THE COMMINUTION OF METAL POWDERS

by

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SUMMARY.

X-ray line broadening and transmission electron microscopy have been used to investigate the deformation structure of aluminium, copper, and nickel powders ball milled in an argon atmosphere. X-ray line broadening was analysed in terms of crystallite size and strain. Ball milling produced a decrease in crystallite size and an increase in the strain function. Electron microscopy indicated that the crystallite size corresponded to a cell or sub-grain structure within the powder particles. The substructure size decreased rapidly during ball milling until a limiting size was reached after which the rate of decrease was only slight. The limiting values were 200 Å, 325 Å, 475 Å for copper, nickel and aluminium respectively. The limiting size effect was thought to be caused by dynamic recovery; the difference in size being explained by the effect of temperature and stacking fault energy.

Annealing increased the crystallite size and was accompanied by a decrease in strain function. The changes in strain function may be considered to be associated with changes in dislocation arrangement in the cell walls and subboundaries. The strain function was seen to vary with crystallographic direction.

Ball milling produced flake-like shaped particles which decreased in size with ball milling. The substructure size did not appear to be related to the particle size.
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Among the comminution processes the technique of ball milling, a procedure in which a large number of particles are comminuted at the same time, has gained considerable industrial importance. Ball milling can produce powders of very fine particle size which in the case of ductile or malleable metals are flake-like in shape, the thickness often below 1 micron. The flake-like nature of such metal particles has been exploited in the paint industry, the manufacture of explosive, and more recently in dispersion strengthened alloys. The majority of investigations concerning ball milling have been directed towards the relationship between conditions of ball milling and the size and shape of the particles produced. In contrast very little attention has been given to the structural changes occurring within the particles.

The object of the present investigation is to study the changes in microstructure occurring within particles of metal powder during ball milling. The metal powders chosen were commercially available aluminium, copper, and nickel powders of good purity. These ductile metals have a face-centred cubic lattice structure whose deformation behaviour has been widely reported in the literature, e.g. references (1,2,3). However, these metals differ in their melting points, strength properties, and stacking fault energies. A comparison between the ball milled structure of the metals should indicate how such properties influence the deformation behaviour.

The methods used in the investigation were the line broadening of x-ray diffraction patterns and transmission electron microscopy. X-ray line broadening can be analysed in terms of crystallite size and strain. Many such investigations have been carried out on powdered materials; however, where ball milled metal powders have been concerned the main interest has been in changes occurring during annealing. Electron microscopy has become a well established method in the study of the structure of metals. Thin metal particles seem suitable as specimens
provided they are thin enough to transmit the electron beam. The advantage of using such specimens is that the changes in structure which can occur during conventional specimen preparation are avoided. It is intended to compare the results from x-ray line broadening with those of electron microscopy especially in terms of the significance of crystallite size broadening and strain broadening. To assist such a comparison a limited number of annealing experiments were performed.

The large surface areas resulting from ball milling can make the particles highly reactive therefore, the powders have been ball milled in a glove box filled with argon. This precaution has been taken, not only to avoid surface oxide films, but also to avoid any pyrophoric reaction which might otherwise occur in air.

Throughout this report the particle size refers to the outer dimensions of a powder particle. The grain size, sub-grain size, and cell size refer to the structure within the particles. The crystallite size refers to the measurement obtained from x-ray line broadening.
COMMINUTION IN THE BALL MILL.

Introduction.

As far as metal powders are concerned the ball mill has been used extensively to investigate the comminution process. Such investigations are made difficult by the wide variety of conditions that can exist inside the mill. The process is strongly influenced by the physical properties of the metal being comminuted. Consideration must also be made of the quantity and size of balls, volume, size, and shape of the metal powder, and the various movements of each caused by the mill rotation.

Theories of comminution.

Comminution theory is concerned with the relationship between the cause and effect of particle size reduction, the cause represented by the energy expended and the effect by the reduction in particle size achieved. Many theories have been suggested defining the energy required to effect reduction in particle size most notable being those of Rittinger (4), Kick (5), and Bond (6). Rittinger's theory states that "the energy necessary for reduction in particle size is directly proportional to the increase of surface," giving the equation

\[ E = K \left(1 - \frac{1}{R}\right) \frac{1}{a} \]

where \( E \) is the energy input required to reduce the material from original size \( D \) to product size \( a \), \( R \) is the reduction ratio \( D/a \), \( K \) is a constant.
Kick's law states "the energy required for producing identical changes in configuration in geometrically similar particles of the same composition varies as the volumes or weights of those particles", giving the equation

$$E = K \frac{\log R}{\log 2}$$

These theories have been derived for brittle materials where the greater part of the energy input to the material during milling is absorbed in elastic deformation. The fraction of this energy appearing as surface energy is extremely small, most of it being dissipated as heat. Attempts to verify Rittinger's theory by experiment have shown that the energy consumption per unit area of new surface produced increased much faster than the theory predicted (7). Holmes (8) considered it unreasonable to suppose that there should exist a fixed relationship, such as Rittinger's, between input energy and new surface, especially as the law had not considered the influence of the variation of particle strength with particle size of the material. Kick's law applies to a perfectly elastic homogeneous material, whose resistance to reduction would not vary with particle size. However, the law does not provide for the variations in the conditions of stress, or for the lack of homogeneity in the material, when cracks and other faults are present. Holmes, therefore, introduced a form of Kick's law modified to allow for the particle characteristics and conditions of stress application, and suggested that the theories of Rittinger and Kick should not be applied to milling problems. Reviewing the experimental evidence on the subject, Bickel (7) suggested that Rittinger's theory is more consistent with finer size reduction and Kick's with coarser reduction, whilst Jones (9) from similar evidence suggested the opposite.

A more recent theory developed by Bond (6) relates the breakage energy to the square root of the reduction ratio. Neither is this theory consistent with the evidence obtained from a large number of experiments nor is it based on the physical properties of the material being
comminuted. Hence Bond's theory is regarded only as an empirical compromise between the two earlier theories. However, the theory has been recognised as a useful method of predicting the power requirements for comminution (8).

It is generally accepted that for most brittle materials, i.e. rock, ore, coal etc., the elastic limit and final yield point are so close together, that, for practical purposes work done in plastic deformation may be neglected. Because of their marked plastic behaviour such assumptions would be unfounded when considering the comminution of metals, where the useful energy would be employed in effecting elastic deformation, plastic deformation and the production of new surface.

An important divergence from the empirical approach to ball milling has been made by Rose (10) who studied the internal dynamics of the ball mill using the theory of probability. In considering both hard and soft materials he postulates that processes occurring in a ball mill are controlled by the probability of the particle entering a circular "zone of operation" surrounding the contact point between two balls. Outside this zone no operation, which demands the trapping of a particle between two balls, can take place. The rate of grinding of the powder was found to be a function of the quantity of powder in the space between the balls, reaching a maximum when this space was full. For harder materials the minimum particle size decreased when the quantity of powder was decreased, a maximum being reached at one tenth of the space between the balls. When a soft material is milled this maximum is reached when the powder occupies from one-half to all the space between the balls. It was shown that the relationship between milling time and the new surface produced is not a simple linear function and the application of Rittinger's law to the ball mill was not experimentally verified. Rose was able to verify his theoretical predictions experimentally by using a ball mill enclosed in a calorimeter, thus correcting for any loss or gain of heat to or from the atmosphere.
With reference to metal powders Hütting and Sales (11) showed that for brittle metals, i.e. tungsten and iron-cobalt-aluminium alloys, the particle size distribution produced by ball milling was related to the oversize material according to the exponential function developed by Rosin and Rammler (12) where:

\[ \% \text{ wt. oversize } (R) = 100 \exp \left( \frac{x}{F} \right)^n \]

x is the width of the aperture considered in determining R, F is the constant of fineness, and n is a constant equal to unity.

Particles of the tough metal, i.e. chromium-nickel-carbon alloy, were slowly abraded. The larger particles of the ductile metals used, i.e. copper and aluminium, were not broken by milling but rather flattened. The finer particles of the ductile metals followed Rosin-Rammler's law until, particularly in the case of copper, an equilibrium of grinding was set up, with the coarse powder becoming finer and the fine powders coarser.

Factors influencing ball milling.

In terms of fineness of product the efficiency of ball milling has been shown to depend upon the conditions inside the mill. The operation of ball milling is usually carried out by rotating a cylinder partially filled with balls and a charge of the metal to be comminuted. As the mill revolves the mill load, i.e. balls and charge, are set in motion. The load rotates with the mill, being carried up to a position where, under gravity, it falls or cascades down. Comminution is therefore achieved by a combination of grinding and impact of those particles caught in the contact point between two balls or between a ball and the mill wall.

The rotation of the ball mill is limited to speeds below that at which the balls rotate completely with the mill. This "critical speed" is reached when the centrifugal and centripetal forces, acting on a small particle travelling on and with the breast of the mill, are equal. Dallavalle (13) quotes the critical speed as
Where \( R \) is the radius of the mill in feet. However, he points out that in general, the efficiency of ball milling does not vary greatly in the range from 30 to 80% of the critical speed. Rose and Trbojevic (14) have shown that, at high rates of revolution, slip does not occur between the charge and the mill shell but between the charge and the first layer of balls, resulting in a possible reduction in mill wear.

If the mill load completely fills the ball mill no comminution will occur at all. Nehm (15) calculated that if the balls are to fall a maximum distance, causing more grinding or higher impact, their volume should fill just less than half the mill. In his theoretical approach Rose (10) considered a volume of balls occupying 40 percent of the mill. Dallavalle (13) has pointed out that the rate of grinding is proportional to the number of ball contacts and is greatest with smaller balls, although larger balls will have more impact. Norris (16) has shown that for efficient milling the ball shape should be spherical. Engels (17) test on industrial mills showed that when grinding hard materials a soft ball should be used but when grinding soft materials a hard ball is desirable.

Studying the effect of temperature on milling, Djingheuzian (18) found that higher milling temperatures increased the absolute mechanical efficiency of milling, part of the heat applied externally or generated in comminution being transformed into useful work. However, Jones (9) has pointed out that the cost and inconvenience of heating may minimise any extra milling efficiency, especially as the risk of oxidising the powder is increased.

In all ball milling processes agglomeration due to welding or flocculation can occur, difficulty often being encountered in grinding ductile metals which have a greater tendency to weld together than do brittle or friable metals, Noel et al. (19) For given grinding
conditions the ultimate particle size is limited to that obtained when equilibrium is reached between the rate of grinding and the rate of agglomeration (11). Advantage of this fact has been taken by West & Llewelyn (20) who ball milled powders of nickel, iron and copper to obtain an increase in particle size, thus improving the packing and flow properties of the original powder. They found that the welding together of particles during milling could be increased if, after removing the oversize particles, the undersized particles were annealed and then remilled.

If fine powders are required it is necessary to add substances in the nature of a lubricant thereby preventing metal surfaces from touching and welding. In the milling of aluminium it is customary to add stearic acid to perform this function (21). This lubricant is often added in the form of a liquid, although Jones (9) points out that welding is not necessarily avoided. Quantnetz et al. (22) studied the effect that surfactants and inorganic salts, added to grinding liquids, had on the ball milling of metal powders. They found that the effectiveness of milling could be increased by use of a suitable inorganic salt although only stearic and oleic acid produced sub-micron particles. Similar work has been carried out by Sands et al. (23), who concluded that the use of an inorganic salt produced inter-particle welding, whereas the organic soaps significantly lowered the particle size at which welding balanced comminution. A slight improvement in fineness could be obtained by milling under argon although welding still occurred in the latter stages of milling. Royen and Romeis (24) ball milled aluminium in various liquids in an atmosphere of argon or argon-oxygen mixtures. However, their results, concerning the effects of the various milling conditions, were inconclusive. Harris (25) pointed out that due to their pyrophoric nature a great amount of care was needed when manufacturing fine metal powders. Such powders are best manufactured and handled under a protective inert atmosphere.
X-RAY DIFFRACTION LINE BROADENING.

Introduction.

Plastic deformation produces broadening of x-ray diffraction lines relative to those of a well annealed metal (26). Although the maximum intensity decreases with broadening the total or integrated intensity of each line remains constant. The observed recovery of line sharpness after annealing (27), (28) is a concentration of the total intensity over a small line breadth.

If the x-ray diffraction lines of an annealed metal are recorded as intensity against angular breadth profiles similar to Fig. la are produced. Symmetric line broadening, Fig. lb, produced by deformation is caused by two factors, broadening due to structural effects and broadening due to the instrument. Correction for instrumental broadening is necessary before the components of structural broadening can be interpreted. An effect of broadening is to cause the peaks of the Kα₁Kα₂ doublet to merge together thus preventing the shape of the Kα₁ profile from being resolved. A method developed by Rachinger (29) is now used to resolve the Kα₁ component. Asymmetric line broadening, Fig. lc, can be caused by the presence of deformation twins (30). A shift in the angular position of the profile peaks similar to Fig. ld, can be caused by the presence of impurities or a change in specimen geometry. A decrease in the separation of neighbouring peaks may be caused by the presence of stacking faults (30). Line broadening can be measured from the profiles in two ways:

a) By measuring the profile breadth at a given fraction of the maximum intensity, (Fig. le).
b) By dividing the integrated intensity, represented by the area under the curve, by the maximum intensity, (Fig. lf).

Interpretation of line broadening.

X-ray line broadening cannot be observed without the effect of broadening due to the experimental conditions. This extraneous cause of broadening is a function of the instrument and is known as instrumental
Fig. 1. X-ray line broadening profiles.

(a) Annealed Profile

(b) Symmetrical Broadening

(c) Asymmetrical Broadening

(d) Peak Shift

(e) Half Peak Breadth

(f) Integral Breadth = $\frac{A}{I}$
broadening. The complexity of the factors involved make calculation of its contributory effect difficult.

Scherrer\(^{(31)}\) originally described line broadening as

\[ \beta = B - b \]

where \(\beta\) is structural broadening, \(B\) is the broadening from a specimen with small crystallite size, and \(b\) the broadening from an infinitely large crystal.

Later Warren and Biscoe \(^{(32)}\) proposed a relationship of the form \(\beta^2 = B^2 - b^2\), but as the experimental accuracy is reported to be no greater than 10 per cent the final result will be similar for both equations.

Correction for instrumental broadening was originally obtained from a "standard" metal mixed with the specimen being studied. For example, Jones \(^{(33)}\) studied the broadening of x-ray lines of colloidal gold using annealed molybdenum to give the instrumental broadening. The same year Brindley and Ridley \(^{(34)}\) published an account of the broadening produced by filing rhodium which was compared with chemically prepared specimens of rhodium powder as a means of eliminating instrumental broadening. Stokes \(^{(35)}\) separated the instrumental broadening by an analytical method using a Fourier series. Correction for instrumental broadening is now achieved by measuring an annealed sample of the metal being studied, it being assumed that the broadening due to deformation is negligible.

Analysis of the structural broadening indicated that it largely consisted of broadening due to crystallite size, lattice strain, and stacking faults.

Cold work causes subdivision of grains into sub-grains, or coherently diffracting domains, smaller than \(10^{-4}\) \(\text{cm}\) giving a resultant broadening of the diffraction profile. The broadened profile can yield the so called "particle" or "crystallite" size only if the contribution due to internal strains and imperfections can be separated. After correction for instrumental broadening, the particle size broadening \(B_p\), according to Scherrer \(^{(31)}\),
\[ B_\theta = \frac{k \lambda}{t \cos^2 \theta} \text{ radians} \]

where \( \lambda \) is the wave length of x-radiation in \( \text{Å} \), \( \theta \) is the diffraction angle, \( k \) is referred to as the Scherrer constant, and \( t \) is the crystallite size in \( \text{Å} \).

The value of \( k \) depends on the way in which line broadening and the crystallite size are defined, Scherrer originally obtained a value of 0.94. Several investigators including von Laue (36), Bragg (37), Warren (38) and Wilson & Stokes (39) have discussed this problem and in each case a value of \( k \) close to unity has been obtained. "t" is defined as the mean apparent crystal size in the direction normal to the reflecting plane when \( k \) is unity. Generally it can be seen from the Scherrer equation that, if \( t \) is larger than \( 10^{-4} \text{ cm} \), the diffraction broadening becomes negligible and the crystallite size determination becomes increasingly inaccurate.

In a review of x-ray diffraction broadening Warren (40) suggested that cold work produces a domain structure within metals, such that the different domains diffract essentially incoherently with respect to one another. If these domains are separated by small angle boundaries, the domain or crystallite size will give an average dimension of the regions between boundaries. Even if dislocations are not arranged to form small angle boundaries the crystallite size can be interpreted as an average separation between dislocations.

Some other effect, such as lattice strain, was considered to be present after deformation since the Scherrer expression relating crystallite size to broadening could only account for part of the structural broadening.

Stokes and Wilson (41) suggested that the origin of strain broadening may be due to the following two causes,

1. The metal is broken down into coherent diffracting domains, each of which has a uniform expansion or contraction so that its lattice parameter differs from the mean.

2. The broadening may be due to distorted crystallites
larger than $10^{-4}$ cm, the distortion takes the form of non-uniform expansions and contractions, as well as twists and bends.

It has been shown (41) that if the integral breadth of the strain distribution is $\xi$, the corresponding line broadening $\beta_s$ due to strain is

$$\beta_s = 2\xi \tan \theta$$

where $\theta$ is Bragg angle. This equation, showing how broadening varies with the diffracting angle $\theta$, can be derived from Bragg's law,

$$n\lambda = 2d \sin \theta,$$

which gives

$$\frac{\Delta d}{d} = \frac{\Delta d}{\tan \theta}$$

where the component of strain in a direction perpendicular to the reflecting planes is

$$2\xi = \frac{\Delta d}{d}$$

Attempts have been made to calculate the mechanical strain, the stored energy, and the distribution and density of dislocations from the strain broadening component.

A further part of structural broadening has been demonstrated when Barrett (42), (43) suggested that stacking faults, introduced during plastic deformation, may contribute significantly to profile broadening.

In 1952 Paterson (30) calculated the effect of stacking faults on the diffraction profiles of face-centred cubic crystals and showed how faulting could be determined from measurement of profile shape and displacement of their peaks. The presence of stacking faults could be detected by comparing the change in the peak separation of two neighbouring reflections of a cold worked specimen, with the separation of the same peaks of a fully annealed specimen. The probability of finding
a stacking fault between any two neighbouring planes, $\alpha$, was given by,

$$\Delta(2\theta)_{200} - \Delta(2\theta)_{111} = -45 \sqrt{3} \alpha / \pi^2 (\tan \theta_{200} + \frac{1}{2} \tan \theta_{111})$$

indicating that the (200) and (111) peaks converge.

Differentiation between broadening caused by stacking faults and that caused by crystallite size is complex.

Two entirely different methods have been developed to interpretate the various components of structural broadening from diffraction profiles. Apart from minor refinements for profile correction both methods remain as they were originally developed.

Averbach and Warren (44) developed a method of interpretation of profiles by using Fourier series, the method is very dependent on the tails of the profiles which are difficult to determine.

An alternative method derived by Williamson and Hall (45), relies on the assumption of a defined line shape to each profile, thus permitting the components of broadening to be separated. The basis for measuring the components that produce the increase in integral line breadth is the Scherrer formula for crystallite size broadening and the Stokes and Wilson equation for strain broadening.

Pearson (45) has pointed out that one of the major points in favour of the Williamson and Hall method is the use of the variation of profile breadth with $2\theta$. He considers that this variation is the feature of x-ray diffraction profiles which is most obviously related to different profiles of broadening and therefore it should not be ignored in any method of analysis.

Fourier analysis requires a large amount of computation and where automation is not available the Williamson and Hall method allows the maximum use to be made of available data without excessive computation.

Pearson (46), and Agnihotri (47) found that the values of crystallite size and strain are of the same order of magnitude for both methods, with Fourier analysis
probably the more precise.

Many of the earlier investigators, including Smith and Stickley (49), Megaw and Stokes (50) and Wood (58) supported the view that broadening is due to randomly directed, slowly varying lattice strains. Warren and Averbach (51) studied the changes in line shape and concluded that lattice strains are not constant over distances greater than about 10 atomic diameters. Warren (40) reported that the root-mean-square strains derived from Fourier analysis decrease noticeably with the distance over which they average. He suggested that the strains are highly inhomogeneous, rather than simple extensions and compressions which are constant over large volumes. However, an accurate description of the broadening due to strain is difficult since it is not clear how it is related to the true physical situation existing in the metal.

Comparisons between theory and experimental evidence are influenced by the anisotropic behaviour of most metals, Youngs modulus varying with crystallographic direction. Smith and Stickley (49) were able to resolve the variation in strain function, with the indices of reflection in terms of elastic anisotropy in brass. They suggested that $\xi/2$ should have the same order of magnitude as tensile strength divided by Youngs modulus, and found good agreement. Warren and Averbach (52) using the root-mean-square strains derived from Fourier analysis found the strain to be nearly inversely proportional to the value of Youngs modulus in the particular crystallographic directions measured.

Some investigators have considered the strain function or root-mean-square strain to be a measure of strain energy or stored energy of the sample and have related this energy to the structure produced by deformation. Michell and Haig (53) calculated the stored energy of ground Nickel from values of root-mean-square using the Stibitz's equation (54),

\[
\text{Stored energy, } V = \frac{3}{2(1+2v^2)} \left(\frac{Ad}{d}\right)^2 \text{ cal/gm}
\]
where $E$ is Youngs modulus, $v$ is Poissons ratio, and $(\Delta d/d)$ is the strain component. These values were in reasonable agreement with values of stored energy measured by calorimetry. However, Faulkner \(^{(55)}\) found much closer agreement after deriving the expression,

$$V = \frac{15 E}{4(1-v)} (\Delta \frac{d}{d})^2 \text{ cal/gm}$$

Williamson & Smallman \(^{(56)}\) calculated the density and distribution of dislocations from values of stored energy derived from the equation of Stibitz. The dislocation density in cold worked filings was higher than that found in annealed filings. They suggested that the distribution of dislocations in annealed metals was more random than the complex arrangement in cold work metals. Their results for both cold worked and annealed aluminium agreed well with the microbeam measurements of Gay et al. \(^{(57)}\). Williamson & Hall \(^{(45)}\) found that the values of strain function for aluminium varied according to the purity, hence they suggested that the impurities restricted the movement of dislocations. From observations on tungsten they concluded that the mobility of dislocations is a function of both the impurity content and the atomic mobility, the latter being a function of the melting point. The effect of atomic mobility was confirmed by Wagner \(^{(58)},(59)\) who reported a decrease in strain function when aluminium and copper filed at $-150^\circ$ C were annealed at room temperature.

Variations in strain function have been observed by Otte and Welch \(^{(60)}\) for different modes of deformation. Tensile deformation of copper-silicon-manganese alloys gave low values of strain, large values being a characteristic of filings whilst values for wire drawing are somewhat less than filings. Commenting upon the work of Michell & Haig \(^{(53)}\), Michell & Lovegrove \(^{(61)}\) pointed out that the strain found in ground nickel was observed to be greater than that of deformed bulk specimens of nickel.

Both the Fourier, and the Williamson & Hall methods
of interpretation have been used in the following summary concerned with aluminium, copper and nickel. Most investigators have used metal filings, which are suitable for diffractometer specimens and can easily be produced in different environments, i.e. under liquid nitrogen. However, Williamson and Hall (45) proposed that during filing plastic deformation may occur under conditions of local temperature much higher than those of cold working, suggesting that the recovery temperature had been exceeded during the filing of aluminium for which a crystallite size of 4000 Å was observed.

To avoid the effect of recovery Wagner (59) filed and measured aluminium at -150° C and found a crystallite size of 320 Å that increased to 650 Å after standing at room temperature for 5 mins. The small crystallite size, he suggested, was due to substructure such as small angle boundaries and that broadening was only due to crystallite size and strain. This was in agreement with Fullman (62), who suggested cold work should not produce stacking faults in aluminium. Wagner (58) carried out a similar experiment on copper concluding that the crystallite size of 155 Å, increasing to 180 Å at room temperature, was due to deformation and twinning faults.

Agnihotri and Mitra (63) obtained for copper deformed at room temperature, a crystallite size of 800 Å and a low stacking fault probability. Greenough & Smith (64) also found a low stacking fault probability for copper deformed at room temperature, a result that Wagner (58) considered when suggesting that the stacking fault probability depended on the amount of cold work that could be put in and maintained.

Examining nickel ground on a diamond wheel, Michell and Haig (53) found a crystallite size of 300 Å, which on annealing at 400° C showed very little change. Later Michell and Lovegrove (61) measuring compressed nickel foil, found a crystallite size, 1000 Å. Both investigations gave a very small stacking fault probability.

Very little investigation, as far as x-ray diffraction is concerned, has been carried out on powders produced by ball milling.
Royen and Romies (24) have used line broadening to study the effectiveness of various fluids on the ball milling of aluminium. The smallest crystallite size measured in the milled powder was 600 Å with a value for strain function of 0.0025. They found on annealing at 500°C an increase in crystallite size and decrease in strain.

Lewis and Pearson (65) found that by milling aluminium filings together with aluminium oxide particles a large increase in strain could be achieved although no change in the crystallite size was observed. On the other hand aluminium ball milled without the oxide present did show a small decrease in particle size but no change in the value of strain function.
DEFORMATION STRUCTURE OF FACE-CENTRED CUBIC METALS.

Introduction.

The structure of deformed face-centred cubic metals was investigated by Gay et al. (57), (66) and Kelly (67) using the x-ray microbeam technique. They concluded that a domain or cell-like structure was present in deformed aluminium, copper, nickel and lead. These observations were confirmed when, following the initial work of Heidenreich (68), Hirsch et al. (69) and Bollmann (70) observed dislocations by transmission electron microscopy of thin metal foils. They observed regions, relatively free from dislocations, separated by walls of high dislocation density.

The cell size is much smaller than the grain size seen in the optical microscope, also the orientation across a cell wall is much smaller than the orientation across a grain boundary.

The formation of a cell structure depends upon a number of factors including the amount of deformation, temperature of deformation, mode of deformation, and properties of the material under consideration, i.e. purity, melting point and stacking fault energy.

The cell structure.

It was suggested from the x-ray microbeam results (57), (66), (67) that the following features were relevant to the cell structure:

(a) The cell size is independent of the initial grain size and decreases to a limiting value after a certain strain.
(b) This limiting value of the cell size increases with the softness of the metal.
(c) The width of the cell walls increases with the hardness of the metal.
(d) The cell size is reduced by increasing the impurity content.
(e) The difference between a boundary region and a cell was simply that the former contains more excess dislocations of one sign than the latter.

The cell structure is caused by an uneven distribution of dislocations in the form of a network. Generally the
cell size is regarded as the dislocation free areas between the cell walls. Often small dislocation loops varying in size are positioned in or near the cell walls, (71), (72). If the density of dislocations in the cell walls increases their arrangement becomes more irregular, hence they are termed dislocation tangles. With large amounts of dislocation tangles it is difficult to decide whether or not a cell structure is present.

Segall et al. (71), Howie (73), Swann (74), and Bartuska (75) have observed that with increasing deformation at room temperature the dislocation density within the cell does not change greatly but the wall density increases and the cell size becomes smaller. Similar effects have been observed in B.C.C. metals, Keh and Weismann (76). Generally the increase in deformation produced a wider and more ragged wall structure, often accompanied by a tendency for some cell walls to lie along certain crystallographic planes. Observations by Warrington (77) and Howie (78) on copper, Swann (74) and Whelan (79) on aluminium and Hirsch (80) on nickel support this idea. The evidence suggests this tendency is greater for higher amounts of deformation. The rate of decrease in cell size decreases as the amount of deformation increases.

The limiting cell size reported by Kelly (67), using the microbeam technique to measure tensile tested aluminium, was confirmed by Swann (74) who measured the cell size of rolled aluminium directly from electron micrographs. Considering the lower resolution of the microbeam technique the cell sizes obtained, microbeam 2.8 microns and micrograph 1.8 microns, are in good agreement. However, Swann pointed out that the mode of deformation could account for the difference in cell size since Segall and Partridge (81) have found a larger limiting cell size, 2 microns, for aluminium deformed in tension. Similarly Embury et al. (82) found a limiting size in cold drawn copper wire of 0.16 microns.

In 1964 Johari & Thomas (83) published a report on the influence of strain rate on the cell size of single and polycrystalline copper. They observed that the cell
size decreased with increasing strain rate and that the dislocation density, for the same strain, was much higher in the polycrystalline samples. It was suggested that the grain boundaries in polycrystalline copper act as sources for dislocations during plastic flow. In the single crystal copper the dislocations in the cell walls lie close to glide planes suggesting that cell formation is favourable when two or more independent slip systems are available. They observed that the cell structure after explosive deformation was smaller and more uniform than that produced by tensile deformation.

Nolder & Thomas \(^{(84)}\) observed a similar effect between static and shock loaded nickel. Increasing the shock loading of nickel resulted in a decrease in cell size. At a critical cell size, about 0.15 microns and below, microtwinning was observed. This cell size was not attained by tensile deformation at temperatures down to \(4^\circ\) K and twinning was not observed.

The flake-like nature of ball milled particles allow the structure to be observed directly by electron microscopy, when thin enough, without alteration of the dislocation structure reported to occur in the conventional preparation of thin foils.

Observations by Szego & Houseman \(^{(85)}\) have shown some form of structure to be present in aluminium flakes produced by micro-rolling, a form of extreme comminution, in a Micromax Fragmentor. However, the substructure was thought to be caused by edges or surfaces of particles that had been welded together during deformation. Royen & Romeis \(^{(24)}\), examined the structure of ball milled aluminium flakes and observed a definite cell structure that was altered very little by annealing at \(450^\circ\) C although there was a decrease in dislocation density at the cell walls. These results were in agreement with their x-ray diffraction studies.

Segall et al.\(^{(71)}\) investigating the effect of alternating stress on copper and nickel found areas of high and low dislocation density of about the same size. The areas were larger than the cell size found in samples deformed unidirectionally to the same average dislocation
density. The same structure has been observed in aluminium by Segall & Partridge (81).

Cell size and the distribution of dislocations in the cell and cell walls are greatly influenced by the temperature of deformation. Heidenreich (68), Swann (74) and Johari and Thomas (83) observed a much greater decrease in cell size of aluminium than found for copper (77) when deformation occurred between room temperature and -196°C. In contrast to copper the number of dislocations within the cells of aluminium increased rapidly as the deformation temperature was lowered. When the deformation temperature of copper was increased from -196°C to 650°C the cell walls seem to sharpen accompanied by an increasing tendency for the walls to lie parallel to the (100), (110) and (111). Swann (74) concluded that the dislocation density for the same strain is increased by decreasing the deformation temperature indicating that dislocation movement was restricted to shorter distances at lower temperatures.

Doubt has been raised as to whether or not the structure seen in the electron microscope is representative of the bulk material. Attempts have been made to study the distribution of dislocations within specimens of aluminium (74) and copper (86). Both investigations showed that the observed density of dislocations at the surface is much less than the interior, indicating that dislocation motion is easier in the surface regions.

It is uncertain whether loss or rearrangement of dislocations occur during the thinning of specimens from the bulk material. Hirsch and Valdre (87) studied these possibilities and concluded that rearrangement of dislocations was insignificant, however, Ham (88) observed a large loss of dislocations. Mader (89) considered that dislocations rearrange by the cross slipping of screw dislocations through the foil surface. On the other hand Hirsch (90) has proposed that the long range stress field around dislocations becomes small as the metal becomes thinner, and the pinning action of the foil surface prevents large rearrangements of dislocations. Swann (74)
observed the absence of a cell structure in thin films deformed in the electron microscope. He suggested that since cell structure forms only when at least two slip systems are present, the thinness of the film must limit the number of systems present.

The many observations conducted on deformed F.C.C. metals by using the electron microscopy may be represented in the following summary.

The size of cell structure formed during deformation depends upon the stacking fault energy of the metal, cell size can be decreased by:

1) increasing the amount of deformation;
2) increasing the strain rate;
3) lowering the temperature of deformation.

The formation of cell structure is hindered by:

1) additions of impurities and alloying elements;
2) precipitates;
3) deformation by alternating stress;
4) lowering the temperature of deformation.

The decrease in cell size is accompanied by:

1) an increase in the total dislocation density;
2) cell walls becoming ragged;
3) an increase in dislocation density of cell walls.

The tendency for cell walls to lie along crystallographic planes increases when:

1) the amount of deformation increases;
2) the temperature of deformation increases;
3) the strain rate increases.

Theories of cell formation.

Several theories have been put forward to account for the formation of cell structure during deformation. An important consideration in any such theory is that, under similar deformation conditions, the cell structure developed will vary from metal to metal. The differences are not confined to cell size alone, the rate of cell formation and the density and distribution of dislocations in the cells and at the cell walls also being affected.

Hirsch (90) considered that cell formation was influenced by the stacking fault energy of the metal since this is a measure of the equilibrium separation of the two
partials of an extended dislocation, which in turn influences the ability of a dislocation to cross slip, to climb, or to intersect other dislocations.

However, Kulman-Wilsdorf et al. (72) considered that the interaction between dislocations and point defects leads to the formation of dislocation tangles and subsequently, cell structure. They suggested that a quasi-equilibrium was reached where the elimination of point defects by dislocations just balances the point defects generated during slip. Under these conditions dislocation loops and superjogs are formed from the original glide dislocation. Some of the superjogs will anchor the dislocation and the free dislocation segment between them bows out into a loop which, if suitably oriented, may cross slip. Such dislocation behaviour has been called "Mushrooming".

The effect of stacking fault energy on cell formation has been studied by Hirsch (80), Swann & Nutting (91), Howie & Swann (92). The method most often employed to change the stacking fault energy is the addition of soluble alloying elements. In general a decrease in stacking fault energy results in a decrease in cell size. In some cases, where the stacking fault energy is very low, dislocations become dissociated and a cell structure is not formed. The effect of stacking fault energy is shown in Fig.2.

![Figure 2](image)

**Fig.2.** The stacking fault energies of some Ag-Al alloys and the dislocation distribution (after Swann (74))

(A) Cell structure observed.
(B) Cross slip very infrequent.
(C) Dislocations completely dissociated.
WORK HARDENING OF FACE-CENTRED CUBIC METALS.

Introduction.

The metal particles used in the present investigation are similar in particle size to the grains found in polycrystalline metals, hence at the most each particle will contain no more than several grains. It is therefore appropriate to consider the deformation behaviour of these metal particles as being closer to that of single crystals than polycrystalline metals.

To understand more fully how plastic deformation may influence the structure of metals it is of interest to consider the stress-strain curves of single crystals. Although single crystal behaviour is very different from that of polycrystalline metals the factors influencing deformation will, in most cases, be common. Also it is possible to consider each grain of a polycrystalline aggregate as a single crystal, however, the restraining effect of the surrounding grains will modify the nature of its behaviour.

Single crystal f.c.c. behaviour.

The shear-stress shear-strain curve of face-centred cubic metal single crystals can be, in general, divided into three distinct stages as indicated in Fig. 3, (93).

Stage I or easy glide stage begins at the onset of plastic flow and is characterised by a low but constant work hardening rate.

Stage II or linear hardening region has a constant work
hardening rate but is higher than Stage I. Stage III or parabolic hardening region is characterised by a work hardening rate which decreases continuously with increasing strain until fracture occurs.

The formation of cell structure relative to the stress strain curve has been studied by Howie (73), and Hirsch and Steads (94) using copper single crystals. During Stage I long straight dislocations on the primary glide plane were seen. The dislocation density remained low and a cell structure was not observed. In Stage II tangles of dislocations appeared which developed into a cell structure with a high density of dislocations in the cell walls and relatively few dislocations in between. In Stage III the overall dislocation density was higher than Stage II although the cell size changed very little. The misorientation between cells increased and these boundaries showed a strong tendency to lie along primary or conjugated slip planes.

The shape of the stress-strain curve will depend upon a number of factors which may influence deformation i.e., orientation, temperature, purity, stacking fault energy, strain rate and specimen size.

The orientation dependence of the stress-strain curve of pure metals has been investigated by many workers. The most obvious effects of orientation are that the extent of easy glide decreases and the hardening rate increases for orientations near the corners and edges of the standard triangles, (Diehl (95), Suzuki et al. (96)). Mitchell & Thornton (97) found that the orientation dependence persisted in copper crystals deformed at 4.2° K. They concluded that the extent of easy glide decreases as the possibility of slip on secondary systems. Masing & Raffelsieper (98) and Lücke & Lange (99) found at suitable orientation, that easy glide in aluminium is strongly influenced by the possibility of slip occurring on a secondary system. In general these investigators found that the influence of orientation on the work hardening rate in Stage II and Stage III is much less apparent than for Stage I.

Stress-strain curves of single crystals are very
dependent on the testing temperature. The most obvious effects of temperature are that the initial flow stress, extent of easy glide, the stress at the onset of Stage III and the fracture stress are all increased with decreasing temperature. Berner (100), Garstone et al. (101), testing aluminium in the temperature range 4.2 to 500° K found that Stage I and II were only well developed at low temperatures and easy glide was not detected at 500° K. Similarly Andrade & Aboav (102) testing copper found that easy glide disappears above 673° K. All these investigators found an increase in initial flow stress with a decrease in temperature. Mitchell & Thornton (97) and Haasen (103) working on copper and nickel respectively found that by decreasing the temperature the rate of work hardening during easy glide decreased, whilst the extent of easy glide increased. The rate of work hardening during Stage II seems to be relatively insensitive to temperature (97).

The stress at the onset of Stage III decreases rapidly with temperature and Mitchell (104) considers it the most temperature dependent hardening characteristic for pure metals. Because of the gradual transition from Stage II to Stage III, Thornton et al. (105) pointed out that this stress is difficult to define. At high temperatures, where easy glide and Stage II may disappear, the onset of Stage III becomes even less apparent. Diehl and Berner (106) and Mitchell & Thornton (97) found that the rate of work hardening during Stage III was more temperature dependent than that during Stage II. Mitchell (104) pointed out that if thermally activated cross slip was prevalent at high temperatures the strong temperature dependence of Stage III hardening was to be expected.

Impurities have a considerable effect on the initial stages of work hardening. Rosi (107) and Garstone et al. (101) found that the easy glide stage and initial flow stress for copper increased with the addition of soluble impurities. Lücke & Lange (99) reported the opposite effect for aluminium; however the main impurity, silicon, was insoluble.

The effect of stacking fault energy on the stress-strain curve is closely connected to impurity or alloying
content as such additions usually change the stacking fault energy of the metal. Mader (89) found that a decrease in stacking fault energy by adding cobalt to nickel resulted in the following changes. The extent of easy glide was increased, the hardening rate during easy glide decreased and the stress and strain at the onset of Stage III were increased. The hardening rate during Stage II was almost unaffected by the change in stacking fault energy. In general a decrease in stacking fault energy is equivalent to lowering the temperature thus preventing cross slip.

Altering the strain rate during deformation has a similar effect as changing the temperature, since at faster strain rates there is less time for thermally activated movements to occur at barriers. Thus Berner (100) using copper, found that an increase in strain rate led to an increase in the initial flow stress and hardening rate during easy glide. Also, the stress at the beginning of Stage III was found to increase.

The effect of specimen size has been studied by Suzuki et al. (96) and Garstone et al. (101) using crystals of copper. Using specimens from 0.21 mm up to 9.5 mm in diameter, they found an increase in the extent of easy glide and a decrease in hardening rate of easy glide as the diameter decreases. Sumino and Yamamoto (103) using specimens of aluminium from 6.6 to 96.7 microns thick, found that the strain hardening rate in Stage II decreased with decreasing specimen thickness until Stage I and II were indistinguishable. Also, they found an increase in initial flow stress with decreasing thickness. The dependence of easy glide strain on specimen size is almost certainly due to the fact that the slip distance is comparable, or even greater than, the specimen radius. Thus most of the dislocations can slip out of the specimen during easy glide. The slow accumulation of dislocations results in the onset of Stage II occurring at higher strains, (104).

The effect of surface oxide films on the stress-strain curve of single crystals has been investigated by Paterson (109). The difference between unoxidised and oxidised specimens of identical orientation, size and
purity was not significant.

The influence of these factors on the three stages of the stress-strain curve can be summarised as follows. The onset of plastic flow is due to the operation of dislocation sources, hence any effect that reduces the mobility of these dislocations will cause the initial flow stress to increase. During easy glide slip only occurs on one slip system, the extent and strain hardening rate of this stage being influenced by the factors that govern the extent of single slip. The change in strain hardening rate from Stage I to Stage II is caused by slip occurring on more than one slip system. During Stage II dislocations accumulate on a number of slip planes and networks of dislocations begin to form. The onset of Stage III is highly sensitive to temperature and stacking fault energy and reflects the ability of the dislocation to cross slip past obstacles thus causing the hardening rate to decrease.

**Polycrystalline behaviour.**

The principal difference between the room temperature deformation of single crystals and polycrystalline metals is due to the presence of grain boundaries in the latter. Polycrystalline metals consist of aggregates of a large number of randomly oriented grains. The simplest type are multicrystals which are aggregates of several crystals, i.e. bicrystals, tricrystals etc. The grain boundaries between the crystals or grains represents a much greater degree of misorientation than that formed in cell boundaries of deformed single crystals. Elbaum (110) has shown the importance of the orientation change across grain boundaries during deformation by experiments on aluminium bicrystals, each crystal having the same direction and plane of slip. As the orientation across the boundary increased, slip on the two primary slip systems generated high elastic stresses at the boundary. In order to relieve these stresses an increasing number of secondary slip systems were activated. The stress-strain curves of bi-, tri-, and quadricrystals showed a higher work hardening rate with increasing grain boundary
misorientation, neither Stage I nor Stage II were observed. Increasing the number of crystals per cross section also resulted in a higher work hardening rate. Fleischer and Hosford (111) observed similar effects for aluminium specimens containing up to 12 crystals per cross section.

Boas and Hargreaves (112) used hardness indentations to measure the work hardening of aluminium multicrystals where the grain boundaries were parallel to each other and perpendicular to the tensile axis. They concluded that multiple slip occurred in the regions near the grain boundaries and that the centre of the grains deform by single slip. Hence the effect of reducing the free surface per crystal by increasing the number of grains per specimen, results in an increased slip activity which leads to higher work hardening rates.

Boas and Ogilvie (113) have shown the operation of up to five slip systems in aluminium polycrystals. Because of this large number of slip systems polycrystals strain harden at a rate near to single crystals oriented to favour multiple slip. The stress-strain curve for polycrystalline metals shows only Stage II and Stage III deformation. In general the factors influencing single crystal behaviour in these regions are applicable to polycrystals.

The increased hardening caused by the grain boundaries is due to difficulty experienced by dislocations moving from one grain to another. However, slip in a polycrystalline aggregate does not occur by dislocations forcing a path through the boundary. Instead dislocations pile up at grain boundaries causing a stress concentration which may be sufficient to activate dislocation sources in neighbouring grains. With increasing deformation a dislocation substructure may be formed within the grains, being similar to the structure developed in single crystals.

**Types of grain boundaries.**

The boundaries in polycrystalline metals are termed high angle due to the magnitude of misorientation between the grains. The grain boundaries represent a region of
random misfit between the adjoining crystal lattices. Such a grain boundary may be described by a complex arrangement of dislocations, often so irregular that individual dislocations are not recognisable. Consequently a high-angle boundary is often regarded more simply as a surface about 2 atoms thick, in which the atomic arrangement is irregular. As the difference in orientation between the grains decreases the state of order in the boundary increases. The low-angle boundaries forming the substructure in single and polycrystalline metals often represent an orientation difference of less than 1° angle. Shockley and Read (114) suggested that low-angle grain boundaries may be described as aggregates of dislocations arranged in different ways depending upon the nature of misorientation between neighbouring grains, i.e. tilt, twist etc. The simplest situation is the case of a tilt boundary composed of an array of edge dislocations.

Because of their simple dislocation arrangement low angle boundaries are lower-energy boundaries than high angle boundaries. Shockley and Read (114) have proposed that the degree of misorientation should be proportional to the number of dislocations per unit length of boundary and that the energy of boundary, $E$, could be computed from this misorientation $\Theta$ by the equation

$$E = \frac{E_m}{\Theta_m} (1 - \ln \frac{\Theta}{\Theta_m})$$

where $E_m$ is the maximum boundary energy at the misorientation of $\Theta_m$. From the slope of the curve of this equation it is shown that the energy of a large boundary is smaller than the total energy of a number of boundaries having a total misorientation equal to the larger.
EXPERIMENTAL PROCEDURE.

Materials.
The following commercial metal powders were used for the investigation.

**Aluminium:**
Atomised powder, "SP" grade, granular in shape.
Specified by the suppliers, The British Aluminium Co. Ltd., as follows:
Size range: 35 mesh to dust.
Chemical composition: 99.991 % Al
0.0025 % Cu
0.0035 % Fe
0.003 % Si

**Copper:**
Electrolytic powder, granular in shape.
Specified by the suppliers, Dohm Industrial Ltd., as follows:
Size range: 200 mesh to dust.
Chemical composition: 99.95 % Cu.

**Nickel:**
Carbonyl powder, type 287(B), of irregular shape in a chainlike structure.
Specified by the suppliers, Mond Nickel Ltd., as follows:
Size range: 2.9 - 3.6 microns.
Chemical composition: 0.05 - 0.15 % C
0.05 - 0.15 % O
Below 0.001 % S
Below 0.01 % Fe
Remainder Ni.

To avoid prolonging the duration of ball milling only the fraction of each metal powder passing through a 350 mesh "British Standard" sieve was used.

Table 1 shows the properties of the resulting powders. The average particle size and surface area were measured by the Fisher Sub Sieve Sizer method.
TABLE 1

Properties of the metal powders.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Average Particle size</th>
<th>Surface area</th>
<th>Apparent density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>25.5 microns</td>
<td>870 cm²/g</td>
<td>0.96 g/cm³</td>
</tr>
<tr>
<td>Copper</td>
<td>12.4 &quot;</td>
<td>550 &quot;</td>
<td>2.93 &quot;</td>
</tr>
<tr>
<td>Nickel</td>
<td>3.1 &quot;</td>
<td>2150 &quot;</td>
<td>0.92 &quot;</td>
</tr>
</tbody>
</table>

**Glove box.**

Because of its large surface area a fine metal powder will combine rapidly with any reactive gas in the surrounding atmosphere. If the reaction is exothermic the heat generated can induce an escalating reaction which results in severe oxidation of the metal powder or possibly an explosion.

Such pyrophoric behaviour can be avoided if the material is manufactured, stored and handled in an inert atmosphere. A suitable method for avoiding these problems, or at least reducing them, is to use a glove box. This is essentially a gas tight box filled and maintained with an inert atmosphere. The material is introduced into the main chamber through a transfer box and manipulated by means of rubber gloves attached permanently to the box. Hence protection of the powder is achieved at the expense of ease of handling.

**Glove box design.**

The shape of the glove box was designed to enable the installation of a compacting press, ball mill and ancillary equipment. The box was 42" high, 24" wide and 22" deep and was constructed in 3/8" thick perspex sheet, the base being separate to enable equipment to be installed. The total volume of the glove box was 13 cubic feet or 375 litres. The front wall of the box had four circular openings 6 inches in diameter with flanges to which latex rubber gloves 28 inches long, 16-28 thousandths of an inch thick were fitted.

The transfer box was built onto the left hand wall of the glove box. The box was constructed from 5/16" thick perspex sheet with 9 inch sides and was fitted with two openings, one to the outside and the other to the main chamber. The doors fitted to these openings were
6 inch glove port-doors, supplied by "Rank Nucleonics Ltd.". During operation one door was always closed and the door to the main chamber was opened only when the transfer box was filled with argon. A vacuum system was connected to the transfer box to remove the air before filling with argon. Two or three purges were given to remove the air from the transfer box.

Gas piping was in P.V.C. tubing 17 mm outside diameter, 12 mm bore and vacuum tight glass taps were used for gas valves. Terminals for the supply of electrical power pass through the box wall and were sealed with araldite.

The glove box and ancillary equipment are shown in Fig. 4, (p. 108).

Inert atmosphere.

The atmosphere chosen was argon, this being the most readily available inert gas. In comparison helium is more expensive, not significantly purer and lower in density, whereas nitrogen is not completely inert. Although slightly higher in density than air, argon can be handled by fans and blowers designed for air.

A typical analysis of the high purity argon supplied by Air Products Ltd., was 2.6 ppm oxygen with a Dew Point below -80° C equivalent to 1 ppm Water Vapour. Nitrogen, the other major impurity is below 20 ppm.

Gas distribution.

Before filling with argon as much air as possible must be removed from the box. Since the glove box was not built to withstand vacuum the air must be purged out by the incoming argon.

The supply of argon was distributed by means of a pipe positioned around the base of the glove box. To achieve uniform distribution holes, 1/16 inch in diameter, were positioned along the length of the pipe, their spacings becoming closer towards the end. The gas was extracted through bell shaped outlets positioned in the top corners of the box, areas where the gas was expected to stagnate.

If no mixing occurs, the argon entering at the bottom
should displace the air through the outlets at the top of the box. However, due to unavoidable mixing of argon and air a number of volume changes were required. According to White \(^{(115)}\) the number of volume changes, \(N\), required is given by the relationship,

\[
N = \log \frac{C_0}{C}
\]

where \(C_0\) is the initial air concentration, \(C\) is the concentration of air remaining.

At least the number of volume changes calculated from the above formula were used when purging the glove box, in order to achieve reasonable extraction of air. During purging the argon leaving the box passed through a flow meter followed by a bubbler before entering the atmosphere.

**Gas leakage.**

A positive pressure was maintained inside the glove box to avoid an inrush of air should one of the rubber gloves become punctured. In maintaining this pressure difference, minimum one inch water gauge, a high standard of box construction with well sealed joints and tight fitting doors was necessary. Gas leakage from the box was detected by the foaming of a soap solution brushed onto the box joints, all leaks being sealed with lacquer.

The leakage of air into the box is mainly by diffusion, the amount depending not upon the pressure difference but upon the concentration of air inside and outside the box. Although some diffusion does occur through the perspex the main problem is the diffusion of \(H_2O\) vapour through the latex rubber gloves. Thus Ayer \(^{(116)}\) has found that the permeability of rubber gloves increased by a factor of ten during use.

The measure of pressure loss against time was used to determine the leak rate. This method is suitable for leak rates in the region of 0.05 per cent box volume per hour, the leak rate standard generally specified by users of inert gas systems. This leakage rate is equivalent to a pressure change of 0.204 inch water gauge (W.G.) per hour which can be caused by an 0.15°C change in temp. or 0.38
mm Hg change in barometric pressure. Any such changes must be corrected for when calculating pressure loss.

To test the leak rate the box was pressurised to plus 2 inches W.G. indicated on a manometer connected to the outlet. Changes in temperature were indicated by thermometers, one inside and one outside the box. Observations were made every 30 minutes over a period of 6 hours.

The leak rate calculations were as follows:

Box pressure difference = 0.79 inch W.G.
Mean temp. difference = 0.3°C = 0.402 inch W.G.
Barometric pressure difference = 0.1 mm Hg = 0.0536 inch W.G.

Corrected box pressure difference =
- 0.79 - 0.402 + 0.0536 = 1.1384 inches W.G.

Average leak rate from box \( \frac{1.1384}{6} \) =
0.189 inch W.G./hour.

Leak rate of one per cent per hour =
\( \frac{1}{100} \times \frac{760}{4} \times 13.6 = 4.07 \) inches W.G. per hour.

Percentage box leak rate = \( \frac{0.189}{4.07} = 0.0465 \) per cent/hour.

Even with this acceptable figure the impurity level inside the glove box will continue to rise. By continuously passing argon through the box the impurity content will reach an equilibrium dependent on the rate of gas flow, purity of incoming gas and the leakage rate. If argon, of impurity level 20 p.p.m., is circulated at a rate of 4 box changes per hour the maximum impurity content in the box will be,

\( \frac{465}{4} + 20 = 140 \) p.p.m.

The average impurity level in the glove box will, therefore, be somewhere between 80 p.p.m. and 140 p.p.m. depending on the degree of mixing.

Purification system.

Because of the need for a continuous flow of argon through the glove box in order to maintain a low impurity level, a recirculation system was used. Recirculation of the exit gas through a purification system was
considered to be more economical than continuous purging with cylinder gas. The principal contaminants to be removed are those which diffuse through the gloves and those which are introduced with materials and instruments entering through the transfer box. Water vapour, oxygen, nitrogen and organic solvents are the most prominent.

To remove water vapour a physical adsorption process using molecular sieves was chosen. Kohl and Riesenfeld (117) have shown that molecular sieves have a higher adsorption capacity than Silica Gel, Activated Alumina, and Bauxite for the range of water vapour content to be expected in the glove box. Linde type 4A molecular sieves in the form of 1/16 inch cylindrical pellets were used enabling a dew point of $-50^\circ C$ to be achieved after recirculation for one hour, as measured by an Alnor Dewpointer instrument. Regeneration of the molecular sieves was carried out at $300^\circ C$ for several hours using a dry inert atmosphere.

Oxygen is removed by the oxidation of MnO to Mn$_2$O$_4$ at $150^\circ C$. Pyrolusite (MnO$_2$), in the form of plus 10 mesh lumps, was reduced to MnO with hydrogen to obtain the purification material. After use the material was regenerated to MnO by reduction with hydrogen at $320^\circ C$. The pyrolusite could be regenerated a number of times until it crumbled to powder. Oxygen removal was carried out after the removal of water vapour from the argon as the process works more effectively on a dry gas.

The removal of nitrogen is difficult when compared with the methods used to remove water vapour and oxygen. An effective method of reducing the nitrogen content is to completely change the argon in the regeneration system at regular intervals, only one or two volume changes being necessary.

Activated charcoal was used to extract organic vapours by adsorption at room temperature. A satisfactory method of regeneration was by vacuum treatment.

**Operation of gas supply.**

A line diagram of the purification system is shown in Fig. 5. Argon leaves the glove box through the outlets
and passes through the activated charcoal bed into recirculation pump. The diaphragm type pump, supplied by Charles Austen Pumps Ltd., has a "no load" rating of 25 litres per minute, equivalent to 3–4 box volume changes per hour at 2 inches water gauge pressure. On leaving the pump the gas then passes through the molecular sieves and then the manganous oxide bed. Both these reactants are housed in pyrex glass reactors 12 inches high by 1\(\frac{1}{2}\) inches in diameter, gas entering through a central pipe that terminates \(\frac{1}{2}\) inch from the bottom. The manganous oxide reactor was heated by a sunvic controlled heating tape. After removal of oxygen the warm gas passes through a glass cooling coil submerged in water before entering the glove box. During handling the gas supply was closed; argon displaced by the glove movements passing to the atmosphere through the bubbler.

Fig. 5. Line diagram of the purification system.
BALL MILLING.

Ball milling was carried out in a cylindrical porcelain container, 6 inches in external diameter, with a capacity of one litre. The open end of the container was sealed by a porcelain end cover secured by a quick-release bar and screw. All edges and corners inside the container were generously radiused to prevent wear. The container material was a hard, dense, non-porous ceramic recommended by the makers for its high resistance to abrasion and its chemical inertness.

The container was rotated by a horizontal pair of parallel rubber rollers. The driving roller (the other idles) was geared by pulley wheels and vee belt to a variable speed electrical motor rated at 1/20 h.p. and 15 lb. in. torque. Both rollers, running in bearings, were mounted on a stand incorporating the electrical motor, the complete assembly being permanently placed inside the glove box and controlled from the outside by a rheostat. The rotational speed of the container was controlled at 70 r.p.m., being within the 30 to 80 per cent critical speed range.

The container was charged with 293 hardened steel balls, \( \frac{1}{2} \) inch in diameter, weighing 245 g. With this amount of balls the cylinder was just under half filled, allowing the balls to fall or cascade the maximum distance. The ball size chosen was a compromise between small balls with many points of contact and large balls with high impact forces. The charge of metal powder was 50 grams, resulting in a ball to powder charge ratio of approximately 50 to 1 by weight. It was found beneficial to add 2.5 g of stearic acid to each charge to act as a lubricant and prevent metal surfaces touching and welding. Coating of the balls and container walls was achieved by milling with stearic acid for 30 mins. prior to the introduction of the metal powder. A dry lubricant was preferred to a liquid lubricant because of the difficulty in maintaining constant conditions with the latter, due to evaporation.
After loading with powder the ball mill container was sealed and continuously milled for the required period. On completion of milling the powder was separated from the balls, the container and balls were removed for cleaning and reloading. The ball milling procedure was identical for each batch of powder, except for the duration of milling which varied from 10 to 150 hrs. No significant loss in ball weight was observed.

Each sample of milled powder was stored inside the glove box after x-ray diffraction and microscopy specimens had been taken.

ANNEALING FURNACE

The metal powders were annealed in a "Nichrome" wire wound horizontal tube furnace with a hot zone 2.5 inches long.

The circuit diagram, Fig. 6, illustrates that power input is controlled by a variac and a rheostat which, when activated by the Ether temperature indicator-controller, give high and low power inputs for under and over temperature conditions instead of the usual, but more abrupt, "on-off" system. Temperature control was within plus or minus 2° C for periods of up to four hours. Temperature was measured inside the furnace with a Pt/13% Rh-Pt thermocouple positioned centrally in the hot zone.

High purity argon, dried by molecular sieves, was passed at a measured rate through the furnace and released through a bubbler to maintain a positive pressure. An inert atmosphere was chosen to avoid any change in particle size that might occur in a reducing atmosphere, thus allowing better comparison with the milled powder.

Samples of ball milled powder were transferred to the furnace, annealed, and returned to the glove box in an air tight container. Annealing treatments were made on powders after ball milling for various times. The aluminium and nickel powders were annealed at 400° C for 4 hrs., the copper powder at 250° C for 4 hrs. Powders
milled for 150 hrs. were given additional treatments varying between 100-600° C. These temperatures were chosen to avoid agglomeration of the particles by sintering.

**SURFACE AREA DETERMINATION**

The surface areas of the powders were measured using the Fisher Sub Sieve Sizer instrument. This instrument developed from the method of Gooden & Smith (123), is based on the principle that a relationship exists between the specific surface of the powder and the rate of fluid flow, pressure head, viscosity of the fluid, density of the powder and porosity of the powder bed. Although the permeability of the packed powder is the property that is actually measured, the method can give a comparison between powders having the same particle shape. Air at a constant pressure, is allowed to flow through a powder bed prepared by a standardised compacting procedure. Since the air also passes through a resistance flow meter the pressure on the exit side of bed varies with the rate of flow, the pressure difference being shown on
a manometer across the flow meter. A chart incorporated in the instrument gives a direct reading of average particle size in microns. The surface area can be calculated from the equation

\[ S = \frac{6 \times 10^4}{d \rho} \]

where \( S \) is the surface area in \( \text{cm}^2/\text{g} \), \( d \) the particle size in microns, and \( \rho \) the density in \( \text{g/cm}^3 \).

The instrument has the advantage over other permeability methods that small amounts of powder can be used.

**APPARENT DENSITY.**

The apparent densities of the powders were measured using a modified form of the standard technique described in ASTM B212 - 48. Because of the limited amount of powder available a smaller container, 8.1 \( \text{cm}^3 \) in volume, was used. The distance between the bottom of the funnel and the top of the container was \( \frac{1}{2} \) inch. The powder sample was poured into the glass funnel and permitted to fall into the container until the powder overfilled the container. After the powder was levelled off with the top of the container, the container was tapped to settle the powder, thus avoiding loss, and transferred from the glove box in an air tight container to a balance and weighed.

The apparent density being calculated as follows:

\[
\frac{\text{Sample weight (g)}}{\text{container volume (cm}^3\text{)}} = \text{Apparent density g/cm}^3
\]

**DIFFRACTION EQUIPMENT AND TECHNIQUES.**

The diffraction equipment used comprised a Philips PW 1010 stabilised x-ray generator with a PW 1050
goniometer, and a proportional counter connected to a 1051 scaler and recording panel. Nickel filtered copper radiation was used with the filter placed between the specimen and the counter.

In order to ensure that a minimum of 50% of the specimen surface area was being irradiated, two slit systems were used to irradiate the specimen, a 4° slit was used from $2\theta = 150^\circ$ to $80^\circ$ and a 2° slit from $2\theta = 80^\circ$ to $40^\circ$. Diffraction profiles were recorded automatically using a ratemeter with a time constant of 1 second. However, in the case of (111) and (200) peaks manual scanning was used to obtain more accurate peak positions.

Because of the pyrophoric nature of the powders the normal technique of preparing diffractometer specimens by packing powder into a recessed metal holder was considered unsuitable. However, the necessary protection could be obtained if the powder was embedded in a material that did not interfere with the x-ray beam.

A material found suitable for this purpose was a cold setting acrylic resin manufactured by North Hill Plastics. Equal parts of the polymer and metal powders were mixed in the glove box, the slurry resulting from addition of the liquid monomer being cast into a rubber mould resting on a flat plate. Cooling the monomer prior to polymerisation reduces the exothermic reaction rate, causing the setting temperature of the specimen to remain below $40^\circ$ C. The resulting specimens were flat enough to be held accurately in the goniometer and at the same time provided sufficient surface area for diffraction of the beam at any value of $2\theta$. Diffraction traces obtained from samples made by this technique showed well defined peaks. The crystallite size and strain function found for annealed samples prepared by this technique did not differ significantly from the values found for annealed samples prepared by the conventional technique.

It was found possible to heat-treat specimens made by this technique below $200^\circ$ C provided that they were supported on a flat surface.
THE ANALYSIS OF DIFFRACTION PROFILES.

Throughout the present study, the integral breadth (integrated intensity/maximum intensity) was used as a measure of line breadth. The integrated intensity is obtained by measuring the area under the resolved profile peak above the estimated background, and the maximum intensity by measuring the height of the resolved peak maximum. This method of analysis was preferred to half peak width (width where the intensity is half its maximum value), particularly where the peaks are very broad and errors may be introduced due to the wrong estimation of background level.

The following sequence of computation was made in the analysis of the profiles. First, a smooth curve was drawn through the recorded profiles, and the background level was indicated by an assumed linear variation between adjacent troughs. The number of squares on the chart paper under the curves, but above background level, were counted and two-thirds of this area was taken as the area under the K\(\alpha_1\) curve. Rachinger's method was used to separate the K\(\alpha_1\) peak from the composite K\(\alpha_1\)\(\alpha_2\) doublet. Having obtained the value of the integral breadth in radians, \(\beta^*\) and \(d^*\) were calculated from the following analysis, using a step by step tabulation procedure.

The diffraction profiles were analysed by the method proposed by Hall and Williamson. The total broadening, \(\beta_T\), is represented by the relationship;

\[
\beta_T = \beta_I + \beta_E
\]

\(\beta_I\), the instrumental broadening, was assumed to be that of an annealed specimen. This was obtained by annealing the original powders of aluminium, copper, and nickel for 4 hours at 400°C in argon. Since the K\(\alpha_1\) and K\(\alpha_2\) doublets could be resolved the broadening due to strain and crystallite size had been reduced to a minimum. The difference between the integral breadth of any given specimen and that from the annealed specimen was taken
to represent the excess broadening.

\[ \beta_E \] represents the excess broadening due to both crystallite size, \( \beta_p \), and strain \( \beta_s \). Studies of profile shapes have shown that the shapes lie between Cauchy and Gaussian curves. A Cauchy assumption gives the relationship \( \beta_E^2 = \beta_p^2 + \beta_s^2 \) whilst a Gaussian form gives

\[ \beta_E^2 = \beta_p^2 + \beta_s^2. \]

If the simpler Cauchy form is assumed the error which is introduced results in the magnitude of the strain function being slightly lower. However, the crystallite size determination is unaltered and qualitative comparisons of strain remain valid. As has been pointed out by Warren \(^{40}\) the Cauchy type of distribution ignores the tails of the profiles, these being of vital concern in the line shape type of analysis based on Fourier analysis. However, it is in the tails that the experimental data is weaker due to overlapping of adjacent peaks. Thus the assumption of a Cauchy shape is considered to be justified. Hence using a Cauchy profile shape.

\[ \beta_E = \beta_p + \beta_s \] \hspace{1cm} (1)

The Scherrer formula relating broadening to mean particle dimension is.

\[ \beta_p = \frac{\lambda K}{t \cos \theta} \] \hspace{1cm} (2)

where \( \beta_p \) is the broadening due to small crystallite size \( t \) is the mean particle dimension, and \( K \) is a constant, close to unity, which varies with the particle shape.

When the broadening is due to lattice strain, Stokes and Wilson \(^{41}\) have shown that the relationship between the integral breadth \( \beta_s \) and the strain distribution, \( \xi \), may be written

\[ \beta_s = 2 \xi \tan \theta \] \hspace{1cm} (3)

Substituting equations 2 and 3 in equation 1 gives
\[ \beta = \frac{\lambda}{t \cos \theta} + 2\xi \tan \theta \]

or \[ \frac{\cos \theta}{\lambda} = \frac{1}{t} + \frac{\xi}{\lambda} \frac{2 \sin \theta}{\lambda} \]

which in terms of reciprocal space may be written

\[ \beta^* = \frac{1}{t} + \xi \frac{d^*}{\lambda} \]

where \( d^* = \frac{2 \sin \theta}{\lambda} \), and \( \lambda = 1.54 \text{ Å} \)

Thus a plot of \( \beta^* \) against \( d^* \) gives an intercept of \( 1/t \), where \( t \) is the crystallite size in Ångström units, and a slope equal to \( \xi \), the strain function.

The scatter of the points on the \( \beta^* \) v. \( d^* \) graph about a mean straight line should constitute a deviation pattern which is typical of a deformed face-centred cubic metal, (113). This pattern is shown by connecting with a straight line, each point in an increasing \( d^* \) value sequence. The slope of the \( \beta^* \) v. \( d^* \) graph was determined by selecting a mean straight line representative of all the points, although less emphasis was placed on the points obtained for the weaker profiles, i.e. the (222) and (400) profiles.

**RACHINGER'S METHOD FOR SEPARATION OF K_\alpha_1 K_\alpha_2 DOUBLETs.**

This is the method which has been used for the isolation of the K_\alpha_1 peak in the present study.

It depends on the assumption of a 2:1 ratio for the maximum peak intensities of the K_\alpha_1 K_\alpha_2 peaks and it requires a knowledge of the 2\( \theta \) separation of the two peaks. This can either be measured from an annealed specimen where the doublet separation is well defined, or it can be calculated using the formula:

\[ \Delta \theta = \sin^{-1} \left( \frac{\lambda_2}{2z_{hk1}} \right) - \sin^{-1} \left( \frac{\lambda_1}{2z_{hk1}} \right) \]
If $z$ is the doublet separation, the first step is to divide the profile into strips by ordinates whose separation is $z$, starting at the termination of the $K\alpha_1$ peak marked by position "a" in the diagram. From $a$ to $a-z$ the $\alpha_1$ peak is the same as the combined trace. By halving the ordinates between $a$ and $a-z$ and translating them through a distance $z$ in the $-2\theta$ direction the $\alpha_2$ curve is obtained for the $a-z$ and $a-2z$. The $\alpha_1$ curve in this range is then obtained by subtraction of the $\alpha_2$ curve from the composite $\alpha_1 - \alpha_2$ curve. The procedure is then repeated, the $\alpha_2$ curve in the range $a-2z$ to $a-3z$ being obtained by halving the $\alpha_1$ ordinates from $a-z$ to $a-2z$ and displacing this reduced curve by a distance $-z$. This process is repeated if necessary until the curve is completely resolved.

\[ \text{Fig. 7. Rachinger's Method.} \]
The electron microscope used in this investigation was the AEI EM6G, operating up to 100 kV and aligned for double condenser working. Transmission electron-microscopy was used throughout the investigation. Selected area diffraction methods were used to study the crystalline state of the particles.

Specimen preparation.

The technique developed was to take a sample of the powder, submerged in alcohol, from the glove box and disperse the powder in the alcohol using an ultra-sonic bath. A droplet of this suspension was placed on a glass slide which had previously been coated with carbon in a vacuum evaporation unit. The carbon film, 100 - 200 Å thick, acts as a support film for the particles when subsequently mounted on a 3 mm grid for examination in the microscope. Squares of a size comparable to the dimension of the microscope grids were then scratched on the carbon film. These were then floated off on alcohol and caught on microscope grids.

OPTICAL MICROSCOPY.

A Vickers projection microscope was used to examine the powders at low magnifications. Samples were prepared by dispersing the particles in a formvar film, on a thin glass slide, by rolling with a glass rod. This method breaks down agglomerates but should not distort soft particles. Light was transmitted through the glass slide to project the image of the particles as silhouettes.

Samples of the original powders were mounted in plastic and polished in the usual metallographic manner. The microstructure of the sectioned particles was revealed by etching in the following solutions:
Aluminium Etch:
90 ml HCl
90 ml HNO$_3$
30 ml HF, 40%  
20 gr Ferric Chloride
Diluted 1 part to 3 parts H$_2$O. Specimen immersed for 5 mins. at room temperature.

Copper Etch:
4 gr CrO$_3$
0.75 gr NH$_4$Cl
5 ml HNO$_3$
5 ml Conc. H$_2$SO$_4$
90 ml H$_2$O
Specimen immersed for 5 secs. at room temperature.

Nickel Etch:
5 gr FeCl$_3$
2 ml HCl
95 ml Ethyl alcohol
Specimen immersed for 3 mins. at room temperature.
(4) EXPERIMENTAL RESULTS.

SIZE AND SHAPE OF DEFORMED PARTICLES.

The effect of ball milling on the size and shape of the powders is shown by the results of surface area measurements, optical and electron microscopy. The effect on packing properties is shown by measurements of apparent density.

The values of surface area for various ball-milling times are shown in table 2 (p. 82), these values being plotted in Figs. 9, 12, & 14 for aluminium, copper and nickel respectively. The surface area is seen to increase with ball milling time for all three metal powders, although this tendency is not so clear in the case of aluminium.

The progressive change in particle size and shape during ball milling can be followed in Figs. 37, 38 & 44, which show optical photomicrographs of representative samples of aluminium and copper respectively. In comparison the particle size of the nickel powder was much smaller and required a larger magnification as shown in the series of electron micrographs Figs. 36 & 51. For all three metals a decrease in particle size was observed as ball milling progressed. However, in the early stages of ball milling, particularly in the case of aluminium, particles larger than the largest particles in the original powder were observed. The presence of larger particles indicated that the particles, originally granular in shape and difficult to focus, were deformed into flake-like particles. The flaky nature of the powders was confirmed by visual observations. Electron microscopy also showed that the particles produced by ball milling have one dimension considerably smaller than the other two. However, the variations in transmitted intensity indicated a variation in thickness from particle to particle and that the thickness across the individual particles varied. The tendency was for the particles to become thinner towards the edges, see for example Figs. 41a, 48c & 54a.
A comparison between the surface area measurements and the particle size range observed in the electron microscope for powders ball milled for 150 hrs. is shown in table 3.

**TABLE 3.**

<table>
<thead>
<tr>
<th>Powder</th>
<th>SIZE IN MICRONS from Surface Area</th>
<th>ELECTRON MICROSCOPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>3.5</td>
<td>0.3 to 5.0</td>
</tr>
<tr>
<td>Cu</td>
<td>0.5</td>
<td>0.1 to 1.2</td>
</tr>
<tr>
<td>Ni</td>
<td>0.8</td>
<td>0.1 to 1.4</td>
</tr>
</tbody>
</table>

Thus in each case the surface area measurement falls within the size observed in the electron microscope.

The apparent density measurements are shown in table 4 (p.83), these values being plotted against ball milling time in Fig. 8, 11 & 13 for aluminium, copper and nickel respectively. In the case of aluminium and of copper the apparent density falls rapidly and reaches a minimum after a relatively short period of ball milling, further ball milling resulting in a slow increase in the apparent density. In comparison the apparent density of the nickel powder was seen to increase continuously with ball milling time.

As the particle size distribution is known to influence the packing properties of a powder, thus affecting the shape of the apparent density curve, histograms of particle size distribution for some of the aluminium powders were calculated. Aluminium was chosen in preference to copper because of the more pronounced minimum in the apparent density curve and its larger particle size.

Fig. 10 shows histograms of particle size distribution for aluminium powders ball milled for times close to those giving the minimum in the apparent density curve, Fig.8, and the original powder. The histograms were calculated from the particle size distribution observed in the optical microscope. This method was chosen because a more representative distribution could be achieved than
in the case of electron microscope. Each particle was cut from a print of known magnification, weighed and the equivalent circular or projected diameter was then calculated.

The histograms show that after 10 hrs. ball milling, particles larger than the original powder are present, the particles being distributed over a wide range of sizes with a high proportion at the coarse end.

With further milling the range of particle sizes decreases, and approaches a more symmetrical distribution after 50 hrs. milling. The particle size median value correspondingly decreases after an initial increase, as follows: original powder: 37 microns 10 hrs. milling: 60 microns 30 hrs. milling: 38 microns 50 hrs. milling: 35 microns

The method is limited by the difficulty in resolving particles less than approximately 5 microns in size, however, the distribution at the coarse end is not significantly affected.

LINE BROADENING RESULTS.

The results of x-ray line broadening for the ball milled aluminium, copper and nickel powders are shown in tables 5,6 & 7 (p. 84 to 86) respectively. The integral line breadth $\beta$, increases with increasing $2\theta$, shown as $d^*$, except in the case of the (222) profiles for which the values are always low. The integral line breadth also increases as the duration of ball milling increases. Values of broadening for some of the ball milled powders after annealing are also shown. The effect of annealing the ball milled powders is to reduce the amount of broadening.

The line broadening was analysed for strain and mean crystallite size by the Williamson and Hall method. The Strain function, $\xi$, was given by the slope of the $\beta'$(excess) v. $d^*$ curve, and the reciprocal of crystallite size from the intercept of this curve on the $\beta'$ axis. The excess broadening due to deformation was determined by subtracting the instrumental broadening,
represented by the broadening of an annealed specimen of the original powder, from the total broadening. Values of $\beta^*$ (equal to $\beta \cos \theta$) and $\beta^*$ (excess) are tabulated with the values of integral breadth.

For comparison the value of $\beta^*$ against $d^*$ for the annealed specimens and ball milled samples are shown in Figs. 15, 16 & 17 for aluminium, copper and nickel respectively. Results on annealed specimens showed negligible broadening due to strain, the broadening being equivalent to a crystallite size effect.

Values of $\beta^*$ (excess) against $d^*$ for both the ball milled and annealed ball milled samples are shown in Figs. 18 to 20 for aluminium, Figs. 21 to 23 for copper and Figs. 25 to 27 for nickel.

Values of strain function and crystallite size, determined from the curves of $\beta^*$ (excess) v. $d^*$, are shown in tables 8 to 10 (p.87 to 89). Because of the possible variations in determining the slope of the curve a range of values for the crystallite size and strain function are given.

If the \{100\}, \{110\}, and \{111\} had shown multiple order reflections the strain function and crystallite size in the [100], [110], and [111] directions could have been determined. Second order reflections were observed for the \{100\} and \{111\}, although their intensities were generally so weak that some inaccuracy could occur in the calculation of $\beta^*$ values. The determinations of strain function and crystallite size in the [100] and [111] are shown in tables 8 to 10 (p.87 to 89). From these values a certain amount of anisotropy can be seen for all three metals in the deformed state. In general a greater strain and crystallite size were present in the [100] direction than in the [111] direction. The difference being most pronounced in the copper and nickel specimens.

Fig. 32 shows the values of crystallite size plotted against ball milling time for all three metals. In each case a decrease in crystallite size was observed as the ball milling time was increased. However, the rate at which the crystallite size decreases becomes less as ball milling proceeds, the curves tending towards a limiting
crystallite size. This limiting value was 200 Å and 475 Å for copper and aluminium respectively, in the case of nickel the limiting value was not reached, but after 150 hrs. ball milling the crystallite size was 325 Å. During the early stages of ball milling the aluminium required less milling time to attain a given crystallite size than did either the nickel or the copper powders.

The values of strain function plotted against ball milling time are shown in Figs. 33a, b & c for aluminium, copper and nickel respectively. For both nickel and aluminium the strain function increased with ball milling time, the rate of increase progressively decreasing. In the case of copper the value of strain function was high initially and did not change significantly during ball milling. The maximum values of strain function, reached after 150 hrs. ball milling, were 0.0041, 0.0035, and 0.0030 for aluminium, nickel, and copper respectively.

The relationship between strain function and crystallite size at a given ball milling time is shown for each metal in Fig. 24. Aluminium shows a large increase in strain function for a small change in crystallite size. The opposite behaviour is seen for copper where the crystallite size decreases with hardly any increase in strain function. The behaviour of nickel showed an almost linear relationship between decreasing crystallite size and increasing strain function.

The effect that annealing at various temperatures has on the strain function and crystallite size of samples ball milled for 150 hrs. is shown in Figs 29, 30 and 31 for aluminium, copper and nickel respectively. In general an increase in annealing temperature caused the strain function to decrease whilst the crystallite size increased. However, the crystallite size did not greatly increase until the strain function, had almost reached its minimum value. The value of strain function and crystallite size for various ball milled samples annealed at the same temperature are shown in tables 8 to 10, these values being plotted in Fig. 28 in the case of aluminium. Again the general effect of annealing is to decrease the strain function and increase the crystallite size.
The relative positions of the (111) and (200) peaks of ball milled and annealed specimens were examined for evidence of stacking faults. However, with the exception of copper ball milled for 150 hrs., only small peak convergences were observed, being within an angular separation, measured in 2θ, of 0.01°. Values below 0.01° are regarded as a limit to the sensitivity of the method, probably due to unavoidable variations in geometry and not to the presence of stacking faults. The peak convergence for the specimen of copper ball milled for 150 hrs. was 0.036°. Derivation of the stacking fault probability, $\pi$, using the Paterson equation, gives a value of 0.0068, indicating that 1 in every 147 close-packed planes are faulted. From these results it would appear that stacking faults caused by deformation were only present in copper ball milled for 150 hrs.

None of the profiles showed any significant peak asymmetry, suggesting the absence of twinning faults. In each metal the relative intensities of the reflections remained constant as a result of ball milling. This would suggest that a deformation texture, i.e. the orientation of the planes with respect to the surface of the flake-like particles, had not been developed. However, the measurement of texture would be completely masked by the random distribution of particles in the diffractometer specimen.

**ELECTRON MICROSCOPY.**

The flake-like shape of the ball milled particles was used to advantage in the electron microscopy of the powders. Because the particles lay horizontally on the carbon support film, the electron beam could be transmitted through the smallest dimension of the particles. The advantage of this method is that the particles require no further preparation and the risk of changing the microstructure is avoided. Generally for transmission of electrons the thickness is between 500 - 5000 Å depending on the metal involved. Since the
transparency of particles depends upon the atomic number of the metal involved, it is to be expected that specimens of copper will need to be thinner than specimens of either nickel or aluminium to give the same transparency. As stated earlier the particles were observed to vary in thickness, some particles being transparent, some only transparent at the edges, whilst other particles were opaque to the electron beam.

It was observed that the structure of the particles was often unstable during examination. Thus the heating effect of the beam caused the structure to change, as well as melting or agglomerating of the particles. Such behaviour was observed more often with thicker particles, especially in the case of nickel where the thermal conductivity is lower than in the case of aluminium or copper. Low beam intensities were therefore used to help in avoiding such behaviour; this however resulted in the structure becoming more difficult to examine.

The effect of ball milling on the general distribution and structure of particles examined in the electron microscope can be followed by the electron micrographs and electron diffraction patterns of representative samples shown in Figs. 38 to 41 for aluminium, Figs. 45 to 48 for copper, and Figs. 52 to 54 for nickel. The micrographs show that in general the structure within the particles becomes finer as the duration of ball milling increases. Accompanying this increase in fineness was a general tendency for the structure to become more diffuse, making focusing, and subsequently photography, more difficult.

This effect is clearly shown in the case of aluminium where grain boundaries, bend extinction contours, and occasionally dislocations are seen in the structure of the sample ball milled for 10 hours, (Fig. 39a). However, the structure after 150 hrs. ball milling was more difficult to examine, even when examined at high magnifications, (Fig. 41b). Examination of this sample showed, where the contrast was sufficient, a cell-like structure of light and dark areas. The contrast of this structure was seen to change when the specimen was tilted with respect to the electron beam.
Since the contrast effect in the electron microscope depends upon the diffraction of electrons from the crystal lattice, grains or crystals with different orientations with respect to the electron beam will show differences in contrast. By changing the diffracting conditions, i.e. tilting the specimen, a change in contrast can occur. This change in contrast is more rapid than the continuous change in contrast due to the sweeping movement of bend extinction contours. Apart from having an extremely small cell size, about 200 Å, the copper samples ball milled for 150 hrs. showed a structure in which the boundaries between the cells were in light contrast when viewed in normal bright field illumination.

**Electron diffraction.**

Electron diffraction studies were made in the electron microscope on some of the ball milled powders. Electron diffraction patterns could be obtained when the particles were thin enough to allow electrons to be transmitted through them; for the thicker particles this was usually only possible at the edges. The selected area diffraction technique used throughout the investigation enabled diffraction patterns taken from a small area to be compared with the features observed in transmission electron microscopy from the same area. The diameter of the selected area was about 1 micron, except where otherwise stated. In most cases it was difficult to obtain strong diffraction patterns due to the intensity of the beam being limited by the unstable behaviour of the ball milled particles.

In each case the electron diffraction pattern consisted of concentric rings corresponding to the face-centred cubic crystal structure. The patterns were indexed by using the diameter of the diffraction rings, \( D \), measured directly from the photographic plates using a travelling microscope, in the equation

\[
D = \frac{2\lambda L}{d}
\]

where \( d \) is the spacing of the planes, \( \lambda \) the electron wave...
length and \( L \) is the distance of the specimen from the plate. The camera constant \( L \) was determined from a sample of thallium chloride at an operating voltage of 100 kV to be \( 15.4 \pm 0.1 \) 

Using the relationship for cubic crystals where

\[
d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}
\]

\( a \) is the crystal cube edge and \( h, k, l \), are the Miller indices, the patterns of aluminium, copper and nickel were confirmed to an accuracy of 1 per cent. The specimens were examined for anomalous rings caused by double diffraction from twinboundaries. However, only in the case of copper were extra rings present, most of these being identified as belonging to the Cu\(_2\)O pattern.

Examination of the patterns showed that the rings were composed of a number of spots, which in some cases merged into a continuous ring. The number of spots increased as the amount of ball milling increased. Tilting the specimen caused some spots to disappear and others to appear. The size of the spots in the copper and the nickel rings was larger than those of aluminium, this being analogous to x-ray diffraction where broadening is greatest in the former two.

The fact that continuous ring patterns are characteristic of polycrystalline samples indicates that the spots were diffracted from individual crystals or cells within the area contributing to the electron diffraction pattern. Therefore it is evident that the particles are not single crystals but are composed of a number of randomly oriented crystallites individually contributing to the diffraction pattern.

If the number of individual spots are counted it is possible to estimate the number of crystals contributing to the pattern. Uncertainty in this method arises because it is known how many crystallites have the correct diffracting conditions to contribute to the pattern. However, in the case of nickel ball milled 150 hrs., where the spots are on the limit of resolution, the size of the crystals or cells in particles examined was
calculated to be 750 Å. Considering the uncertainty of the method the value obtained has at least the same order of magnitude when compared with the structure in the electron micrographs.

Some of the rings showed a lack of uniformity, the spots tending to form into arcs indicating a preferred orientation of some sort. As ball milling progressed these arcs broke up into spots suggesting a more random orientation of the crystals. This is shown in the case of aluminium in Figs. 39c, 40c & 41c. Because of the weakness of the higher order rings the interpretation of any texture was not possible.

Examination of the particles by dark field illumination proved difficult due to the low beam intensity used. Where a higher beam intensity could be tolerated, namely for aluminium ball milled for 150 hrs., each spot in the electron diffraction patterns that was examined corresponded to a cell in the transmission micrographs.

Examination of the aluminium powders which had been annealed after ball milled showed that in each case the cell structure had slightly increased in size as well as clarity, Figs. 42 to 43a. The specimen ball milled for 10 hrs. showed after annealing, a structure with well defined grain boundaries and more dislocation structure within the grains than before annealing. In general more extinction contours were observed and the stability of the particles was less than in the case of ball milled particles.

The ball milled nickel powders also showed a clearer and larger cell structure after annealing, Figs. 55 & 56. Where electron diffraction studies were made the number of spots decreased on annealing.

The structure of the copper powder consisted of an agglomeration of small globules, Figs. 49a & 50a. Electron diffraction patterns of the annealed copper specimens showed the face-centred cubic sequence of rings belonging to copper, although the intensities of the Cu₂O rings were considerably weaker than in the ball milled specimens. This decrease in Cu₂O intensity was confirmed by x-ray
diffraction studies which also showed a slight increase in the strongest CuO peak.

From the results of electron microscopy, complemented by electron diffraction studies, there is enough evidence to suggest that the ball milled particles have a cell-like structure, the size of which decreases as the duration of ball milling increases. The cell structure was observed to be influenced by annealing treatments, the cell size increasing when the specimens were annealed. The cell size does not appear to be related to either the ball milled particles planer dimension or to the thickness. However, observation can only be made in the regions where the particles are thin enough to be transparent in the electron beam.

Estimates of grain or cell size from the electron micrographs are shown in table 11.

<table>
<thead>
<tr>
<th>Ball milling time (hrs.)</th>
<th>Ball milled size (Å)</th>
<th>Annealed size (Å)</th>
<th>400°C/4hrs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2000 - 6000</td>
<td>4000 - 10,000</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>800 - 2000</td>
<td>3000 - 4000</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>300 - 1000</td>
<td>1000 - 2000</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>200 - 700</td>
<td>400 - 1000</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1000 - 3000</td>
<td>400 - 850</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>400 - 1200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>100 - 400</td>
<td>250 - 850</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1500 - 3000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>600 - 1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>200 - 400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>100 - 300</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Optical micrographs of the original aluminium and copper powders show that the particles are polycrystalline with an average grain size of 20 microns and 5 microns respectively, (Figs. 34 & 35). The structure of the nickel powder could not be resolved in the optical microscope.
SHAPE OF DEFORMED PARTICLES.

In the case of the ductile face-centred cubic metal powders investigated such properties as ductility, or perhaps more accurately malleability, Young's modulus, and the rate of work hardening will have a large influence on the effectiveness of ball milling, whether in terms of surface area produced or decrease in particle size. The effectiveness of ball milling will decrease as ball milling progresses since the particles work harden and become more difficult to deform, causing the energy required to continue deformation to increase continuously. Apart from the mechanical properties of the powders the effectiveness of ball milling can also be influenced by other factors such as the quantity of powder in the space between the balls (14). Therefore the change observed in apparent density could also have some influence on the effectiveness of ball milling.

Both surface area measurement and microscopy indicate that the original particles are deformed during ball milling to produce fine flake-like particles where the surface area per volume is larger than in the original granular particles. The flake-like particles produced show that plastic deformation has occurred even in the early stages of ball milling. The decrease in size of these flake-like particles is possibly caused by fracture occurring in areas where the particles are thin enough for large stresses to be set up under the impact conditions. It is also possible that the particles fracture by a shearing process similar to that occurring in the final fracture zone of ductile metals.

The change in apparent density during the ball milling of aluminium and of copper may be explained by the following process: At the onset of ball milling the original particles are deformed into a flake-like shape, this being accompanied by a simultaneous comminution of the particles resulting in a decrease in particle size. Due to this change from granular to a flake-like shape
the particles do not pack as well and the apparent density is seen to decrease. The minimum in the curve corresponds to a situation where all the particles are flake-like in shape. If ball milling is then continued a gradual decrease in the size of these flake-like particles is produced. However, as the flake shape is mechanically weak, the particles will tend to decrease in size, by bending, breaking, and loss of material from the edges. This occurs in preference to reducing the flake thickness, this becoming increasingly difficult because of work hardening. As the flake-like particles decreases in size their packing properties improve and the apparent density increases. As verification of this fact the author has observed the packing of squares of paper, used to represent flakes of constant thickness. The apparent density was seen to increase as the size of the paper squares decreased.

The low apparent density value of the original nickel powder is probably due to the "spikey" nature of the particles, this being shown in Fig. 36 where the particles are seen to have agglomerated into a chainlike pattern. The removal of these spikes during the early stages of ball milling causes an improvement in the packing properties which overshadows any deterioration in packing due to the formation of flake-like particles. Hence the apparent density increases throughout ball milling due to removal of the spikes, and at a later stage to the decreasing size of the flake-like particles. The increase in apparent density for all three metal powders does not appear to be caused by particle agglomeration; however, any such agglomeration might have been destroyed during specimen preparation.

PROBLEM OF "SIZE".

Some confusion exists in what is meant by the size as measured by the different methods. The size obtained by x-ray line broadening is often taken as the particle size of a powder without consideration of the
microstructure of the particles. To avoid such confusion the following definitions have been used in the present investigation: The particle size of a powder refers to the outer dimensions of a powder particle. The crystallite size refers to the measurement obtained from x-ray line broadening. The cell size refers to the structure within the particles as seen in the electron microscope. When comparing the sizes measured by different methods it is possible that the difference in size could be accounted for by the difference in accuracy of the methods. The large number of diffracted x-rays involved indicates that the crystallite size measurement is a statistical mean value. This value becomes less accurate in the size range above 1000 Å due to the fact that the size is calculated from the reciprocal of excess broadening, which in turn depends upon the accurate determination of the instrumental broadening. In comparison the accuracy of the electron microscopy size determination decreases as the structure becomes finer and therefore more difficult to resolve. A more accurate comparison between the particle size measured by electron microscopy and that determined from surface area measurements would be possible if a more direct method, e.g. surface adsorption (119), than air permeability had been used.

The results enabled an interesting comparison to be made between crystallite size derived from x-ray line broadening and size of particles and cell size as seen in the electron microscope. The crystallite size did not appear to be related to the planar dimensions of the powder particles which were much larger than the crystallite size. As seen from their transparency in the electron microscope the thinnest particles must approach the crystallite size in thickness. However, the variations in transparency show that there are many thicker particles present hence the mean particles thickness does not appear to be related to the crystallite size. It is evident that both the crystallite size and the cell size decrease as deformation increases. Similarly both the crystallite size and cell size increase after the ball milled particles are annealed, although the overall dimensions of the
particles does not appear to change. The difference between cell size and crystallite size becomes less pronounced as ball milling progresses, approaching the same order of magnitude when the particles had been ball milled for the longest time. A comparison between the size measured after 150 hrs. ball milling is shown in Table 12.

<table>
<thead>
<tr>
<th>Material</th>
<th>Crystallite size</th>
<th>Cell size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>450 - 500 Å</td>
<td>200 - 700 Å</td>
</tr>
<tr>
<td>Copper</td>
<td>190 - 200 Å</td>
<td>100 - 300 Å</td>
</tr>
<tr>
<td>Nickel</td>
<td>310 - 340 Å</td>
<td>100 - 400 Å</td>
</tr>
</tbody>
</table>

As ball milling continues the rate of decrease in crystallite size becomes much slower until a limiting crystallite size is reached. This effect being less apparent for copper and for nickel than for aluminium. A limiting cell size has also been observed by Gay et al. (57), (66), Kelly (67), Swann (74), Segall and Partridge (81) and Embury et al. (82).

The smallest values of crystallite size determined by x-ray line broadening are compared with the values obtained by other investigators using the same method in Table 13.

<table>
<thead>
<tr>
<th>Material</th>
<th>Crystallite size</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al, ball milled</td>
<td>475 Å</td>
<td>current work</td>
</tr>
<tr>
<td>Al, &quot;</td>
<td>600 Å</td>
<td>(24)</td>
</tr>
<tr>
<td>Al, filings (-150°C)</td>
<td>320 Å</td>
<td>(59)</td>
</tr>
<tr>
<td>Al, &quot;</td>
<td>650 Å</td>
<td>(59)</td>
</tr>
<tr>
<td>Al, &quot;</td>
<td>4000 Å</td>
<td>(45)</td>
</tr>
<tr>
<td>Cu, ball milled</td>
<td>200 Å</td>
<td>current work</td>
</tr>
<tr>
<td>Cu, filings (-150°C)</td>
<td>155 Å</td>
<td>(58)</td>
</tr>
<tr>
<td>Cu, &quot;</td>
<td>180 Å</td>
<td>(58)</td>
</tr>
<tr>
<td>Cu, &quot;</td>
<td>800 Å</td>
<td>(63)</td>
</tr>
<tr>
<td>Ni, ball milled</td>
<td>325 Å</td>
<td>current work</td>
</tr>
<tr>
<td>Ni, compressed foil</td>
<td>1000 Å</td>
<td>(61)</td>
</tr>
</tbody>
</table>
Similarly the cell sizes observed in the ball milled particles are compared in Table 14 with the smallest sizes observed in the electron microscope by other investigators.

<table>
<thead>
<tr>
<th>Material</th>
<th>Cell size</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al, ball milled</td>
<td>200 - 700 Å</td>
<td>current work</td>
</tr>
<tr>
<td>Al, &quot; &quot;</td>
<td>1000 - 20,000 Å</td>
<td>(24)</td>
</tr>
<tr>
<td>Al, rolled</td>
<td>18,000 Å</td>
<td>(74)</td>
</tr>
<tr>
<td>Cu, ball milled</td>
<td>100 - 300 Å</td>
<td>current work</td>
</tr>
<tr>
<td>Cu, cold drawn</td>
<td>1600 Å</td>
<td>(82)</td>
</tr>
<tr>
<td>Ni, ball milled</td>
<td>100 - 400 Å</td>
<td>current work</td>
</tr>
<tr>
<td>Ni, shock loaded</td>
<td>700 - 2500 Å</td>
<td>(84)</td>
</tr>
</tbody>
</table>

The crystallite size can therefore be considered to represent a substructure similar to the cell structure observed by electron microscopy. The substructure is formed by a network of dislocations introduced during deformation. The dislocation networks subdivide grains of the polycrystalline powder particles into cells which are slightly misoriented with respect to each other. The distance between the cell walls decreases as the number of dislocations to be accommodated increases during deformation. Hence the cell size decreases. As the number of boundaries within each grain increases, the crystalline structure of the grain becomes increasingly misoriented. The increasing random structure indicated by the electron diffraction patterns also suggest a similar effect. Whether or not the heavily deformed particles consist of one or a number of grains is not clear. However, dislocation "pile-ups", which occur at large angle grain boundaries, were not observed.

The limiting cell size effect can be explained by reference to Stages II and III of the stress-strain curve, where both poly- and singlecrystals are influenced by similar factors. During Stage II a network of dislocations appears, developing into a cell structure which decreases in size as the strain increases. At a strain corresponding to the onset of Stage III, characterised by a decrease in
the rate of work hardening, the dislocations cross slip to avoid each other and also annihilate dislocations of opposite sign. This cross slip of dislocations results in fewer dislocations being available for cell wall formation, and hence the cell size changes very little as deformation continues. This type of behaviour has been seen, for example, by Howie (73), Hirsch & Steeds (94). The decrease in stress with temperature at the onset of Stage III (104), is coincident with the temperature dependence of cross slip. Seeger (120) has termed this thermal activity, aided by stress, "dynamic recovery".

The temperature dependence of cross slip could explain why the ball milling time necessary to produce the limiting crystallite size became increasingly longer for aluminium, copper, and nickel respectively. The deformation temperature, relative to the absolute melting temperature, is higher for aluminium and lower for nickel than for copper. Therefore the amount of deformation necessary to reach the limiting crystallite size will increase as the melting temperature of the metal increases. In the region before the limiting crystallite size is reached the deformation required to produce a given crystallite size is greater for nickel and lower for aluminium than for copper. This region, where the crystallite size decreases with deformation, is similar to Stage II of the stress-strain curve. The rate of hardening during Stage II has no temperature-dependence (97) but has been related to the shear modulus (5). However, for the metals investigated the higher the melting temperature the higher is the shear modulus and the influence of these two factors on the crystallite size during this stage of ball milling is not clear.

The ability of dislocations to cross slip is also influenced by the stacking fault energy of the metal, in general a decrease in stacking fault energy being equivalent to lowering the temperature thus preventing cross slip. Accompanying this lack of cross slip is a decrease in cell size (80). The difference observed between the limiting crystallite size of aluminium and of copper, can be explained by the difference in stacking
fault energy of the two metals. The low stacking fault energy of copper will prevent cross slip from occurring readily and a smaller cell size will result than in the case of aluminium where the stacking fault energy is much higher. The limiting crystallite size of nickel, although continuing to fall slightly, lies between the values of aluminium and copper. However, the stacking fault energy of nickel is less certain, the published values (84),(100) falling to either side of aluminium.

Investigations by Mader(89) and Hirsch & Steeds(94) have shown that dislocations frequently escape at the specimen surface. Mitchell (104) has shown that this effect can influence the stress-strain curve depending on the specimen size. From the difficulty in observing dislocation tangles, even in the copper particles where cross slip is relatively difficult, it is possible that there has been a loss of dislocations at the particle surface by cross slip of screw dislocations. Such dislocation behaviour would assist the effect of dynamic recovery. However, the presence of oxide films on the surface of the particles would offer some resistance to the loss of dislocations. Such oxide films were not entirely prevented, even though the precaution of ball milling the powders in an inert atmosphere of argon was taken.

**PROBLEM OF "STRAIN".**

The explanation of broadening due to strain is less apparent than the explanation of broadening due to size. It has been suggested (40), (51) that strain broadening is due to the lattice strains concentrated over distances corresponding to a few atomic diameters. Furthermore values of strain function have been related to values of Young's modulus (52), the stored energy introduced by deformation (53), mode of deformation (60), distribution of dislocations (56) and atomic mobility (45). Therefore it is difficult to describe strain broadening in relation to the structure of the metal. However, a comparison of
the present investigation with previous results might confirm, if not clarify this relationship.

Comparison between strain function and mechanical properties are influenced by the anisotropic behaviour of most metals, Young's modulus varying with crystallographic direction. As the values of strain function have been determined in the [100] and [111] directions a comparison can be made with the value of Young's modulus in each direction. The higher values of strain function found in the [100] direction compared to the values found in the [111] direction are in good agreement with the observations of Lewis & Pearson (118) and Warren & Averbach (57). The former found higher than average strain function in the direction of minimum value of Young's modulus whilst the latter found the strain to be nearly inversely proportional to Young's modulus. The difference between the values of strain function in the [100] direction and [111] direction, which are much larger for copper and nickel than for aluminium, can therefore be explained by the anisotropy of the metals concerned. Such anisotropy is shown by the values of Young's modulus, calculated from elastic constants, in the following crystallographic directions:

<table>
<thead>
<tr>
<th></th>
<th>[100]</th>
<th>[110]</th>
<th>[111]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>6.05</td>
<td>7.5</td>
<td>7.76</td>
</tr>
<tr>
<td>Copper</td>
<td>6.68</td>
<td>13.3</td>
<td>19.2</td>
</tr>
<tr>
<td>Nickel</td>
<td>13.6</td>
<td>23.2</td>
<td>30.3</td>
</tr>
</tbody>
</table>

During ball milling the average strain function increases even after the limiting crystallite size has been reached. However, this effect is more apparent for aluminium and nickel than for copper. If the strain function is a measure of the lattice strain then the arrangement of dislocations must cause additional strain even when the crystallite size is constant. Howie (73) and Hirsch and Steeds (94) have observed that the misorientation between cells increases after the limiting size has been reached. The results of the electron diffraction studies indicate that the structure becomes more random which suggests a greater misorientation between the cells during this stage. When the limiting cell size is reached cross slip can also cause a local
rearrangement of dislocations in the cell walls to form subboundaries. As the orientation across the cell boundary increases the number of dislocations per unit length of boundary also increase and the energy of the boundary becomes greater (114).

On the other hand annealing the ball milled powders caused the strain function to decrease rapidly to almost a minimum value before any appreciable change in crystallite size had occurred. The well defined subgrains observed during the electron microscopy of the annealed ball milled aluminium and nickel powders support these findings. However, the structure of the annealed copper powder is not understood. During annealing the thermally activated process of polygonisation takes place whereby the dislocations climb from their glide planes to annihilate each other (121). Simultaneously there is a rearrangement of the remaining dislocations to form subboundaries of the tilt type. As annealing continues more dislocations are annihilated and the boundary energy decreases. Thus the energy of the subboundaries is substantially reduced before the onset of such processes as boundary migration which cause the subgrains to increase in size.

It is therefore possible that the increase in strain function observed during ball milling, and its subsequent decrease during annealing, is in some way associated with the changes in lattice strain caused by the arrangement of dislocations in the cell walls and subboundaries. The high initial value of strain function of copper is possibly due to the reduced mobility of the dislocations caused by grain boundaries and a low stacking fault energy.

DEFORMATION IN BALL MILLING.

From the observed changes in particle size, microstructure and x-ray line broadening it is possible to consider ball milling as a continuous deformation process. An increase in the duration of ball milling may be compared to an increase in mechanical deformation,
similar to that observed in other deformation processes such as rolling or drawing. However, a direct comparison in terms of the magnitude of deformation is not possible.

It can be seen that the substructure is smaller in the case of ball milling than in the other deformation process. This is probably connected with the deformation process since the deformation conditions, e.g. amount and rate of deformation, strongly influence the substructure formed.

The amount of deformation during ball milling, as shown by the thin flake-like particles produced, is very high. The mode of deformation, a combination of impact and attrition, produces a very high strain rate. As shown by Johari & Thomas (83) and Nolder & Thomas (84) the cell size decreases with increasing strain rate, this being very pronounced in the case of shock loading, since at faster strain rates there is less time for cross-slip to occur. The geometry of deformation is another factor to be considered. During ball milling the deformation takes place in a random manner as compared to rolling where deformation is confined to a definite geometry. During rolling and wire drawing it has been observed that the cell structure forms in a preferred direction (82). The formation of a cell structure in a preferred direction during ball milling is probably prevented by the random type of deformation. The size of the particles produced during ball milling is much smaller than the size of specimens produced by other deformation processes and hence could have some effect on the size difference.

GENERAL.

It is reasonable to assume that the fine powders produced by ball milling have some use in powder technology if, and when, their pyrophoric properties can be properly controlled. The combination of small particle size and fine substructure within the particles could play an important role in the sintering behaviour of such powders. Again the size and structure of the powder particles are
of interest in the field of dispersion strengthened alloys made from powders, where the size of the substructure as well as the distance between the dispersed oxide particles is known to influence the strengthening properties (122). However, it has been shown during the annealing experiments that the particle substructure is changed by thermal treatments and the influence of sintering on particle substructure remains a matter for investigation.

(6) CONCLUSIONS.

From the results presented the following conclusions can be developed.
1) Ball milling produces flake-like shaped particles which decrease in size as ball milling continues. The observed anomalous changes in apparent density during ball milling may be caused by these changes in particle size and shape.

2) The results of x-ray line broadening and electron microscopy indicate that ball milling produces a substructure within the particles. The crystallite size obtained from x-ray line broadening measurements is considered to represent a substructure similar to the cell structure observed in the electron microscope. The substructure size decreases rapidly with ball milling time until a limiting size is reached after which the rate of decrease is only slight. This limiting size effect is thought to be due to dynamic recovery; the difference in size and amount of ball milling at which this occurs for the different metals is caused by the effect of temperature and stacking fault energy.

3) The extremely small size of the substructure may be caused by the severe and complex nature of the deformation process.
4) The observed changes in strain function during the ball milling and annealing of the particles may be associated with the changes in lattice strain caused by the arrangement of dislocations in the cell walls and subboundaries. The variations in strain function with crystallographic direction appears to be related to the anisotropy of the metals investigated.

5) Because the crystallite size measurements do not appear to be related to the outer dimensions of the particles it is suggested that x-ray line broadening is not a suitable method for the measurement of the particle size of deformed metal powders.
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TABLE 2.
Average values of surface area for aluminium, copper and nickel, determined by the Fisher Sub-sieve method.

<table>
<thead>
<tr>
<th>Metal powder</th>
<th>Ball milling time, hours.</th>
<th>Average surface area with standard deviation cm$^2$/g</th>
<th>Equivalent diameter, microns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>0</td>
<td>871±14</td>
<td>25.5</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>5797±156</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>8889±144</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>6006±139</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>4141±75</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>6404±169</td>
<td>3.5</td>
</tr>
<tr>
<td>Copper</td>
<td>0</td>
<td>545±8</td>
<td>12.4</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>3644±169</td>
<td>1.85</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>4921±0</td>
<td>1.37</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>7844±0</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>13219±400</td>
<td>0.51</td>
</tr>
<tr>
<td>Nickel</td>
<td>0</td>
<td>2152±19</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>5186±169</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>7963±150</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>8498±131</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Average surface area value equal to the arithmetic mean of 3 measurements.

Standard deviation = $\sqrt{\frac{\sum x^2}{N} - (\frac{\sum x}{N})^2}$

where $x$ is a value of surface area, and $N$ the number of values.
TABLE 4.

Average values of apparent density for Aluminium, Copper, and Nickel.

<table>
<thead>
<tr>
<th>Metal Powder</th>
<th>Ball Milling Time, hours.</th>
<th>Average Apparent Density with Standard Deviation.</th>
<th>Grammes per cm³</th>
<th>Per Cent Theoretical Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>0</td>
<td>0.959±0.015</td>
<td>35.52±0.56</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.373±0.003</td>
<td>13.82±0.11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.345±0.006</td>
<td>12.78±0.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.309±0.007</td>
<td>11.44±0.26</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.281±0.008</td>
<td>10.41±0.30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.374±0.009</td>
<td>13.85±0.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.513±0.028</td>
<td>19.00±1.60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.618±0.015</td>
<td>22.89±0.55</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
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Average Apparent density equals the arithmetic mean of 3 measurements. Standard deviation calculated as shown in Table 1.
Table 5. Values of X-ray line broadening for Aluminium.
(A) Integral line breadth, $\beta \times 10^{-3}$ radians. (B) $\beta^* \times 10^{-3}$. (C) $\beta^*$ (excess) $\times 10^{-3}$.

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* hkl: Miller indices of the diffraction plane.
* d*: Interplanar spacing.
* Ball Milling Time, hrs.: Time spent milling the sample.
* Annealing Temperature, °C.: Temperature at which the sample was annealed.

Note: The values for $\beta^*$ (excess) are calculated as the difference between the integral line breadth and the $\beta^*$ values.
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Table 7. Values of X-ray line broadening for Nickel.

(A) Integral line breadth $L \times 10^{-3}$ radians. (B) $S \times 10^{-3}$. (C) $S \times (\text{excess}) \times 10^{-3}$.  

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<td>190</td>
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<td>1250</td>
<td>0.40</td>
<td>1.00</td>
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<td>3333</td>
<td>0.81</td>
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<td>1111</td>
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<td>2500</td>
<td>1053</td>
<td>3.10</td>
<td>0.69</td>
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<td>Ball Milling Time, hrs.</td>
<td>Annealing Temp. °C.</td>
<td>Mean Crystallite Size, Å (Lower:Upper)</td>
<td>Mean Strain Function x10⁻³ (Lower:Upper)</td>
<td>Crystallite Size Å [100] [111]</td>
<td>Strain⁻³ Function [100] [111]</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>------------------------</td>
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</tr>
<tr>
<td>0</td>
<td>-</td>
<td>&gt;10.000:10.000</td>
<td>0.60:1.20</td>
<td>&gt;10.000:10.000</td>
<td>1.12:0.65</td>
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<tr>
<td>20</td>
<td>-</td>
<td>1667:2350</td>
<td>2.00:2.50</td>
<td>952:1587</td>
<td>9.81:1.41</td>
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</tr>
<tr>
<td>40</td>
<td>-</td>
<td>1000:1250</td>
<td>2.45:3.00</td>
<td>505:535</td>
<td>2.05:0.88</td>
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<td></td>
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<tr>
<td>60</td>
<td>-</td>
<td>625:800</td>
<td>2.80:3.50</td>
<td>472:741</td>
<td>2.83:1.95</td>
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<td></td>
<td></td>
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<tr>
<td>80</td>
<td>-</td>
<td>435:556</td>
<td>2.80:3.45</td>
<td>313:348</td>
<td>2.40:0.83</td>
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<td></td>
<td></td>
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<tr>
<td>100</td>
<td>-</td>
<td>385:455</td>
<td>3.10:3.55</td>
<td>273:412</td>
<td>2.53:1.88</td>
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<tr>
<td>150</td>
<td>-</td>
<td>305:339</td>
<td>3.25:3.85</td>
<td>250:348</td>
<td>3.35:2.08</td>
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<tr>
<td>150</td>
<td>105</td>
<td>333:400</td>
<td>2.10:2.80</td>
<td>230:483</td>
<td>1.10:2.70</td>
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<tr>
<td>150</td>
<td>300</td>
<td>526:625</td>
<td>0.68:1.12</td>
<td>599:500</td>
<td>1.04:0.23</td>
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<tr>
<td>150</td>
<td>400</td>
<td>833:952</td>
<td>0.56:0.85</td>
<td>1149:680</td>
<td>1.20:0.07</td>
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<tr>
<td>20</td>
<td>400</td>
<td>&gt;10.000:10.000</td>
<td>0:0.15</td>
<td>&gt;10.000:2857</td>
<td>0.3:-0.75</td>
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<td>60</td>
<td>400</td>
<td>2222:3333</td>
<td>0.50:0.75</td>
<td>2222:3333</td>
<td>0.6:0.35</td>
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</table>
Fig. 8. Apparent density of aluminium plotted against ball milling time.

0.8 - 0.6 - 0.4 - 0.2 - 0

Ball Milling Time, (hrs.)

Fig. 9. Surface area of aluminium plotted against ball milling time.

0.8 - 0.6 - 0.4 - 0.2 - 0

Ball Milling Time, (hrs.)
Fig. 10 Histograms showing particle size distribution of aluminium powder in the non-milled and milled condition.
Apparent Density, \((\text{g/cm}^3)\)

Fig. 11. Apparent density of copper plotted against ball milling time.

Surface Area, \((\text{m}^2/\text{g})\)

Fig. 12. Surface area of copper plotted against ball milling time.
Fig. 13. Apparent density of Nickel plotted against ball milling time.

Fig. 14. Surface area of Nickel plotted against ball milling time.
Fig. 15. $\beta^* \text{ vs } d^*$ for aluminium powder ball milled for various times and the annealed powder.

A = Annealed  
B = 10 Hrs.  
C = 20 Hrs.  
D = 30 Hrs.

E = 50 Hrs.  
F = 80 Hrs.  
G = 100 Hrs.  
H = 150 Hrs.
For various times and for annealed copper powder:

A = Annealed, D = 40 Hrs, G = 100 Hrs.
B = 0 Hrs, E = 60
C = 20
F = 80

\( \beta^{*} \times 10^{-3} \)

0 0.2 0.4 0.6 0.8 1.0 1.2

111 200 220 311 222 400 331 420

H  G  F  E  D  C  B  A
Fig. 17. $\beta^* vs d^*$ for nickel powder ball milled for various times and for annealed nickel powder.

A = Annealed.  D = 40 Hrs.  G = 100 Hrs.
B = 0 Hrs.    E = 60 Hrs.  H = 150 Hrs.
C = 20 Hrs.   F = 80 Hrs.
Fig. 18. $\beta^*(\text{excess})$ vs $d^*$ for ball milled aluminium powders.

A = 10 Hrs.  E = 80 Hrs.
B = 20 Hrs.  F = 100 Hrs.
C = 30 Hrs.  G = 150 Hrs.
D = 50 Hrs.

$\beta^*(\text{excess}) \times 10^{-3}$
Fig. 20. $\beta^*(\text{excess})$ vs $d^*$ for aluminium ball milled 150 hrs. and annealed at various temperatures.

- $A = 600^\circ \text{C}$
- $B = 500^\circ \text{C}$
- $C = 400^\circ \text{C}$
- $D = 110^\circ \text{C}$
- $E = 20^\circ \text{C}$
Fig. 21. $\beta^*(\text{excess})$ vs $d^*$ for copper powder ball milled for various times.

A = 0 Hrs. D = 60 Hrs. G = 150 Hrs.
B = 20 Hrs. E = 80 Hrs.
C = 40 Hrs. F = 100 Hrs.
Fig. 22. $\beta^*(\text{excess})$ vs $d^*$ for copper powder ball milled 150hrs. and annealed at various temperatures.

A = 400°C, D = 105°C
B = 300°C, E = 20°C
C = 250°C
Fig. 23. $\beta^t$ (excess) vs $d^t$ for copper ball milled various times and annealed for 4 hrs. at 250°C.

$A = 20$ Hrs.
$B = 40$ Hrs.
$C = 150$ Hrs.

Fig. 24. The relationship between crystallite size ($t$) and strain function at a given ball milling time for aluminium (A), copper (B), and nickel (C).
Fig. 25: $\beta^*(\text{excess})$ vs $d^*$ for nickel powder ball milled for various times.

A = 20 Hrs.  \hspace{1cm} D = 80 Hrs.
B = 40       \hspace{1cm} E = 100
C = 60       \hspace{1cm} F = 150
Fig. 27. $\beta^*$ (excess) vs $d^*$ for nickel ball milled 150 hrs. and annealed for 4 hrs. at various temperatures.

- **A**: 400°C
- **B**: 300°C
- **C**: 105°C
- **D**: 20°C

$A = 20$ hrs,
$B = 60$ hrs,
$C = 150$ hrs,
Fig. 29. Crystallite size (t) and strain function (ξ) for aluminium ball milled 150 hrs. and annealed at various temperatures for 4 hours.
Fig. 31. Crystallite size ($t$) and strain function ($\xi$) of nickel ball milled 150 hrs. and annealed for 4 hrs. at various temperatures.
Crystallite size (Å) as a function of ball milling time.
or Dali milling time.

Aluminium Fig. 33a.

Nickel Fig. 33b.

Copper Fig. 33c.

Ball milling time (hours)
Fig. 4. View of the glove box.
Fig. 34.
Aluminium powder sectioned, polished and etched.
(x 250)

Fig. 35.
Copper powder sectioned, polished and etched.
(x 500)

Fig. 36.
Nickel powder.
(x 5000)
FIG. 37a.
Aluminium powder.
(x 100)

FIG. 37b.
Aluminium powder ball milled 10 hrs.
(x 100)

FIG. 37c.
Aluminium powder ball milled 30 hrs.
(x 100)
Fig. 37d.
Aluminium powder
ball milled 50 hrs.
(x 100)

Fig. 37e.
Aluminium powder
ball milled 150 hrs.
(x 250)

Fig. 38.
Aluminium powder
ball milled 150 hrs.
(x 3000)
Fig. 39a.
Aluminium powder ball milled 10 hrs.
(x 20000)

Fig. 39b.
Aluminium powder ball milled 30 hrs.

Fig. 39c.
Electron diffraction pattern of 39b.
(x 2)
Fig. 40a.
Aluminium powder
ball milled 50 hrs.
(x 2000)

Fig. 40b.
Aluminium powder
ball milled 50 hrs.
(x 50000)

Fig. 40c.
Electron diffraction
pattern of 40b.
(x 2)
Fig. 41a. Aluminium powder ball milled 150 hrs. (x 20000)

Fig. 41b. Aluminium powder ball milled 150 hrs. (x 100000)

Fig. 41c. Electron diffraction pattern of 41b. (x 2)
Fig. 42a.
Aluminium powder ball milled 10 hrs, annealed for 4 hrs. at 400°C. (x 20000)

Fig. 42b.
Aluminium powder ball milled 30 hrs, annealed for 4 hrs. at 400°C (x 20000)

Fig. 42c.
Aluminium powder ball milled 50 hrs, annealed for 4 hrs. at 400°C. (x 20000)
Fig. 43a.
Aluminium powder ball milled 150 hrs. and annealed at 400°C for 4 hrs. (x 50000)

Fig. 43b.
Electron diffraction pattern of 43a. (x 2)
Fig. 44a.
Copper powder.
(x 100)

Fig. 44b.
Copper powder
ball milled 10 hrs.
(x 150)

Fig. 44c.
Copper powder
ball milled 20 hrs.
(x 150)
Fig. 45a.
Copper powder
ball milled 20 hrs.
(x 1500)

Fig. 45b.
Copper powder
ball milled 20 hrs.
(x 50000)

Fig. 45c.
Electron diffraction
pattern of 45b.
(x 2)
Fig. 46a.
Copper powder ball milled 40 hrs. 
(x 2500)

Fig. 46b.
Copper powder ball milled 40 hrs. 
(x 50000)

Fig. 46c.
Electron diffraction pattern of 46b. 
(x 2)
Fig. 47a.
Copper powder
ball milled 100 hrs.
(x 5000)

Fig. 47b.
Copper powder
ball milled 100 hrs.
(x 50000)

Fig. 47c.
Electron diffraction
pattern of 47b.
(x 2)
Fig. 48a. Copper powder ball milled 150 hrs. (x 5000)

Fig. 48b. Copper powder ball milled 3.50 hrs. (x 50000)
Fig. 48c.
Copper powder ball milled 150 hrs.
(x 100000)

Fig. 48d.
Electron diffraction pattern of 48c.
(x 2)
Fig. 49a.
Copper powder
ball milled 150 hrs.
and annealed for
4 hrs. at 250°C.
(x 50000x)

Fig. 49b.
Electron diffraction
pattern of 49a.
(Selected area dia.
5 microns)
(x 2)
Fig. 50a.
Copper powder ball milled 40 hrs. and annealed for 4 hrs. at 250°C. (x 50000)

Fig. 50b.
Electron diffraction pattern of 50a. (selected area dia. 5 microns) (x 2)
Fig. 51a.
Nickel powder
ball milled 10 hrs.
(x 5000)

Fig. 51b.
Nickel powder
ball milled 60 hrs.
(x 5000)

Fig. 51c.
Nickel powder
ball milled 150 hrs.
(x 5000)
Fig. 52.
Nickel powder
ball milled 20 hrs.
(x 50000)

Fig. 53a.
Nickel powder
ball milled 60 hrs.
(x 50000)

Fig. 53b.
Electron diffraction
pattern of 53a.
(x 2)
Fig. 54a.
Nickel powder
ball milled 150 hrs.
(x 50000)

Fig. 54b.
Nickel powder
ball milled 150 hrs.
(x 100000)

Fig. 54c.
Electron diffraction
pattern of 54b.
(x 2)
Fig. 55a.
Nickel powder ball milled 150 hrs. and annealed for 4 hrs. at 400°C.
(x 80000)

Fig. 55b.
Electron diffraction pattern of 55a.
(x 2)
Fig. 56a.
Nickel powder ball milled 60 hrs. and annealed for 4 hrs. at 400°C. (x 50000)

Fig. 56b.
electron diffraction pattern of a particle (top/centre) in 56a. (x 2)