The STRUCTURE OF VAPOUR DEPOSITED ALLOYS OF IRON WITH PLATINUM AND PALLADIUM

by

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Abstract

The structure of Fe$_x$-Pd$_{1-x}$ (0.85 > $x$ > 0.5) and Fe$_x$-Pt$_{1-x}$ (0.85 > $x$ > 0.3) thin film alloys co-deposited from the vapour phase over substrate temperatures ($T_S$) ranging over 200-700 °C have been examined at room temperature, using X-Ray, Microprobe, TEM and SEM techniques.

The sequence of phases developed as $T_S$ is changed have been explained in terms of three factors:

a) The structure of the initial phase, which in turn is a function of the $T_0$ temperature where $\Delta G^{bcc-fcc} = 0$.

b) Diffusion at the designated temperature, which depends on both $T_S$ and the rate of deposition.

c) Further transformations which occur on cooling through critical ordering or martensite start temperatures.

Based on the co-deposited thin film results, a model is proposed which facilitates the determination of alloy phase diagrams.

A direct determination of $T_0$ temperature in certain composition ranges is also possible through vapour deposition techniques. Preliminary calculation of $T_0$ confirms the experimental results and the role played by magnetic contributions.

The combined experimental data for Fe-Pt alloys confirm the earlier assumption of a eutectoid transformation at about 17at% Pt at around 600 °C and provides evidence of the efficacy of thin films for the rapid assessment of low temperature equilibria.
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CHAPTER ONE

Introduction
The experimental determination of equilibrium phase diagrams of alloys containing high melting point components is hindered by the low mobility of the constituent atoms in the bulk samples. Thus the currently available Fe-Pt phase diagram for iron rich alloys still exhibits only metastable lines indicating a diffusionless transformation on cooling and heating and no real phase boundaries are available in this system. Up to 25 at%Pt, ordering behaviour has not been linked to the bcc/fcc transformation in such a way as to conclusively show there is a eutectoid transformation. Neither is there any reliable information for $T_0$ temperatures related to either martensitic start temperature or critical ordering temperature.

In many respects, Fe-Pt and Fe-Pd alloys have common structural characteristics ie. martensitic transformation, critical ordering temperature, eutectoid transformation, ordering behaviour and magnetic ordering to a ferromagnetic state. It is clear that a technique is required to accelerate the kinetics of diffusion in order to explore the true structures in these alloys. This will also help in understanding the analogous Fe-Ni alloys which still exhibit problems in interpretation due to slow diffusion at low temperatures alloys. This will form a separate study in its own right.

The use of thin films in equilibrium phase diagram studies holds great promise in that an alloy film can be produced which
exhibits the same transformations as occur in bulk phase diagrams. The ability to generate a thin film equilibrium phase diagram could dramatically reduce the time required to study an alloy system.\(^{(152)}\)

The phase diagrams of Fe-Pt and Fe-Pd alloys have been studied using the ion beam sputtering technique for thin film deposition. The technique allows for a rapid examination of metastable and stable phases in binary and ternary alloys. In alloy thin films, equilibrium is obtained at temperatures which are unlikely to be reached in techniques involving bulk specimens.

The unique characteristic features of vapour deposition technique used in this work is the high surface diffusion which is controlled by substrate temperature \((T_s)\). Depending on the \(T_s\), either equilibrium or metastable phases can be distinguished. The formation of multiphase structures in co-deposited alloy films is controlled by the diffusional breakdown of fully intermixed depositing atoms \((152)\), so that a reference to three kinetic regimes can be made with respect to \(T_s\). The diffusion depends on deposition rate as well as \(T_s\). At low \(T_s\), the surface mobility of atoms is insufficient for the deposition of the fully intermixed depositing atoms and films can contain metastable single phase structure. With increasing \(T_s\), surface mobility of atoms increases and subsequently a metastable two phase structure can be identified. Finally, with a further increase in \(T_s\), the atomic mobility at the surface is sufficient to allow the full atomic rearrangements necessary for the formation of equilibrium
phases.
It is clear that by using the vapour deposition technique it is possible to determine phase boundaries of the alloys at low and high $T_s$. In addition, $T_o$ temperature can be determined independently from martensitic start temperature ($M_s$).

This thesis is divided into four major parts. The first part is a survey of the literature concerned with structural characteristics of Fe-Pd and Fe-Pt alloys with reference to phase transformations and some physical properties in both bulk and thin film alloys. Additionally, specific references have been made to the structure of vapour deposited alloys and the factors that can affect the final structures.

The second part describes the sputtering technique used for producing thin films and the techniques used for their subsequent examination.

The third part concerns the results and the analysis of vapour deposited Fe$_x$-Pd$_{1-x}$ (x = 0.85, 0.75, 0.70, 0.60, 0.50), Fe$_x$-Pt$_{1-x}$ (x = 0.85, 0.75, 0.70) and Fe-Pt-Ni alloys followed by a discussion.

The mechanism and sequence of phases developed as $T_s$ changed is explained in terms of the following factors:
1) The structure of the most stable single phase initially formed on deposition, which is a function of the $T_o$ temperature.
2) Decomposition of the initial phase at the designated temperature by diffusion.
3) Transformations of the decomposed structures which occur on cooling through $T_{o1}$ or $T_{o2}$ temperatures.
In Fe-Pt thin film alloys, an increase in fcc lattice spacing as $T_s$ decreases is considered to be due to an increase in degree of ordering. At lower $T_s$, an ordered fct structure is considered to be due to the fcc lattice transformation through $T_{o2}$ (FePt) temperature.

In Fe-Pd thin film alloys, an increase in degree of tetragonality in fct structure with decrease in $T_s$, is considered to be due to an increase in degree of ordering.

The results for Fe-Pd structures suggest that in the vicinity of the Curie temperature, phase stability can be affected. However, in Fe-Pt thin film alloys, this effect is less obvious. This is because the Curie temperature in Fe-Pt is much lower than the one in Fe-Pd alloys.

Considering the surface morphology of the thin films, a relation can be established that relates type and number of phases with surface morphology. Based on various theories and the surface morphology, the surface diffusion of Fe-Pt alloys has been estimated. Based on that, the relationship between diffusion distance $\bar{X}$ and $T_s$ is examined. This will subsequently allow an estimate of the region of equilibrium to metastable structures with respect to $T_s$. Subsequently a model for formation of an equilibrium vapour deposited thin film phase diagram is proposed. The true phase boundaries are determined as the results of both diffusion and transformation mechanisms.

In addition, the experimental data for Fe-Pt alloys confirms the formation of a eutectoid transformation.
The fourth part concerns the effect of magnetism on phase boundaries and calculation of the $T_{O1}$ temperature in the Fe-Pt system. Finally, comparison is made of experimental and calculated ways of determining $T_{O}$ and the phase boundaries.
CHAPTER TWO

2. Iron-Palladium Phase Diagram

2.1 Introduction
The Fe-Pd phase diagram resembles the Fe-Ni and Fe-Pt systems, belonging to the expanded gamma field type. It exhibits a continuous series of solid solutions between fcc gamma Fe and Pd and two ordered phases at lower temperatures, (FePd) and (FePd\textsubscript{3}) respectively. In contrast with the Fe-Ni and Fe-Pt systems, a miscibility gap instead of an ordered Fe\textsubscript{3}Pd phase has been observed in the fcc solid solution. It shows an Invar effect in compositions centred around 30 at\%Pd. It also has the ability to form thermoelastic martensites that exhibit a shape memory effect. The Fe - Pd phase diagram (fig.1c) reported by Kubaschewski (1) is a combination of results investigated by thermal, magnetic and X-Ray techniques.

2.1.1 Phase Transformation and Crystal structure

In 1936 Grigojew (2) determined the gamma to alpha transformation temperature in Fe-Pd alloys using hardness and thermal techniques (fig.1a). Cooling curves indicate two arrests which suggest a change in transformations. In the Iron rich Palladium alloys (6.68-25.09 at\%Pd), a very significant heat release was observed. However, with increasing Palladium content, transformation temperature drops rapidly. Extrapolating the results to the Fe-rich region, the curve intersects the Y-axis below 700\degree C.

In 1938 Fallot (3) found an isothermal phase transformation
occurring at a constant temperature $(840-850)^0\text{C}$ for 5.5 and 15 at\%Pd and at $756^0\text{C}$ up to 33.3 at\%Pd. Furthermore, the $\alpha \rightarrow \chi$ transformation temperature remains constant at about $669-695^0\text{C}$ up to at least 25 at\%Pd using magnetic techniques. This differs considerably from the thermal and hardness techniques employed by Grigojew (2).

Hultgren and Zapffe (4,5,6) in 1938-39 examined the structure of alloys with 5 to 20 at\%Pd quenched from the gamma phase and found only a supersaturated bcc alpha Fe solid solution. Diffraction lines of the bcc single phase were diffuse, with the diffuseness increasing with the amount of palladium in the sample. However, alloys with 5.5, 10, and 20 at\%Pd annealed at $750^0\text{C}$ were two phase (bcc + fcc) extending to beyond 40 at\%Pd. The solubility of Pd in bcc alpha-Fe was estimated from lattice parameter data to be 2.4, 1.8, and 0.9 at\%Pd at 740, 690, and $500^0\text{C}$ respectively. It is emphasised (4) that the phase boundaries drawn in fig.(1b) are not to be regarded as exact.

In 1963, Raub et al(7) and Kussmann and Jessen (8) re-investigated the Fe-Pd phase diagram below $950^0\text{C}$. Raub et al(7) carried out high and low temperature X-Ray analysis, supplemented by optical microscopy on long term annealed alloys in the 6-85 at\%Pd range. They found the addition of Pd converts the bcc/fcc transformation to a monotectoid which extends from 7-23 at\%Pd with a critical temperature at about $815^0\text{C}$. With an alloy of 6 at\%Pd and in the temperature range of $640-825^0\text{C}$, both bcc and fcc phase are formed whereas at $833^0\text{C}$ only a single bcc phase is observed.
In the temperature range of 825-850°C with 11 at%Pd two fcc phases with clearly different lattice spacings exist in equilibrium. Similar behaviour was observed for 17 at%Pd with a high temperature camera. Samples quenched from 800-580°C with 6-40 at%Pd always remained as fcc phase, but after quenching from 575°C, a distorted tetragonal L1₀ phase was formed. Even low temperature X-Ray showed only bcc and fct phases in equilibrium.

Kussman and Jessen (8) employed thermomagnetic and dilatometric measurements. This permitted more precise positioning of phase boundaries. The eutectoid at which the fcc phase is in equilibrium with bcc and L₁₂ phase was placed at about 620°C with 43 at%Pd by Raub et al (7) but at 605°C with 46 at%Pd by Kussmann and Jesen (8). This is very close to the saturation concentration of L₁₀ structure at 49 at%Pd.

In the course of an X-Ray study of the Fe-Pd system, a rigorous determination of the crystal structures of the FePd and FePd₃ superlattices was conducted by Hultgren and Zapffe (4). The existence of an order-disorder transformation based on FePd₃ in the range of 62.81-74.39 at%Pd at 810°C was first indicated by Grigorjew (2) on the basis of thermal measurements, hardness, and electrical conductivity. At intermediate temperatures, a mixture of two phases was present. At lower temperatures, c/a decreased and also decreased with higher Palladium concentrations.

Alaverdov (9) in 1939 reported a composition range for the FePd
ordered phase from about 40 to about 62.6 at%Pd (with c/a = 1.027 for 62.6 at%Pd) with an observed transformation temperature of 880\,^\circ C at 60-61.5 at%Pd.

Raub et al (7) in 1963 found that for alloys greater than 40 at%Pd, the fct phase formation temperature reached a maximum of 800\,^\circ C. At 62 at%Pd, Ll_2 phase appears in conjunction with the Ll_0 phase with an indication that the Ll_2 phase has a higher critical temperature than the Ll_0 phase.

The two ordered phases FePd and FePd_3 formed at about 790\,\pm\,20\,^\circ C and 820\,\pm\,20\,^\circ C respectively and are separated by a narrow two phase field.

Although there has been no direct evidence for the existence of an ordered Fe_3Pd phase, Grum-Grzhimailo (10) postulated the existence of such a phase based entirely on a theoretical treatment.

Hocart and Fallot (11) performed magnetic measurements over the entire range of Pd composition, and their results were confirmed by Hultgren and Zapffe (6). They found anamalous magnetic properties at the composition FePd and also FePd_3. X-Ray diffraction showed that the disordered fcc phase predominated in both cases with a few weak lines of another phase present.

Two Curie points were found in the range of 5-40 at%Pd at 764 and at 432\,^\circ C respectively which is a characteristic indication of two phases. For high Pd content, the Curie point depends on the heat treatment. The Curie points reached a maximum at 48 and 74 at%Pd when alloys cooled slowly for 100 hours between 400\,^\circ C and 800\,^\circ C.
Fig. (1a) The Fe-Pd phase diagram proposed by ref. (2).

Fig. (1b) The Fe-Pd phase diagram by ref. (4).

Fig. (1c) The Fe-Pd phase diagram.
2.1.2 Fe-Pt Phase diagram

2.1.3 Introduction

The Fe-Pt phase diagram resembles in many respects the Fe-Ni and Fe-Pd systems. At higher temperatures Fe and Pt are mutually soluble in all proportions and have a fcc crystal structure. At lower temperatures there are complications associated with the fcc to bcc cubic transition in Fe rich alloys and there are regions of stability of superlattices centred near the compositions Fe$_3$Pt, FePt and FePt$_3$. It shows an Invar effect in alloys containing 22-35 at\%Pt and like Fe-Pd, has the desirable ability to form thermoelastic martensites that exhibit the shape memory effect, which is linked to prior ordering in the austenite. The Fe-Pt phase diagram (fig.2c & 2d) reported by Hansen (12) and Kubaschewski (1) respectively is a combination of results investigated by thermal, electrical, microscopic, magnetic, dilatometric, hardness and X-Ray diffraction techniques.

2.1.4 Phase transformation and crystal structure in Fe-Pt alloys

The Fe-Pt phase diagram was first investigated in 1907 by Isaac and Tammon (13) by means of thermal analysis. The liquidus transition temperatures were studied by means of thermal analysis. The continuous solid solution found at higher temperatures transformed into two regions, at approximately 25at\% Pt and 30-100 at\%Pt as shown in fig.(2a). Nemilov (14) postulated that the region between 30-100 at\%Pt
was attributable to the FePt phase, as both hardness measurements and thermal expansion coefficients gave anomalous results for these regions.

In 1938 Fallot (3) and Martelly (15) investigated the alpha to gamma phase transformation by measurement of magnetization as a function of temperature and observed a discontinuity in these curves. They found that with increasing platinum content, the separation of the alpha to gamma transus lines decreased and that the transus line reached ambient temperature at approximately 21 at% Pt at 25°C. This was confirmed by Kussman and Rittberg (16) who showed this transformation in alloys with 22, 25, 26 at% Pt starts at 50, 20, and -60°C respectively.

In 1935 Graf and Kussman (17) investigated the structure of Fe-Pt alloys for temperatures up to 1100°C by measuring coercive force, the saturation magnetization for quenched and annealed specimens, metallographic and X-Ray diffraction techniques. They (17) examined the exact nature of magnetic properties and made a distinction between the Curie temperature of quenched fcc phase and that of the FePt phase produced on annealing (fig.2b).

In 1950, Kussman and Rittberg (16) used linear expansion techniques to determine bcc to fcc transition points. In addition, transition was shown to occur between low temperature bcc alpha and the high temperature gamma phase. This transition is of the shear type, as in the martensite reaction.

The Fe-Pt phase diagram cited by Hansen (12) (fig.2c) and Kubaschewski (1) (fig.2d) is based principally on the work of
In 1957 Berkowitz et al (18) used resistivity and magnetization measurements, supported by X-Ray and metallographic examination, to show that certain modifications should be made to this diagram. They suggested that the line marking the beginning of fcc gamma to bcc alpha phase transformation for disordered gamma phase should be moved to higher temperature and Pt concentration, passing through 25at% Pt at 0°C. Alloys containing 14.4 and 24.2 at%Pt, quenched from 1000°C, transformed to alpha phase with traces of gamma phase in the latter composition. The small amount of gamma phase present was above its Curie temperature.

Kussman and Rittberg (16) showed the same results as Berkowitz et al (18) for 14.4 at%Pt alloy but the 24.2 at%Pt alloy remained as gamma phase. The difference in results was suggested to be due to a more rapid cooling adopted by Berkowitz et al (18).

Under equilibrium conditions, the disordered gamma phase decomposes into alpha phase and ordered gamma phase. The alpha phase and the ordered gamma phase should, at equilibrium, be separated by a eutectoid. The change of resistivity in the 14.4 at%Pt specimen during annealing at 550°C and the isothermal decomposition of this alloy at 550°C suggests that this eutectoid would be placed somewhat above 550°C (18).

Eutectoid transformation in Fe-Pt alloys was similarly proposed by Vlasova et al (19) by magnetic study of an approximately 13.4 at%Pt alloy.
In 1963 Sundaresen et al. (20) investigated thermodynamic properties of Fe-Pt alloys by an electromotive force method in the ranges 600 - 700°C and 700 - 900°C. They suggested the possibility of three eutectoid equilibria between the bcc, fcc phase, Fe₃Pt and FePt. A tentative modification of the phase diagram is shown in fig. (3).

Kussman and Rittberg (16) using magnetic, dilatometric and X-Ray measurement showed the existence of an Fe₃Pt superlattice. Its range of existence extends from about 19 to 33 at%Pt. This occurs in the region of the reversible alpha to gamma transformation. They identified a two phase region between gamma and Fe₃Pt and between FePt and FePt₃, but actual phase boundaries were not established. A tentative maximum ordering point for FePt was drawn according to the related Fe-Pd phase diagram (fig. 2c).

In 1962, Crangle and Shaw (21) suggested the existence of superlattices based on composition Fe₃Pt, FePt, FePt₃. However the exact conditions under which they occur are somewhat uncertain. The existence of FePt₃ were confirmed with maximum ordering temperature occurring at 1350°C at an approximately 65 at%Pt. Additional phases Fe₃Pt and FePt was also postulated.

Berkowitz et al. (18) had concluded from their resistivity measurements on Fe-Pt that the ordering temperature suggested by Kussman (16) for the Fe₃Pt phase was 100°C too high. This temperature marks the limits below which appreciable short range order appears rather than the temperature at which long
range order vanishes. In 1973 Dunne and Wayman (22) using metallography, electrical resistivity measurements on alloys near the composition Fe$_3$Pt confirmed the transformation from fcc austenite to bcc martensite and furthermore established that the ordering of 25 at% alloy prior to the martensite transformation results in a reverse martensite transformation with a small temperature hysteresis.

Meysner et al.(23) examined the high temperature Fe-Pt phase diagram in the Fe$_3$Pt region with a high temperature X-Ray camera. They suggested Fe$_3$Pt alloy is in a dual-phase state in the temperature range 670-750°C, with one phase an ordered Ll$_2$ structure and the other ordered Ll$_0$ (FePt). Fig.(4a) shows the temperature dependences of phase Ll$_2$ and lattice parameters of phase Ll$_0$ in Fe-24at%Pt. Part of Fe-Pt phase diagram near Fe$_3$Pt composition is illustrated in fig.(4b).
Fig. (2a) the Fe-Pt phase diagram proposed by ref. (13).

Fig. (2b) the Fe-Pt phase diagram proposed by ref. (?).
Fig. (2d) The Fe-Pt phase diagram published by ref. (1).

Fig. (3) A section of Fe-Pt phase diagram proposed by ref. (20).

Fig. (4) a) Temperature dependences of lattices Fe-24 at% Pt
b) Part of Fe-Pt phase diagram ref. (23).
2.2 Order-Disorder in alloys

2.2.1 Introduction

Numerous substitutional alloys are ordered at low temperatures and disordered at high temperatures. "Ordered" means that the lattice site can be grouped into sublattices, each of which is occupied predominantly by one kind of atom. In the "disordered" state no such grouping is possible, each sublattice being occupied by the various constituents at random. Over certain ranges of concentration and temperature, the structures are neither perfectly ordered nor perfectly random. When the alloys are "ordered", as defined above, there are non-zero correlations between the kind of atom on a given site and the kind on a distant site, and the system is said to have "long-range order". When the alloys are "disordered" there are still correlations, called "short-range order parameter" between the kinds of atoms at sites close to each other. Order parameters can be measured experimentally by their effects on the scattering of X-Rays and neutrons. The degree of long range order affects the intensities of the "superlattice reflection" while the presence of short-range order affects the intensity of the diffuse scattering (24).

The formation of a superlattice takes place at the ideal or near compositions $A_3B$, $AB$, and $AB_3$. The superlattices derived from the fcc structures (Al) are known as $Ll_0$ and $Ll_2$ in the structurbericht notation.

The $Ll_2$ structure corresponds to the ideal composition $A_3B$. The "B" atoms are in the [000] positions and the "A" atoms are in
the remaining sites of the conventional unit cell of the fcc structure. In this superlattice the "B" atoms each have twelve unlike nearest neighbours, compared with an average of three like and nine unlike nearest neighbours in a random fcc solid solution.

The L10 has tetragonal symmetry where the "A" atoms are at points [0 0 0] and [1/2 1/2 0] of the unit cell, and "B" atoms are at points [1/2 0 1/2] and [0 1/2 1/2]. The structure consists of alternate layers of "A" and "B" atoms parallel to the (001) planes. The attraction between "A" and "B" atoms results in slightly smaller interatomic distances between nearest neighbours in adjacent layers, so the structure is tetragonal with axial c/a ratio slightly different from unity. Each atom has four nearest neighbours of its own type in the same (001) layer, and eight nearest neighbours of the opposite type in the two adjacent (001) layers. This contrasts with the completely disordered structure, where each atom, on average, has six like and six unlike nearest neighbours (25).

Fig.(5a & 5b) shows the unit cells of the disordered and ordered structures in copper-gold forming, Cu3Au and AuCu respectively.

Table (1) illustrates the position of atoms in superlattices derived from fcc structures.

Like other phase transformations in solids, order-disorder transformations occur by nucleation and growth, and therefore are often slow.

In this section the kinetics of order-disorder transformations in alloys in general with an emphasis on the ordering behaviour
of iron rich Fe-Pt alloys and Fe-Pd alloys are underlined.

2.2.2 Kinetics of Order-Disorder transformations in alloys

2.2.3 Theory

Theoretical treatments of kinetics of order-disorder transformations have been attracting a great deal of attention, and various models have been proposed with different degrees of sophistication.

Theoretical treatments of superlattices have been given by Borelius (26), Johnson and Linde (27), Gorsky (28), Dehlinger (29), and Dehlinger and Graf (30), chiefly on the basis of formal thermodynamic relations. It was considered anew by Bragg and Williams (31), Bethe (32), and Peierls (33), who as a group, started with simple assumptions about atomic forces and calculated quantitative results that compared very favourably with experiment.

In 1919 Tammann (34), in order to explain changes in resistivity, put forward the hypothesis that the atoms, in alloys subjected to long annealing, segregate into regular positions. The existence of such a segregation in gold-copper alloys was experimentally observed by Johnson and Linde (27) by means of X-Ray analysis.

Dehlinger and Graf (30) have given an account of the effect of thermal treatment on the AuCu system, and compared the X-Ray results with observations of physical properties of the alloy and have discussed the theory of the effects.

Bragg and Williams (31) considered the kinetics of ordering in
a binary system and the problem of the rate of approach to the equilibrium state associated with annealing and quenching. They concluded that the ordered structure has a lower potential energy than the disordered structure, but thermal agitation promotes disorder. It is also shown above a certain critical temperature the structure is completely random. As the temperature is lowered, order sets in abruptly at the critical temperature, and at first rapidly increases. It only becomes complete as absolute zero is approached. They realised the dependence of rate of relaxation upon temperature, which enables the effects of annealing and quenching to be predicted. The rate of relaxation depends upon the magnitude of the "activation energy" required to surmount a potential barrier when two atoms interchange position. Because interchange of atomic position at room temperature is infrequent, the alloy structure relates to some previous point in its history when the temperature was just sufficiently high for interchange to be important.

2.2.4 Thermodynamics of the Order-Disorder

The equilibrium state at a given temperature is the state which makes the thermodynamic potential a minimum. For a solid the thermodynamic potential may with very good approximation, be represented by the free energy:

\[ F = U - T \Phi \]  

where \( U = \) internal energy
\[ S = \text{entropy} \]
\[ T = \text{absolute temperature.} \]

Both "U" and \( S \) depend upon the degree of order, defined by a suitable parameter "S". Bragg and Williams (31) defined the degree of order "S" for the more general case of alloy in which the "A" atoms were a fraction "r" of the whole, the remaining fraction \((1 - r)\) being "B" atoms. "S" is defined as:

\[ S = \frac{p - r}{1 - r} \quad (2) \]

where "p" is the probability of finding an "A" atom in the site appropriate to such an atom. "S" varies from unity for complete order to zero for complete disorder.

The quantity "V" may be defined as the increase in the potential energy of the crystal when one atom is moved from an ordered to a disordered position. The actual value of "V" depends on the value of "S" and the actual equilibrium state is that which gives self-consistent values of "S" and "V".

Fig.(6a & 6b) shows the general nature of a family \( S (V, T) \) and \( V (S, T) \) curves respectively. The characteristic relation shows that "V" depends upon "S", and tends to zero as "S" tends to zero. If "V" was constant, there would be a gradual falling off of the degree of order with increasing temperature, as in fig.(6c). The decrease in "S" involves a decrease in "V", and hence the degree of order falls off more steeply and reaches zero at the critical temperature as shown by the dotted curve.

In contrast to the above school of thought, Dehlinger (29) supposed that "U" and \( S \) depend upon both the degree of order
and upon the "tetragonality" of the crystal, which he regards as another variable not defined by the degree of order. By assuming various curves for the external energy "U" as a function of order and tetragonality, Dehlinger (29) drew the free energy curves and showed that the order-disorder transition may be continuous or partly continuous and partly sudden.

Borelius (26) makes the more natural assumption that c/a axial ratio depends on the degree of order.

The variation of "S" with temperature can be calculated for different superlattices by choosing a suitable model (quasi-chemical theory). Fig.(7) shows the variation of long range order "S" for A₃B type transformations. The degree of variation of short range order is shown as the dashed lines. A substantial change in order takes place discontinuously at order-disorder transition temperature \( T_c \), i.e. a first order transformation.

The transformation is said to be the first order, if the free energies are equal at the transformation temperature, but the entropies and volumes of the two phases differ. The transformation is said to be of the second order if the free energies, the entropies and volumes are equal but the heat capacities or compressibilities differ.

The order-disorder transition for Ll₂ type superlattice alloys is known to be a first-order reaction which involves a latent heat of transformation on the basis of classical thermodynamics (31). From the viewpoint of ordering kinetics a similar explanation has been given for the ordering in Ll₂ type alloys by Dienes (35), and Vineyard (36), but in this case it was
shown that the ordering behaviour is strongly dependent on the ordering temperature near Tc; a large fluctuation in local degree of order is required to initiate the ordering reaction and hence the ordering for the alloy takes place by a nucleation and growth mechanism. This is a feature of first order reactions.

The nucleation and growth process is illustrated in fig.(8). Atoms within the ordered regions, or domains, are marked; the unmarked sites are disordered. The sublattices are generally equivalent, so that at any given nucleation site either "A" or "B" atoms can occupy the sublattice. The independently nucleated domains will often be out of phase. An antiphase domain boundary (APB) will form as a result of domain growth across which the atoms will have the wrong kind of neighbours. APBs are, therefore, high energy regions of the lattice and are associated with an APB energy.(37)

Generally, stoichiometric alloys transform from disorder to order phase with varying degree of ordering. However, in non-stoichiometric alloys, the disordered phase transforms to a disordered matrix + ordered precipitates which involves composition changes. An ordered structure can be formed in non-stoichiometric phases either when some atom sites are left vacant or when some atoms are located on wrong sites.
Fig. (5) a) Superlattice of CuAu (Ll₂)
b) derived from the fcc structure (Al) (a).

Fig. (5b) Superlattice CuAu (Ll₀)

Table 1 Position of atoms in superlattices derived from fcc structures.

<table>
<thead>
<tr>
<th>Disordered Structure</th>
<th>Superlattice Type</th>
<th>Composition</th>
<th>Atom Positions</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>f.c.c.</td>
<td>Ll₀ (Tetragonal)</td>
<td>AB</td>
<td>2A @ (000; 000)</td>
<td>Ni₃Pt, FePd</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2B @ (000; 000)</td>
<td>AuCu, CoPt</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>MgIn, MnNi, FePt</td>
</tr>
<tr>
<td>f.c.c.</td>
<td>Ll₂</td>
<td>A₃B</td>
<td>3A @ (0½; 000)</td>
<td>Cu₃Au, Au₃Cu</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3B @ (000; 000)</td>
<td>Pt₃Co, Fe₃Pt</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pt₃Fe, Cu₃Pt</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ni₃Mn, etc.</td>
</tr>
</tbody>
</table>
Fig. (6) General nature of the (a) $V(S,T)$ and (b) $S(V,T)$ relations. ref (31)

Fig. (6c) General falling off of the degree of order with increasing temperature when $(V)$ is constant. ref (31)

Fig. (7) The variation of long range order $(L)$ and short range order $(s)$. ref (160)

Fig. (8) The formation of an antiphase boundary (APB) when out-of-phase ordered domains grow together. ref (37)
2.2.5 Rate of approach to ordering

The time required for ordering in an alloy to be established is determined by atomic movements, i.e. diffusion. In ordering, unlike in precipitation and decomposition processes, no large concentration differences arise which necessitate transport of material over large distances. It is much more a question of atomic exchange between neighbouring sublattice sites.

It is expected that the rate of diffusion in small particles will be enhanced due to surface effects. This was demonstrated by Kachi et al. (38).

A greater rate of ordering was observed for FeNi alloy at 250°C by increasing the diffusion by means of electron irradiation (39). Also Weil (40) observed that the FePt superlattice was directly formed in a very short period when particles of Pt(CN)₄Fe were reduced in hydrogen at a temperature below the critical point.

Considering the above results, it appears that the rate at which order sets in depends on composition, particle size, time, defects and annealing temperature.

2.2.6 Detection of long range order

Of the various methods of investigating order-disorder changes, X-Ray diffraction is the most direct.

In 1923, Bain (41) detected, on X-Ray photographs of AuCu₃, lines that could only be attributed to a superlattice. This conclusions were firmly established by Johnson and Linde (27). Considering AuCu₃ where atoms with scattering power f_Au are at
positions with coordinates (000) and atoms with scattering
power $f_{Cu}$ are at $(1/2 1/2 0)$, $(1/2 0 1/2)$, and $(0 1/2 1/2)$, it
will be seen that there are two classes of reflections.
The main reflections occur when indices are all "odd" or all
"even", and have intensities proportional to:

$$|F|^2 = (f_{Au} + 3f_{Cu})^2 \quad (3)$$

The superlattice lines occur when indices are mixed "odd" and
"even", and have intensities proportional to:

$$|F|^2 = (f_{Au} - f_{Cu})^2 \quad (4)$$

This is when the alloy is completely ordered. Also they are
proportional to:

$$|F|^2 = S^2 (f_{Au} - f_{Cu})^2 \quad (5)$$

ie. in a partially ordered alloy. Thus, in fully disordered
alloys "S" = 0 and the superlattice lines vanishes, since each
lattice point, then has on the average the same scattering
power. From the above statements, for a fully ordered Fe$_3$Pt
alloy it is found that :

Intensity (superlattice line)/Intensity (fundamental line)

$$|F|^2/|F|^2 = (f_{Pt} - f_{Fe})^2/(f_{Pt} + 3f_{Fe})^2 \quad (6)$$

At $\sin \theta/\lambda = 0$, $f = Z$ ie. atomic scattering power is equal to
atomic number.
\[
\frac{I_s}{I_f} = \frac{(78 - 26)^2}{(78 + 3 \times 26)^2} = 0.11
\] (7)

Superlattice lines are only about one-tenth as strong as fundamental lines in the case of Fe₃Pt. In the case of Fe₃Ni, even when fully ordered, the intensity of the superlattice lines becomes so weak that they can only be detected under special circumstances. The corresponding intensity ratio for Fe₃Pd alloy is about 0.15.

A method which can be employed to detect these faint superlattice lines is to take into account the slight dependence of scattering factors on the wavelength of the radiation. If the wavelength is near to that at which the element would itself emit as target of an X-Ray tube, then the scattering factor is reduced.

Jones (42) has detected the superlattice lines in the alloy of CuZn by the use of zinc Kₗ radiation. With other radiations, the difference between the scattering power of copper and zinc is so small that the superlattice lines can not be detected.

Fig.(9) demonstrates the variation of the scattering power correction Δf with \( \frac{\lambda}{\lambda_k} \). When \( \frac{\lambda}{\lambda_k} \) is \(<0.8\), the correction is practically constant and independent of small variation in \( \lambda_k \). But when \( \lambda \) is near \( \lambda_k \), the slope of the correction can be quite different for two elements of nearly the same atomic number. By taking advantage of this fact, the intensity of a superlattice line can be increased above its normal value (160).

The difficulty of having to observe weak diffracted beams can also be avoided by of neutron diffraction (43). The scattering cross sections vary from atom to atom quite differently from
Fig. (9) Variation of the scattering factor correction $\Delta f$ with $\lambda/\lambda_K$.
X-Ray scattering factor and are not related to atomic number.

2.2.7 Ordering behaviour in Fe-Pd and Fe-Pt alloys

In this section the characteristics of ordering in FePd, Fe$_3$Pt, and FePt alloys are considered. In FePd alloys degree of order increases with an increase in degree of tetragonality, whereas in Fe$_3$Pt alloy the marked increase in lattice spacing is consistent with increase in degree of ordering.

a) FePd superlattice

Reference to ordering in FePd$_3$ alloy is given in section 2.1.1. In this section, ordering in FePd alloy is considered. Atomic ordering takes place in the equiatomic alloy FePd at temperatures below 680°C and as a result a Ll$_0$-type superlattice is formed. It is found that the tetragonality of the FePd crystal lattice increases with the degree of long range ordering (44). In the temperature range 620-680°C, the ordered phase and disordered solid solution can co-exist in the equilibrium state (45), but in the temperature range below 620°C, only the ordered phase is thermodynamically stable.

In 1938, Hultgren and Zaffe (4) studied a 51.9 at%Pd alloy which was quenched from 700°C. A disordered fcc structure was observed. But at 650°C and below, a tetragonal FePd structure with a = 0.3852 nm, c = 0.3723 nm was observed. This is in disagreement with Jewllinhaus (46) who identified an FePd ordered phase in range of 50 at%Pd by X-Ray analysis and found the ordered phase to be a tetragonal Ll$_0$ type structure with
c/a = 1.03 and a = 0.38 nm. The same alloy quenched from higher temperature had a disordered fcc structure with a = 0.378 nm. He also found that annealing the alloy at 500°C, markedly affected the coercive magnetic properties of the FePd phase. At lower temperatures c/a decreased, and surprisingly, it decreased at higher palladium contents. The volume of this ordered tetragonal unit cell is 0.5524 nm$^3$, (where a = 0.30815 nm) compared with 0.5494 nm$^3$ for the disordered gamma phase, an increase of 0.5 per cent on ordering. Hultgren and Zaremba (4) suggested that this anomaly might be due to ferromagnetism.  

Hocart and Fallot (43) and Jewllinhaus (46) also found that ordering profoundly influenced magnetic properties. Although in an AuCu type of superlattice the critical temperature of ordering normally has a maximum at 50 at%, the only composition at which perfect order is possible, this is not true for FePd. The critical temperature for the 51.9 at%Pd alloy was near 700°C, but order persisted up to 770°C, with 60 at%Pd.

b) FePt superlattice

Lipson et al (47) determined the crystal structure of the ordered FePt alloy that places the Fe atoms at (000) and (1/2 1/2 0) and Pt atoms at (1/2 0 1/2), (0 1/2 1/2) with a = 0.3838 and c/a = 0.968.

In the disordered state, the atoms would be situated at random in the four positions and the axial ratio would be unity with fcc structure.
c) Fe$_3$Pt superlattice

Fe$_3$Pt austenites undergo an fcc to Ll$_2$ ordering reaction below $T_{c/od}$ (12) with iron atoms occupying the face centre position and the platinum atom the corners of a fcc in the fully ordered state. This type of ordering can be attained when the alloy is annealed below the atomic ordering temperature $T_{c/od}$. The disordered phase can also be retained by rapid quenching from a temperature higher than $T_{c/od}$.

Chang and Sastri (48) suggested that $T_{c/od}$ for 24 and 22 at%Pt to be 835 and 765°C respectively. The temperature $T_{c/od}$ result for 24 at%Pt is in excellent agreement with Kussmann and Rittberg's data (16), but it is lower (as opposed to 825°C) for 22 at%Pt. The discrepancy is thought to be due to lack of heat treatment of any sample between 700°C and 800°C by (16).

The extent to which substituting Nickel for Platinum could reduce the critical ordering temperature in Fe$_3$Pt is predicted by Inden (49) in quasi-binary section (Fe$_3$Pt -Fe$_3$Ni). Skinner (50) showed both experimentally and by calculation a lower $T_{c/od}$ fig.(10).

However, from the available information on the kinetics of ordering in Fe$_3$Pt, the rate of approach to the equilibrium order is slow at temperature below 725°C (51), while at higher temperature, the equilibrium value of "S" increases rapidly with increasing temperature (52).

Ling and Owen (53) studied Fe-25at%Pt powder at room temperature in a quenched specimen. A gradual variation of "S"
with ordering temperature near the critical temperature was observed. The room temperature lattice parameter "a" was found to be 0.3724 nm, between $S = 0$, and $S = 0.4$ and then increased linearly to 0.3736 nm as "S" approaches unity (fig. 11). Similarly Dunne et al(54) support the idea that ordering results in a significant increase in austenite lattice spacings.

Tadaki et al(55) examined Fe-24at% Pt alloy austenitised, at 650°C, by low temperature X-Ray and electron microscopy. They found the lattice parameter tends to increase with increasing order as the time increases at constant temperature, and tends to increase with decreasing temperature. Table (2) is a summary of the lattice spacings measurements for Fe$_3$Pt alloys indicating the increase in "a" because of ordering. It is therefore commonly held that in Fe$_3$Pt alloys, an increase in lattice parameter at room temperature is associated with the ordering of the fcc structure (52,53,55). However, the reasons for this behaviour are dealt with in the Invar section 4.2.2.

X-Ray diffraction results from Fe$_3$Pt-Fe$_3$Ni alloys showed the austenite to consist of two austenites(fcc + fcc'), with significant differences in lattice parameter. On cooling, fcc transformed to martensite (bcc') leaving the fcc'phase at $-130^0$C untransformed (50) (fig.12). When Miodownik (56) sought evidence for ordered gamma phase in Fe-Ni-Pt alloys it was concluded that (fcc/fcc') phase separation is more likely to occur than ordering as the alloy composition moves towards Fe-25at% Ni.
Fig. (10) Variation of ordering temperature with composition. ref. (50)

Fig. (11) Room temperature lattice 'a' as a function of the degree of order "S" in Fe₃Pt. ref. (53)

Fig. (12) Changes in the diffraction pattern obtained on cooling an aged Fe₃Pt₀.5Ni₀.5 alloy. ref. (50)

Table (2) Lattice spacings measured at room temperature for powder Fe-Pt alloys.

<table>
<thead>
<tr>
<th>at% Pt</th>
<th>fcc(nm)-od</th>
<th>fcc(nm)-do</th>
<th>bcc(nm)</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.25</td>
<td>0.3721</td>
<td>0.964</td>
<td></td>
<td>48</td>
</tr>
<tr>
<td>24.0</td>
<td>0.3718</td>
<td>0.2966</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>24.5</td>
<td>0.3725</td>
<td>0.2989</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>25.0</td>
<td>0.372</td>
<td>0.296</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>25.5</td>
<td>0.3725</td>
<td>0.2962</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>27.0</td>
<td>0.372</td>
<td>0.372</td>
<td>-</td>
<td>53</td>
</tr>
<tr>
<td>28.0</td>
<td>0.375</td>
<td>0.375</td>
<td>-</td>
<td>83</td>
</tr>
<tr>
<td>30.0</td>
<td>0.3756</td>
<td>0.3756</td>
<td>-</td>
<td>83</td>
</tr>
<tr>
<td>31.0</td>
<td>0.3761</td>
<td>0.3761</td>
<td>-</td>
<td>This work</td>
</tr>
<tr>
<td>32.0</td>
<td>0.3762</td>
<td>0.3762</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
2.3 Martensitic transformation

2.3.1 Introduction

Martensitic transformation is influenced by many factors mainly sensitive to composition, austenite heat treatment, particle size and ordering.

The transformation temperature \( M_s \) in Fe-Pt and Fe-Pd progressively decreases with ordering and the morphology of martensite varies correspondingly from a lenticular type to a thin plate one (57). Associated with the thermoelastic martensite transformation, the shape memory effect was found in an ordered Fe\(_3\)Pt alloy (58). However, in the case of Fe-Pd alloy this effect is not always connected with the ordered structure in fcc-fct martensitic transformation.

This section will consider the theory of martensitic transformation in general, in particular the one in Fe-Pt and Fe-Pd alloys and the factors that may influence the transformation.

2.3.2 Theory of martensitic transformation

Burke (59) defines martensitic transformation as one in which the growth of the product crystals takes place by the systematic coordinated movement of many atoms of the parent crystal in such a way as to generate the product structure, the distance through which any one atom moves in the course of the transformation being a fraction of one lattice spacing. Any atom has the same neighbours in the product phase as in the parent crystal, only the relative positions are different. Thus the chemical composition of parent and product is identical and
if the parent is ordered so also is the product. Furthermore, a martensite crystal contains the same number of atoms as the region of the parent crystal from which it is generated but, since there is a change of lattice, the shape and volume of the martensite crystal is different.

The theory of the geometry of martensitic transformations is studied by Wechsler, Lieberman, Read (60), Bowles, Mackenzie (61), and is outlined in the review paper by Lieberman (62). In 1924 Bain (63) demonstrated how the bct lattice could be obtained from the fcc structure with the minimum of atomic movement and the minimum of strain in the parent lattice. As shown in fig. (13a & 13b), an elongated unit cell of the bcc cell can be drawn within two fcc cells. It is interesting that the Bain deformation involves the absolute minimum of atomic movements in generating the bcc from the fcc lattice. The reason for martensitic transformation is the difference between the free energies \( \Delta F < 0 \) (64,65) of the two alternative structures of the given assembly of atoms. In basic terms this means that one kind of interatomic bonding is energetically favoured at lower temperatures below some equilibrium temperature \( T_0 \). However, on account of the effect of non-chemical free energy (interfacial and strain energy, \( \Delta G > 0 \)), the net free energy difference is:

\[
\Delta W = \Delta F + \Delta G
\]  

When the \( \Delta W < 0 \), the embryo can grow. Both free energies are affected by alloying with consequent effects on \( M_s \) temperature. Further, defects present in the parent effect the nucleation and growth of the martensite, but it is difficult to isolate
specific effects.
The kinetic feature of most martensitic transformations is described as athermal, a transformation on cooling that begins at a certain temperature ($M_s$) but progresses only if the temperature is continuously lowered, until a certain temperature ($M'_f$) is reached. The corresponding temperatures for the reverse transformation are ($A'_s$) and ($A'_f$).

A temperature $T < T_0$ is necessary for the onset of martensitic phase transformation (66). The next section is an attempt to define $T_0$.

2.3.3 Thermodynamical equilibrium temperature $T_0$

Transformation starts at an undercooling temperature $\Delta T$ below the thermodynamical equilibrium temperature $T_0$. $T_0$ is strongly affected by alloying additions. A schematic definition of the temperature $T_0$ in a phase diagram and free energy diagram is shown in fig. (14). It is defined as the equilibrium temperature at which the free energies of the austenite and the martensite of comparably high structural perfection are equal (66). Most frequently it is claimed that $T_0$ is to be found intermediate between "$M_s$" and "$A_s$". This implies an equivalent undercooling ($T_0 - M_s$) and overheating ($A_s - T_0$) for the formation of martensite and austenite respectively. This method is however inapplicable for thermoelastic martensite. It is very likely that it also does not apply for martensitic transformations which take place reversibly with a few $^0K$ hysteresis at low temperatures. The condition ($T_0 - M_s$) $\sim$ ($A_s - T_0$) is better fulfilled in low yield stress alloys, where the lattice invariant shear is accompanied by dislocation movement, such as
2.3.4 Thermoelastic and non-thermoelastic martensite

Two types of martensitic transformation are realised.

a) Thermoelastic

b) Non-thermoelastic.

Thermoelastic martensite was first observed in aluminum bronze by Kurdjumov and Khandros (67) and later found in non-ferrous alloys. Kurdjumov (68) considered the necessary condition for thermoelastic transformation as that the martensite interface remains glissile during transformation so that reverse movement of the interface can occur on raising the temperature or applying an appropriate stress. Christian (69) reported that thermoelastic transformations appear to fall into two categories:

Class I in which the temperature range $M_s^' \to M_f^'$ is small and $A_s^' \geq M_s^'$, and class II, in which $M_s^' \to M_f^'$ is large and $M_s^' < A_s^'$ (fig.15). It appears that a small chemical driving force and a small volume change are associated with class I transformation.

However, a thermoelastic transformation is characterised by a small thermal hysteresis compared with that of non-thermoelastic one (for example about 400°C in Fe-Ni alloys) (70).

Another significant difference between the two transformations is in the manner of the forward and reverse transformations. In the former case transformation proceeds by the continuous growth of martensite upon cooling, and the reverse transformation occurs by the "backwards" movement of the interface. The typical morphology of non-thermoelastic martensite is
characterised by a curved interface like the lenticular martensite observed in many ferrous alloys. While the morphology of the thermoelastic martensite is characterised by a smooth planar interface. Such differences in appearance may be closely related the above mentioned difference in the mobility of the martensite interface in transformation kinetics (57).

2.3.5 On Nucleation of martensite

Fisher et al (71) have developed a theory for the nucleation of martensite. The major factor influencing nucleation of martensite was considered to be statistical composition fluctuations occurring in small regions at high temperature and frozen-in on quenching. These local regions of varying size and composition serve as nucleation centres. They become supercritical, one by one, as temperature is progressively lowered, resulting a temperature dependent or athermal transformation.

Fisher (72) applied nucleation theory to substitutional solid solution alloys (Fe-Ni in this case). He predicted a time and composition dependent on nucleation frequency. Machlin and Cohen (73) have shown that single crystals would transform to a large extent in a single burst. In large grain polycrystalline specimens frequently more than one grain and sometimes the whole specimen would transform at the same instant in this manner. Results on filing indicated that different particles would undergo the burst transformation at widely different temperatures. These results support the
conclusion that the transformation behaviour could not be described by a single nucleation frequency as would be the case if the nucleation were homogeneous.

Cech and Turnbull (74) studied powders of Fe-Ni alloy and showed that the martensite transformation appears to start on heterogeneous nucleation sites. Their data supports the hypothesis that heterogeneities in a spectrum of radii exist in the particles. Nucleation occurs at these sites and, once nucleated, martensite proceeds to form through the particles. The probability of finding a heterogeneity of a given radius in a particle increases with increasing particle size.

2.3.6 Parameters that influence martensitic transformation

The object of this part of the thesis is to clarify the relative influences of each of the critical austenitising parameters in relation to the martensitic transformation in the alloys of interest. These parameters include, grain size, composition of alloy, magnetism, defects, austenitising temperature and degree of order.

In thin films the grain size is considered to be of the same order of the film thickness, and much smaller than in the powder of Cech and Turnbull (74). This fine grain size in the evaporated film was considered to be responsible for the depression of the transformation temperature. The reason for this behaviour could be explained as follows: A grain boundary might be considered as a preferential site for martensite nucleation because it is an extensive defect.
However, a grain boundary also serves to stabilise the parent phase and thus hinder the martensitic transformation. Grain boundary atoms are relatively stable to martensitic transformation for they are partly free from restriction by neighbouring atoms and tend not to take part in the coordinated atom movements of such transformations. Also lattice defects near the grain boundary can migrate to the boundary and disappear and thus the number of nucleation sites is expected to decrease. Finally dislocations in a fine particle will diffuse out of the surface by the climbing motion caused by excess vacancies or other surface effect.

Leslie and Miller (75) used an Fe-31 %Ni-0.02 %C for grain refinement studies and established that the amount of retained austenite increases as the austenite grain size decreases. This indicates that the austenite grain boundaries impeded the formation of martensite. Similarly Kachi et al(76) studied fine particles of Fe-27.4 at%Ni produced from elevated temperature. The X-Ray diffraction results showed particles smaller than 0.8 microns hardly transformed. This suggests that austenite in fine particles is highly stabilised(fig.16).

Nagakura et al(77) observed a lower Ms temperature in vapour-deposited film of Fe-(14.35, -27.1)at%Ni alloys, 50-150 nm thick. The films were austenitised by heating and subsequently cooled in liquid nitrogen. The Ms temperature was lower than that in corresponding bulk alloy, and falls both with increasing nickel content, and with decreasing film thickness. However, from the data published by Cech and Turnbull (74) it is apparent that it is the relative number of particles
undergoing transformation at a given temperature that varies with particle size. From the values of the martensite percentages in specimens before and after separation, the relative fractions of the particles containing martensite have been calculated. The amount of martensite decreased with a decrease in particle diameter for a constant cooling rate below 0°C.

They concluded the relative number of particles that undergo transformation to martensite on quenching to a given temperature is proportional to diameter squared or cubed.

Machlin and Cohen (73) concluded from studies of an Fe-29.5 %Ni alloy that the amount of phase transformed is independent of the austenitising temperature, if the grain size is maintained constant. But, Entwisle and Feeney (78) who studied the formation of athermal martensite, expressed the opinion that the "austenitising treatment" is the dominating factor controlling the start of transformation.

It has been shown that the martensitic transformation can be affected by the particle size, but the heat treatment of austenite is also an apparent controlling factor in decreasing $M_s$ temperature.

Martensitic transformation can also be affected by a static magnetic field. The free energy of the $\alpha$ phase in a magnetic field decreases and it is roughly proportional to the strength of the field.

$$\Delta T = \frac{\Delta E_m}{\Delta F (T_0 - M_s)}$$
where $\Delta E_m$ = Magnetic energy
$\Delta F$ = Driving force of transformation
$T_o$ = Equilibrium temperature
$\Delta T$ = Increase in $M_s$ temperature

$\Delta E_m = J_\alpha H$ \hspace{1cm} (10)

where $J_\alpha$ = Intensity of magnetisation of martensitic phase.
and $H$ = Strength of magnetic field.

Satyanarayan et al(79) found a reasonable agreement between the increase in $\Delta T$ obtained by calculation and that found by direct measurement. Increasing the intensities of the magnetic energy gave increasing $M_s$ temperature (fig.17).

\(\alpha\) Effect of lattice vacancies

Since neutron irradiation produces vacancies and interstitials, it must also have an effect on the martensitic transformation. Porter and Dienes (80) observed the effect of neutron irradiation promoting the martensitic transformation in an Fe-25.5 at%Ni alloy. The $M_s$ temperature of the alloy determined after irradiation, however, was found to be lowered by the damage produced. This means that the austenite retained after irradiation is stabilised by the lattice defects introduced by the irradiation.
Fig. (13) The lattice correspondence for the martensite formation in steel, (a) the tetragonal unit cell outlined in the austenite matrix, (b) the lattice pure deformation (Bain strain) carrying the austenite cell into the martensite cell of axial ratio c/a (62).

Fig. (14) Definition of the temperature $T_0$ in a phase diagram and a free energy diagram.
Fig. (15) Schematic representation of electrical resistivity vs. temperature hysteresis loops for presently designated class I and class II thermoelastic transformations. \textit{ref.}(52,69)

Fig. (16). Dependence of the amount of martensite on the particle size of Fe-27.4 at%Ni powders \textit{(76)}.

Fig. (17) Effect of a magnetic field on the free energy. \textit{ref.}(79)
b) The effect of atomic order on the martensitic transformation

The austenite to martensite transformation in the alloy of near Fe₃Pt composition is markedly affected by the degree of atomic order in the austenite. Ordering will lower the energy of both phases, but the ordered inherited from the ordered parent phase will not necessarily have the most stable atomic arrangement for the martensite (81). The lowering of the energy due to ordering may therefore not be so large as in the parent and so generally the ordering in the parent phase lowers the $M_s$ temperature.

Dunne and Wayman (22) have postulated that martensite formation from ordered austenite occurs with a small undercooling and with a small chemical free energy change. In addition, the stability of the austenite relative to martensite increases. A reduction in the chemical energy $\Delta G$, implies lower resistance to shear i.e. ordering has decreased the driving force. Fig.(18) shows schematically how these factors would bring about both a decrease in $M_s$ and a decrease in the change of chemical free energy at $M_s$. (See section 2.5.4)

Table (3) gives calorimetric measurements $\Delta H$ for a number of alloys exhibiting martensitic transformation along with the corresponding free energy change. A large difference in $\Delta G$ for ordered and disordered parent is noticeable, the ordered parent leading to a relatively small undercooling (37).
Fig. (18) Schematic diagram showing variation of chemical free energy change with temperature for both the ordered and disordered transformations.

Ref. (22)

Table (3) Calorimetric measurements of enthalpy and undercooling in some martensitic alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$\Delta H^{\gamma\rightarrow\alpha}$ (J mol$^{-1}$)</th>
<th>$T_0 - M_s$ (K)</th>
<th>$-\Delta G^\gamma_{M\rightarrow\alpha}$ (J mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-Ni</td>
<td>1550</td>
<td>20</td>
<td>92</td>
</tr>
<tr>
<td>Cu-Al</td>
<td>170–270</td>
<td>20–60</td>
<td>19.3 ± 7.6</td>
</tr>
<tr>
<td>Au-Cd</td>
<td>290</td>
<td>10</td>
<td>11.8</td>
</tr>
<tr>
<td>Fe-Ni 28%</td>
<td>1930</td>
<td>140</td>
<td>840</td>
</tr>
<tr>
<td>Fe-C</td>
<td></td>
<td></td>
<td>1260</td>
</tr>
<tr>
<td>Fe-Pt 24% ordered</td>
<td></td>
<td></td>
<td>17</td>
</tr>
<tr>
<td>Fe-Pt disordered</td>
<td></td>
<td>~150</td>
<td>~1260</td>
</tr>
</tbody>
</table>
2.3.7 Martensite tetragonality

Martensite transformed from disordered austenite has a bcc structure (82). Once the austenite is annealed below the ordering temperature, i.e. is ordered, the resultant transformed martensite is now bct, with a c/a ratio of greater than unity. The c/a ratio increases with increasing time at temperature, decreasing $M_s$ (58), or degree of order (56), and all three are inextricably linked together.

Umemoto and Wayman (58) measured the martensite tetragonality in Fe-23, 24, and 25 at%Pt alloys as a function of $M_s$ temperature and ordering time. The c/a ratio of the tetragonal martensite formed from partially ordered austenite indicates that this ratio increases with the decrease in Platinum composition (fig.19) and increases with the ordering time (fig.20). It also indicates that $M_s$ temperature decreases with increase in tetragonality and with departure from stoichiometry.

2.3.8 Martensitic transformations in Fe-Pd and Fe-Pt alloys

a) Introduction

The martensitic transformations of Fe-Pd alloys (30 at%Pd) have shown various interesting characteristics. It is shown that the fcc-fct transition is a thermoelastic transformation. On further cooling the fct martensite transforms to bct martensite non-thermoelastically. 

It has been shown (22,57) that the martensitic transformation in Fe-Pt alloy near the composition Fe$_3$Pt changes from fcc to bcc (non-thermoelastic) and from fcc to bct (thermoelastic)
with increase in the degree of long range order of the austenite. Several transformation characteristics such as $M_s$ temperature and martensite tetragonality are influenced. In the following section, the characteristics of martensitic transformation and the parameters that might influence the transformations in Fe-Pd and Fe-Pt alloys are outlined.

b) Martensitic transformation in Fe-Pd alloys

The martensitic transformations in Fe-Pd alloys with Palladium composition in the range of ~ 23-34 at% has been investigated by many authors (83,84,85,86,87,88) and the following characteristics of the transformation have been reported:

1) The fcc-fct transition is a thermoelastic martensitic transformation, and the c/a ratio of the fct martensite gradually decreases from unity with decreasing temperature. Associated with the fcc-fct transformation there exists the shape memory effect.

2) The fct martensite transforms to bct martensite non-thermoelastically on further cooling.

Matsui et al (87) reported a new fct phase in Fe-Pd system using a low temperature X-Ray diffraction technique in the Pd composition range 24-34 at%. Their results suggest that the transformation occurs in the successive sequence of fcc - fct - bct and the transformation fcc - fct is almost reversible while the transformation fct - bct is irreversible. It is also found that the $M_s$ temperature is very sensitive to the Pd content. The metastable phase diagram of the Fe-Pd system determined by the $M_s$ temperature measurements (86) fig.(21) suggests that the fct
and bct martensite phases co-exist at room temperature in an Fe-29.4 at% Pd alloy, and the bct martensite is not observed in an Fe-30.6 at% Pd alloy after being cooled to liquid helium temperature. In this region, the volume ratio of bcc and fct phases at room temperature depends on the quenching rate from 1150°C.

Historically, Hultgren and Zapffe (4) reported that the bcc martensite phase exists in the Fe-Pd alloys containing less than 20 at% Pd. But, Sugiyama et al (86) found the fcc austenite phase containing less than 24.9 at% Pd was transformed to a bcc martensite phase and an Fe-27.7 at% Pd alloy was transformed to bct martensites.

Oshima et al (88) determined the structure and phase transition of Fe-Pd alloys in the 23.6 and 49 at% Pd range by means of X-Ray diffractometry, optical and TEM techniques. They have shown (fig. 22) the transition temperature depends sensitively on the Pd concentration, and that the axial ratio is progressively reduced from unity with decreasing temperature. Fig. (23), shows the temperature dependence of lattice constants and c/a axial ratio for various Fe-Pd alloys after cooling.

The transformation temperature from fcc - fct structure occurred at 280, 186, and 84 K for 30, 32, and 33 at% Pd alloys respectively.

The above results are also consistent with the phase transformation for a single crystal of thermally quenched 28 at% Pd. Sato et al (89) demonstrated fcc - fct transformation at about 265 K using neutron inelastic scattering measurements. A 37 at% Pd alloy did not undergo a structural transition.

Table (4) illustrates a summary of structures with
corresponding lattice parameters for a given composition in Fe-Pd alloys.

Furthermore, the relation between the fct and bcc martensites in the Fe-Pd alloy with 23.6-30.6 at%Pd was examined using X-Ray and TEM by Oshima (90). The bct martensite was observed for alloys with 25 and 28.7 at%Pd quenched from austenite to room temperature. Although no fct martensite was observed in these alloys, the morphology of the bct martensite strongly suggested that the austenite transformed to the martensite through a prior fct structure.

Oshima (90) investigated successive martensitic transformations of fcc-fct-bct in Fe-Pd (~30at%). It is found that the transformation temperature from fcc to bct becomes lower than that of fcc-fct, and the fct phase is not a transitional phase to bct but an independent phase.

Alternatively, Foos et al (91) considered the fct phase as a transitional phase or a precursor of bct martensite rather than an independent martensite phase.

However, it is now concluded that the fct phase is not a transition phase in the fcc-bct martensite transformation but a low temperature phase, since in the composition range 30.6 to 32 at%Pd it never transforms to bct martensite on further cooling.

A characteristic precursor, "tweed" structure has been observed within these alloys in a certain temperature range above the fcc-fct transformation temperature; the origin of tweed was found to be the thin platelets with tetragonal distortion formed in the fcc austenite.(90)

It has been suggested that tetragonal distortion of bct
Martensites of disordered Fe-Pd alloys are associated with the tetragonal (fct) distortion of the fcc austenite. Oshima et al (92) observed the tweed microstructure in Fe-Pd alloys with Pd less than 32 at% in which fcc-fct martensitic transformation takes place. It appeared in the temperature range up to 100°K above the $M_s$ temperature.

c) Martensitic transformation in Fe-Pt alloys

Disordered Fe-Pt alloys near the composition Fe$_3$Pt transform non-thermoelastically, from fcc austenite to bcc martensite. With increasing degree of order in the austenite, the transformation changes to a thermoelastic type. The martensite transformation is dependent upon both the degree of order and the Platinum composition. The characteristics of thermoelastic and non-thermoelastic martensitic transformation in 24 at%Pt alloy were studied by Tadaki et al (55). They concluded that the thermoelastic martensite has a bct structure, and the tetragonality becomes still higher with progress of austenite ordering, reaching $c/a = 1.106$ in an alloy with "S" = 0.8.

In 1978, Foos et al (93) observed a slight tetragonal distortion in an ordered fcc Fe$_3$Pt alloys before transformation to bct and considered this fct structure as a transitional phase leading to bct martensite.

Muto et al (94) systematically studied the fcc-fct and fcc-bct martensitic transformations in ordered and disordered Fe$_3$Pt in the range of 22.6-26.5 at%Pt. By means of "in situ" observation it is found that the transformation did not proceed
successively as fcc-fct-bct. They suggested that the fcc-fct transition is not a precursor of the transformation to the bct phase as suggested by Foos et al(93), but a competing transformation. It is considered that the presence of tweed is a precursor of the fcc-fct transition independent of the fcc-bct(bcc) transformation.

A similar transformation sequence was observed in Fe-Pd alloys. But the fct phase is considered to be a stable low temperature structure. This is because the fct phase no longer transformed to bct in the region 30.6-32 at%Pd.

the Matsui et al(95) studied low temperature structure of Fe-Pt alloys and an fct structure was found for the well-ordered alloys near 25 at%. Though the structure was not observed by (96,97), the discrepancy between the results is explained to be due to the degree of order "S" of Fe₃Pt superlattice. Fig.24 shows a low temperature phase diagram of Fe-Pt alloys (95). The following conclusions have been drawn:

<table>
<thead>
<tr>
<th>at%Pt</th>
<th>phase transformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>fcc      bct      Order</td>
</tr>
<tr>
<td>24-26</td>
<td>fcc      fct      &quot;</td>
</tr>
<tr>
<td>26</td>
<td>no transformation   &quot;</td>
</tr>
<tr>
<td>25</td>
<td>fcc      bcc      Disorder</td>
</tr>
<tr>
<td>27</td>
<td>fcc      fct      &quot;</td>
</tr>
<tr>
<td>28</td>
<td>no transformation   &quot;</td>
</tr>
</tbody>
</table>

The partially ordered 25 at%Pt transforms as fcc-fct-bct and it is found that the transformation depends on the degree of order. The new fct phase found in the ordered and disordered Fe-Pt alloys is similar to the case of Fe-Pd alloys.
Fig. (19) Variation in Ms temperature as a function of martensite tetragonality (c/a) for Fe-23, 24 and 25 at%Pt alloys. ref. (58)

Fig. (20) Variation in martensite tetragonalities as a function of ordering time at 550°C for Fe-23, 24 and 25 at%Pt alloys. ref. (58)
Fig. (21) Change in Ms temperatures of martensite in Fe-Pd alloys as a function of Palladium concentration.

ref. (86)

Fig. (22) Temperature dependence of lattice constants and c/a ratio for 32 and 30 at% Pd alloys.

ref. (88)
Fig. (23) Changes in lattice parameters (a) and c/a (b) for Fe-Pd alloys by cooling. (90)

Table (4) Structure and lattice spacings in Fe-Pd alloys. ref. (94)

<table>
<thead>
<tr>
<th>at% Pd</th>
<th>structure</th>
<th>a(nm)</th>
<th>c(nm)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.0</td>
<td>bcc</td>
<td>0.2953</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>23.6</td>
<td>bcc</td>
<td>0.2952</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>25.0</td>
<td>bcc</td>
<td>0.2942</td>
<td>0.2998</td>
<td>1.019</td>
</tr>
<tr>
<td>27.7</td>
<td>bct</td>
<td>0.2942</td>
<td>0.2998</td>
<td>1.019</td>
</tr>
<tr>
<td>28.0</td>
<td>fcc</td>
<td>0.3755</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>27.0</td>
<td>fcc-fct-bct</td>
<td>0.375</td>
<td>0.3636</td>
<td>0.916</td>
</tr>
<tr>
<td>29.7</td>
<td>fcc</td>
<td>0.386</td>
<td>0.3636</td>
<td>0.916</td>
</tr>
<tr>
<td>30.0</td>
<td>fcc</td>
<td>0.3758</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>37.0</td>
<td>fcc</td>
<td>0.3775</td>
<td>0.3712</td>
<td>0.983</td>
</tr>
</tbody>
</table>
Fig. (24) Low temperature phase diagram of Fe-Pt Invar alloys proposed by (95). Solid and dashed curves indicate the disordered and well ordered alloys respectively.
2.4 The Invar effect

2.4.1 Introduction
Invar alloys are characterised by an anomalously small thermal expansion coefficient over a wide temperature range. Fe based alloys such as fcc \( \text{Fe}_{1-x} \text{Ni}_x \), \( \text{Fe}_{1-x} \text{Pt}_x \) and \( \text{Fe}_{1-x} \text{Pd}_x \) (containing 60 to 76 at% Fe) are typical examples of Invar alloys. The composition is normally situated close to where the martensitic transformations temperature starts to decrease rapidly.

In addition, Invar alloys possess other anomalous properties, such as a large pressure dependence of the Curie temperature and a positive temperature dependence of the elastic constant below the Curie temperature, large forced magnetostriction, large magnetic susceptibility in the saturation range and anomalous electrical resistivity.

The Invar properties of Fe-Pt and Fe-Pd alloys have not been investigated specifically in the present work, but some of the Invar effects could be significant, particularly changes in lattice constant and Curie temperature \( (T_C) \) and the possibility that heterogeneous fluctuations in composition arise in this composition range.

2.4.2 Theory

The Invar behavior was first observed by Guillaume in 1896 in a 30 at% Ni which was magnetic and had an expansion coefficient two-thirds of Platinum (98).

Several theories have been suggested to explain the Invar
effect. For example, statistical microstructural composition fluctuations of the Fe-Ni alloy by Kachi et al. (99), the band theory by Mathon and Wohlfarth (100), competing electronic states suggested by Weiss (101). However, the true explanation is likely to encompass all three approaches (102).

Weiss (101) extended the idea that there are two electronic configurations of the iron atom in an fcc lattice to Fe-Ni Invar alloys. He proposed that the energy difference, between the two electron levels depends upon the surroundings of the iron atom, with the difference going through zero near the Invar composition. In pure fcc iron, the antiferromagnetic fcc\textsubscript{1} state is the ground state with a smaller lattice constant. On alloying the ferromagnetic fcc\textsubscript{2} state becomes the ground state above 29 at\%Ni.

Asano and coworkers (103) have investigated many aspects of the Invar anomaly in fine grained Fe-Ni alloys. Their results indicate the co-existence of ferromagnetic and anti-ferromagnetic phases, enabling them to propose a concentration function model explaining the Invar characteristics. In this model, the paramagnetic lattice constant is assumed to be smaller than the ferromagnetic lattice and a distribution of Curie temperature causes successive regions to transform to the paramagnetic state as the temperature is increased.

2.4.3 Fe-Pt Invar alloy

The Invar effect in Fe-24-30 at\%Pt is even more pronounced when
compared with Fe-30 at%Ni. The thermal expansion coefficient becomes negative below the Curie temperature (104). As a result the room temperature lattice parameter as a function of platinum concentration shows a small deviation from Vegards law in the Invar range.

Ordering stabilises the ferromagnetic state and therefore generally reduces the Invar effect. However, partial ordering of the alloy with less than 25 at%Pt may show an increased Invar effect because particular combinations of order and solute content place the iron atoms into a condition of critical ferromagnetism.

Tadaki et al (55) considered an increase of lattice parameter in ordered 24 at%Pt is associated with the Invar effect of the austenite. They also showed that the Invar effect does not have significant influence on the martensite transformation in an alloy annealed for short periods; but for the alloy annealed for longer periods, Curie temperature (T_c) becomes higher than M_s and the Invar effect can possibly influence the transformation. However, for the Invar effect to become decisive, a critical temperature interval between T_c and M_s is considered to be necessary.

2.4.4 Fe-Pd Invar alloy

Invar properties of fcc Fe-Pd alloys were first investigated by Kussmann and Jessen (8). They reported that the thermal expansion coefficient of Fe-Pd alloys quenched from high temperature fcc phase shows a deep minimum around 30 %Pd, while
in the equilibrium phase diagram, the Invar composition is in
the two phase bcc + fcc region.
Foos et al (105) suggested that tetragonal distortion of the
c/a parameter with decrease in temperature in the Fe-Pd
austenite alloys (25-32 at%Pd) is associated with the strong
Invar effect. This was characterised by special features in
electron microscopy. It is suggested that the Invar effect
exists for a wide range of temperatures from the Curie
temperature (350°C) to room temperature.
2.5 Magnetic effects

2.5.1 Introduction

It is well known that in Fe-Pt alloys, chemical ordering depresses martensite transformation temperatures as well as increasing the Curie temperature (106). The extent to which, magnetic ordering can affect $M_s$ temperature and consequently $T_0$ is less documented but equally important. Kaufman and Cohen (107) made a detailed study of the relation of martensite formation to the intrinsic thermodynamic properties of iron alloys including magnetic components for pure iron. However, they did not include an explicit formula for the effect of solutes on the magnetic force energy.

Although in this thesis, magnetism will not be dealt with in detail, the effect of magnetism on the phase boundaries and the calculation of $T_0$ has to be considered.

2.5.2 Theory

The importance of a magnetic contribution to the stabilities of magnetic metals and alloys was recognised by Zener (108) who associated the bcc/fcc phase transformation with changes in magnetic properties.

Initially, it was considered that the total free energy in pure iron splits into magnetic ($\Delta G_{\text{mag}}$) and non-magnetic ($\Delta G_{\text{nm}}$) components and the magnetic terms are taken to be responsible for deviation at high temperatures. This implies a normal behaviour of free energy at low temperature.

Weiss and Tauer (109) extended Zener's ideas and proposed
further additional features to consider the magnetic component. They are:
a) The use of the Bohr magneton number "B" as well as the Curie temperature "T_c" for an evaluation of the magnetic component.
b) A formal conversion of the relative magnitudes of $\Delta G_{\text{mag}}$ and $\Delta G_{\text{nmag}}$ into proper quantitative thermodynamic functions.
c) The inclusion of entropy of mixing terms.

Miodownik (110) has expressed the relationship between the free energy of ferromagnetic and paramagnetic bcc iron in the vicinity of the Curie point essentially by graphical means (fig.25). This model has advantages over the Zener treatment in analysing the effect of alloying elements. Various modifications have since been made by Inden (111) and Hillert (112). More recently, Chang et al (113) considered the magnetic contribution by using an alternative empirical model provided the Curie temperature and the magnetic moment of the alloy are known. Combining this magnetic term with the non-magnetic term, extrapolated from higher temperature, they calculated appropriate free energies for the Fe-Ni system, but did not specifically apply this to the martensite transformation.

2.5.3 Effect of magnetic and chemical ordering on $T_c$ and $M_s$

The extent to which atomic ordering and disordering and Pt composition can effect Curie and $M_s$ temperature for Fe-Pt the alloys around fcc-bcc phase boundary is shown by Sumiayma et al (106) in fig. (26).
Skinner and Miodownik (114) considered the effect of chemical ordering on the martensite transformation of ordered Fe-24.5 at%Pt alloys. By making certain assumptions, a new model is proposed which quantitatively explains the observed effects when both chemical and magnetic order are taken into account. The following sequence of effects was considered:

a) The free energy of a chemical disordered alloy without any magnetic effect (fig.27a).
b) A chemically disordered alloy with magnetic contributions (fig.27b).
c) The effect of chemical ordering plus increased magnetic effects due to higher $T_c$ are shown in fig.(27c).
d) The effect of reducing elastic constraints (fig.27d).

Fig.(27e) shows the overall effects.

The free energy of the martensite phase is taken as the ground state ($\Delta G = 0$) and the positions of the free energy curves of the austenite phase are fixed by the available data, as shown in Table (5).

Experimentally, it is shown $M_s^{(do)} - M_s^{(od)} = 125^0K$, while correspondingly $T_o^{(do)} - T_o^{(od)} = 300^0K$. This basically takes both magnetic and chemical ordering into account. However, the shift in $M_s$ that can be directly attributed to chemical ordering for alloys where $M_s > T_c$ (58) is only $\sim 50^0K$. fig.(28).

This shows that the effect of chemical ordering is small when the Curie temperature is well below the $M_s$, and emphasises the need to make allowance for magnetic contributions.
2.5.4 Estimation of magnetic free energy

The energy of magnetization is generally a function of two variables, the Curie temperature $T_c$ and the number of magnetic electrons $B$ (Bohr Magnetons). Because there can be a continuous variation in the degree of long range order, the transformation is spread over a range of temperature below $T_c$. Miodownik (115) assumed that the enthalpy ($H$) and entropy ($S$) as a function of temperature can be derived from "$H"(max)$ and "$S"(max)$ as the following:

$$\Delta G_{mag}(T) = \left[ -0.9RT_c \ln (B^0 + 1) \right] \frac{B^t}{B^0} - RT \ln \left( \frac{B^0 - B^t}{B^0} \right) + 1$$

(11)

Where $B^t = B^0 \left[ 1 - (T/T_c)^6 \right], \quad (T < 0.9T_c)$ \hspace{2cm} (12)

$B^t = B^0 \left[ \frac{1}{2} + 10(T/T_c - 1) \right], \quad T > 0.9T_c$ \hspace{2cm} (13)

$$\Delta G_{mag} = RT \ln(B + 1) \phi(t)$$

(14)

Where $\phi(t) = T/T_c$

for $t > 1$,

$$t = \frac{1}{K} \left( t^{-n_1}/C_1 + t^{-n_2}/C_2 + t^{-n_3}/C_3 \right)$$

(15)

for $t < 1$,

$$t = \frac{1}{K} \left( -K + \frac{n_4}{C_4} pt + \frac{n_5}{C_5} (1/p - 1) \frac{t^{n_6}}{C_6} + \frac{t^{n_7}}{C_7} + \frac{t^{n_8}}{C_8} \right)$$

(16)

Where $K = \frac{C_9}{C_{10}} \left( 1 + \frac{C_{11}}{C_{12}} (1/p - 1) \right)$ \hspace{2cm} (17)

$n = \text{constant}$

The function is the same for both bcc and fcc states except $p = 0.4$ for bcc and $p = 0.28$ for fcc state. The overall magnitude
of the magnetic free energies of the two methods is in good agreement and each have their advantages and disadvantages. The Swedish (116) formulation has been incorporated into a method for minimising free energies in binary and multicomponent systems (poly) and is the method used in chapter 6 to calculate the phase boundaries in the Fe-Pt (disordered) system.

Returning to the case of the 24.5 at%Pt alloy, the magnetic free energy contribution below $T_c$ (od & do) has a large effect in both ordered and disordered cases. The overall $\Delta g^{fcc-bcc}$ reaches a maximum value, followed by a rapid decrease in free energy as the temperature decreases fig.(27a). The model also predicts the possibility of reversion of $bcc'$-fcc on cooling, for alloys which exhibit a critical combination of $T_o$ and $T_c$. This is because sufficient magnetic free energy can cause the $G(fcc)$ curve to bend back and potentially recross the $G(bcc')$ curve at low temperature (fig.27c).

Not only does the magnetic ordering affect $\Delta G$, but it also plays a part in reducing the elastic constants with temperature and therefore the elastic constraints operating at $M_S$.

2.5.5 The effect of magnetic transition on phase boundaries

The most obvious effect of a magnetic transition on phase boundaries is a change in solubility of a second phase. It occurs whenever the Curie temperature intersects a transus line (116). In this region the relative magnetic contribution to the thermodynamic functions and phase stabilities of magnetic metals and alloys becomes important. In a review Miodownik (117) discussed the various possible changes in phase.
equilibria due to magnetic interactions.

The stability of the magnetic phase alloy is governed by two terms: the chemical and magnetic contributions. The compositional dependences of the magnetic free energy vary in such a way that when added to the chemical term a hump in the free energy curve is produced. This hump then causes the formation of a miscibility gap. Fig. (29) shows a schematic phase diagram displaying a tricritical point. (118). A similar miscibility gap has been calculated by Chaung et al. (119) in the Fe-Ni system. Absolute proof is difficult to illustrate in this system because of the similarities in lattice parameters of the two phases. Mossbauer spectra of the alloy determined at room temperature do reveal the presence of two magnetic states of iron, but it is still not clear whether this reveals segregation or real phase separation.
Fig. (25) Treatment of ferromagnetism in the vicinity of the Curie temperature

ref. (110)

Fig. (26) Effect of ordering on Tc and Ms in Fe-Pt alloys

ref. (106)

Fig. (29) Schematic phase diagram exhibiting a tricritical point due to magnetic interaction.

ref. (118)

Fig. (28) Depression of the Ms on ordering for selected Fe-Pt alloys.

ref. (58)
Fig. (27)a Absence of both chemical ordering and magnetic effect.

b) No chemical ordering, but magnetic effect, Tc low.

c) Hypothetical chemical ordering. It is assumed Tc(od) > Tc(do).

d) Chemical and magnetic ordering reduces elastic constant.
e) Effect of magnetic and chemical ordering on $T_c$ and $M_s$.
ref.(50)

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Table (5) Quantitative values used in Figs.27.
2.6 Thin films deposition Techniques

2.6.1 Introduction
There are various methods of producing thin films, and these may broadly be classified into two separate groups:
   a) Chemical methods
   b) Physical methods
Among chemical methods, the most important are electrolytic, electroless, anodic oxidation and chemical vapour deposition. In the present work, the use of the vapour deposition technique has been implemented to study the structure of Fe-Pd and Fe-Pt alloys in thin films and so discussion will be confined to physical methods.

2.6.2 The physical methods for producing thin films
The physical methods for preparation of thin films are classified in two groups:
   1) Vacuum evaporation
   2) Cathodic sputtering

a) Vacuum evaporation
In this method, thin films are produced by the condensation of vapourised material on to a cooler substrate. An excellent review of the subject is given by Holland (120). As a summary, the process is outlined as the following sequences:
   a) Transformation of solid material to a vapourised state by means of sufficient heat.
b) Deposition of these particles and rearrangement on the surface of the substrate. The liberated particles travel in space with their thermal velocities along a straight line until collision with another particle. The fraction of evaporated atoms that undergo no collision in traversing the source to substrate distance "d" is \( \exp(-d/\lambda) \), where \( \lambda \) is the mean free path of molecules in the residual gas in the vacuum chamber. According to Chopra (121), in order to prevent considerable dispersion of evaporated particles for distance "d" of 10 to 50 cm in a vacuum evaporator, a pressure less than \( 10^{-5} \) torr is necessary, Table (6).

b) Cathodic sputtering

Sputtering occurs when a target (the cathode) is bombarded with energetic particles which cause the ejection of surface atoms. The ejected atoms may then be condensed on a substrate to form a thin film. If ejection is due to positive ion bombardment, it is referred to as cathodic sputtering. Sputtering minimises the problem of controlling the composition of multicomponent films, because under steady conditions material arriving at the substrate should have the same composition as the cathode. Winter et al (122) proposed a simple model which predicts the composition of sputtered multicomponent thin films. The results of their studies suggest that the film composition is a function of vapour pressure, sputtering rate, atomic size, system geometry, sticking probabilities, and the sputtering coefficient.
Kay (123) and Maissel (124) have given an excellent review on sputtering. A simple cross section of a sputtering system is shown in fig.(30). The main types of sputtering systems may be distinguished as:

a) Glow discharge system
b) Ion beam system
c) Glow discharge sputtering

d) Ion beam sputtering

This process occurs when an electric field is applied between the cathode and substrate in a gas at low pressure, \(10^{-1}\) to \(10^{-3}\) torr. The gas is ionised positively.

Sputtering was first recorded in 1852 by Grove (125) who noticed the disintegration of cathodes in a glow discharge tube with tube pressure of order of 0.1 torr.

Penning and Moubis (126), considered the dependence of mean free path on pressure, and coupled a magnetic field to their discharge tube which increased the electron path length and enabled the discharge to be maintained at a lower pressure.

d) Ion beam sputtering

Features of ion beam sputtering are that, sputtering can take place under high vacuum condition with a field free region between target and substrate. In addition, the target can be bombarded under oblique incidence. Considering the reaction at the target, the material is ejected in a neutral form. The ejection is a function of the crystallographic orientation of the target (127) and the
velocity of the ejected material is much higher than that in the evaporation case. The velocity distribution of sputtered atoms compared with evaporated atoms for a polycrystalline target is shown in fig. (31).

Frank and Ghander (128) have developed a simple ion beam source using a saddle field. An increase in efficiency of ionisation enables low chamber pressures to be maintained during deposition ($10^{-5}$-$10^{-4}$ torr). However even with this design the flux of ions is much smaller than with evaporation sources. In the event this proves to be an advantage in relation to attaining equilibrium in the deposited films (see section 4.3).

### 2.6.3 Composition of multicomponent alloys

It has become apparent that in sputtering from a multicomponent target, the target composition is not necessarily reproduced in the film if the preferential loss of one constituent occurs. Winters et al (122) suggested a model to predict the composition of sputtered multicomponent films as a function of vapour pressure, sputtering rate, atomic size, system geometry, probability and sputtering coefficients.

However, the composition of deposited films can also be predicted from the Raults law:

$$n_a/n_b = \left(\frac{c_a}{c_b} \cdot \frac{P_a}{P_b}\right) \cdot \left(\frac{m_b}{m_a}\right)^{1/2} \quad (18)$$

where
- $c$ = fraction of component in target
- $m$ = mol. wt. of the element
- $n$ = mole fraction of element in thin film
- $p$ = equilibrium vapour pressure of element.
A satisfactory method of preparing alloys and compounds with precisely controlled composition is to evaporate each component from a separate source, and having the substrate itself at an elevated temperature. This so-called three temperature method gives good results (120, 129).

Whener et al (130) found that different materials possess different sputtering yields. This is defined as the average number of atoms ejected from the target per incident ion. It increases with the increase of ion energy and mass. It was realised that the sputtering yield is closely related to the electron concentration in the "d" shells and to the reciprocal of the heat of sublimation of the target material.

In order to increase the evaporation rate and avoid some of the problems existing in direct heating of the materials, other methods such as electron beam evaporation can be utilised. In this method, energised electrons heat the surface of the source material, a small molten pool forms and the material evaporates.

During ion beam bombardment, the target temperature could increase and it depends on the ion beam flux intensity. This is due to the collision between particles of ionised gas and target alloy. This is consistent with Baders and Snouses (131) result that the yield for polycrystalline copper is decreased as the temperature is increased. By means of water cooling the target, consistent deposition conditions can be obtained.
Table (6) Some facts about the residual air at 25°C in a typical vacuum used for film deposition. ref.(121)

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<th>Pressure, Torr</th>
<th>Mean free path, cm (between collisions)</th>
<th>Collisions/sec (between molecules)</th>
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<th>Monolayers/sec †</th>
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<td>900</td>
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<td>44</td>
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<tr>
<td>10⁻⁵</td>
<td>510</td>
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<td>3.8 × 10¹⁵</td>
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<td>3.8 × 10¹³</td>
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<td>10⁻⁹</td>
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<td>9 × 10⁻³</td>
<td>3.8 × 10¹¹</td>
<td>4.4 × 10⁻⁴</td>
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*1 Torr = 1 mm Hg.
†Assuming the condensation coefficient is unity.

Fig.(30) Simple cross section of sputtering system.

Fig.(31) Velocity distribution of sputtered atoms compared with evaporated atoms. ref.(127)
2.6.4 Stages in formation of thin films

a) Condensation
Thin film specimens can be prepared by any of the methods described in section 2.6. Atoms arrive at the substrate randomly and move to find a suitable minimum energy position. The ratio of atoms that are absorbed by the surface to those arriving is called the sticking coefficient (120, 121). A sticking coefficient of less than unity is achieved when the impinging atom has a high kinetic energy. The adsorbed adatom losses some of its energy by a series of atomic collisions to the substrate (121). The time required for an incident atom to lose its excess kinetic energy and achieve thermal equilibrium with the substrate is of order of "2/ν" where "ν" is the adatom surface vibration frequency (132). The adatom moves over surface due to a combination of thermal energy from the substrate and excess energy which is retained from the particle and has not yet been fully accommodated. The basic atomic processes in thin film deposition are shown in an energy diagram (129) (fig.32).

b) Nucleation and growth

Film growth may be divided into certain stages as distinguished by Pashley et al (133):

a) Nucleation, formation of statistically distributed nuclei over the substrate.

b) Growth of the nuclei and formation of larger islands.

c) Coalescence of islands and formation of a connected network.
d) Filling of the holes in the network structure often involves secondary nucleation within the holes. Processes occurring in the nucleation and growth of crystals on a substrate is shown schematically in fig.(33).

c) **Basic modes of growth**

Three basic growth mechanisms can be considered, depending on the strength of interaction between the deposited atoms and the substrate material. The three basic modes of thin film growth are illustrated schematically in fig.(34).

1) The Frank and Van der Merwe (134) mechanism leading to layer by layer growth. The layer growth occurs when the extension of the smallest stable nucleus occurs overwhelmingly in two dimensions, resulting in planar sheets of atoms or molecules.

2) The Volmer-Weber (135) mechanism, characterised by three dimensional nucleation and island growth. The rates of growth in the different directions are, in general, not uniform.

3) The Stranski-Krastanov (136) mechanism, starting with the adsorption of a monolayer of the deposited material with subsequent nucleation on top of this layer.

When island growth occurs, the density of islands as a function of deposition rate, substrate temperature, and time is important, as is the manner in which islands coalesce to form a continuous film.

The mechanism of coalescence is analogous to that of sintering (137) of two spheres. In terms of surface mobility of adatoms over the surfaces of the deposit and islands, Pashley et
al(133) interpreted various coalescence effects.

2.6.5 Physical properties of thin films

Physical properties of vacuum deposited films are well known to depend on experimental parameters, such as evaporation rate, substrate temperature and residual gas pressure. Thin films contain a high density of defects, namely grain boundaries and dislocations in addition to vacancies present within the grains. The metallurgical and physical properties of bulk alloys and formation of thin films were discussed in the preceding sections.

The main differences in the physical properties of thin films in comparison to bulk materials are outlined as the following:

a) Thin films have finer grain size than bulk materials.

b) At temperatures below which recovery processes occur, thin films have a high dislocation and vacancy density, compared to the bulk samples.

c) High ratio of surface area/volume in thin films.

a) Grain size in thin films

In general, thin films contain a larger grain boundary area than bulk materials because the average grain size is generally smaller. In thin films, the grain size increases with the increasing surface mobility of adatoms and clusters during deposition when substrate temperature increases during deposition (138,139). Murr (138) and Matthews (139) showed a critical temperature where epitaxial effects cause a massive
increase in grain size to the order of 1000 nm.

Epitaxy occurs usually in a narrow temperature band with specific substrate deposit combinations and can be described as the growth of single crystal films.

Parameters such as deposition rate, substrate temperature, annealing temperature, thickness of the films, vacuum pressure, and presence of impurities have a significant effect on the structure and properties of vapour deposited thin films (138,139,121). Fig.(35) shows the schematic variation of the grain size of pure metal films as a function of (a) substrate temperature during deposition, (b) rate of deposition, (c) film thickness, (d) annealing temperature subsequent to deposition.

At a reasonable deposition rate, the condensed nuclei on the substrate are very close to each other, of the order of 10 nm. This distance can be further reduced by increasing the nucleation rate. A grain size of this magnitude is often reported in thin films (121,140).

The mobility of the impinged atoms on the surface increases with increasing deposition rate, but, atoms becomes buried under subsequent layers before much diffusion can take place (141). A smaller grain size is observed at higher deposition rate (138,139).

Pashley et al(141) have suggested vacuum deposition pressure, influence the structure and properties of thin films. In poor vacuum, mobility of the surface atoms on the growing film reduces due to the gas entrapment on the surface and hence
affects the grain size (138, 139, 141).

b) Defects in thin films

Basset et al (142), Pashley (141), showed that evaporated single crystal films of metals commonly contained an extremely high density of lattice defects. Defects in thin films include dislocations, point defects, twins, grain boundaries and stacking faults.

High dislocation density is reported in thin films (143). Dislocations are the most frequently encountered lattice defect in thin films and may be formed on coalescence of islands (138). If the islands are very small, they can move or rotate somewhat to eliminate the difference in orientation.

Dislocations are built into the films during its final stage of growth, as the continuous network of deposits develops into a continuous film, free of holes.

Generally, the lattice constants of sputtered alloys are slightly larger (~0.5%) than those of the bulk alloys (145). The lattice expansion may be related to a loosely packed structure produced by incorporation of gas atoms (eg. Ar) (146).
Fig. (32) Energy diagram of the basic atomic processes in thin film deposition. \textit{ref.} (129)

Fig. (33) Processes occurring in the nucleation and growth of crystals in substrates.

Fig. (34) The three basic modes of thin film growth.

Fig. (35) Schematic variation of the grain size of pure metal films as a function of a) substrate temperature during deposition; b) rate of deposition; c) film thickness; and d) annealing temperature subsequent to deposition. \textit{ref.} (121)
2.7 Diffusion in thin films

2.7.1 Atomic theory of diffusion

The rate of structural changes when metals and alloys are heat treated is controlled by the rate at which the atoms in the lattice change position. There are two common mechanisms by which atoms can diffuse through a solid and the operative mechanism depends on the type of site occupied in the lattice. Substitutional atoms usually diffuse by a vacancy mechanism whereas interstitial atoms migrate by forcing their way between the larger atoms, i.e. interstitially. In this section, mainly transport mechanisms by surface diffusion have been considered.

2.7.2 Transport mechanisms in surface diffusion

The surface transport of atoms plays an important role in the growth of crystals from the vapour. A thin film has a high density of defects, fine grain size (∼10 nm) and dislocation density as high as $10^{10} - 10^{11}$ /cm$^2$ (121,140). These defects are normally in close proximity or directly connected to the surface.

Grain boundary and dislocations in thin films are known as short circuit paths for diffusion, because diffusion along them is orders of magnitude faster than in the lattice (144). Gupta and Ho (147) distinguished between the various diffusion processes and found a correlation between activation energies for diffusion along the individual paths and melting temperature.
The molecules incident on a surface may do one of several things. They may desorb from the surface immediately, or after undergoing some surface diffusion. The mean stay time of an adatom on the surface "t" depends upon its desorption energy $Q_a$.

$$t = \frac{1}{v} \exp\left( \frac{Q_a}{k'T} \right)$$  \hspace{1cm} (19)$$

where "v" = the adatom surface vibration frequency. In a time "t", the mean square distance that an adatom diffuses in a particular direction,

$$\langle X \rangle = (2D_s \cdot t)^{1/2}$$

$$= (2vt)^{1/2} a \exp \left( -\frac{Q_s}{2kT_s} \right)$$  \hspace{1cm} (21)$$

where $D_s$ = the surface diffusivity;

$$D_s = D_0 \exp\left( -\frac{Q_s}{kT_s} \right)$$  \hspace{1cm} (22)$$

t = the time an atom can move on the surface before being covered by incoming atoms.

v = the atomic vibrational frequency.

$Q_s$ = the activation energy for surface energy.

$k'$ = the Boltzmann's constant.

$T_s$ = the substrate temperature.

Each atom diffuses for $(a/r)$ second before being surrounded and restricted by the adjacent atoms, where;

a = atomic spacing

r = deposition rate.

Thus the mean diffusion distance per depositing atom is (121);

$$\overline{X} = (2v \cdot a/r)^{1/2} a \exp \left( -\frac{Q_s}{2kT_s} \right)$$  \hspace{1cm} (23)$$
The temperature dependence of the diffusion coefficient \(D\) is
described by the Arrhenius equation:

\[
D = D_0 \exp \left(- \frac{Q}{kT} \right) \tag{24}
\]

where \(D_0\) = Temperature "frequency factor"

\(Q\) = Activation energy

\(T\) = Temperature in (K).

Gupta (148) in his remarks concluded that diffusion in thin films is generally controlled by their microstructure which largely involves fast atomic transport along the grain boundaries, to a lesser extent along dislocations and lattice diffusion within the grains.

He has measured some important techniques for measuring diffusion with their capabilities in terms of the magnitude of the diffusion coefficient. Experimental techniques which measure lattice diffusion coefficients less than \(10^{-10}\) cm\(^2\)/sec are suitable for thin films.

Balluffi and Blakely (149) discussed the effect of contribution of the lattice, grain boundary and dislocation to the penetration profile as a function of grain size or the nature of the dislocation and the density present in the films at the temperature of diffusion. Fig.(36) illustrates the dominant mass transport processes for steady state diffusion in broken rectangles as a function of the grain size, the dislocation density and the melting point normalised temperature \((T/T_m)\). \(T_m\)
is melting temperature.

2.7.3 Effects of impurities

Relatively high concentrations of uncontrolled impurities may be present during the film diffusion as a result of the particular fabrication or diffusion conditions which are employed. Two ways in which impurities may affect the diffusion may be distinguished:

1) Impurities may be incorporated in the bulk of the film during initial fabrication and thereby exert an effect on the subsequent diffusion;

2) Impurities in the specimen environment (ie either the atmosphere or the specimen surface or substrate) may diffuse into the film or else produce reactions at the film surface during diffusion in a manner to perturb the diffusion in the nearby specimen volume. Such "near-surface " effects could be especially important in thin films, since all volume elements are close to the surface (148).

Fig.(36) Regimes of grain size and dislocation density over which lattice, G.B, or dislocation diffusion is dominant during steady state diffusion through a thin film specimen of an fcc metal as a function of $T/T_m$.

ref.(149)
2.8 Phase transformation in thin films

2.8.1 Introduction

Most crystalline metals and alloys are produced by the process of solidification from the liquid phase. Crystallisation begins with the formation of solid nuclei, which then grow by consuming the melt. These two processes generally govern the formation of new phases.

The determination of an equilibrium state of solid phase reaction in bulk samples is often a lengthy process which requires a long annealing time at moderately low temperatures. The main factors that accelerate the mixing process in thin film alloys are firstly the diffusion distance \((D_t)^{1/2}\) which is often comparable to the film thickness. Secondly, it is also due to the presence of high defect concentrations in thin films. Consequently, \(D_s \gg D_b\) where \(D_s\) and \(D_b\) are the surface and bulk diffusion coefficients respectively. Therefore, equilibrium state at low temperatures can be reached in a much shorter time (150).

Alloy thin films can be produced by either of two main techniques;

a) Sequential deposition in which layers of the pure elements are sequentially deposited in the required ratio on a substrate to produce a homogenised film by subsequent annealing.

b) Simultaneous deposition: in which a homogeneous film of desired composition is formed as a result of simultaneous deposition of the pure elements, without annealing. However, the initial structure and phase formation of the films produced by each technique are different. At this stage, only thin films
produced by the simultaneous deposition technique are considered.

The objective of this section is to review the capability of utilising thin films for the investigations of structure and relation between phases and substrate temperatures.

2.8.2 Substrate temperature and phase transformation

The growth of a thin film is strongly dependent on the mobility of the atoms deposited on the surface of the growing film. Therefore, the crystallography and structural order of the film can, to a large extent, be controlled by the substrate temperature ($T_s$) during deposition. The distance over which atoms have to migrate to transform into a phase or a multiphase mixture will increase with increasing substrate temperature. At low $T_s$, metastable structures can form because the surface mobility of the adatom is low, while for higher $T_s$, the increased surface mobility of the adatom makes it possible to form equilibrium phases.

2.8.3 Kinetics of phase formation in thin films

Cantor and Cahn (151), found that vapour quenched Al-Ni and Al-Fe alloys prepared by co-sputtering have a higher solid solubility than those prepared by thermal evaporation, and all the equilibrium intermetallic compounds were suppressed and replaced by disordered bcc structures. The $T_s$, below which only
the disordered phase would be formed is predicted based on the mean diffusion distance $\bar{X}$ (equ. 21) a depositing atom could move on the surface before being covered and trapped by further incoming atoms.

If the mean diffusion distance is less than one interatomic spacing, the initially homogeneous depositing atoms cannot move to ordered positions. Equation (21) indicates that the critical temperature for ordering is determined largely by the surface activation energy.

However, the mean diffusion distance per depositing atom increases due to the adsorbed impurities which may lower the effective value of $Q_s$, and the larger value of $v$ for the surface than the bulk value of $10^{13}$/sec.

Cantor and Cahn's (151) work was performed at temperatures of less than $100^0K$ where bulk diffusion could be ignored.

Saunders and Miodownik (152) considered the significance of bulk diffusion at higher temperatures where the atoms that are initially buried by the depositing atoms will be able to move back to the surface and participate again in the diffusional breakdown of the initial homogeneous mixture. This can occur when the distance $a$ recently deposited atom can move due to bulk diffusion, is greater than the thickness of the film covering it. Therefore, an additional time that an atom can spend on the surface is derived. Equation (21) is further modified by including a free energy gradient associated with the breakdown to a two phase mixture.

$$\bar{X} = \left[2v(a/r + D/r^2)\right]^{1/2} \cdot a \cdot \exp\left(-\frac{Q_s}{2kT_s}\right) (\Delta Gt/kT_s)$$

(23)

(see p. 85)
where $\Delta G_t = \text{Integral free energy change on the formation of the equilibrium structure from the initial single phase mixture.}$

and $D_b = D_o \exp(-Q_b/\kT_s)$ \hspace{1cm} (24)

where $Q_b = \text{Bulk activation energy}$

$D_o = \text{Constant.}$

The formation of multiphase structures in co-deposited alloy thin films is controlled by the diffusional breakdown of fully intermixed depositing atoms, so that three kinetic regimes are observed (152).

1) At low $T_s$ the surface mobility is insufficient for the decomposition of fully intermixed depositing atoms and the films contain non-equilibrium single-phase structures.

2) With increasing $T_s$, partial breakdown to non-equilibrium phases takes place.

3) With a further increase in $T_s$ the atomic mobility at the surface is sufficient to allow the full atomic rearrangements necessary to form equilibrium phases.

As the surface diffusion is involved, the kinetics of this breakdown are very rapid and equilibrium can be achieved at surprisingly low temperatures.

2.8.4 Structure of alloys produced by vapour deposition

Vapour quenching techniques such as sputter-deposition and thermal evaporation have been known as a powerful method for producing new alloys. Structure of thin films can be affected
profoundly by the parameters such as rate of deposition, quenching rate and impurities.

In this section, the nature of phase boundaries obtained by vapour deposition techniques are illustrated by a few examples.

Muckherjee and Rogalla (153) in their studies on Fe-Ni-Cr system found a reduction in size of the two phase field as a result of low temperature vapour quenching, (fig.37). The deposition rate was 2 nm/s and the $T_s$ were in the range of $77 - 700^0K$.

The shape and position of the fcc + bcc region was explained by assumption that fcc phase decomposed to (bcc + fcc) at high temperatures by diffusion and at low temperatures, an incomplete diffusionless fcc $\rightarrow$ bcc martensitic transformation occurred during film growth and/or subsequent cooling. From the broadening X-Ray diffraction peaks, the grain size of the films deposited at temperature between 77 and $523^0K$ was estimated to be 20 - 80 nm. They suggested that the two phase bcc + fcc structure is not likely to be formed during condensation even at temperatures as high as $673^0K$. This is because diffusion is too slow to form the two phase structures which requires material to be transported over comparatively long distances before it is buried by newly deposited material.

Similarly, Hentzell et al(154) showed for co-evaporated Ni-Al alloys, that with a decrease in $T_s$, the solid solubility of Al in Ni increases, (fig.38).

Suzuki and Wilts (155) used electron diffraction to determine
the phase boundary of Fe-Ni alloys. Thin films deposited on a single crystal at the rate of about 2 nm/s in the substrate temperature range 25 to 500°C. The phase diagram determined in this way has boundaries which are in fair agreement with the equilibrium boundaries for bulk material above 400°C and deviates markedly below 300°C.

It is shown that the (bcc + fcc) mixture phase disappears below 100°C (fig. 39).

Zhang et al(156) investigated the Fe-Pd phase boundaries by X-Ray diffraction which was produced by an rf sputtering technique. Operational parameter is shown in Table (7). Fig.(40), shows the non-equilibrium phase diagram of the sputter-deposited Fe_{1-x}Pd_x alloys, together with the results of solid quenched Fe_{1-x}Pd_x alloys and the equilibrium phase diagram. Vapour quenching which has quite a high cooling rate produces wider ranges of single bcc and fcc phases. It gives a disordered fcc phase similar to solid quenching.
Fig. (37) Structure of Fe-Ni-Cr films deposited at various substrate temperatures. In (a) A is the equilibrium two phase region determined experimentally for bulk Fe-Ni alloys, whereas (B) was calculated from thermodynamic data for alloys below 673K. The dotted curves labelled (C) are the martensitic start and finish temperatures of bulk Fe-Ni alloys. ref. (153)

Fig. (38) Structure of vapour deposited Al-Ni alloy films for varying substrate temperature. ref. (154)
Fig. (39) Crystal structure of evaporated Ni-Fe films. ref. (153)

Fig. (40) Phase boundaries of Fe_{1-x}Pd_x alloys.
- a) the sputtered deposited alloys.
- b) the solid quenched alloys.
- c) the equilibrium phase diagram at RT. ref. (156)

Table (7) Sputtering parameter ref. (156)

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</tr>
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<td>Deposition rate</td>
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CHAPTER THREE

3. Experimental methods

The vacuum sputter deposition technique has been applied to produce thick films (1000 - 2000 nm) onto amorphous silica glass (20x5mm$^2$) substrates, with substrate temperature range 650 - 25 °C, and thin films (~100 nm) on single crystal rock salt. The deposition rate is estimated by considering the deposition time and thickness of the film for a known current and voltage. The thickness of the film is measured using a Tallystep which has a resolution of one nm. Both single and composition gradient films have been produced and examined chemically by a JEOL 35 X-Ray microprobe analyser, structurally by X-Ray diffraction and Transmission Electron Microscope (TEM). The morphologies of the thick films have been examined using Scanning Electron Microscopy (SEM).

The vacuum chamber is pumped down by a rotary pump and water cooled diffusion pump with a typical pressure $\sim 10^{-5}$ mbar. The ion beam sources used were water cooled B11W fine beam saddle-field ion sources manufactured by Ion Tech Ltd. which are characterised by a slow deposition rate, fig.(41a). The source operates by cold cathode discharge at low pressure using 99.999% pure argon.

The argon gas is further purified by a getter before entering the ion beam sources. The getter consists of a glass tube filled with granules of titanium placed into a furnace jacket.
held at 800°C.

A power supply model B50 with a maximum 10 Kv and 10 mA output has been supplied by Ion Tech Ltd. enabling the ion beams and electron currents as well as high voltage to be monitored.

The target(s) which is directly placed about 5 cm. below the substrate is presputtered for about 3-4 hours and this allows the target(s) to be sputter-cleaned before deposition. The sources require time to thermally equilibriate and during this stabilization period the substrate is protected by a shutter.

The substrate is heated by means of small heating coils placed within a water cooled substrate holder. The heater is held at a fixed distance from a Nicrome heat spreader (back plate) to produce an even temperature profile over the substrate. A schematic diagram of water cooled substrate holder with the heater in position is shown in fig.(41b).

3.1 **Accuracy of substrate temperature**

Direct substrate temperature measurement during film deposition is made possible by attaching a Cr/Alumel thermocouple into the substrate by drilling a hole of 1.5 mm diameter. In addition the substrate temperature is measured indirectly by calibrating the heater by attaching a thermocouple onto the back plate. The results are plotted as temperature versus current fig.(42). Both back plate and substrate temperature-current curves appear to be very smooth and consistent. The differences of about 10% in the two curves can be accounted for by the heat transported
(in the form of energy) by the target atoms onto the substrate during deposition.

3.1.1 Production of single and gradient composition alloy films
The single composition method involves sputtering of the target alloy so that a uniform composition is deposited. This is satisfactory if the target contains a single-phase structure.

Composition gradient alloy films have been produced successfully by means of placing two alloy targets close to each other and utilising the near cosine deposition geometry of sputtered films in the fashion of Adams et al(157).

Fig.(43) shows schematically the experimental configuration used.

The deposition rate is estimated by considering the deposition time, and the thickness of the films for a given current and voltage. The film thickness is measured using a Tallystep. However for the films deposited by composition gradient method, variation of thickness across the film is observed. This is because according to the property of each element, different currents are used for each ion beam source.

In the present work, primarily, single composition alloy films from single Fe-Pd and Fe-Pt alloy targets have been produced. Fe-Ni-Pt films with composition gradient have been produced to show the capability of the technique.
3.1.2 Powder work

Powders from the target alloys were produced by filing. The particle size was measured using a Cambridge Instruments Quantimet 920. The powders were encased in molybdenum foil to prevent contamination and reaction at high annealing temperature. Subsequently placed in a quartz vacuum tube with a vacuum better than $10^{-3}$ mbar. The powders were annealed in a furnace for given periods and were subsequently water quenched.

The structure of the annealed powders were analysed with a Debye-Scherrer powder camera using Cu $K_\alpha$ radiation. The X-Ray film was filtered with aluminum foil with the sample exposed to the X-Ray for 2.5h.

3.1.3 X-Ray diffraction

Films were examined structurally using a Philips 1010 X-Ray diffractometer with Cu$K_\alpha$ radiation ($\lambda = 0.154178$ nm) equipped with a monochromator. The lattice parameters of different phases were measured at room temperature with a slow scanning speed. The films contained sufficient volume for X-Ray diffraction. The room lattice parameters for each diffraction peak was measured, utilising Braggs law.

$$n\lambda = 2d \sin \theta$$  \hspace{1cm} (25)

Where $\lambda$ = the wave length of radiation

$d$ = distance between adjacent planes(hkl)

$2\theta$ = the angle at which diffraction occurs for each plane
An extrapolation of the lattice parameter values using the Nelson-Riley function (158) was made for correction.

In all the measurements a standard sample holder was used in order to reduce the sources of error.

The lowest X-Ray scanning speed (20 = 1/8 min-1) with an appropriate time constant was applied for accurate lattice parameter measurements and better resolution of the peaks. An accuracy of ±0.0095 nm in X-Ray lattice parameter measurements was calculated using pure Cu.

The phase boundary determination by X-Ray diffraction technique in composition gradient Fe-Ni alloys films was hindered because of narrow composition changes, slit size effects and thickness variations along the composition gradient thin films.

X-Ray resolution of Kα1, Kα2 peaks at high angles was found to be difficult as peaks were broadened. The line broadening which is basically due to structural defects and grain size, caused the peaks of the Kα doublet to merge together. A method developed by Rachinger (159) is used when possible to resolve the Kα component. Otherwise an average peak position is considered.

Utilising Debye and Scherrer (160) camera, KαCo radiation (λ = 0.17902 nm), with an iron filter, operating at 32 Kv and 10 mA, a glancing angle technique was applied. The exposure time used was two and half hours with 1.5 mm collimators. This method proved much more useful for observing faint superlattice lines.

Co-deposited films often contain preferred orientation (161),
and the identification of structure is not possible from the measured X-ray intensities.

3.1.4 TEM and SEM

In order that electron beam can penetrate the specimen, it must generally be only 100 nm thick or less. Thin films were examined using JEOL 200CX and 400T TEMs.

The deposited thin film on rock salt was subsequently dissolved in distilled water and transferred to a fine 3mm diameter copper grid. In some cases a double sided grid was used to prevent the lose of sample in the TEM column.

Decomposition of the NaCl substrate temperature prohibited any film deposition above 450°C.

In the diffraction mode, crystalline specimens give rise to patterns of spots in a ring from which ‘d’ spacings can be measured.

\[ r_d = \frac{L}{\lambda} \]  \hspace{1cm} (26)

where \( r \) = ring radius

\( L \) = camera length

\( \lambda \) = wavelength for a given electron energy.

If the crystal size is very small, a cloudy pattern refers to an amorphous structure.

Use of a dark field image in the microscope enables us to examine the location of each individual phases. However, the lattice parameter determination from TEM diffraction patterns is not accurate.
Annealing thin films in situ during examination in JEOL 200CX which contains a heating stage is ideal for direct observation of phase transformations. In the present work, due to the magnetic property of the samples, a stable condition during hot stage process was difficult to maintain. Also different kinetics of diffusion are expected when compared with thin films deposited directly at the same temperatures.

SEM is primarily used to study the surface, or near the surface structure of the thick film specimens. In general films deposited at low $T/T_m$ showed no surface roughening, whereas at higher $T/T_m$ surface roughening was observed.
3.1.5 Materials

The materials used in this work were supplied by Johnson Matthey Co. The experimental results are based on the following alloy targets:

a) **Iron – Palladium alloys**

Table (8) illustrates the composition of the alloys used to produce single composition thin films. The actual composition was determined by a JEOL 200 microprobe analyser.

<table>
<thead>
<tr>
<th>No.</th>
<th>Nominal comp. at%</th>
<th>Actual comp. at%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe Pd</td>
<td>Fe Pd</td>
</tr>
<tr>
<td>1</td>
<td>85 15</td>
<td>84.9 15.1</td>
</tr>
<tr>
<td>2*</td>
<td>75 25</td>
<td>75 25</td>
</tr>
<tr>
<td>3*</td>
<td>70 30</td>
<td>70.2 28 x</td>
</tr>
<tr>
<td>4</td>
<td>60 40</td>
<td>60.1 39.9</td>
</tr>
<tr>
<td>5</td>
<td>50 50</td>
<td>50 50</td>
</tr>
</tbody>
</table>

*: These alloys were produced by melting the alloy at 1600°C in a vacuum furnace, then annealed for 72h at 1100°C. (water quenched) x: 1.8 at% Si was detected in this alloy.
b) Iron - Platinum alloys

Table (9) shows the composition of the Fe-Pt alloys used. The actual composition was determined in the same manner as Fe-Pd alloys.

<table>
<thead>
<tr>
<th>No.</th>
<th>Nominal comp. at%</th>
<th>Actual comp. at%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>Pt</td>
</tr>
<tr>
<td>1</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>70</td>
<td>30</td>
</tr>
</tbody>
</table>

c) \( \text{Fe}_{1-x} (\text{Pt Ni})_x \) Alloys

Single and composition gradient films were produced from \( \text{Fe}_3 (\text{Pt}_{0.9} \text{Ni}_{0.1}) \) and \( \text{Fe}_3 (\text{Pt}_{0.6} \text{Ni}_{0.4}) \) targets. Table (10) illustrates the nominal and actual composition determined by JEOL 200 microprobe.

<table>
<thead>
<tr>
<th>No.</th>
<th>Nominal comp. at%</th>
<th>Actual comp. at%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>Pt</td>
</tr>
<tr>
<td>1</td>
<td>75</td>
<td>22.5</td>
</tr>
<tr>
<td>2</td>
<td>75</td>
<td>15.0</td>
</tr>
</tbody>
</table>
Fig. (41a) Water cooled B11W fine beam saddle-field ion source.

Fig. (41b) Schematic diagram of water cooled substrate holder with heater in position.
Comparing the Temperatures of Substrate and Backplate.

- △ Backplate Temp.
- Substrate Temp.

Fig. (42) Substrate temperature-current curves.

Substrate

Target
d

Element A

Element B

Film rich in A

Film rich in B

Ion beam

~ 5 cm.

Fig. (43) Schematic representation of experimental configuration used for deposition of an alloy containing a) single composition b) composition gradient.
CHAPTER FOUR

4. Results and discussion

4.1 Introduction

Room temperature structures of vapour deposit Fe-Pd and Fe-Pt alloys with the substrate temperature between 200-700°C have been examined. Relatively few assumptions need to be made to explain the mechanism of phase formation by diffusion and transformation on cooling to room temperature. The rapid assessment of the alloy phase diagram using deposition technique has been demonstrated by introducing a model to relate composition with $T_s$, associated with diffusion distance an atom can move.

Phase boundary and $T_0$ temperature calculations have been carried out and compared with the experimental results.

a) Results and discussion based on Fe-Pd thin film alloy

Fe-Pd alloys with the chemical composition shown in Table (8) have been used as the sputtering target to deposit single composition thin film alloys with substrate temperature between 300-650°C. The sputtering parameters are shown in Table (11). A hypothesis has been put forward which satisfactorily explains the results on the basis of phase formation by diffusion at deposition temperatures and transformation on cooling to room temperature. It has been assumed that above temperature $T_{01}'$ (where $\Delta G_{fcc-bcc} = 0$) on deposition, fcc structures form and subsequently decompose to bcc + fcc structures. When deposition
takes place below $T_{01}$, a bcc structure is formed and subsequently decomposes to (fcc + bcc) structures.
Although in this system the magnetic effect has not been calculated, it has been considered to explain some anomalous results.
Further, a hypothetical relationship between substrate temperatures and decomposition of the alloy has been devised.

b) Results and discussion based on Fe-Pt thin film alloys

Fe-Pt target alloys, Table (9) have been used to deposit single composition thin film alloy with substrate temperatures between 200-650°C. Similar assumptions as for the case of Fe-Pd alloy have been made.
Models similar to those indicated in the Fe-Pd system, were used to explain the relationship between substrate temperatures and phase decompositions. Thus enabling us to demonstrate the results in the form of a thin film phase diagram.
"$T_0$" has been calculated, since in this thesis, it is a key issue to explain the phase transformations.

c) Results and discussion based on Fe-Pt-Ni thin film alloys

Composition of the alloy target(s) used to codeposit composition gradient thin films are illustrated in Table (10). The deposition parameters are shown in Table (12). The objectives of depositing these alloys were:
1) To demonstrate the capability of the sputtering techniques for reproducibility of both single and composition gradient thin films.
2) To examine the effect of addition of small amount of Ni (3-7 at\%) into Fe\textsubscript{3}Pt alloy when quasi binary Fe\textsubscript{x-1} (Pt\textsubscript{0.6} Ni\textsubscript{0.4}) - Fe\textsubscript{x-1} (Pt\textsubscript{0.9} Ni\textsubscript{0.1}) alloys are codeposited.

In the following sections, results and discussion based on Fe-Pd, Fe-Pt and Fe-Pt-Ni vapour deposited alloys are presented. This is followed by the analysis of the relation between diffusion distance (\(\bar{X}\)) an atom can move on the surface with substrate temperature (\(T_s\)). This will enable us to estimate a model to relate the relation between \(T_s\), \(\bar{X}\) and subsequently the composition of the vapour deposited alloy.

The thin film phase diagram which has been developed by the proposed model, represents a true picture of equilibrium structure at high temperatures and non-equilibrium structure at low temperatures.

<table>
<thead>
<tr>
<th>Table (11) Deposition parameters for the sputtered single composition alloy.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage</td>
</tr>
<tr>
<td>Current</td>
</tr>
<tr>
<td>Vacuum pressure</td>
</tr>
<tr>
<td>Ar.gas pressure</td>
</tr>
<tr>
<td>Substrate temp. (^\circ)C</td>
</tr>
<tr>
<td>Deposition rate</td>
</tr>
<tr>
<td>Low deposition rate</td>
</tr>
<tr>
<td>Deposition time</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table (12) Deposition parameters for the sputtered composition gradient alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage</td>
</tr>
<tr>
<td>Current</td>
</tr>
<tr>
<td>Target &quot;A&quot;&amp;&quot;B&quot;</td>
</tr>
<tr>
<td>Vacuum pressure</td>
</tr>
<tr>
<td>Ar.gas pressure</td>
</tr>
<tr>
<td>Substrate temp. (^\circ)C</td>
</tr>
<tr>
<td>Deposition rate</td>
</tr>
<tr>
<td>Deposition time</td>
</tr>
</tbody>
</table>
Results and discussion based on Fe-Pd thin film alloys

4.1.2 Results and discussion based on Fe\textsubscript{85}Pd\textsubscript{15} thin film alloy.

a) Introduction

In this section the results and discussion for the mechanism of phase formation and transformation in deposited Fe\textsubscript{85}Pd\textsubscript{15} single composition thin film alloy are presented. The alloys are deposited both with low ion energy in addition to some normal deposition rate. Here the effect of using two types of ion beam energies are shown qualitatively. But a quantitative treatment has been examined in a latter section.

b) Results

Room temperature X-Ray results for Fe\textsubscript{85}Pd\textsubscript{15} thin film alloys are shown in Table (13a & 13b).

Fig.(44a) shows the changes of face centred fcc(fct) lattice parameter with substrate temperature (T_s). It is predominantly fcc structure over 300-650°C, but a definite fct lattice can be observed at 550°C. At lower temperatures, determination of the fct structure by observing anomalies in the (111) X-Ray diffraction only is not possible. However, judging from (111) lattice spacings and its equivalent corresponding high Palladium composition, it appears that this reflection is associated with the long axis of a fct phase (c/a<1.0) and the face centred phase should be considered as being fcc/fct.

Fig.(44b) illustrates the variation of body centred bcc(bct) lattice spacings with T_s. When T_s is above 525°C a bcc lattice
with essentially constant lattice parameter is observed. When \( T_s \) is between \( 525 - 300^\circ C \), it shows a bct structure with c/a axial ratio decreasing from 1.036 to unity as the deposition temperature is decreased (fig.44c). Subsequently three regions of body centred phases are distinguished. ie. bcc-bct-bcc.

The volume ratio changes of body centred/face centred phase as measured by the ratio 110(bc)/111(fc) X-Ray diffraction, increases continuously as the deposition temperature is decreased (fig.44d).

The low angle X-Ray diffraction peaks measured at room temperature for this alloy are shown in fig.(44e).

The effect of \( T_s \) on structure and morphology of the deposited alloy film can be used to show the characteristics of equilibrium and non equilibrium phases.

c) Discussion

Consider a schematic portion of Fe-Pd phase diagram shown in fig (45). At high \( T_s \), we can assume above \( T_{01} \), an initial fcc single phase forms on deposition and then decomposes to equilibrium bcc + fcc structure by diffusion. On cooling to room temperature the fcc phase enriched in Pd transforms to an fct structure as it crosses the boundaries associated with \( T_{02} \) of gamma1/gamma2. ie.

\[
\begin{align*}
\text{fcc} & \quad \text{fcc} + \text{bcc} \\
\downarrow & \quad \text{cool} \\
\downarrow & \quad \text{through } T_{02} \\
& \quad \text{fct(at RT)}
\end{align*}
\]
The corresponding composition found in this work for equilibrium bcc is ~ 0.5 at%Pd. The corresponding composition for the equilibrium bcc/bcc+fcc phase boundary in the Fe-Pd phase diagram cited in Hansen (12) is ~ 2 at%Pd. This difference in Palladium composition in equilibrium bcc could be due to:
a) inaccuracy in lattice parameter measurement due to the weak X-Ray peak resolution for bcc phase and its subsequent translation to composition or,
b) whether the bcc phase precipitated out of the initially assumed deposited fcc phase or vice versa[(position of T_01 (bcc/fcc)].

Alloys deposited between eutectoid transformation temperature (~ 600°C) and T_s above 525°C, follow a similar phase formation by diffusion and transformation mechanism as above, but are consistent with a gamma1(gamma2) composition corresponding to about 40-36 at%Pd. This composition change is associated with the gradient of the extrapolated T_02 to lower temperature (fig.45).

When T_s is between 525-300°C it is assumed initially a bcc phase is deposited below T_01 (fcc/bcc), which then decomposes by diffusion to (bcc + fcc). Then on cooling to room temperature the fcc structure partially transforms to bct through T_01 (fcc/bct). i.e.

\[ \text{bcc} \rightarrow \text{bcc + fcc} \]
\[ \text{cool through } T_{01} \]
\[ \text{bct(at RT)} \]

The bcc lattice in this temperature range was not detected at room temperature. This might be due to;
a) the small amount of this phase which is present could have been hidden in the X-Ray diffraction background.
b) since the X-Ray diffraction peaks for bct phase ie. (110) and (011), are broad, they could include the bcc (110) diffraction in their envelope.

The results published by Oshima (90) and Foss (91) has been used as a standard calibration curve shown in fig.(44f). The corresponding composition for the metastable bct phase can then be determined. The Palladium composition varies (26 - 30 at%Pd) with (c/a) the degree of tetragonality. This is consistent with the metastable phase diagram (fig.21) by Oshima (90).

Considering the body centred lattice spacings with $T_s$, three distinct regimes of deposition can be proposed depending on $T_s$ (fig.44b & 44c). When $T_s$ is above 525°C a c/a ratio of unity is observed, indicating the formation of a bcc phase. Subsequent departure from unity at $T_s$ less than 525°C, indicates the formation of a bct phase.

Extrapolation of body centred lattice spacings, to lower $T_s$, indicates that below $\sim$ 300°C, on deposition, a single bcc phase will form which depending on the diffusion flux, will either decompose to bcc + fcc structures, or, alternatively exhibit very little decomposition. This estimation is also supported by considering the changes in c/a ratio with $T_s$ (fig.44d) which again approaches unity at $\sim$ 300°C.

These results are consistent with the known fcc-bct and fcc --- fct + bcc phase transformation in Fe-Pd alloys.

The volume ratio of body centred/face centred structure shows a
continuous increase as $T_s$ decreases. This suggests that as $T_s$ decreases, less face centred structure is precipitated from the initial bcc phase deposit, i.e. less diffusion. However, to a certain extent, preferred orientation growth of one phase relative to the other cannot be excluded.

A SEM micrograph of Fe$_{15}$Pd thin film deposited at 650°C is shown in fig. (46a). An equilibrium characteristics of solid solution fcc + bcc phases together with the mechanism of faceting and growth is evident. The particle sizes are about two microns. A SEM micrograph for the film deposited with substrate temperature at 550°C is shown in fig. (46b), which shows a metastable two phase structure. It is proposed that the smaller particles represent the bcc phase whereas the larger particles could be the fcc(fct) phase. It also indicates how a decrease in $T_s$ can bring about a large reduction in particle size when compared with higher deposition temperatures. This particle size is related to the diffusion in thin films and is proportional to $\overline{X}$ (150).

The proposed bcc phase can be identified by using TEM dark field mode. But with present work, high temperature deposition on NaCl substrate is not possible due to decomposition of the substrate at elevated temperatures. Alternative substrates which do not react with the deposition materials might be promising.

d) Summary

Fe$_{85}$Pd$_{15}$ deposited above $T_{01}$, show equilibrium bcc and fct structure at room temperature.
Alloys deposited below $T_0$, show martensitic bct and fcc(fct) structures.

It is shown that phase formation is dependent on the $T_s$ and on the rate of deposition. At relatively high $T_s$, the initially deposited single phase decomposes into two phases. At intermediate $T_s$, non-equilibrium phases are formed as a result of diffusion slow down. Further, at lower $T_s$, diffusion becomes so restricted that deposited atoms remain as bcc single phase.
Table (13a) Room temperature X-Ray results for fcc(fct) $\text{Fe}_{85}\text{Pd}_{15}$ thin film alloys.

<table>
<thead>
<tr>
<th>$T_s$ (°C)</th>
<th>fcc(fct)(nm)</th>
<th>c/a</th>
<th>c(nm)</th>
<th>at%Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>640</td>
<td>0.378</td>
<td>0.997</td>
<td>0.3769</td>
<td>34.0</td>
</tr>
<tr>
<td>560</td>
<td>0.3848</td>
<td>0.952</td>
<td>0.3663</td>
<td>36.0</td>
</tr>
<tr>
<td>525+</td>
<td>0.3798</td>
<td>-</td>
<td>-</td>
<td>40.0</td>
</tr>
<tr>
<td>450</td>
<td>0.3794*</td>
<td>-</td>
<td>-</td>
<td>39.0</td>
</tr>
<tr>
<td>420+</td>
<td>0.3797</td>
<td>-</td>
<td>-</td>
<td>40.0</td>
</tr>
<tr>
<td>420</td>
<td>0.3787*</td>
<td>-</td>
<td>-</td>
<td>35.0</td>
</tr>
<tr>
<td>370++</td>
<td>0.3803</td>
<td>-</td>
<td>-</td>
<td>42.0</td>
</tr>
<tr>
<td>315+</td>
<td>0.3712 (111) diffraction</td>
<td>18.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*: Only (111),(110),(211) diffractions.
+: Sputtered with low ion energy.

Table (13b) Room temperature X-Ray results for bcc(bct) $\text{Fe}_{85}\text{Pd}_{15}$ thin film alloys.

<table>
<thead>
<tr>
<th>$T_s$ (°C)</th>
<th>bcc(bct)(nm)</th>
<th>c/a</th>
<th>at%Pd</th>
<th>ratio of bcc/fcc</th>
</tr>
</thead>
<tbody>
<tr>
<td>640</td>
<td>0.2863</td>
<td>-</td>
<td>0.5</td>
<td>0.69</td>
</tr>
<tr>
<td>560</td>
<td>0.2859</td>
<td>-</td>
<td>0.5</td>
<td>1.75</td>
</tr>
<tr>
<td>525+</td>
<td>0.2865</td>
<td>1.036</td>
<td>7.5</td>
<td>1.67</td>
</tr>
<tr>
<td>450</td>
<td>0.2862</td>
<td>-</td>
<td>0.5</td>
<td>2.41</td>
</tr>
<tr>
<td>420+</td>
<td>0.2877</td>
<td>1.024</td>
<td>7.5</td>
<td>2.23</td>
</tr>
<tr>
<td>420</td>
<td>0.289</td>
<td>1.019</td>
<td>10.0</td>
<td>2.1</td>
</tr>
<tr>
<td>370+</td>
<td>0.2872</td>
<td>1.017</td>
<td>6.0</td>
<td>3.3</td>
</tr>
<tr>
<td>315+*</td>
<td>0.2932</td>
<td>-</td>
<td>15.0</td>
<td></td>
</tr>
</tbody>
</table>

*: Only (111),(110),(211) diffractions.
+: Sputtered with low ion energy.
Fig. (44a) Room temperature X-Ray results for Fe₈₅Pd₁₅ thin film alloy deposited at designated temperatures $T_s$. 

Fig. (44b) 

Fig. (44c) 

Fig. (44d)
Fig. (44e) RT low angle X-Ray diffractions in Fe$_{85}$Pd$_{55}$ thin film alloys.
*: Sputtered with low ion beam energy.

Fig. (44f) Pd composition dependance on c/a axial ratio for bct structure.
Fig.(45) Schematic representation of Fe-Pd phase diagram. (x) indicates the experimental results for $T_0$ in this work.

* low ion beam energy

E : eutectoid
Fig. (46a) SEM micrograph for Fe$_{85}$Pd thin film alloy deposited at 650°C.

Fig. (46b) SEM micrograph for Fe$_{85}$Pd thin film alloy deposited at 550°C.
4.2.2 Results and discussion based on Fe₃Pd thin film alloy

a) Introduction

The room temperature structure of Fe₃Pd single composition thin film alloys deposited at various substrate temperatures (300 - 670°C) has been examined. A similar pattern of phase formation and transformation, as in the Fe₈₅Pd thin film alloys was observed.

In addition, a Fe₃Pd powder study was conducted in order to compare the results with the bulk alloys. This will be discussed later.

b) Results

Room temperature X-Ray results for face centred and body centred Fe₃Pd thin film alloys are shown in Table (14a & 14b). The variation in lattice spacings with Tₛ in fig.(47a) shows the changes from an fct structure at high Tₛ, to a fcc(fct) phase as Tₛ decreases. The corresponding variation in face centred c/a axial ratio with Tₛ is shown in fig.(47b).

Similarly, the bct(bcc) lattice spacing changes from an equilibrium bcc to a metastable bct phase and subsequently to a bcc structure as Tₛ decreases fig.(47c). The variation of c/a axial ratio with Tₛ for bct(bcc) phases shows that the c/a ratio approaches unity as Tₛ decreases, (fig.47d).

The volume ratio of bct(bcc)/fct(fcc) phases as a function of Tₛ shows (fig.47e) an increase in the volume as Tₛ decreases.

The room temperature low angle 2θ X-Ray diffractions are shown in fig.(47f).
c) Discussion

Above the eutectoid transformation temperature (~600°C), it is assumed that initially a fcc phase is deposited. Subsequently as a result of diffusion, the fcc structure decomposes to equilibrium fcc + bcc structures. On cooling to room temperature the fcc phase transforms by passing through $T_{o2}$ (schematic diagram fig.45) of the FePd phase to a tetragonal fct structure with a c/a axial ratio of about 0.95. If an equivalent lattice spacing for fcc is considered, then the corresponding composition is about 43 at%Pd. This corresponds to the extrapolated FePd boundary with a narrow field of fcc + fct phases.

Alloys deposited with $T_s$ between 600 - ~475°C, transform by a similar mechanism, but with different corresponding compositions due to the change in the gradient of $T_{o2}$. Determination of the tetragonal fct structure becomes increasingly difficult in the lower range of $T_s$. This is because diffusion becomes more restricted rendering the surface mobility of the atoms insufficient for complete decomposition of the depositing atoms. The estimated fcc lattice spacing in fig.(47a), indicates a corresponding composition in the range of 41 to 27 at%Pd for $T_s$ of 450 to 300°C.

Fig.(47b), confirms the gradual transformation from an fct to a fcc structure with the c/a axial ratio approaching to unity as $T_s$ decreases. i.e. diffusion is decreased.

The bcc lattice parameter remains fairly constant for $T_s$ above 475°C, but a tetragonal bct structure with c/a > 1 develops as the deposition temperature decreased.
Below the $T_{01}$ temperature, the initial deposit is a bcc phase which by diffusion then decomposes to fcc + bcc phases. On cooling to room temperature, depending on deposition conditions ($T_s$, deposition rates), the fcc structure partially transforms to bct phase with the remainder transforming to fct(fcc) phase (fig. 47d).

The results in fig. (47c) indicate a critical deposition temperature in the region of 475-450°C, in which there exists competition between formation of the equilibrium bcc structure or bcc martensite.

With decreasing $T_s$, the c/a axial ratio for the bcc structure approaches unity. This indicates that as the $T_s$ decreases, diffusion becomes restricted. Thus for the initial deposited bcc phase, further decomposition become difficult. Subsequently a single bcc structure with composition corresponding to 25 at%Pd is observed.

Similar to Fe$_{85}$Pd alloys, three regimes for bct(bcc) phase transformation with respect to $T_s$ are considered:

1) When $T_s > 475^\circ$C, equilibrium bcc + fcc(fct) structures with bcc composition less than 3 at%Pd

2) When $T_s$ is in the range $475^\circ - 200^\circ$C, a bct phase forms with composition in the range of $\sim 31 - 26$ at%Pd respectively.

3) When $T_s < 200^\circ$C, a bcc phase with composition close to the target composition appears to form.

This sequence is supported by examining the volume ratio of the phases with respect to $T_s$. Fig. (47c) indicates, the variation of bcc with fct above $T_{01}$, is according to the lever rule. i.e. equilibrium conditions. However, on decreasing $T_s$, the volume of bct phase increases sharply with $500-450^\circ$C representing a
critical transition state.

TEM examination of this alloy with temperature between 150-250°C supports the results obtained from X-Ray diffraction. Two cubic phases were observed by TEM at T_s = 250°C. At T_s = 150°C the TEM electron diffraction shows a broad single phase. This is consistent with X-Ray results and the conclusion that decomposition of the initially deposited single phase, becomes difficult as T_s decreases.

SEM micrographs have shown a correlation between the structures and morphology. An example is given in fig. (48) which shows the presence of two types of particles; the elongated particles are associated with the fct phase while the small particles in the background probably represent the bcc(bct) structure. Identification of the proposed phases with TEM is hindered due to restriction in substrate temperature of (NaCl).

d) Summary

Generally, two mechanisms dominate the formation of phases in Fe_3Pd alloy, namely, diffusion and transformation. Although the sequences of phase formation and transformation in these alloys are found to be effectively the same as Fe_{85}Pd alloys, the critical value of T_{01}, for the transformation between equilibrium bcc phase to metastable bct structure is decreased.

Detection of tetragonal phase became easier as compared with Fe_{85}Pd alloy. This illustrates the link between X, composition of the alloy and T_s.
Table (14b) Room temperature X-Ray results for bcc(bct) Fe$_3$Pd thin films alloys.

<table>
<thead>
<tr>
<th>$T_s$ (°C)</th>
<th>bcc(bct) (nm)</th>
<th>c/a</th>
<th>at%Pd</th>
<th>ratio of bcc/fcc</th>
</tr>
</thead>
<tbody>
<tr>
<td>670</td>
<td>0.287</td>
<td>-</td>
<td>2.5</td>
<td>0.71</td>
</tr>
<tr>
<td>600</td>
<td>0.2869</td>
<td>-</td>
<td>2.5</td>
<td>0.84</td>
</tr>
<tr>
<td>575</td>
<td>0.2868</td>
<td>-</td>
<td>2.4</td>
<td>0.82</td>
</tr>
<tr>
<td>550</td>
<td>0.2866</td>
<td>-</td>
<td>2.0</td>
<td>0.92</td>
</tr>
<tr>
<td>525*</td>
<td>0.2874</td>
<td>0.995</td>
<td>2.2</td>
<td>0.92</td>
</tr>
<tr>
<td>500</td>
<td>0.2864</td>
<td>-</td>
<td>2.0</td>
<td>0.9</td>
</tr>
<tr>
<td>450</td>
<td>0.2897</td>
<td>1.024</td>
<td>12.5</td>
<td>0.55</td>
</tr>
<tr>
<td>425+</td>
<td>0.2882</td>
<td>1.027</td>
<td>9.5</td>
<td>0.65</td>
</tr>
<tr>
<td>400</td>
<td>0.2905</td>
<td>1.033</td>
<td>15.5</td>
<td>0.61</td>
</tr>
<tr>
<td>370</td>
<td>0.2936</td>
<td>1.02</td>
<td>19.0</td>
<td>0.85</td>
</tr>
<tr>
<td>300</td>
<td>0.2982</td>
<td>1.01</td>
<td>25.0</td>
<td>2.41</td>
</tr>
</tbody>
</table>

*: Sputtered with lower ion beam energy.
+: Post annealed at 425°C
Fig. (47a) RT X-Ray results for Fe<sub>75</sub>Pd<sub>25</sub> thin film alloys deposited at designated T<sub>s</sub>.

Fig. (47b) Variation of c/a axial ratio for face centred structure with T<sub>s</sub> in Fe<sub>75</sub>Pd<sub>25</sub> thin film alloy.
Fig. (47c) Room temperature X-Ray results for Fe$_{75}$Pd thin film alloy deposited at designated $T_S$. 

Fig. (47d)
Fig. (48) SEM micrograph of Fe₃Pd thin film alloy deposited at 650°C.
4.2.3 Results and discussion based on Fe\textsubscript{70}Pd thin film alloy

a) Results

Room temperature X-Ray results for Fe\textsubscript{70}Pd thin films are shown in Table (15). The actual Pd content is about 29at\%Pd.

The lattice spacings as a function of $T_s$ show, an fct structure with $c/a \sim 0.95$ at lower $T_s$, and a fcc phase at high $T_s$ (fig.49a). The $c/a$ ratio approaches unity as $T_s$ decreases (fig.49b).

The lattice spacings for the bcc phase remain fairly constant at high $T_s$, and increase with decrease in $T_s$, shown in fig.(49c).

The volume ratio of bcc/fct(fcc) shows a minimum at $T_s$ about 370$^\circ$C and subsequently increases as $T_s$ decreases further, (fig.49d).

The low X-Ray diffraction Bragg angle $2\theta$ measured at room temperature is shown in fig.(49e).

b) Discussion

A similar mechanism occurs in terms of phase decomposition by diffusion and transformation. However, at lower $T_s$, there are complications in this alloy which are associated with the Invar region and intersection of $T_{o1}$ and $T_{o2}$ temperatures.

When $T_s$ is above the eutectoid transformation temperature, it is assumed as before that the initial deposit is the most stable single phase at that temperature (fcc) which then by diffusion, decomposes to a mixture of (fcc + bcc) phases. On
cooling to room temperature, the fcc phase transforms to an fct structure through $T_{O2}$ temperature with a composition corresponding to about 41 at%Pd. The equilibrium composition in bcc phase corresponds to about 3 at%Pd.

When $T_S$ is between 600-400°C, the initially deposited fcc phase decomposes to a mixture of (fcc + bcc) structures directly at temperature $T_S$. Then on cooling to room temperature, the fcc phase transforms to an fct structure through $T_{O2}$ temperature. The corresponding composition for an fct phase boundary varies from 47 - 40 at%Pd over this temperature range, whereas the bcc phase retains its equilibrium composition.

When $T_S$ is less than 400°C, the results indicate the initial formation of a metastable bcc phase below $T_{O1}$ temperature with a subsequent decomposition to bcc + fct(fcc) structures by diffusion. The initially deposited bcc phase can decompose to bct + fct(fcc) structure, but diffusion in the thin films is still sufficient to give a lower bcc Pd content. The corresponding composition for the fcc phase deposited at $T_S \approx 300°C$ is 34 at%Pd and for the corresponding bcc is about 27 at%Pd. The ratio of c/a for fct(fcc) phase approaches unity when $T_S$ is below 400°C. This supports the results based on the changes of fct structures to fcc phase as $T_S$ is reduced. Fig.(49e) shows diffuse X-Ray diffraction peaks at low $T_S$, which indicates that diffusion is being restricted.

The volume ratio changes with $T_S$ for the bcc/fct(fct), indicating a minimum for deposition temperature at about 370°C.
followed by a sharp increase in volume in the bcc structure
fig. (49d). This may be used to locate $T_{01}$. This supports the
erlier assumption and is confirmed by the increase in bcc
lattice spacings for $T_5$ less than 400°C (fig. 49c).

Room temperature TEM examination of these alloys deposited at
300°C on rock salt, supports the results of X-Ray diffraction
studies. Diffuse electron diffraction rings with grain sizes
estimated less than 10 nm have been observed. The extent to
which ion beam energy can effect the diffusion process and
grain growth are compared in micrographs (50a & 50b). The
 corresponding thin film morphology is shown in fig. (50c &
50d). The fct(fcc) and bcc electron diffraction rings are
clearly separated and grain size increases when ion beam energy
is lowered.

SEM morphology demonstrates the possible presence of two phases
(bcc + fct) with elongated particles in fct structure. Similar
behaviour is observed in Fe$_3$Pd thin film alloy. As $T_5$
decreases, the particle size decreases and the surface of the
films become smoother.
Table (15) Room temperature X-Ray results for fct(fcc) and bcc Fe$_{70}$Pd$_{30}$ thin film alloys.

<table>
<thead>
<tr>
<th>$T_s$ ($^\circ$C)</th>
<th>fct(fcc)(nm)</th>
<th>c/a</th>
<th>at%Pd</th>
<th>bcc(nm)</th>
<th>at%Pd</th>
<th>ratio of bcc/fcc</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>0.3867</td>
<td>0.95</td>
<td>42</td>
<td>0.2873</td>
<td>28</td>
<td>0.68</td>
</tr>
<tr>
<td>550</td>
<td>0.388</td>
<td>0.955</td>
<td>48</td>
<td>0.2873</td>
<td>28</td>
<td>0.73</td>
</tr>
<tr>
<td>480</td>
<td>0.3866</td>
<td>0.968</td>
<td>42</td>
<td>0.287</td>
<td></td>
<td>0.53</td>
</tr>
<tr>
<td>375</td>
<td>0.3866</td>
<td>0.95</td>
<td>40</td>
<td>0.293</td>
<td>14</td>
<td>0.38</td>
</tr>
<tr>
<td>290+</td>
<td>0.3786*</td>
<td>-</td>
<td>36</td>
<td>0.2792</td>
<td>27.5</td>
<td>0.69</td>
</tr>
<tr>
<td>290</td>
<td>0.3785*</td>
<td>-</td>
<td>35</td>
<td>0.2988</td>
<td>26</td>
<td>0.78</td>
</tr>
</tbody>
</table>

*: Only (111) X-Ray diffraction.

+: Sputtered with low ion beam energy.
Fig. (49) Room temperature X-Ray results for Fe\textsubscript{70}Pd\textsubscript{30} thin film alloy deposited at designated $T_s$. 

**Fig. (49a)**

**Fig. (49b)**
Fig. (49c) RT low angle X-ray diffractions for Fe$_{70}$Pd$_{30}$ thin film alloy deposited at designated $T_s$. 

Fig. (49d) 

Fig. (49e) 

b.c.c. lattice spacings (nm) 

$X_{jQ} - 3$ b.c.c. lattice spacing (nm) 

Low sp. rate (-53 nmt/min) 

Substrate temperature C ($T_s$) $\times 10^2$ 

Intensity ratio bcc/FCC $V T_s$ in Fe$_{70}$Pd$_{30}$ J.F.
Fig. (50) a) TEM 200 micrograph of Fe$_{70}$Pd$_{30}$ thin film alloy deposited at 300°C. x500000. b) TEM 200 electron diffraction of (a) (200KV).

c) TEM 200 micrograph of Fe$_{70}$Pd$_{30}$ thin film alloy deposited at 300°C with low ion beam energy x750000. d) TEM 200 electron diffraction of (c) (200KV).
4.2.4 Results and discussion based on Fe_{60}Pd_{40} thin film alloy

a) Results

Room temperature X-Ray results based on Fe_{60}Pd_{40} thin film alloys are shown in Table (16).

The variation of fct(fcc) lattice spacings with T_s in fig.(5la), shows an fct structure at high T_s. In the intermediate deposition temperatures, the c/a ratio approaches unity. When T_s is lowered, the c/a axial ratio decreases as shown in fig.(5lb).

Weak bcc X-Ray diffraction peaks together with an fct structure are observed for T_s above 550^0C. No further evidence for a bcc structure is observed at lower T_s. Variation of the bcc lattice parameter for T_s is shown in fig.(5lc).

The low angle 2 θ X-Ray diffraction patterns with T_s are shown in fig.(5ld).

b) Discussion

As previously assumed, at high T_s, and above T_{02}, an initially deposited fcc structure decomposes into fcc and bcc phases by diffusion. On cooling to room temperature the fcc phase transforms to an fct structure as the temperature passes through T_{02} (FePd). Alloys deposited just above eutectoid temperature, retain an fcc structure at room temperature. Similarly, when T_s is between 600-550^0C, the initial deposit is an fcc phase, which then decomposes into (fcc + bcc) by diffusion. On cooling to room temperature the fcc phase transforms to an fct structure and the bcc phase remains
unchanged.
The bcc lattice parameter changes smoothly with $T_s$, with a composition corresponding to the range of $4 - 0.5$ at%Pd. No bcc structure is observed for $T_s$ less than about $500^\circ$C. However, when $T_s$ is in the range $\sim 550 > T_s > 420^\circ$C, an fcc structure forms on deposition, but on cooling through $T_{02}$ it transforms to an fct(fcc) phase with c/a close to unity fig.(51b). It is not easy to give a reason for this behaviour, but the presence of stable fcc phase in this region could be due to the magnetic effect caused in the vicinity of the Curie temperature. In order to examine the possible magnetic effect in this region, 50at%Pd alloy is examined. This is discussed in a later section. Alternatively, the absence of a bcc phase may reflect reduced prior chemical microsegregation.

When $T_s$ is below $\sim 420^\circ$C, an fct structure is formed directly on deposition with a decreasing c/a ratio as $T_s$ is lowered. The sudden increase in degree of tetragonality, with $T_s$ around $400^\circ$C, suggests that this is the location of $T_{02}$ for this alloy. The increased tetragonality with decrease in $T_s$, can be considered to be due to the increase in degree of ordering (46). When $T_s$ is at room temperature, diffusion becomes restricted and only a single fcc phase is observed.

c) **TEM and SEM analysis**

The structure of Fe$_{60}$Pd alloys at low temperature was also examined by TEM. Thin films (less than 100 nm thickness) deposited on rock salt, were crystalline at room temperature with grain size less than 10 nm. Electron diffraction patterns
show in fig. (52a & 52b) a single cubic phase. However, with the limited accuracy (camera length, line width, measurement) it is not possible to conclude whether this is fct or fcc, but it is consistent with an fct structure with c/a ~ 1.

At $T_s$ about $300^0C$, for thin films deposited with low ion energy, an ordered fct phase is grown epitaxially. Electron diffraction pattern also shows possible anisotropic growth. Micrographs show a crystal size of less than a few tens of nm (fig.53a & 53b).

A comparison was made between a thin film deposited at $300^0C$ and another thin film deposited at room temperature, then annealed at $300^0C$ "in situ". It is clearly shown in micrograph (54a & 54b) that diffusion in thin films deposited at the temperature is faster than the one annealed "in situ".

An analysis of the SEM morphology confirms the presence of a number of identifiable phases. At high $T_s$, a micrograph of Fe$_{60}$Pd alloys shows (fig.55a & 55b) an equilibrium structure characteristic of the fct(fcc) phase. It is observed that particles have grown by the coalescence and faceting mechanism. The concentration of bcc phase is almost negligible.

d) **Summary**

At high $T_s$, mainly a diffusion mechanism dominates the decomposition of the initial single phase deposit. At intermediate $T_s$, in the vicinity of $T_c$, the absence of bcc phase particles is assumed to reduce diffusion at interphase boundaries. Below the $T_{02}$ temperature, the fct phase forms
directly on deposition and the increase of degree of
tetragonality is considered to be due to the increase in degree
of ordering with an unchanged Pd chemical composition.
TEM examination confirms the presence of an fct ordered phase,
and there is an increase in the degree of ordering when the ion
beam energy is reduced.

Footnote
It was noticed that thin films deposited at high $T_s$, peeled off
from the substrate when exposed to air. This behaviour was not
observed for the alloy deposits with $T_s$ less than $500^\circ$C. This
effect could again be linked to the presence of a Curie
temperature and possibly even to shape memory properties in
this region.
Table (16) Room temperature X-Ray results for Fe$_{60}$Pd$_{40}$ thin film alloys

<table>
<thead>
<tr>
<th>$T_s$ (°C)</th>
<th>fct(nm)</th>
<th>c/a</th>
<th>at%Pd</th>
<th>(nm)</th>
<th>at%Pd</th>
<th>bcc/fct ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>0.3869</td>
<td>0.956</td>
<td>43</td>
<td>0.2882</td>
<td>4</td>
<td>0.18</td>
</tr>
<tr>
<td>625</td>
<td>0.3797</td>
<td>-</td>
<td>40</td>
<td>0.2877</td>
<td>3</td>
<td>0.1</td>
</tr>
<tr>
<td>575*</td>
<td>0.3858</td>
<td>0.957</td>
<td>40</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>550</td>
<td>0.3807</td>
<td>0.997</td>
<td>40.5</td>
<td>0.2857</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>425*</td>
<td>0.3827</td>
<td>0.993</td>
<td>46</td>
<td>trace</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>415</td>
<td>0.3810</td>
<td>0.998</td>
<td>42</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>370</td>
<td>0.3817</td>
<td>0.988</td>
<td>40</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>325*</td>
<td>0.3837</td>
<td>0.984</td>
<td>45</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>0.3841</td>
<td>0.975</td>
<td>43</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>0.3866</td>
<td>0.976</td>
<td>51</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.3858</td>
<td>0.99</td>
<td>55</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*: Sputtered with low ion beam energy
Fig. (51a) Room temperature X-Ray results for Fe₆₅Pd₃₅ thin film alloy deposited at designated $T_s$. 

Fig. (51b)
Fig.(52) a) TEM 200 micrograph of Fe,Pd thin film alloy deposited at room temperature x60000.
b) TEM 200 electron micrograph of (a). (200KV).

Fig.(53) a) TEM 200 micrograph of Fe,Pd thin film deposited at 300°C with low ion beam energy. It shows fringes and twins x400000.
b) TEM 200 electron diffraction of (a) indicating epitaxy.

Fig.(54) Comparison between TEM 200 electron diffractions of Fe,Pd thin film deposited a) at 300°C. b) deposited at RT, then annealed at 300°C in situ.
Fig.(55a) SEM 250 micrograph of equilibrium characteristic Fe_{50}Pd thin film alloy deposited at 625°C (tilted 45°).

Fig.(55b) SEM 250 micrograph of equilibrium characteristic Fe_{60}Pd thin film alloy deposited at 650°C (flat).
4.2.5 Results and discussion based on FePd thin film alloy

a) Results

This alloy is examined to clarify the anomalous results observed in the Fe\textsubscript{60}Pd thin film alloy around the Curie temperature ($T_c$) regions. Table (17) shows the room temperature X-Ray results based on FePd thin film alloys.

Variation of room temperature lattice spacings and c/a axial ratio with $T_S$ is shown in fig. (56a & 56b). Well above $T_c$, an fct structure with $c/a \approx 0.962$ is observed, whereas with a decrease in $T_S$, in the vicinity of $T_c$, c/a approaches to unity. With further decreasing $T_S$, there follows an increase in the degree of tetragonality.

All the deposition took place below $T_{02}$ temperature.

b) Discussion

When $T_S$ is just below the eutectoid transformation temperature, an ordered fct structure forms directly on deposition. The corresponding composition for the fcc structure is above 50 at\%Pd. Similarly, when $T_S$ is just below the Curie region, an fct(fcc) structure is formed directly on deposition with increasing c/a axial ratio. The corresponding composition for the equivalent fcc structure is about 39 at\%Pd. It appears that the structure and ordering close to the Curie temperature is affected by magnetism. A similar effect is observed in Fe\textsubscript{60}Pd thin film alloys (section 4.2.4).

When $T_S$ is well below Curie temperature, an fct phase forms
directly on deposition with an increase in the degree of
tetragonality. As before, this suggests that on decreasing \( T_s \)
below \( T_C \), the degree of tetragonality increases, and
subsequently the degree of ordering increases. This is
supported by the characteristic of c/a ratio versus \( T_s \), shown
in fig.(56b).

A similar behaviour is observed in Fe_{60}Pd thin film alloys. In
Fe_{60}Pd thin film alloy, initially the approach to unity of c/a
ratio just above Curie temperature is considered to be due to
the absence of bcc phase, thus the fct structure becomes less
stable. However, since in FePd thin film alloy the presence of
bcc structure is not expected, there should therefore, be an
effect from magnetism on the structure which controls the c/a
ratio in fct phase. When \( T_s \) is well below the Curie
temperature, the decrease in c/a could indicate an increase in
the degree of ordering.

c) Summary

At high temperatures, an ordered fct structure forms directly
on deposition. At intermediate temperatures, near \( T_C \), both the
FePd phase boundary and the degree of tetragonality is affected
by magnetism.

The increase in the degree of tetragonality is considered to be
due to the increase in degree of ordering. When \( T_s \) is well
below \( T_C \), an FePd phase with increasing degree of ordering is
observed.

Table (18) summarises the results based on FePd thin film
alloys.
Table (18) Summary of the results for Fe-Pd thin film alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>STRUCTURES OBSERVED WITHIN DEPOSITION TEMP. RANGE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T=°C 650 600 550 500 450 400 350 300 250 200 150 100</td>
</tr>
<tr>
<td></td>
<td>Fct. (D+T.Thro.T02) +→ Fcc. (ext) (D)</td>
</tr>
<tr>
<td></td>
<td>Fct. (c/a &lt; 1) +→ Fcc (fct) +→ Fcc (ext) (D)</td>
</tr>
<tr>
<td></td>
<td>Fct. (c/a &lt; 1) +→ Fcc (fct.) +→ Fct. (c/a &lt; 1) (Due to DEG. ORD.)</td>
</tr>
<tr>
<td></td>
<td>Fct. +→ Fct. (fct.) +→ Fct. (c/a &lt; 1) (Due to DEG. ORD.)</td>
</tr>
</tbody>
</table>

D : Diffusion
T : Transformation
Ts : Substrate Temperature
Table (17) Room temperature X-Ray results for fct FePd thin film alloy

<table>
<thead>
<tr>
<th>$T_s$ (°C)</th>
<th>fct (nm)</th>
<th>c/a</th>
<th>at%Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>0.3867</td>
<td>0.962</td>
<td>46.0</td>
</tr>
<tr>
<td>470</td>
<td>0.3795</td>
<td>0.997</td>
<td>39.0</td>
</tr>
<tr>
<td>300</td>
<td>0.3838</td>
<td>0.98</td>
<td>50</td>
</tr>
</tbody>
</table>

Fig. (56a) Room temperature X-ray result for FePd thin film deposited at designated $T_s$.

Fig. (56b) Fct lattice c/a axial ratio $V T_s$ in FePd T.F
4.2.6 Discussion on Fe-Pd thin film alloys

The structure of Fe\textsubscript{x}-Pd\textsubscript{1-x} (0.85 > x > 0.50) thin films, codeposited at substrate temperatures between 300-700°C has been examined at room temperature. The sequence of phases developed as \( T_s \) changed can be explained in terms of three factors.

a) the structure of the initial phase,

b) diffusion at the designated temperature,

c) transformations which occurs on cooling through temperature \( T_{ol} \) (where \( \Delta G^{fcc-bcc} = 0 \) or \( T_{o2} \).

The structure of the initial phase depends whether \( T_s \) is above or below \( T_o \).

At high \( T_s \), above \( T_{ol} \), for the Fe\textsubscript{85}Pd, Fe\textsubscript{75}Pd, Fe\textsubscript{70}Pd and Fe\textsubscript{60}Pd alloys, if the initial deposit is a single fcc phase, then by diffusion it decomposes to a mixture of equilibrium (fcc + bcc) phases; on cooling to room temperature, the fcc phase transforms to an fct structure as it crosses \( T_{o2} \), while the bcc phase remains unchanged.

With the lowering the value of \( T_s \) and decreased diffusion, depending on the effect of Pd on the \( M_s \) and whether \( T_s \) is above or below \( T_o \), the following sequences can be interpreted.

With Fe\textsubscript{85}Pd alloy when the deposition is below \( T_{ol} \), initially a bcc single phase forms on deposition which then decomposes into (bcc + fcc) structures. With decreased diffusion due to lowering \( T_s \), a small amount of fcc phase can precipitate from bcc phase. Subsequently, on cooling to room temperature, the fcc phase transforms through \( T_{ol} \) to a bct structure with the bcc phase retained unchanged but not detected due to the scattering noise in X-Ray diffraction traces.
At lower $T_s$ diffusion becomes restricted and further decomposition of the initial deposited phase is no longer possible. Therefore a single phase with composition close to the target alloy is observed.

With decrease in $T_s$, the relative volume ratio of bcc(bct)/fcc(fct) phases increases. This is interpreted as a decrease in fcc(fct) precipitation with lowering $T_s$.

The above mechanism highlights the important relation between diffusion distance $\overline{X}$, $T_s$ and subsequently $T_0$ temperature.

Similar characteristics have been observed in Fe$_3$Pd and Fe$_{70}$Pd alloys. However in the Fe$_{70}$Pd alloy, at lower temperature, there exists some complication associated with Invar effect and where the two $T_0$ ($T_{01}$ and $T_{02}$) cross each other. With increase in Pd content in the target alloy, a lower $T_{01}$ temperature has been detected.

The Fe-Pd alloys with 40at% and 50at% Pd content which were used as sputtering targets, illustrate additional features on which reflects the effect of magnetism and ordering. These alloys did not show a bcc structure for $T_s$ less than 500°C, but in the range of 550 $T_s$ 450°C, a stable fcc structure was observed. Although the results are consistent an unambiguous reason for this behaviour is not known. But the presence of stable fcc phase in this region could be due to the magnetic effect caused in the vicinity of the Curie temperature. Alternatively, the absence of a bcc phase may reflect reduced prior chemical microsegregation. A continuous increase in degree of tetragonality for fct structure when $T_s$ is below 400°C, can be considered to be due to the increase in degree of ordering. When $T_s$ decreases, diffusion becomes restricted and only fcc single phase is observed.
4.3 Results and discussion based on Fe-Pt thin film alloys

4.3.1 Results and discussion based on Fe\textsubscript{85}Pt thin film alloy

a) Results

Room temperature X-Ray results for sputtered Fe\textsubscript{85}Pt thin film alloys are shown in Table (19a & 19b). Structure of thin films deposited from a Fe\textsubscript{85}Pt target with T\textsubscript{s}, between 650-500\textdegree C, show an fcc and a mixture of bcc phases. At lower T\textsubscript{s}, (below T\textsubscript{01} (where $\Delta G^{fcc-bcc} = 0$) only single bcc phase is observed. At higher deposition temperatures equilibrium (fcc + bcc) phases are formed. At intermediate T\textsubscript{s}, metastable bcc(bct) + fcc phases are formed. At lower T\textsubscript{s}, only a single bcc (bct) structure is observed.

The variation of fcc lattice spacings with T\textsubscript{s} is shown in fig.(57a).

At high T\textsubscript{s}, the fcc lattice spacings remain fairly constant within a scattered band, and then increase as the T\textsubscript{s} is decreased (when low ion beam energy is used).

The changes in the bcc lattice spacings at high T\textsubscript{s} is small, but as the deposition temperature decreases, a bcc(bct) structure with c/a $> 1$ is observed. At lower deposition temperatures, only a bcc(bct) structure is observed (fig.57b).

The room temperature low angle 2\theta X-Ray diffraction patterns corresponding to the deposition temperatures shows the presence of (fcc + bcc + bcc') phases.

In this alloy, the accuracy of the measurement for the fcc phase is poor, mainly because of the peak broadening due to the presence of phase mixtures.
b) **Discussion**

At $T_s$ above $600^\circ$C, the initial deposit is a disordered fcc structure above $T_{01}$ temperature. This then decomposes by diffusion to an equilibrium disordered (fcc + bcc) structures. On cooling to room temperature, the disordered fcc structure transforms partially to martensite on passing the $M_s$ temperature. The equilibrium bcc structure remains unchanged. In the equilibrium two phase regions, the lattice parameters of both phases increases slightly with $T_s$.

When $T_s$ is between $600-500^\circ$C, the same sequences as before take place. However, on further quenching in liquid nitrogen, the residual disordered fcc structure transforms to a bcc(bct) martensite, leaving an fcc phase with high lattice spacings. ie.the fcc' ordered structure.

Fig.(57c) shows a disordered and ordered fcc phase with larger lattice parameters (before and after quench in liquid nitrogen). The bcc'/fcc volume ratio with $T_s$ (fig.57c), suggests that disordered fcc phase is further transformed to martensite. Therefore an increase in volume of bcc'is observed.

It can be assumed that the room temperature fcc phase in this temperature range is a mixture of two phases. ie. fcc'(ordered) + fcc-(disordered). This hypothesis is supported by deposition of single composition thin films with a lower rate of deposition. As shown in fig.(57d) by allowing more time for atomic rearrangement at the surface for a given $T_s$, the rate of diffusion becomes enhanced and there is a lattice parameter increase corresponding to an increase in Pt content. Also, no martensitic structure is observed when the deposition rate is
lowered.
Skinner (50) also observed the emergence of an fcc phase with larger lattice spacings in alloys with a higher Pt content at low temperatures due to martensite formation resulting is an austenite component with lower Pt content (higher $M_s$).

When $T_s$ is in the region below $450^0C$, a bcc structure forms directly below the $T_{01}$ temperature, and at room temperature, only a metastable single phase bcc(bct) is observed. Although no fcc structure was detected for the alloy deposited below $T_{01}$, it appears that the initially deposited bcc phase has decomposed to bcc + fcc structures. Since the initial deposit is the most stable phase, with the restricted diffusion at low $T_s$, very little fcc phase is precipitated, which with available techniques is difficult to detect.

X-Ray diffraction in fig.(57e) show the sequence of phase formation. As $T_s$ decreases, diffusion becomes more restricted and subsequently a single bcc phase close to target composition is formed.

c) Summary

When $T_s$ is above $600^0C$, above $T_{01}$, equilibrium (bcc + fcc) phases are formed. Below this temperature and above the $T_{01}$ temperature, similar phases are formed with the fcc being a mixture of ordered and disordered phases. This hypothesis is supported by increasing the rate of diffusion through a reduction of ion beam energy. Below the $T_{01}$ temperature, only a bcc(bct) structure is observed, but the decomposition of the bcc phase to (bcc + fcc) structures cannot be excluded.
Table (19a) Room temperature X-Ray results for fcc Fe$_{85}$Pt thin film alloys before and after quench in LN.

<table>
<thead>
<tr>
<th>$T_\circ$ (°C)</th>
<th>fcc(nm)</th>
<th>at%Pt</th>
<th>fcc(nm)</th>
<th>at%Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>670</td>
<td>0.370</td>
<td>16.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>650</td>
<td>0.3704</td>
<td>18.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>625</td>
<td>0.3697</td>
<td>15.5</td>
<td>0.3723</td>
<td>19</td>
</tr>
<tr>
<td>610</td>
<td>0.3705</td>
<td>19.0</td>
<td>0.3718</td>
<td>18.0</td>
</tr>
<tr>
<td>590</td>
<td>0.3695</td>
<td>14.0</td>
<td>0.3715</td>
<td>16.5</td>
</tr>
<tr>
<td>575</td>
<td>0.3698</td>
<td>16.0</td>
<td>0.3713</td>
<td>16.0</td>
</tr>
<tr>
<td>550*</td>
<td>0.3729</td>
<td>23.0</td>
<td>0.373</td>
<td>23.0</td>
</tr>
<tr>
<td>525</td>
<td>0.370</td>
<td>16.0</td>
<td>0.372</td>
<td>18.3</td>
</tr>
<tr>
<td>500*</td>
<td>0.3742</td>
<td>25.0</td>
<td>0.374</td>
<td>25.0</td>
</tr>
</tbody>
</table>

*: Sputtered with low ion energy

LN: Liquid Nitrogen
bQ: before quench
aQ: after quench

Table (19b) Room temperature X-Ray results for bcc(bct) Fe$_{85}$Pt thin film alloys.

<table>
<thead>
<tr>
<th>$T_\circ$ (°C)</th>
<th>a(nm)</th>
<th>c(nm)</th>
<th>c/a</th>
<th>at%Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>670</td>
<td>0.29</td>
<td>-</td>
<td>-</td>
<td>7.0</td>
</tr>
<tr>
<td>650</td>
<td>0.291</td>
<td>-</td>
<td>-</td>
<td>8.5</td>
</tr>
<tr>
<td>625</td>
<td>0.29</td>
<td>-</td>
<td>-</td>
<td>8.5</td>
</tr>
<tr>
<td>610</td>
<td>0.291</td>
<td>-</td>
<td>-</td>
<td>8.5</td>
</tr>
<tr>
<td>590</td>
<td>0.291</td>
<td>-</td>
<td>-</td>
<td>8.5</td>
</tr>
<tr>
<td>575</td>
<td>0.29</td>
<td>-</td>
<td>-</td>
<td>7.0</td>
</tr>
<tr>
<td>550*</td>
<td>0.2932</td>
<td>0.2924</td>
<td>1.003</td>
<td>9.0</td>
</tr>
<tr>
<td>525</td>
<td>0.29</td>
<td>-</td>
<td>-</td>
<td>7.5</td>
</tr>
<tr>
<td>500*</td>
<td>0.2874</td>
<td>0.2932</td>
<td>1.02</td>
<td>6.5</td>
</tr>
<tr>
<td>450</td>
<td>0.293</td>
<td>0.2935</td>
<td>1.002</td>
<td>13.0</td>
</tr>
<tr>
<td>350</td>
<td>0.2923</td>
<td>0.2943</td>
<td>1.008</td>
<td>14.5</td>
</tr>
<tr>
<td>250</td>
<td>0.2953</td>
<td>0.306</td>
<td>1.03</td>
<td>17.0</td>
</tr>
</tbody>
</table>

*: Sputtered with low ion energy.
Fig. (57) Room temperature X-Ray results for Fe$_{85}$Pt$_{15}$ thin film alloy deposited at designated $T_s$. 
Fig. (57e) Room temperature low angle X-Ray diffractions for Fe$_{85}$Pt$_{15}$ thin film alloys deposited at designated Ts.
4.3.2 Results and discussion based on Fe₃Pt thin film alloy

a) Results

Room temperature X-Ray results for sputtered Fe₃Pt thin films are shown in Table (20a & 20b). At high $T_s$, the structure of the thin film alloy corresponds with the expected equilibrium single fcc phase with fairly constant lattice parameters. As the $T_s$ is reduced, an increasing amount of an additional bcc structure is formed together with an ordered fcc(fct) phase. The fcc lattice spacings increase as $T_s$ decreases. As a result of further decrease in $T_s$, an fct structure with a c/a axial ratio close to unity is observed (fig.58a).

Determination of the c/a axial ratio in the fct structure is based on (111), (200), (220) and (222) X-Ray reflections only. At high $T_s$, no bcc phase is observed, but as the deposition temperatures are reduced, the bcc lattice parameter increases continuously (fig.58b).

The intensity ratio of the bcc/fcc (fct) based on (110)/(111) diffractions shows an increase with decreasing $T_s$. At intermediate values of $T_s$, a decrease in the volume ratio is observed, (fig.58c).(dashed line)

Room temperature X-Ray diffraction at low diffraction angles, shows the sequence of phases observed as $T_s$ changes (fig.58d). TEM electron diffraction supports the X-Ray diffraction results.

b) Discussion

Fe₃Pt alloys deposited at $T_s$ above 600°C, are ordered single
fcc phases with corresponding chemical composition about 25 at%Pt. This is because at high $T_s$, both kinetics of ordering and diffusion are high. The glancing angle technique using a Debye-Scherrer camera and subsequent densitometer measurement proved to be useful to show the relative intensity of the ordered diffractions.

When $T_s$ is between $600 > T_s > 450^\circ C$, both the fcc and bcc lattice parameters increase. It is assumed that the initial phase formed on deposition when above $T_{01}$ temperature, is fcc and this decomposes into (fcc + bcc) phases by diffusion. These phases remain unchanged on cooling to room temperature. The chemical composition of the bcc phase increases (continuous increase in lattice parameters) as $T_s$ decreases. But for the ordered fcc phase the composition remains constant over the $T_s$ range.

When $T_s$ is below $\sim 425^\circ C$, an fcc phase is formed on deposition, which then decomposes to fcc + metastable bcc structures by diffusion. On cooling to room temperature, the fcc phase then transforms to an ordered fct structure by crossing the $T_{02}$ temperature of FePt phase. The c/a axial ratio in the fct structure remains fairly constant as $T_s$ decreases. The c/a ratio was detected from line broadening and the mismatch of the lattice parameter for each individual reflection. At low $T_s$, only (110) and (111) diffractions are observed. Analysis of stacking fault effects showed an inconclusive result. This does not totally exclude the presence of strain and defects in the thin film, but supports the interpretation of the presence of an fct structure.

The lattice spacings of the bcc phase increased as $T_s$. 
decreased. With this alloy composition, since all depositions took place above $T_0$, a bcc phase precipitated from the initially deposited fcc structure.

The Pt composition of the bcc phase, Table (20b), varies from about 10 at%Pt at high deposition temperatures to about 24 at%Pt at $T_s \approx 200^\circ$C. This is consistent with the increase in bcc/fcc (fct) volume ratio with decreasing $T_s$ (fig.58c).

It is clear that as $T_s$ decreases, diffusion become more difficult and the composition of thin film alloy is close to the target alloy composition. In addition to the diffusion, transformations of phases through $T_q$ temperatures are important in determining room temperature structures.

4.3.3 Detection of ordering in Fe₃Pt thin film alloy

The detection of Fe₃Pt superlattice lines becomes increasingly difficult as the substrate temperature decreases. However, a marked increase of the fcc lattice spacing with decrease in substrate temperature is consistent with significant ordering (53-56).

In order to relate the increase of lattice spacing with an ordering effect, some assumptions have to be made. An increase in lattice parameter with the decrease in deposition temperature can be interpreted as the result of:

a) Chemical ordering.

b) An increase in Platinum content.

Using Ling and Owen's results (53) (fig.59), by assuming a continuous incremental increase in the fcc lattice spacings with composition, a standard calibration curve is established. When $T_s$ is above $600^\circ$C, the ordered fcc phase has a
corresponding degree of ordering of about 0.8 (53). In the $T_s$ range $600 > T_s > 450^0C$ the increase of fcc lattice spacings is initially considered to be due to the chemical ordering.

If the increase in the lattice spacings is considered to be due only to an increase in the chemical composition, the Pt composition differences between case (a) and (b) in the fcc phase is increased by about 2at% Pt.

For $T_s$ below $425^0C$, the composition of the fct structure is determined by calculating the equivalent volume corresponding to fcc lattice spacings. A composition variation in the range of 27.5-33 at%Pt with $T_s$ is then observed, which contradicts the hypothesis of a constant chemical composition on ordering. However, if the $c/a$ ratio for fct phase in this work is compared with other reported values (21,91,161), a composition close to the alloy target (25 at%Pt) is deduced. At low $T_s$, due to the lack of necessary diffraction lines, accurate determination of $c/a$ ratio is difficult, but the results are consistent. This tetragonality is likely to be the combined result of chemical and magnetic ordering.

A microstructural study of the Fe$_3$Pt thin film alloy deposited at $T_s$ $350^0C$ and $230^0C$ confirms the X-Ray diffraction results. Electron diffraction for thin films deposited at $350^0C$ shows the presence of two cubic phases with a weak bcc diffraction intensity. This is associated with a decrease in the volume of bcc phase shown in fig.(60b). Whether this decrease is related to the appearance of the fct structure is not known. The corresponding micrograph (fig.60a), shows a grain size of the order of less than 10 nm, together with the presence of twin or
distorted plates. These plates could be related to the strains in the thin film.

For the films deposited at 230°C, two cubic phases are observed. From broad electron diffractions, a bcc and fct phase with c/a ratio close to unity is identified (fig. 61a & 61b). The presence of texture on electron diffractions patterns could be due to the grain alignment in the vicinity of Curie temperature. The corresponding micrograph shows much smaller grain sizes when compared with the one deposited at 350°C. This indicates that as Tₛ decreases, diffusion become more restricted and subsequently a smaller grain size is observed.

c) Summary

The mechanism of phase formation is considered to be dependent on both diffusion and the thermodynamics of phase transformation. Although, except at high Tₛ, the expected superlattice diffractions are not detected, the increase in lattice spacings with decreasing Tₛ has been interpreted to be due to ordering. The following interpretation can then be made. At high Tₛ, because of high surface diffusion dominant in sputtered thin films (152,153), an ordered fcc structure with a high degree of ordering is formed. By reducing Tₛ, the high degree of ordered fcc phase persists together with a bcc structure. At lower Tₛ, diffusion becomes restricted, but in transforming the fcc to fct structure through Tₒ₂, the thermodynamics of phase transformation becomes dominant. The lattice spacing and volume of the bcc phase increase with decreasing Tₛ.
Table (20a) Room temperature X-Ray results for Fe$_3$Pt thin film alloys.

<table>
<thead>
<tr>
<th>$T_s$ ($^\circ$C)</th>
<th>a (nm)</th>
<th>c/a</th>
<th>at%Pt (od)</th>
<th>ratio of bcc/fcc(fct)</th>
</tr>
</thead>
<tbody>
<tr>
<td>675</td>
<td>0.3733</td>
<td>-</td>
<td>24.0</td>
<td>-</td>
</tr>
<tr>
<td>650</td>
<td>0.3733</td>
<td>-</td>
<td>24.0</td>
<td>-</td>
</tr>
<tr>
<td>625</td>
<td>0.3732</td>
<td>-</td>
<td>23.9</td>
<td>-</td>
</tr>
<tr>
<td>600</td>
<td>0.3733</td>
<td>-</td>
<td>24.0</td>
<td>-</td>
</tr>
<tr>
<td>550</td>
<td>0.3753</td>
<td>-</td>
<td>26.5</td>
<td>0.16</td>
</tr>
<tr>
<td>475</td>
<td>0.3753</td>
<td>-</td>
<td>26.5</td>
<td>0.22</td>
</tr>
<tr>
<td>450</td>
<td>0.3625</td>
<td>-</td>
<td>27.5</td>
<td>0.22</td>
</tr>
<tr>
<td>415</td>
<td>0.3777</td>
<td>0.995</td>
<td>25.0</td>
<td>0.37</td>
</tr>
<tr>
<td>360</td>
<td>0.3793</td>
<td>0.99</td>
<td>25.0</td>
<td>0.16</td>
</tr>
<tr>
<td>340</td>
<td>0.3775</td>
<td>0.994</td>
<td>25.0</td>
<td>0.24</td>
</tr>
<tr>
<td>280</td>
<td>0.3788</td>
<td>0.995</td>
<td>25.0</td>
<td>0.4</td>
</tr>
<tr>
<td>230</td>
<td>0.3767</td>
<td>-</td>
<td>25.0</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table (20b) Room temperature X-Ray results (body centred) for Fe$_3$Pt thin film alloys.

<table>
<thead>
<tr>
<th>$T_s$ ($^\circ$C)</th>
<th>a (nm)</th>
<th>at%Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>0.2921</td>
<td>10.5</td>
</tr>
<tr>
<td>475</td>
<td>0.293</td>
<td>13.0</td>
</tr>
<tr>
<td>450</td>
<td>0.294</td>
<td>15.5</td>
</tr>
<tr>
<td>415</td>
<td>0.295</td>
<td>16.8</td>
</tr>
<tr>
<td>360</td>
<td>0.296</td>
<td>18.0</td>
</tr>
<tr>
<td>340</td>
<td>0.296</td>
<td>20.0</td>
</tr>
<tr>
<td>280</td>
<td>0.298</td>
<td>22.0</td>
</tr>
<tr>
<td>230</td>
<td>0.299</td>
<td>24.0</td>
</tr>
</tbody>
</table>
Fig. (58) Room temperature X-Ray results for Fe$_2$Pt thin film alloy deposited at designated $T_s$. 

Fig. (58a) 

Fig. (58b) 

Fig. (58c) 

Fig. (58d)
Fig. (59) Room temperature fcc lattice spacings vs. Pt composition in Fe-Pt alloys.
Fig. (60) a) TEM 200 micrograph of Fe$_2$Pt thin film alloy deposited at 350°C. x720000.
   b) TEM electron micrograph of (a).

Fig. (61) a) TEM 200 micrograph of Fe$_2$Pt thin film deposited at 230°C x720000.
    b) TEM electron diffractions of alloy (a).
4.3.4 Results and discussion based on Fe$_{70}$Pt thin film alloy

a) Results

The purpose of examining this alloy is to support the assumptions made for interpreting the results on Fe$_3$Pt thin film alloys.

Fe$_{70}$Pt thin film alloys were deposited with $T_s$ between 500-230°C. Room temperature X-Ray results for sputtered Fe$_{70}$Pt alloys are shown in Table (21). The microprobe results show an actual composition of 29.8 at% Pt.

At high $T_s$, an fcc structure is observed. As $T_s$ decreases, a fct structure becomes predominant (fig.62a). The degree of tetragonality increases with decreasing $T_s$. The variation in c/a axial ratio with $T_s$ is shown in (fig.62b).

Unlike Fe$_3$Pt thin film alloys, no bcc phase is observed in the Fe$_{70}$Pt alloy.

b) Discussion

The Fe$_{70}$Pt alloy which is assumed initially to be deposited as an ordered fcc phase at 500°C retains its structure without any changes on cooling to room temperature. The corresponding composition for the fcc lattice parameter is found to be 29.9 at% Pt.

If this phase is formed above the $T_{02}$ of the FePt phase, theoretically, the fcc phase should transform into an fct structure on further cooling. By not doing so, it suggests that the ordered Ll$_2$ fcc phase has been stabilised and subsequently no further phase transformation takes place on cooling to room
temperature.
As the $T_s$ decreases, an ordered fct structure is formed on deposition. This indicates the deposition took place below the $T_{02}$ temperature.
The decrease in the c/a axial ratio for fct with the decrease in $T_s$ is consistent with an increase in the degree of ordering and a tendency for the Platinum composition to remain constant.

If the decrease in the c/a ratio is interpreted as a change of composition, the corresponding Platinum composition will be greater than 50 at%Pt. which is unlikely, unless there is a further eutectoid reaction of the form $\text{Fe}_3\text{Pt} \rightarrow \text{bcc} + \text{FePt}$. Table (22) summarises the results based on vapour deposited Fe-Pt alloys.
Table (21) Room temperature X-Ray results for Fe\textsubscript{70}Pt\textsubscript{30} thin film alloy fcc(fct) structure

<table>
<thead>
<tr>
<th>$T_s$ (°C)</th>
<th>a (nm)</th>
<th>c/a</th>
<th>c (nm)</th>
<th>at%pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.3772</td>
<td>-</td>
<td>-</td>
<td>29.9</td>
</tr>
<tr>
<td>400</td>
<td>0.3793</td>
<td>0.99</td>
<td>0.3785</td>
<td>29.7</td>
</tr>
<tr>
<td>360</td>
<td>0.380</td>
<td>0.99</td>
<td>0.3766</td>
<td>29.2</td>
</tr>
<tr>
<td>280</td>
<td>0.3831</td>
<td>0.972</td>
<td>0.3706</td>
<td>30.0</td>
</tr>
<tr>
<td>230</td>
<td>0.383</td>
<td>0.962</td>
<td>0.3685</td>
<td>30.0</td>
</tr>
</tbody>
</table>

Table (22) Summary of the results in Fe-Pt thin film alloys

OBSERVED PHASES AND MECHANISM OF PHASE FORMATION AND TRANSFORMATION IN Fe-Pt THIN FILM ALLOYS

<table>
<thead>
<tr>
<th>Alloy</th>
<th>STRUCTURES OBSERVED WITHIN DEPOSITION TEMP. RANGE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>700 650 600 550 500 450 400 350 300 250 200</td>
</tr>
<tr>
<td>$T_s$</td>
<td></td>
</tr>
<tr>
<td>Fe\textsubscript{80}Pt\textsubscript{20}</td>
<td>fcc+bcc+bcc(bcc)</td>
</tr>
<tr>
<td></td>
<td>(D)</td>
</tr>
<tr>
<td></td>
<td>+ fcc+bcc+bcc'</td>
</tr>
<tr>
<td></td>
<td>D+T.Thro.$T_{o1}$ below $T_{o1}$</td>
</tr>
<tr>
<td>Fe\textsubscript{75}Pt\textsubscript{25}</td>
<td>fcc+bcc+bcc(bcc)</td>
</tr>
<tr>
<td></td>
<td>(D)</td>
</tr>
<tr>
<td></td>
<td>+ fct+bcc(bcc)</td>
</tr>
<tr>
<td></td>
<td>(D+T.Thro.$T_{o2}$)</td>
</tr>
<tr>
<td>Fe\textsubscript{70}Pt\textsubscript{30}</td>
<td>fcc+bcc+bcc(bcc)</td>
</tr>
<tr>
<td></td>
<td>(D)</td>
</tr>
<tr>
<td></td>
<td>+ fct+bcc(bcc)</td>
</tr>
<tr>
<td></td>
<td>(D+T.Thro.$T_{o3}$)</td>
</tr>
<tr>
<td></td>
<td>fcc</td>
</tr>
<tr>
<td></td>
<td>+ fct(oc)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

D: Diffusion
T: Transformation
$T_s$: Substrate Temperature (°C)
od: Order
Fig. (62) Room temperature X-Ray results for Fe$_{70}$Pt$_{30}$ thin film alloy deposited at designated temperature.
4.3.5 Discussion on Fe-Pt thin film alloys

The structure of Fe$_x$-Pt$_{1-x}$ (0.85 $>$ x $>$ 0.70) alloys co-deposited at substrate temperatures between 200-700°C has been examined at room temperature. Similar assumptions as the ones in the Fe-Pd alloys (see section 4.2.6) are made to explain the sequence of phases developed as $T_s$ changed.

With a Fe$_{85}$Pt thin film alloy, at high $T_s$, above $T_{01}$, the initial deposit fcc single phase decomposes to equilibrium (fcc + bcc) phases by diffusion. This structure is retained on cooling to room temperature. With intermediate $T_s$ (600 $>$ $T_s$ $>$ 450°C), in addition to (fcc + bcc) phases, a martensite structure is observed at room temperature. The fcc phase partially transforms to a bct(bcc) structure through $T_{01}$ temperature. On further quenching in liquid nitrogen the residual fcc shows an increase in lattice parameter. Based on this observation it is postulated that the fcc phase in these temperature ranges is a mixture of two phases, i.e. ordered fcc', and disordered fcc. This hypothesis is supported by the enhancement of the rate of diffusion (lowering sputtering ion beam energy) and subsequent observation of an increase in fcc lattice spacing in the absence of martensitic structure.

For all depositions below $T_{01}$, only bcc(bct) single phase with very little (if at all) decomposition to fcc + bct(bcc) is observed, which underlines the reduction of diffusion with decrease in $T_s$. This supports the decrease in diffusion due to low $T_s$. 
With Fe$_3$Pt thin film alloy, ordered fcc single phase is observed at high $T_s$.

At the intermediate $T_s$ (600 > $T_s$ > 400°C), above $T_{01}$, the initially deposited fcc phase decomposes to (fcc + bcc) structures. These structures are retained on cooling to room temperature.

Combined experimental results from Fe$_{85}$Pt and Fe$_3$Pt in the $T_s$ range (575-600°C), yielded the formation of a eutectoid with composition ~17at% Pt.

As $T_s$ decreases, an increase in fcc lattice parameter is interpreted as an increase in degree of ordering. This hypothesis is supported by unchanged Pt chemical composition within its $T_s$ range.

An increase in the bcc lattice spacings is due to increase in composition of Pt in the metastable phase.

When $T_s$ is <400°C, the initial deposit above $T_{01}$ is fcc which then decomposes to (bcc +fcc) structures by diffusion. On cooling to the room temperature, the fcc phase transforms to an fct structure through temperature $T_{02}$. The anomalous results were initially interpreted as to be due to magnetic effect in the vicinity of $T_c$. But the effect had already started about 150°C above the $T_c$ (od) temperature. Although the magnetic effect at the phase boundary cannot be denied (115), the examination of Fe$_{70}$Pt thin film alloy confirmed the formation of an fct structure through $T_{02}$. However, an fct phase stabilisation by the magnetic effect is likely.
Furthermore with Fe$_{70}$Pt thin film an increase in degree of
tetragonality with constant Pt chemical composition as $T_s$
decrease is interpreted to be due to the increase in degree of
ordering.

As $T_s$ decreases more bcc phase is segregated and the
bcc(bct)/fcc(fct) volume ratio illustrates an increase with
decrease in $T_s$. Fig.(58c)

With lowering $T_s$ diffusion becomes more difficult so that no
further decomposition can take place and the composition of
thin film alloy approaches to the composition of the target
alloy.

It is clear that both $T_0$ temperature and $T_s$ play an important
role in determining thin film alloy structures.
4.4 Results and discussion based on Fe-Pt-Ni thin film alloys

4.4.1 Results and discussion based on Fe$_3$(Pt$_{0.9}$Ni$_{0.1}$) - Fe$_3$(Pt$_{0.6}$Ni$_{0.4}$) thin film alloys

a) Introduction

Two alloys Fe$_3$(Pt$_{0.9}$Ni$_{0.1}$) and Fe$_3$(Pt$_{0.6}$Ni$_{0.4}$) were used as two independent sputtering targets. The geometry relative to the ion beam and the substrate position was arranged so that two cones of sputtered atoms would overlap and produce a composition gradient on a thin film (fig.43). The composition range spans the compositions of the two target alloys, and $T_s$ was varied in the range of 150 to 675°C. As before, the structure of the alloy was examined mainly by X-Ray diffractometry.

The structures of these alloys had similar characteristics to the Fe-Pt alloys discussed in section 4.3.1, but by using the composition gradient deposition technique, a more rapid assessment of phase equilibria and its related characteristics can be illustrated. Furthermore, the effect of substituting 3-7 at% Ni for Pt in a Fe$_3$Pt alloy is obtained.

b) Results

Three areas across the films were measured and the composition variation was measured by a JEOL 200 microprobe.

The deposition parameters of the alloys are shown in Table (12).

Table (23) shows the room temperature lattice parameters
measured for fcc and bcc phases by X-Ray diffraction for Fe$_3$
(Pt$_{0.9}$Ni$_{0.1}$) - Fe$_3$ (Pt$_{0.6}$Ni$_{0.4}$) composition gradient film 
alloy.

Results are presented for only one of the measured positions 
along the film composition Fe$_3$Pt$_{0.7}$Ni$_{0.3}$.
The variation of the fcc and bcc lattice parameters with the 
T$_s$, together with the low 20 Bragg diffraction angle is shown 
in fig (63a, 63b & 63c).

When T$_s$ is high, in addition to the fcc structure, an fcc' 
phase with a larger lattice parameter is observed. This 
diffraction corresponds to the ordered phase. The fcc lattice 
spacing increases continuously with decreasing T$_s$. A deviation 
to this trend is observed at lower T$_s$.
The room temperature bcc lattice spacings increase continuously 
as the T$_s$ decreases. At low T$_s$, only (111)fcc and (110)bcc 
X-Ray reflections are observed.
The X-Ray diffraction intensity ratio of the bcc(110)/fcc(111) 
increases with decreasing T$_s$ (fig.63d).

Although the method potentially reduces the number of 
experiments needed to cover the ternary system, the lattice 
parameter measurements for the co-deposited composition 
gradiant alloys are difficult to measure accurately. This 
is mainly because of the X-Ray diffractometer slit size effect 
and the unavoidable irradiation of a range of alloy film 
compositions in the film. The schematic diagram in fig.(64) 
illustrates this effect. Nevertheless, a significant 
consistency in the results is observed. Fig.(65a & 65b) shows 
the effect of substituting Ni for Pt in Fe$_3$Pt alloy, 
 ie. measuring the lattice spacings with (Fe$_3$Pt$_{0.7}$Ni$_{0.3}$) and 
(Fe$_3$Pt$_{0.9}$Ni$_{0.1}$) compositions.
The accuracy is further decreased as $T_s$ decreased. Although X-Ray reflections indicates a possible fct structure at low temperatures, sufficient diffractions are not available for a definite structure determination.

b) Discussion

At high $T_s$, a single fcc phase is initially formed directly on deposition. Superlattice lines were not detected from X-Ray diffraction patterns. This is due to the effect of the addition of Ni (about 7 at%Ni) to Fe-Pt alloy which reduced the ordering temperature (50). When the alloys are deposited at $650^0$C, two fcc phases are formed by diffusion at the deposition temperature, the ordered phase with high lattice parameter and a disordered structure with lower lattice parameter. This is consistent with the expected phase boundary at high temperature (49). The diffraction pattern illustrates the presence of two fcc phases.

When $T_s$ is between $650-550^0$C, a single fcc phase with constant lattice spacing is followed by the appearance of a bcc phase for $T_s$ below $550^0$C. This suggests, that when $T_s$ is below $550^0$C, but above $T_{01}$, the initial fcc structure decomposes by diffusion to (fcc + bcc) phases which remain unchanged on cooling to room temperature.

When $T_s$ is lowered, the continuous increases in the volume of the bcc phase suggest that a bcc structure is formed directly on deposition below $T_{01}$. This then decomposes to (bcc + fcc) structures by diffusion. This is also supported by continuous increase in volume ratio of bcc/fcc with decreasing $T_s$. 
Depending on $T_5$, the Ni composition and subsequently diffusion flux, the fcc phase either retains its structure on cooling, or transforms to an fct structure. On crossing $T_{02}$ temperature. Although the tetragonal structure is not detected unambiguously, the anomalous behaviour of the lattice spacings at lower $T_5$ (about $300^\circ C$) supports the possibility of formation of an fct structure in this region. A similar behaviour is observed in a Fe$_3$Pt thin film alloy where the fct structure forms at about $400^\circ C$.

At lower $T_5$, diffusion is reduced and the mobility of the deposited atoms are reduced. Therefore the initially deposited single phase remains undecomposed.

4.4.2 Effect of substituting of Ni for Pt in Fe$_3$Pt alloy thin films

As for the binary Fe-Pt alloys, the increase in the fcc lattice spacings with the decrease in $T_5$ is considered to be due to the increase in degree of ordering. As Ni content increases, the lattice spacings decrease with $T_5$. This is taken to indicate a lower degree of ordering and/or lower diffusion.

The results support the earlier study by Skinner (50) that the addition of Ni to a Fe$_3$Pt alloy, substantially reduces the ordering temperature.

The Pt content of the fcc phase decreases with increasing Ni concentration in Fe-Pt alloys. This effect is further discussed later when changes in chemical composition with $T_5$ is considered (see section 6).
Table (23) Room temperature lattice spacings and structures for composition gradient $\text{Fe}_x(\text{Pt Ni})_{1-x}$ Thin film alloys.

<table>
<thead>
<tr>
<th>$T_\circ (^\circ\text{C})$</th>
<th>Structure observed</th>
<th>Lattice parameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{Fe}_3(\text{Pt} 0.9 \text{ Ni}0.1)$</td>
<td>$\text{Fe}_3(\text{Pt} 0.8 \text{ Ni}0.2)$</td>
</tr>
<tr>
<td>200</td>
<td>f.c.c 0.3762</td>
<td>0.3752</td>
</tr>
<tr>
<td></td>
<td>b.c.c 0.2984</td>
<td>0.298</td>
</tr>
<tr>
<td>275</td>
<td>f.c.c 0.3778</td>
<td>0.3764</td>
</tr>
<tr>
<td></td>
<td>b.c.c 0.2973</td>
<td>0.297</td>
</tr>
<tr>
<td>325</td>
<td>f.c.c 0.3762</td>
<td>0.376</td>
</tr>
<tr>
<td></td>
<td>b.c.c 0.2968</td>
<td>0.2966</td>
</tr>
<tr>
<td>375</td>
<td>f.c.c 0.3748</td>
<td>0.3741</td>
</tr>
<tr>
<td></td>
<td>b.c.c 0.2941</td>
<td>0.2927</td>
</tr>
<tr>
<td>425</td>
<td>f.c.c 0.3742</td>
<td>0.3731</td>
</tr>
<tr>
<td></td>
<td>b.c.c 0.2932</td>
<td>0.2928</td>
</tr>
<tr>
<td>450</td>
<td>f.c.c 0.3748</td>
<td>0.3745</td>
</tr>
<tr>
<td></td>
<td>b.c.c 0.2906</td>
<td>0.2902</td>
</tr>
<tr>
<td>525</td>
<td>f.c.c 0.3749</td>
<td>0.3745</td>
</tr>
<tr>
<td></td>
<td>b.c.c 0.2898</td>
<td>0.29</td>
</tr>
<tr>
<td>575</td>
<td>f.c.c 0.3698</td>
<td>0.3696</td>
</tr>
<tr>
<td></td>
<td>(f.c.c) -</td>
<td>0.372</td>
</tr>
<tr>
<td>650</td>
<td>f.c.c 0.3697</td>
<td>0.3693</td>
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<tr>
<td></td>
<td>(f.c.c) 0.372</td>
<td>0.3718</td>
</tr>
<tr>
<td>675</td>
<td>f.c.c 0.3706</td>
<td>0.371</td>
</tr>
</tbody>
</table>
Fig. (63) Room temperature X-Ray results for Fe$_3$Pt$_{0.7}$Ni$_{0.3}$ thin film alloys (composition gradient) deposited at designated $T_s$. 

Fig. (63a)fcc lattice spacings (a) 

Fig. (63b)bcc lattice spacings (a) 

Fig. (63c) 

Fig. (63d) Int. ratio $T_s$ in comp. gradient Fe-Pt-Ni.
Fig. (64) Schematic representation of X-Ray slit with respect to specimen

Fig. (65a) and (65b) Overall room temperature X-Ray results for composition gradient Fe$_3$Pt$_{0.9}$Ni$_{0.1}$-Fe$_3$Pt$_{0.7}$Ni$_{0.3}$ thin film alloys deposited at designated $T_s$. 
CHAPTER FIVE

5. Calculation of surface diffusion in Fe-Pt alloys

5.1 Introduction

The controlling factors that define the shape of the phase diagram which apply to vapour deposited alloys are related to the kinetic conditions during deposition and transformation on cooling.

The distance an atom can move on the surface $X$, is limited by the surface diffusion (121). Therefore at low $T_s$, the mobility of atoms is insufficient for the decomposition of mixed depositing atoms, and films are expected to contain non-equilibrium single phase structures. With increasing $T_s$, $X$ increases and the mobility at the surface will be sufficient for atoms to rearrange themselves and to decompose to a supersaturated two phase structure. Further increases in $T_s$ causes the full atomic rearrangement necessary for equilibrium phase formation.

In this section the extent to which deposition temperature can affect diffusion distance $X$ is underlined and examined more quantitatively. In order to characterise $X$ versus $T_s$, it is first necessary to determine the surface diffusion energy in Fe-Pt thin film alloys.

5.1.1 Estimation of surface diffusion

There is a scarcity of surface diffusion data for low
temperatures in particular for fcc iron base alloys. In order to estimate $D_s$ and subsequently $Q_s$, for Fe-Pt thin film alloy, two approaches are considered.

a) extrapolation from available empirical diffusion data
b) the use of parameters derived from experimental surface morphology of the thin films.

(a) The activation energy for surface diffusion suggested by Gjostein (146) is $13T^\frac{1}{2}$ J/mol, with a frequency factor of 0.014 cm$^2$/sec. From this the magnitude of $D_s$ can be calculated for various $T_s$. By extrapolating the data for pure fcc iron to lower temperatures, at $T_m/T_s = 2.27$, $D_0$ and $D_s$ are found to be about $5.25 \times 10^{-14}$ cm$^2$/sec respectively corresponding to $Q_s = 220$ kJ/mol. This is irrespective of Pt concentration.

(b) The $D_s$ also can be estimated by considering the sizes of SEM hillocks at a given $T_s$. In this model "r" is assumed to be the radius of a complete hemisphere and all the diffusional flux available at the surface is used to form these hillocks. However, these assumptions are not strictly true because, some energy is spent to create phases and also the hillocks are not completely hemispherical.

A similar approach has been used by Goodhew and Smith (162) for the spheroidisation of Au thin films. The diffusion flux necessary to form a hemisphere on the surface of the film is given by the expression:

\[
D_s \cdot t = \int_{R=0}^{R=L} 2 \pi R^2 \, dR
\]  

(27)
Where \( R \) = radius of the hemisphere

\[ 2L = \text{distance between the hemispheres} \]

\[ 2\pi R^2 = \text{volume element of a hemisphere moving a distance } L. \]

Equation (27), is used to calculate \( D_5 \) and subsequently \( Q_5 \) for Fe\(_3\)Pt thin film when \( T_5 \) is about 575°C. It is found to be about \( 10^{-14} \text{ cm}^2/\text{sec} \) and 148 kJ/mol respectively. The distance between two hillocks estimated to be \( \approx 750 \text{ nm} \), and "t" as half the deposition time. "D\(_0\)" is assumed to be 0.014 cm\(^2\)/sec (146).

Experimental results suggest that as well as deposition temperature effect, deposition rate, substrate-target distance and thickness of the film can profoundly effect the surface roughening of the films. Consequently \( Q_5 \) decreases with increase in the size of hillocks (grain size). Similar results for the variation of the surface grain size with deposition rate has been shown (163) for Al films. Fig. (66a) shows the variation of \( \log D_5 \) versus \( T_m/T_5 \). As \( T_5 \) increases, the estimated and evaluated \( D \) come to a closer agreement. The diffusion variations with temperature for the bulk alloys are shown for comparison. From the ranges of estimated \( Q_5 \), and taking into account the presence of impurities such as entrapped Ar gas, oxide and target impurities, an average \( Q_5 = 163 \text{ kJ/mol} \) for the \( T_s \) range is chosen.

5.1.2 Relationship between \( \bar{X}-T_5 \) and morphology of the alloy films

Based on the surface morphology and estimated \( Q_5 \), the variation
of \( \bar{X} \) with \( T_s \) required to change from non-equilibrium structures to equilibrium structures is calculated using equation (21) and is shown in fig.(66b). When \( T_s \) is around 550\(^{\circ}\)C the bulk diffusion becomes important. A critical temperature "\( T_{\text{crit}} \)" can be defined (152) as:

\[
T_{\text{crit}} = -\frac{Q}{k_b} \ln \left( \frac{r_a}{D} \right) \quad \text{(see p.85)} \tag{28}
\]

The kink in \( X-T_s \) graph (fig.66b) suggests the regime where bulk diffusion becomes important. Equilibrium in thin films is achieved at a temperature about 575-600\(^{\circ}\)C which is unlikely to occur in the bulk materials.

As a first approximation, it is assumed that \( \bar{X} \) needs to be about 1000 nm for equilibrium structures, which is the same magnitude as the film thickness. Film thickness and the grain size in some cases are the same order as the effective diffusion distance (121). The corresponding \( T_s \) calculated from \( \bar{X} = (2D_s t)^{1/2} \) is about 600\(^{\circ}\)C, which is consistent with our previous study based on Fe-Cu-P alloys when an equilibrium structure was achieved at \( T_s = 600^{\circ}\)C (164).

The calculated \( \bar{X} \) for the alloy film at \( T_s = 575^{\circ}\)C is about 650 nm, which is about 100 nm lower than the actual measurements. This suggests the estimated \( Q_s = 163 \text{ kJ/mol} \) is still too high.

The SEM micrograph for the alloy film deposited at \( T_s = 650^{\circ}\)C, showed complete equilibrium characteristics with particle sizes about 2000 nm. This is actually larger than the calculated \( \bar{X} \) for the corresponding \( T_s \). This confirms the necessity for a lower \( Q_s \).
This is probably due to the fact that phase formation energy and other diffusion processes defined by Harrison (165) have been neglected in the original assumption. No comparison has been made between diffusion distance "X" in Fe₃Pt and Fe₃Pd thin film alloys based on morphological features since the structures in the two systems are different. However, it is expected that $Q_s$ is lower in Fe-Pd alloys.

5.1.3 Alternative calculation of surface diffusion

An alternative approach to calculate $Q_s$ in Fe-Pt thin film alloys is by using the changes in composition occurring at different values of $T_s$ and relating these to the composition that should be produced if full equilibrium is obtained. Table (24) shows the initial calculated results. Values of $Dt/L^2$ corresponding to the fractional saturation $Co - C/Co - Cequ$ for a Cylindrical geometry (166) can be made for various values of $T_s$ (fig.66c).

where $Co =$ initial concentration

$C =$ mean concentration at time "t"

$Cequ.$ = equilibrium concentration.

A cylindrical geometry is the closest geometry to thin film if the thickness of the cylinder is considered to be approximately the same magnitude as film thickness.

By making the assumptions shown in Table (24), the following equation is devised for "D":

$$D = AL^2/\Delta T_s^2 t \ (cm^2/s) \quad (29)$$

Subsequently from a graph of $(ln D_s)$ versus $(T_s)$ (fig.66c), $Q_s$ is found to be about 150 kJ/mol. This is in good agreement with the other methods used to estimate $Q_s$ in Fe-Pt alloys.
**Table (24) Experimental data for surface diffusion in Fe-Pt thin films**

<table>
<thead>
<tr>
<th>$T_s ($^\circ$C)</th>
<th>$1 \times 10^3 / T_s$ (K)</th>
<th>$T_s$</th>
<th>$D t / L^2 = A$</th>
<th>$D = A L^2 / \Delta T_s^2$</th>
<th>$t$ (m/s)</th>
<th>$\ln D_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>2.11</td>
<td>350</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>250</td>
<td>1.191</td>
<td>300</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>300</td>
<td>1.74</td>
<td>250</td>
<td>0.003</td>
<td>$5.45 \times 10^{-8}$</td>
<td>-16.72</td>
<td>-</td>
</tr>
<tr>
<td>350</td>
<td>1.60</td>
<td>200</td>
<td>0.02</td>
<td>$6.25 \times 10^{-7}$</td>
<td>-14.28</td>
<td>-</td>
</tr>
<tr>
<td>400</td>
<td>1.48</td>
<td>150</td>
<td>0.08</td>
<td>$4.44 \times 10^{-6}$</td>
<td>-12.32</td>
<td>-</td>
</tr>
<tr>
<td>425</td>
<td>1.43</td>
<td>125</td>
<td>0.15</td>
<td>$1.20 \times 10^{-5}$</td>
<td>-11.33</td>
<td>-</td>
</tr>
<tr>
<td>450</td>
<td>1.38</td>
<td>100</td>
<td>0.25</td>
<td>$3.13 \times 10^{-5}$</td>
<td>-10.37</td>
<td>-</td>
</tr>
<tr>
<td>475</td>
<td>1.34</td>
<td>75</td>
<td>0.38</td>
<td>$8.40 \times 10^{-5}$</td>
<td>-9.38</td>
<td>-</td>
</tr>
<tr>
<td>500</td>
<td>1.29</td>
<td>50</td>
<td>0.45</td>
<td>$2.25 \times 10^{-4}$</td>
<td>-8.4</td>
<td>-</td>
</tr>
<tr>
<td>525</td>
<td>1.25</td>
<td>25</td>
<td>0.7</td>
<td>$1.40 \times 10^{-3}$</td>
<td>-6.57</td>
<td>-</td>
</tr>
<tr>
<td>550</td>
<td>1.22</td>
<td>-</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Assumptions:

$L = $ Few atomic layers of the Fe-Pt thin films with homogeneous growth (5nm).

$t = $ The time an atom can move on the surface before being covered by incoming atoms, (20 sec.).

$\Delta T = $ The deposition temperature difference between the bcc/bcc+fcc equilibrium phase and the initial composition.

$A = $ Approximate value of erf.(error function)
I n D SURFACE
BULK DIFFUSION IN Fe Pt
X nm Variation of Subs.Temp, with X in Fe^Pt
-22.
-24.
-26.
-28.
-30.

 bulk diffusion
Average Surface diffusion
Estimated Surface diffusion

Substrate Temperature °C (b)

Fig.(66) a) A comparison between bulk and surface diffusion.

b) Variation of X with Ts in Fe₃Pt thin film: alloy

[Graph showing bulk and surface diffusion]

0ₜ = 2/αT²
A = err.
L = A T (5 - 500 nm)
t = the time an atom can stay on the surface before being covered by incoming atoms

Qs/R = 10x10⁻³
Qs = 35.6 Kcal/mol
(150 kJ/mol)

Fig.(66) c) Variation of composition concentration of Pt
in Fe-Pt thin film alloy.
d) Estimate of Qs using (c).

[Graph showing composition variation]

0.1
0.01
0.001

Substrate Temperature °C

Region where bulk diffusion becomes important

Qs = 39 Kcal/mol
(163 kJ/mol)

Co - Co - Cequ

equilibrium

non-equilibrium

measure of diffusion

Cequ

Co
6. A model to relate variation of chemical composition with deposition temperature

6.1 Introduction

In the previous sections the sequences of phase formation and transformations with deposition temperatures are outlined. The mechanisms by which $T_s$ can affect the structure of vapour deposit alloys have been discussed and the profound effect of $T_s$ on diffusion distance ($\bar{X}$) demonstrated.

In this section, the extent to which $T_s$ can affect the chemical segregation in vapour deposited alloys are examined. The model enables us to establish a thin film phase diagram of the alloys as an alternative to the standard available phase diagrams. The model presented in this section is based on the experimental results obtained in Fe-Pt, Fe-Pd and Fe-Pt-Ni thin film alloys.

6.1.1 Vapour deposition phase diagram of Fe-Pt alloy

The measured lattice spacings for both fcc(fct) and bcc(bct) structures in thin films Fe$_{85}$Pt, Fe$_{75}$Pt and Fe$_{70}$Pt are translated to the corresponding chemical composition in the following manner.

1) The variation of the bcc iron lattice spacings due to the addition of Platinum is calculated shown using the following relationship (168):

$$a_{\text{alloy}} = a_0 + (50 \pm 1) \times 10^{-4}c$$  \hspace{1cm} (30)
Where $a_{\text{alloy}}$ = lattice parameter of solid solution,

$a_0$ = lattice parameter of pure iron,

c = at% of solute concentration.

Table (19b & 20b) illustrates the variation of $T_s$ with bcc Pt chemical composition. By making the assumption that the increase in lattice parameter is due to ordering, the corresponding fcc Pt chemical compositions, can be found using the results published by Ling and Owen (53) as a calibration curve. In addition, the results from annealed powders in this study is shown in fig.(59). The ordered fcc lattice parameters measured for the annealed powder Fe$_3$Pt, are in close agreement with the results obtained by (53). Table (2) shows the lattice parameter results obtained from the powdered Fe-Pt alloys. When $T_s$ is less than about 400°C, fct structures are observed in Fe$_3$Pt thin films, and the corresponding Pt composition is determined.

Using above model, a Fe-Pt thin film phase diagram (fig.67a,67b & 67c) is established. The following sequence of phase formation is observed:

At high $T_s$, because of high diffusion in thin films, an equilibrium structure is formed. As $T_s$ decreases a non-equilibrium two phase field is observed. This indicates diffusion is reduced and subsequently $X$ is decreased. At even lower $T_s$, a single phase with composition corresponding to the target alloy is expected. This is when almost no diffusion takes place and the initial deposit remains as single phase.

Combination of the experimental data obtained from Fe$_{85}$Pt and
Fe₃Pt thin film alloys suggest the formation of a eutectoid transformation with about 17 at% Pt at about 600°C. Fig. 67c. This supports the earlier assumption made by Berkowitz et al (18) of a eutectoid transformation based on resistivity and magnetization measurements.

6.2 Vapour deposition phase diagram of Fe-Pd alloy

The extent to which deposition temperature can affect the composition in Fe-Pd alloys has been examined in the same way as for Fe-Pt alloys.

Fe-Pd alloys with 15, 25, 30, 40, and 50 at% Pd predominantly exhibited an fct structure at high Tₜ. This was followed by an appearance of fcc(fct) and bcc(bct) structures at lower Tₜ. A suitable calibration curve for translating the lattice spacings with Pd composition in Fe-Pd alloy is not available. However, the results obtained from Fe₇₅Pd powders alloy in this work (Table 25) are in close agreement with the ones published by Raub et al (7). Recently, Zhang et al (156) produced thin film Fe-Pd alloys by an r.f sputtering technique. No fct structure was observed in their study, but equivalent fcc lattice spacings have been estimated from the fct lattice obtained in this work. Using this approximation, the lattice parameters are converted to the Pd chemical composition.

An equivalent fcc lattice spacing is obtained by assuming

\[ a = (\alpha^2 c)^{1/3} \quad (31) \]

The change of bcc(bct) lattice spacings with Pd composition was determined using data published by (4).
From the above data, the sequences of phases with $T_s$ and composition are shown in fig.(68a, 68b & 68c) for 15, 25, and 30 at%Pd respectively. At high $T_s$, with high diffusion, equilibrium phases are formed. At intermediate $T_s$, non-equilibrium structures are observed. At even lower $T_s$, diffusion becomes restricted and single phase with corresponding composition close to the target alloy is expected.

Due to the absence of bcc(bct) structures in 40 and 50at%Pd alloys, the model has not been applied to this range. Both ordering and the magnetic effect can affect the model.

Since an fcc equivalent to the fct lattice spacing is used for the conversion to the corresponding chemical composition, the accuracy is poor. But in principle, with the limited experimental results, the characteristics of the vapour deposit phase diagram is clearly demonstrated and it is shown how the rate of vapourisation can effect the structures.

6.3 Vapour deposition phase diagram of Fe-Pt-Ni alloy

Using the model, the effect of addition of 3-7 at%Ni to the Fe-Pt vapour deposited thin film alloy is shown in fig.(67d). Although due to the slit size effect (see section 4.4) the accuracy of measurement is poor, the diagram qualitatively demonstrates a similar characteristic as for binary Fe-Pt alloys. It appears that addition of Ni to Fe-Pt alloy, has reduced the "$X$" distance i.e. decrease in diffusion. Additionally, detection of tetragonal phase at lower
temperatures can be due to the presence of Ni content. With the limited results, the eutectoid transformation is estimated to be about 575-600°C with Pt content about 14-16 at%Pt. It appears that the addition of Ni, decreases the eutectoid composition. This illustrates the capability of the technique for determination of thin film phase diagrams in both binary and ternary alloys.
Fig. (67a) Ts V composition in Fe₈₀Pt₂₀ T.F alloy

Fig. (67b) Ts V composition in Fe₈₀Pt₂₀ T.F alloy

Fig. (67c) Structure of vapour deposit Fe-Pt alloys

Fig. (67d) Effect of addition 3-7 at% in vapour deposited Fe-Pt phase diagram.

Fig. (67) Sequence of phases developed as Ts changes with composition in vapour deposited Fe-Pt alloys.
Table (25) Room temperature X-Ray results for Fe$_3$Pd powders with annealing temperature and time.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>fcc(fct)(nm)</th>
<th>c/a</th>
<th>bcc(nm)</th>
<th>ratio of bcc*/fcc</th>
<th>time(h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>0.3726*</td>
<td>-</td>
<td>0.296</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>650</td>
<td>0.37775</td>
<td>-</td>
<td>0.2872</td>
<td>0.54</td>
<td>78</td>
</tr>
<tr>
<td>550</td>
<td>0.3857</td>
<td>0.953</td>
<td>0.2865</td>
<td>0.74</td>
<td>240</td>
</tr>
<tr>
<td>500</td>
<td>0.3878</td>
<td>0.944</td>
<td>0.2865</td>
<td>0.76</td>
<td>240</td>
</tr>
<tr>
<td>500#</td>
<td>0.3867</td>
<td>0.953</td>
<td>0.2869</td>
<td>0.60</td>
<td>240</td>
</tr>
</tbody>
</table>

*: Weak trace of (111) diffraction on X-Ray sensitive film.
#: Subsequent annealing after water quenched at 1100°C.
Fig. (68) Variation of $T_S$ with Pd composition and sequence of phases in vapour deposited Fe-Pd alloys.
CHAPTER SEVEN

7. Calculation of $T_0$ in Fe-Pt (Pd) alloys

7.1 Introduction

Assuming the concept of depositing the most stable single phase at $T_5$, the vapour deposition method allows an experimental way of determining $T_0$. It is therefore useful to compare it with a calculated $T_0$. Also the critical driving force to overcome elastic constraints for disordered Fe-Pt alloys can then be obtained by comparing $T_0$ and $M_S$.

A Fe$_3$Pt alloy is particularly interesting because it exhibits thermoelastic martensite when chemically ordered. The chemical ordering decreases the free energy changes and lowers the $M_S$ temperature (54), compared to the disordered alloy when it is quenched from high temperatures (and $M_S$ is above $T_C$).

The following calculation has been performed by courtesy of Dr. N. Saunders (167).

The position of $T_0$ and bcc/bcc+fcc, bcc + fcc/fcc phase boundaries in Fe-Pt system has been calculated for the chemically disordered phase with magnetic ordering below $T_C$ by using a Lucas optimiser on all available thermodynamic data and subsequently THERMOCALC.

$T_0$ can be evaluated from $(M_S + A_S)/2$ or similar models (69). But in this calculation, $T_0$ has been determined by an independent method via phase diagram characterisation. In this calculation, the experimental $T_0$ results have not been used as part of the optimisation.
7.1.1 Evaluation of $T_q$ via phase diagram characterisation

Only chemical disordered and magnetic ordered/disordered states are considered in the first instance. The relative stability of different phase states is determined by the values of Gibbs energies of the phases under consideration. The phase stability is calculated by using equation (11-17) section 2.5.3, Table (5). The following features are necessary to be able to calculate $T_q(107)$.

a) Phase stability of the elements.

b) Chemical interaction parameters.

c) Magnetic energies.

The non-magnetic interaction parameters are calculated as the following:

The free energy of the fcc and bcc phase for iron base alloy (in this case Fe-Pt alloy) is given by:

$$\Delta G^{fcc}(x_{Fe}, x_{Pt}, T) = x_{Fe} x_{Pt} (98000) + x_{Fe} x_{Pt} (x_{Fe} - x_{Pt}) (30000) + RT (x_{Fe} \ln x_{Fe} + x_{Pt} \ln x_{Pt})$$

(32)

Where "R" is the gas constant.

$$\Delta G^{bcc}(x_{Fe}, x_{Pt}, T) = x_{Fe} x_{Pt} (-106000) + x_{Fe} x_{Pt} (x_{Fe} - x_{Pt}) (30000) + RT (x_{Fe} \ln x_{Fe} + x_{Pt} \ln x_{Pt})$$

(33)

The magnetic terms which dominate the fcc/bcc transformation in pure iron must be extended to the whole Fe-Pt system. Therefore, expressions must be devised for "$T_c$", and "B" which are functions of Pt concentration for both fcc and bcc. The Curie temperature ($T_c$) and Bohr magneton "B" were calculated as a Pt composition function from the following functions:
\[ T_c^{(bcc)} = -1043 \times \text{Fe} + \times \text{Fe} \times \text{Pt} \left[ 1019 - 1205 \times (\text{Fe} - \text{Pt}) + 1012 \times (\text{Fe} - \text{xPt})^2 \right]. \]  

(34)

\[ B^{(bcc)} = 2.22 + \times \text{Fe} \times \text{Pt} \left[ 2.256 - 1.177 \times (\text{Fe} - \text{Pt}) \right] + 0.063(\times \text{Fe} - \times \text{Pt})^2. \]  

(35)

\[ T_c^{fcc} = -201 \times \text{Fe} + \times \text{Fe} \times \text{Pt} \left[ 2832 + 1330 \times (\text{Fe} - \text{Pt}) - (5512) \times \text{Pt} \times (\text{Fe} - \text{Pt})^2 \right]. \]  

(36)

\[ B^{fcc} = 2.1 \times \text{Fe} + \times \text{Fe} \times \text{Pt} \left[ 11.72 + 9.75 \times (\text{Fe} - \text{Pt}) - (7.04)(\times \text{Fe} - \text{Pt}) \right] \]  

(37)

From the above evaluations, the following results were obtained:

a) A plot of bcc/bcc + fcc and fcc + bcc/fcc phase boundaries fig.(69).

b) Plot of \( T_0 \), (fig.69).

c) The changes of free energy for bcc and fcc versus temperature associated with magnetism onset for 25 and 30 at\% Pt. are shown in fig.(70a & 70b). The free energy change in 25at\% Pt is found to be nearly twice as large when compared with 30at\% Pt.

7.2 A comparison between Experimental and calculated results

7.2.1 Phase boundaries

The calculated phase boundary is shown in fig.(69). A deviation at lower temperatures in the vicinity of \( T_c \) indicates the importance of the magnetic effect as the fcc + bcc/fcc phase boundary approaches the Curie region. This is confirmed by the
calculated decrease in free energy $\Delta g^{\text{fcc-bcc}}$ in 30 at%Pt (fig.70b).

The above phase boundary is for the chemical disordered system. Although Skinner and Miodownik (114) made a calculation for both ordered and disordered 24.5 at%Pt alloys, it is in fact very difficult to extend this treatment to the whole range of alloys, as the chemical and magnetic terms interact in a complex way with changes in composition. However, an earlier treatment of Inden (49) for chemical ordering only can be combined with the present calculation at temperatures above $T_c$ as a first approximation, bearing in mind that the Inden treatment assumed composition independent interactive parameters.

Considering the relation between the phase boundaries calculated by Inden (fig.71) who used a BWG model (31) and the calculated and the experimental results in this work, the following remarks can be made:
The point where the bcc/fcc phase boundaries in the Fe-Pt diagram, calculated in this work, cross the fcc/fcc' boundaries calculated by Inden, should give an indication of the position for the eutectoid transformation. This is found to be consistent with the experimental results. However, the present results also support the views of others (12,56) that the chemical ordering temperature calculated by Inden for Fe$_3$Pt is rather high, which is much related to the original assumptions made by Inden in calculating the ordering temperature, for Fe$_3$Pt based on the characteristics of FePt and ignoring magnetic effects.
7.2.2 Comparisons of $T_0$ obtained by calculated, experimental, and $(M_s + A_s)/2$ model

Fig. (69) also illustrates the results obtained for (a) calculated $T_0$, (b) the experimental $T_0$ observed in Fe$_3$Pt and Fe$_8$Pt thin film alloys and (c) the $T_0$ estimated using $(M_s + A_s)/2$. A good correlation between the three results is observed at high temperatures. At lower temperatures, the experimental $T_0$ is observed to be lower than the calculated one. As the deviation increases towards higher Pt contents, it may be assumed some short range ordering may be responsible which is excluded from the model.

7.3 $T_0$ in Fe-Pd alloys

Calculations of $T_0$ in Fe-Pd alloys are hindered because not enough thermodynamic data is available. However, experimental results in Fe$_{85}$Pd, Fe$_{75}$Pd and Fe$_{60}$Pd thin film alloys confirm that the $T_{0_1}$ fcc-bcc and $T_{0_2}$ fcc-fct occur in the regions where "overlap" of different martensites are observed.

7.4 A comparison between $T_0$'s in Fe-Pt and Fe-Pd alloys

The calculated $T_{0_1}$ in this work, experimental $T_{0_1}$ and the calculated $T_0$(od) by Inden (49) in Fe-Pt alloys are shown in fig(72). As these lines cross each other, four distinctive regions can be predicted for non-equilibrium structures.

a) Above $T_{0_1}$ and $T_0$(od), a region of disordered fcc phase,
b) Above $T_{01}$, but below $T_{0(\text{od})}$, a region for ordered face centred structure as the Pt concentration increases,
c) A body centred structure for Pt concentration less than about 18 at\% below $T_{01}$,
d) A mixture of body centred and face centred structures in the region below both $T_{01}$ and $T_{0(\text{od})}$.

By extrapolating (or estimating) the equivalent $T_0$ values from higher temperatures to lower temperatures in Fe-Pd alloys, a similar phase characterisation can be considered as for Fe-Pt alloys. Considering the experimental results for $T_0$s in fig. (45), the following remarks can be made:

a) Above both $T_0$s, a disordered face centred structure is obtained.
b) With increase in Pd composition above 31 at\%, and below $T_{02}$, an ordered fct structure appears.
c) The region below $T_{01}$, with Pd concentration less than 31 at\%, gives a body centred structure.
d) The region below both $T_0$s, yields mixtures of face centred + body centred structures.

These predictions are consistent with the experimental results in both bulk and vapour deposited alloys for both Fe-Pt and Fe-Pd.

Table (26) shows a summary of comparison of the $T_0$ regions and its related structure characteristics for Fe-Pt and Fe-Pd systems. The temperature at which $T_0$ cross over takes place in Fe-Pd alloys is about $100^\circ\text{C}$ lower than the corresponding
temperature in Fe-Pt alloys.
Both systems also have a common characteristic with respect to the Invar composition range.
It is still not clear whether the Invar characteristics play a major part in the non-equilibrium transformations near the $T_0$ cross-over or whether they are separately dependent on similar underlying bonding characteristics.

Table (26) A comparison in structures in Fe-Pt and Fe-Pd alloys with respect to $T_0$ temperature.

<table>
<thead>
<tr>
<th>$T_0$ region</th>
<th>Fe-Pt</th>
<th>Fe-Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>do fcc</td>
<td>do fct</td>
</tr>
<tr>
<td>B</td>
<td>od face centred</td>
<td>od fct</td>
</tr>
<tr>
<td>C</td>
<td>body centred</td>
<td>body centred</td>
</tr>
<tr>
<td>D</td>
<td>&quot; &quot; &quot; +</td>
<td>&quot; &quot; &quot; +</td>
</tr>
<tr>
<td></td>
<td>face centred</td>
<td>face centred</td>
</tr>
</tbody>
</table>
Fig. (69) Calculated phase boundaries and $T_0$ in Fe-Pt alloys.

Fig. (70) Free energy changes for bcc and fcc vs. temperature associated with magnetism onset for (a) 25 at%Pt, (b) for 30 at%Pt.
Fig. (71) Phase boundaries relations

Fig. (72) Relation between $T_{0s}$ (Fe-Pt alloys)
8. Conclusions

The structures of Fe-Pd and Fe-Pt thin film alloys have been studied, and both the experimental work and theoretical evaluations lead to the following conclusions.

1) In both Fe-Pd and Fe-Pt thin film alloys, the sequence of phases developed as $T_s$ changed was found to be dependent on three factors:
   a) the structure of the initial phase, which in turn depends on whether $T_s$ is above or below $T_0$. ($T_{01}$ or $T_{02}$).
   b) diffusion at designated temperature.
   c) further transformations which may occur on cooling through critical ordering or martensite start temperatures.

2) It has been shown that the sputter deposition of relatively few alloys can provide a significant addition to the experimental input needed to define phase equilibrium in thin films, as well as allowing determination of the relevant phase boundaries at low temperatures. In addition, a direct determination of $T_0$ temperature is possible in certain composition ranges.

3) A diffusion mechanism can be used as a means to relate the structure of vapour deposited alloys to variations of $T_s$. In thin films, at high $T_s$, when both bulk and surface diffusions are involved, equilibrium structures are observed.
   At intermediate $T_s$, non-equilibrium structures are observed. At even lower $T_s$, where diffusion is slow, the most stable single
phase with composition close to the target material is observed.

4) Consequently, the most stable phase formed on deposition above $T_{01}$ is fcc and below $T_{01}$ is bcc with both phases subsequently decomposing to (fcc+bcc) structures by diffusion. A decrease in deposition rate (ie. lower ion beam energy) increases diffusion distance $\bar{X}$, changing a non-equilibrium to an equilibrium structure at intermediate $T_s$.

5) The presence of a eutectoid transformation with $T_s$ about 600 $^0$C and about 17 at%Pt is confirmed.

6) In Fe-Pt thin film alloys, the increase in fcc lattice spacings with decrease in $T_s$ is due to an increase in the degree of ordering. Likewise, an increase in degree of tetragonality with decrease in $T_s$, for both Fe-Pd and Fe-Pt thin film alloys are found to be associated with the increase in degree of ordering in the fct structure.

7) Gradient deposition of quasi binary ($Fe_3Pt_{0.9}Ni_{0.1} - Fe_3Pt_{0.7}Ni_{0.3}$) thin film alloy has further demonstrated the capacity of the technique for determination of vapour deposition phase diagrams with a limited number of alloys. Substitution of 3-7 at%Ni for Pt in Fe$_3$Pt alloys reduces the ordering temperature and decreases the diffusion rate.

8) An empirical relationship between surface morphology and structure in thin film alloys is consistent with the proposed diffusion model.
9) In Fe-Pt alloys the results confirm the leading role played by magnetic contributions in determining the $T_0$. Phase stability with continuous increase in degree of ordering in Fe-Pd alloys appears to be due to the effect of magnetism. In Fe-Pt alloys the stability of fct structures appears to be due to the ordering below $T_{02}$ temperature.
CHAPTER NINE

Suggestions for further work

In the present study the assessment of Fe-Pd and Fe-Pt alloy phase equilibria has been demonstrated by using a vapour deposition technique.

1) Lowering sputtered ion beam energy has shown to have a significant effect on the structure of deposited alloys. A detailed examination of the extent to which "X" can be effected by sputtering rate and substrate temperature is desirable.

2) At low $T_S$, the structure of both Fe-Pd and Fe-Pt thin film alloys is found to be tetragonal. Determination of c/a axial ratios are not very accurate due to insufficient X-Ray diffraction peaks. Therefore repetition with a more accurate method of the lattice parameter measurement is required.

3) An accurate lattice parameter measurement in composition gradient thin film alloys was hindered because of the slit size effect in X-Ray diffractometer. Due to this effect a large composition range of deposited film may be irradiated. An alternative technique to eliminate the slit size effect is needed.

4) In Fe-Pd thin film alloys, anomalous results were observed in the vicinity of the Curie temperature. It is proposed that magnetism in this region has stabilised the cubic phase. A
detailed investigation in this region is required.

5) Better calculation of $T_0$ temperature is possible when more experimental data are included. Therefore examination of further alloys will be required.

6) Surface morphologies are known to be useful to catalysts and the experimental results indicate that a relationship between the structure and the surface morphology persists. The use of TEM dark field imaging for identification of vapour deposit phases is promising, but NaCl substrate decomposes at temperature above 400$^\circ$C. Therefore a stable high temperature substrate which does not interact with depositing materials is required which can subsequently be removed by solution.
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