Formation of new materials in the solid state by mechanical alloying

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This paper studies the mechanisms of formation of new materials in the solid state using mechanical alloying. Several key factors have been observed to control the formation of new alloys. These factors are: activation energy, which is related to the formation of defects during collision of powder particles; temperature, which is associated with the plastic deformation of powder particles and sliding between these particles, and between high energetic balls and powder particles; and crystalline size, which is related to the formation of nanometer crystalline during mechanical alloying. It is found that the diffusion process during mechanical alloying is controlled by both mechanical and thermal energy. The activation energy can be lowered by introducing defects, which in turn results in an increase in diffusivity. By reducing grain size, effective diffusivity can be increased significantly. Grain boundary and free surface diffusions are found to prevail to enable diffusion to proceed at relatively low temperature.

Keywords: solid stat diffusion; mechanical alloying; new alloys; activation energy; defects

Introduction

Mechanical alloying (MA), usually carried out under an inert atmosphere in a ball mill¹⁻³ is an alternative technique for producing metallic powders in the solid state. Powder particles in the ball mill are subjected to highenergy collision⁴ which causes the powder particles to be cold welded together and fractured. Cold welding and fracturing enable powder particles to be always in contact with each other and atomically clean surfaces and with minimized diffusion distance. Microstructurally, the MA process can be divided into three stages: at the initial stage, powder particles are cold welded together to form a laminated structure. The chemical composition of the composite particles varies significantly within the particles and from particle to particle. At the second stage, the laminated structure is further refined as fracture takes place. Thickness of the lamellae is decreased. Although dissolution may have occurred, chemical composition of the powders is still not homogeneous. At the final stage, the lamellae become finer and eventually disappear. A homogeneous chemical composition is achieved for all particles, resulting in the formation of a new alloy with a composition corresponding to the starting powder mixture. Using this technique, alloys⁵⁻⁷ and non-equilibrium phases⁸⁻⁹ can be produced. The application of MA to exotic systems began with the work of Schwarz and Koch¹⁰. Since then, formation of amorphous materials¹¹⁻¹³ using MA has received much attention. The fundamentals of formation of amorphous are now well understood.

It is known that all solid-state reactions involve the formation of one product phase or more between the reactants, and that the reaction volume is continually reduced as the reactants become specially separated. Reaction rates are therefore influenced by the initial contact area and by the diffusion of the reactant species through the product phases¹⁴. For most solid-state processes, the initial contact area is fixed and the diffusion rate is limited. Therefore solid-state reactions are temperature dependent. This is not the case for MAinduced reactions since a reaction can actually increase with decrease in temperature and a change of phase¹⁵. With fracturing and rewelding of the powder particles, the reaction area increases. Thus the chemical reactivity increases during MA¹⁷. As pointed out by Schaffer¹⁴, owing to the introduction of a large number of crystal defects¹⁶, MA minimizes the effect of product barriers on reaction kinetics and provides the conditions required for the promulgation of solid-state reactions at low temperature. The change in microstructure is critically dependent on the ductility of the powders. In ductile systems, a composite layered structure is developed on the powder particles during the early stages of MA. This structure is gradually refined and homogenized until finally, a truly alloyed powder with very fine structures from any combination of elements can be produced¹⁸⁻²⁰ from the bottom of a phase diagram (solid state) upward rather than from the top (liquid state)²¹.

The objectives of the present paper are to discuss the mechanisms of mechanical alloying and to study the significance of each key factor during the alloying process.

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Mechanisms of mechanical alloying

Effect of temperature

The increase in temperature during MA is of particular concern. It has been argued that the large plastic deformation that takes place in the process induces local melting leading to the formation of new alloys²². According to this hypothesis, new alloys are produced through a melting mechanism and/or diffusion at relative high temperature. For some materials with low melting temperature it is quite possible that local melting is induced by high collision energy. For most materials, however, melting cannot take place during MA. To achieve cold welding, which is an essential condition for MA, at least one material should normally be ductile. The latter acts as a binder to bind powder particles together²³. However, it has been found that brittle materials such as solid solution Si + Ge, intermetallic compound Mn + Bi and amorphous alloys $NiZr_2 + Ni_{11}Zr_9$ can also be mechanically alloyed^{24,25}. A key feature of the possible mechanisms for MA of brittle components is the temperature of the powder particles during milling. No alloying was observed when the milling vial was cooled by liquid nitrogen²⁵. It has been claimed that pure ceramic materials of WC, TiN and TaN can partially be mechanically alloyed at certain conditions²⁶. The temperature during MA is believed to be far from the melting temperatures of WC, TiN and TaN or their diffusion temperature. The temperature measured after certain duration of MA was only about 120°C. Because the change in temperature of the powder particles is a dynamic process, it is very difficult to monitor directly the temperature during the MA process.

Davis and co-workers²⁵ used an indirect method to determine the change in temperature. In their test, an Fe-1.2 wt% C alloy was prepared by melting electrolytic pure iron and graphite in an induction furnace. The sample was placed in an evacuated guartz tube containing Zr getter and austenized at 1150 K followed by ice-water quenching. Finally about 140 mesh powder with martensitic structure was produced. The resultant powder particles were then milled and their microstructure was analysed. Since a martensitic structure will decomposite into ε -carbide and a lower carbon martensite at 418 K and into cementite and ferrite at 575 K, the temperature of the MA process can be evaluated by examination of the remaining convertible cementite in the sample. The result showed that a change in temperature occurred during MA. The maximum temperature was about 559 K, which is far from the normal diffusion temperature.

Lu et al.27 measured the thermodynamic properties of a nickel and aluminium mixture and of a copper-zinc and aluminium powder mixture using a differential scanning colorimeter (DSC) after different MA times. It was found that the lowest exothermic reaction in the copper-zinc-aluminium system was about 200°C corresponding to the recovery and partial release of the stored energy in the particles. This means that the temperature of the powder particles during MA was

lower than 200°C, otherwise they would be annealed during the process. DSC measurement of nickelaluminium also revealed that the lowest exothermic reaction occurred at about 260°C.

Although the maximum temperature during MA is dependent on several factors, such as the type of ball mill used, speed of rotation employed and properties of the powder particles to be mechanically alloyed, according to the above measurements it is believed that the global temperature is relatively low. The temperature at certain locations under high-energy collision, however, could be higher due to large amounts of plastic deformation and sliding but heat is very rapidly dissipated by the large mass of milling vial, balls and powder particles. Nevertheless, the increase in milling temperature certainly plays a very important role in MA not only in the diffusion process but also in controlling the size of the particles.

As discussed earlier, two major phenomena can contribute to the increase in milling temperature: friction during collision and localized plastic deformation. Schwarz and Koch¹⁰ proposed a model by which temperature rise due to localized deformation can be predicted:

$$\Delta T = \frac{\phi}{2} \sqrt{\frac{\Delta t}{\pi k_0 \rho_{\rm p} c_{\rm p}}} \tag{1}$$

where ΔT is the increase in milling temperature, ϕ the dissipated energy flux given as σv where σ is normal stress due to a head-on collision and v is relative velocity of the ball before impact, Δt the stress state life, $\rho_{\rm p}$ the density of the powder particles, k_0 the thermal conductivity of the particles and c_p the specific heat of the powders. If the values of $k_0 = 2.37$ W cm⁻¹ K⁻¹, $\rho_p = 2.70$ g cm⁻³, $c_p = 900$ J kg⁻¹ K⁻¹ and $\sigma = 170$ MN m^{-2 28}, the increase in temperature during MA can be calculated as a function of collision speed and stress state life using this model. Figure 1 shows the change in temperature of aluminium powder at different MA conditions. Although strongly dependent on stress state life and collision velocity, it has been pointed out by Davis²⁵ that the temperature rise in most collision events is about 100-350 K.

In addition to the heating due to plastic deformation,



Figure 1 Change in temperature as a function of collision speed and stress state life during mechanical alloying

an increase in temperature on a microscopic level as a result of sliding friction can also be predicted²⁹. The method of prediction considers a system where a body comes into contact with another over a limited area and moves over the surface of the other body at a constant velocity. The contact area is considered to be square. Under these conditions, the microscopic temperature rise is given by:

$$\Delta T = \frac{\mu P V_{\rm r}}{4.24 l J (K_1 + K_2)} \tag{2}$$

where $\mu = 0.6$ is the frictional coefficient, P the load, l the half-length of the side of the contact area, J the mechanical equivalent of heat, and K_1 and K_2 the thermal conductivity of the respective bodies.

In addition to the temperature change due to localized plastic deformation and friction, combustion³⁰, reaction of enthalpy¹⁴ and precipitations can also contribute to the increase in temperature. All these contributions, however, cannot supply a sufficiently high temperature for diffusion to proceed.

Effect of diffusivity

Change in diffusivity due to activation energy

Due to the thermal energy of the solid, all the atoms vibrate about their rest positions. Occasionally a particularly violent oscillation of an interstitial atom, or some chance coincidence of the movements of the matrix and interstitial atoms, will result in a jump. In order to move an interstitial atom to an adjacent interstice, the atoms of the parent lattice must be forced apart into higherenergy positions as shown in *Figure 2(a)*. The increase in free energy is referred to as activation energy. Activation energy for diffusion is equal to the sum of the activation energy to form a vacancy and the activation energy to move the vacancy (*Figure 2(b)*), that is,

$$\Delta Q = \Delta Q_{\rm f} + \Delta Q_{\rm m} \tag{3}$$

where $\Delta Q_{\rm f}$ is the activation energy for creating vacancies and $\Delta Q_{\rm m}$ the activation energy for moving vacancies. It appears that in most of MA processes temperature is not a dominating factor. From equations (1) and (2), the temperature generated by a collision is also far from reaching the diffusion temperature. Therefore, factors other than temperature must contribute significantly to the diffusion process.

During MA, mechanical energy can be partially stored by the creation of dislocations and grain boundaries in the mechanically alloyed material. There are two primary classes of point defects: vacancies and interstitials. If there is sufficient activation energy present, atoms can move in crystal lattices from one atomic site to another. As a result of the formation of large amount of defects (dislocations and vacancies which are normally generated by thermal energy in thermally induced diffusion process) due to a highenergy collision of the powder particles, the total acti-



Figure 2 Schematic illustration of activation energy

vation energy required by diffusion is lower because the part of activation energy required to form vacancies may or may not be required completely as graphically shown in *Figure 2(c)*. In general, diffusivity³⁵ can be written as:

$$D = D_0 \exp\left(\frac{-\Delta Q}{RT}\right) \tag{4}$$

where D is the diffusion coefficient, D_0 the material constant, ΔQ the activation energy, R the universal gas constant and T the temperature. Substituting equation (3), equation (4) can be rewritten as:

$$D = D_0 \exp\left[\frac{-(\Delta Q_{\rm f} + \Delta Q_{\rm m})}{RT}\right]$$
(5)

- Equation (5) establishes that at the same value of D, a decrease in activation energy, such as a decrease in activation energy to create vacancies, is equivalent to an increase in temperature. Therefore, it is possible that activation energy can be significantly lowered by reducing $Q_{\rm f}$. It is believed that lowering of activation energy plays a main role in the MA process. In the thermally induced diffusion, lattice defects may be annealed out very rapidly, leading to a decrease in diffusion coefficients. Defects probably contribute little to the increase in homogenization kinetics in such diffusion processes. However, defect density during MA increases with MA duration and therefore significantly contributes to homogenization kinetics. Taking MA of an Al-Cu system as an example, the following parameters may be used^{31,32}: material constant $D_0 = 1.5*10^{-5}$ m²/s, activation energy for lattice diffusion $Q_1 = 126$ kJ/mole, and diffusivities D are $1.0307*10^{-18}$. m²/s at 500 K and 8.8968*10⁻¹⁴ m²/s at 800 K. If defect diffusion is considered where activation energy is only 82 kJ/mole, the diffusivity will be 4.071*10⁻¹⁴ m²/s, which is equivalent to a diffusion process at 800 K.

Bhattacharya and Arzt³³ calculated diffusivity. In the equation, diffusivity includes two parts as formulated in the following equation:*

* The original equation is

$$D = D_{\rm l} \exp\left(-\frac{Q_{\rm l}}{RT}\right) + \beta b^2 \rho D_{\rm c} \exp\left(-\frac{Q_{\rm c}}{RT}\right)$$

$$D = D_{\rm l} \exp\left(-\frac{Q_{\rm l}}{RT}\right) + \beta b^2 \rho D_{\rm c} \exp\left(-\frac{Q_{\rm c}}{RT}\right)$$
(6)

where D_1 and D_c are, respectively, the material constant for the lattice and the core, Q_1 and Q_c are, respectively, the activation energy of the lattice and core diffusion, *b* is Burgers vector, ρ is dislocation density and β is a core diffusivity factor. In principle, the model considers the effect of dislocation accumulation which takes place due to a large amount of plastic deformation causing enhancement of the diffusion coefficient due to extra mobility along the dislocation cores.

Furthermore, it is known³⁵ that at any temperature, the magnitudes of diffusivity along the grain boundary (D_b) and the free surface (D_s) relative to the diffusivity through defect-free lattice (D_l) are such that

$$D_{\rm s} > D_{\rm b} > D_{\rm l} \tag{7}$$

Equation (7) mainly reflects the relative ease with which atoms can migrate along a free surface because surfaces tend to be regions of relatively higher disorder and lower activation energy for diffusion than the interior. *Figure 3* shows the relationship between diffusion via the surface, the grain boundary and the lattice³⁴. It can be seen that lattice diffusion has the largest slope and surface diffusion the smallest. As a result, at low temperatures, surface diffusions. As the temperature is increased, grain boundary diffusion predominates and at a higher temperature, lattice diffusion becomes the principal rout for diffusion³⁴. The change from one predominant mechanism to another depends upon the natures of the grain boundaries and surfaces.

The process of MA consists of fracturing and welding. Hence, at a microscopic level, MA results in three types of free surfaces for diffusion processes to proceed during MA. The first type is microcracks. These can be introduced either by fracture (Figure 4(a)) or by the motion of dislocations (Figure 5). Figure 5 gives an example of the formation of microcrack in a bcc structure. Dislocations move along the slip planes of (101) and (101) to form a microcrack at the (001) plane. Due to the formation of microcracks, the internal energy is increased by the increase in



1/T (T in Kelvin)

Figure 3 Schematic diagram showing the dependence of surface, grain boundary and lattice diffusions on temperature (after reference 34)



Figure 4 Formation of microcracks creates free surfaces for surface diffusion

(b)

(a)



Figure 5 Formation of a microcrack by dislocations

surface energy. To stabilize the powder particles (minimize internal energy), the atoms would attempt to diffuse along the surface of the microcracks to fill the crack as shown in *Figure* 4(b). As the process is driven by the reduction in surface area, the driving force is reduced when the microcracks are filled by diffused atoms. This process proceeds throughout the entire MA processing even after a homogeneous material is eventually formed.

Like the first type of free surface, the second type of macrocrack-like free surface is due to cold welding between different particles as shown in *Figure 6*. The mechanism of diffusion here is similar to the sintering of powder particles. The difference in radii L and r at the valley means that the vapour pressure is lower in the valley than over the rest of the particles and thus atoms can be transferred through the gaseous phase from the main surface of the particle to the valley. There is, however, an outward-acting force on the surface of the valley due to surface tension γ which gives rise to a stress. According to sintering theory, the magnitude of the stress is approximately equal to γ/r . If the ratio at the valley is very small, the magnitude of the stress will be very large.

The third type of free surface is a pre-cold welding surface, which is actually a mechanically bonded surface without real welding. Atoms can diffuse along the



Figure 6 Formation of a macrocrack-like free surface by cold welding between different powder particles

rough free surface to finally form a welded boundary with the disappearance of mechanical bonding. The three types of free surfaces will be generated by fracturing and plastic deformation but will disappear as diffusion proceeds.

In addition, fracturing and cold welding during MA enable different particles to be always in contact with each other with fresh surfaces. The diffused layer between different particles is in turn repeatedly broken, leading to a minimized diffusion distance under high hydrostatic pressure, which is a major difference from normal diffusion process. The formation of layered structure also creates more free surfaces. It is noted that increased collision pressure results in higher compact density of the powder particles. The latter leads to better interparticle contact which should improve interdiffusion between particles. It occurs during a collision event. On the other hand, a lower density results in a higher surface area in the collision and thus a larger contribution of surface diffusion to homogenization. Therefore, it is believed that diffusivity along the free surface D_s dominates the MA process.

Hilda³⁶ and Lu²⁷ have also found that the stored enthalpy increases with prolonged MA duration. The decrease in transition temperature from disordered γ' to ordered γ' when MA duration is increased²⁷ is the result of the increase in stored energy.

Change in diffusivity due to crystal size

With prolonged MA duration, a high density of defects is generated, leading to an increase in microhardness of the powder particles. Because of large plastic deformation and repeated fracturing, the crystalline size can be reduced to a nanometre scale, which normally may be manifested by the change in width at half of maximum X-ray peak. As reported by Horvath et al.37, measurement of self-diffusivity in nanocrystalline copper revealed an enhancement of its self-diffusivity by a factor of about 10¹⁹. This remarkable enhancement may be understood in terms of the large amount of boundaries that provide a connective network of short-circuit diffusion paths. An enhancement of self-diffusivity in comparison to boundary diffusion of a factor of about 100 has been reported³⁷. Because a large volume fraction of the atoms resides in the grain boundaries, nanocrystalline materials have high reactivity and high diffusivity, thus enabling the alloying of normally immiscible metals³⁸. Schumacher³⁹ found that silver can be diffused into copper between 303 and 373 K if the copper crystalline size is in nanometres. This is normally not possible when ordinary copper is used. It implies that the diffusivity of nanocrystalline materials at low temperatures is very high in comparison to materials with a normal crystalline size. This can be represented using a simple mathematical expression³⁴:

$$D_{\rm eff} = (1 - F) D_1 + F D_b$$
 (8)

where D_{eff} is the effective diffusivity and F the area fraction of short-circuit paths (i.e. grain boundaries) in a plane perpendicular to the direction of diffusion. It may be understood that the effective diffusivity can be increased by decreasing grain size (i.e. increasing the area of the grain boundaries). This situation is well promoted in the MA process. If the grain boundary width is δ and grain size d, then roughly, $F = 2\delta/d$. Still taking the Al-Cu system as an example, if the thickness of the grain boundary is $7*10^{-6}$ mm³², the effective diffusivity of this system will be increased from $1.03*10^{-18}$ to $5.70*10^{-15}$ when the grain size is reduced from 50 μ m to 100 nm.

Using equation (8) grain boundary diffusion takes place if the following expression is satisfied³⁴:

$$FD_{\rm b} > (1 - F) D_{\rm 1} \tag{9}$$

For such a situation to occur, the grain size must be small (see the Appendix).

It is believed that diffusivities of stress-free and deforming samples are different. Under high collision stress during MA, the lattice parameter in some locations of the deformed particles can be increased, leading to a large diffusion path. Consequently the activation energy required by moving atoms is lowered. The solute atoms easily diffuse into a diffusion couple under this high collision stress.

Effect of crystal structure

Diffusivities, in addition to being affected by temperature, are also dependent upon crystal structure. In particular, elements with small atomic diameters that form interstitial solid solutions diffuse very rapidly. Carbon diffuses faster in fcc iron than in bcc iron. However, more carbon can be dissolved in fcc iron than in bcc iron because the bcc structure is a less dense structure. Therefore, although the fcc structure has more room for the carbon atoms, the passages through the unit cell are smaller for the movement of carbon.

During MA, the crystal structure of the powder particles can be changed, resulting in a change in diffusivity. An example of such occurrence is the mechanically alloyed CuZnAl alloy from fcc crystal structure α -phase CuZn pre-alloyed powders and element Al powder⁴⁰. During MA, the Al atoms diffused into the CuZn alloy, resulting in the formation of CuZnAl alloy with low Al content. With an increase in milling duration, more Al atoms diffuse into CuZnAl to form a β -phase, which is a bcc crystal structure. As the diffusivity of an α -phase structure at 700°C is only about 4.5*10–11 cm²/s, while in a β -phase structure at 550°C it is about 3*10–8 cm²/s, diffusion in the β -phase can be seen to be much faster than an α -phase.

Conclusions

The key factors controlling the formation of new alloys are found to be: activation energy, which is related to the formation of defects during collision of powder particles with milling balls and vial; temperature, which is associated with plastic deformation of the powder particles and sliding between powder particles, and between high energetic balls and powder particles; and crystalline size, which is related to the formation of a nanometre crystalline during mechanical alloying. From the present study, some primary conclusions may be summarized as follows:

- 1. Diffusion is a mechanism of formation of new alloys during mechanical alloying. The diffusion process in mechanical alloying, however, differs from the thermally induced diffusion process. In the latter process, diffusion is controlled by thermal energy, but in mechanical alloying, formation of new alloys is controlled by both thermal and mechanical energies. During the alloving process, a large number of defects are created by large plastic deformation. According to thermodynamic theory, at a constant temperature, a decrease in activation energy can result in an increase in diffusivity. Therefore, a decrease in activation energy is equivalent to an increase in temperature. High diffusivity can be achieved by creating a large amount of defects through mechanical alloying. It is suggested that the decrease in activation energy due to increase in vacancies gives rise to an increase in diffusivity, thereby the diffusion process is eased.
- 2. As the mechanical alloying process consists of fracturing and welding, at least three types of free surfaces can contribute to surface diffusion mechanisms. Because of the formation of more free surfaces and grain boundaries, surface diffusion, which is driven by the reduction in surface area and the radius of the crack tip, dominates during MA. For thermally induced diffusion processes the driving forces due to surface tension and surface stress always tend to be lower with diffusion duration, while for MA-induced diffusion processes, the opposite trend can be observed due to the formation of microcracks and other defects. By creating nanometre crystalline through repeated fracturing and cold welding of powder particles, diffusion can easily take place through the grain boundaries. Consequently, elements which are difficult to diffuse may be alloyed using this technique.
- 3. Grain boundary and free surface diffusions are always prevalent in the MA process. Although the diffusion temperature is relatively low, the diffusivity is very high. Because of small grain size, lattice

diffusion will be significant only at relatively high temperatures.

4. With an increase in mechanical alloying duration, the temperature of the powder particles is raised by plastic deformation, sliding, chemical, transformation, precipitation and other reactions. All these further enhance the diffusion process.

Appendix

For the transition from grain boundary to lattice diffusion, the following criterion should be satisfied:

$$FD_{\rm b} = (1 - F) D_{\rm l}$$
 (A1)

Thus,

$$\frac{D_1}{D_b} = \frac{F}{(1-F)}$$
 (A2)

Since

$$D_1 = D_0^1 \exp\left(\frac{-\Delta Q}{RT}\right) \tag{A3}$$

and

$$D_{\rm b} = D_0^{\rm b} \exp\left(\frac{-\Delta Q}{RT}\right) \tag{A4}$$

it follows that

$$\frac{F}{1-F} = \frac{D_1}{D_b} = \frac{D_0^1}{D_0^b} \left[\exp \frac{\Delta Q_b - \Delta Q_1}{RT_{\text{trans}}} \right]$$
(A5)

Taking the natural log of equation (A5),

$$\ln\left(\frac{F}{1-F}\frac{D_0^{\rm b}}{D_0^{\rm l}}\right) = \frac{\Delta Q_{\rm b} - \Delta Q_{\rm l}}{RT_{\rm trans}} \tag{A6}$$

and

$$T_{\rm trans} = \frac{Q_{\rm b} - Q_{\rm l}}{R \ln \left(\frac{F}{1 - F} \frac{D_0^{\rm b}}{D_0^{\rm l}}\right)}$$
(A7)

To evaluate the transition temperature, the following data have been taken into account in the calculations³²:

$$Q_1 = 126 \text{ kJ/mole}, Q_b = 84 \text{ kJ/mole}, D_0^1 = 1.5*10^{-5} \text{ m}^2/\text{s}, D_0^b = 15D_0^1, \text{ and } \delta \cong 7 \text{ Å}.$$

If $d = 50 \ \mu \text{m}$

$$F = 2\delta/G = 2*7*10^{-10}/50*10^{-6} = 2.8*10^{-5}$$
(A8)

If $d = 5 \ \mu m$

$$F = 2\delta/G = 2*7*10^{-10}/5*10^{-6} = 2.8*10^{-4}$$
(A9)

From the above it can be seen that grain boundary diffusion begins to dominate over lattice diffusion below 649 K if the grain size is 50 μ m, or below 923 K if the grain size is reduced to 5 μ m. This explains why for MA, only boundary and free surface diffusions are prevalent. Lattice diffusion can be avoided because of small grain size.

References

- I Gilman, P. S. and Nix, W. D. The structure and properties of aluminium alloys produced by mechanical alloying. *Metall. Trans. A* 1981, **12A**, 813–823
- 2 Burgio, N., Guo, W., Magini, M. and Padella, F. Mechanical alloying of the Ti-Al system. Structural Applications of Mechanical Alloying, Proc. ASM Intern. Conf., Myrtle Beach, South Carolina, 27-29 March 1990, Eds Froes, F. H. and deBarbadillo, J. J., ASM Intern. Mat. Park, Ohio, 1990, pp. 175-183
- 3 Otsuka, M., Ishiara, T., Sugamata, M. and Kaneko, J. Deformation of mechanically alloyed Al-TiB2 alloys at elevated temperatures, *Ibid*, pp. 221-228
- 4 Benjamin, J. S. Mechanical alloying history and potential. Proc. of the Novel Powder Metall. World Congr., San Francisco, CA, 21-26 June 1992, pp. 155-168
- 5 Suryanarayana, C., Chen, G. H. and Freos, F. H. Milling maps for phase identification during mechanical alloying. *Script Metall.* 1992, 26, 1727-1732
- 6 Calka, A. and Kaczmerk, W. A. The effect of milling condition on the formation of nanostructures: synthesis of vanadium carbides. Script. Metall. 1992, 26, 249-253
- 7 C. Suryanarayana, G. H. Chen, A. Frefer and F. H. Freos, Structural evolution of mechanically alloyed Ti-Al alloys, *Mat. Sci. Eng.* 1992, A158, 93-101
- 8 Inous, A. and Masumoto, T. Mechanical alloyed metals with non-equilibrium phases. In New Materials by Mechanical Alloying Technique, Eds Arzt, E. and Schultz, L., DGM Informationsgesellschaft Verlag, Calw-Hirsau, Germany, October 1988, pp. 327-342
- 9 Cocco, G., Enzo, S., Schiffini, L. and Battezzati, L. Structural and thermal analysis of new systems prepared by mechanical alloying. *Ibid* pp. 343-348
- 10 Schwarz, R. B. and Koch, C. C. Formation of amorphous alloys by the mechanical alloying of crystalline powders of pure metals and powders of intermetallics. *Appl. Phys. Lett.* 1986, 49, 146-148
- 11 Weeber, A. W. and Bakker, H. Amorphization of ball milling. A review. *Physica* 1988, **B153**, 93–135
- 12 Hellstern, E. and Schultz, L. Glass formation in mechanically alloyed transition metal-titanium alloys. *Mat. Sci. Eng.* 1987 93, 213-2165
- 13 Gaffet, E., Faudot, F. and Harmelin, M. Crystal-to-amorphousphase transition induced by mechanical alloying in the Ge-Si system. *Mat. Sci. Eng.* 1991 A149, 85-94
- 14 Schaffer, G. B. and McCormick P. G. Mechanical alloying. Mat. Forum 1992, 16, 91–97
- 15 McCormick, P. G., Wharton, V. N., Royhani, M. M. and Schaffer, G. B. In *Microcomposites and Nanophase Materials*, Eds Van Aken, D. C., Was, G. S. and Gosh, A. K., TMS, Warrendale, PA, 1991, p. 65
- 16 Schaffer, G. B. and McCormick, P. G. Metall. Trans. A 1992, 23A, 1285
- 17 Schaffer, G. B. and McCormick, P. G. Anomalous combustion effects during mechanical alloying. *Metall Trans. A* 1991 22A, 3019-3024

- 18 Morris, M. A. Composition and structure variations during mechanical alloying to produce the intermetallic Cr₂Nb. J. Mat. Sci. 1991 A150, 1157-1164
- 19 Suryanarayana, C and Schultz, L. Glass formation in mechanically alloyed transition and metal-titanium alloys. *Mat. Sci. & Eng.* 1987 93, 213-216
- 20 Murty, B. S., Ranganathan, S. and Mohan Rao, M. Solid state amorphization in binary Ti-Ni, Ti-Cu and ternary Ti-Ni-Si systems by mechanical alloying. *Mat. Sci. & Eng.* 1991, A149, 231-240
- 21 Johson, A. Topical discussion. In New Materials by Mechanical Alloying Techniques, Eds Arzt, E. and Schultz, L. October 1988, Calw-Hirsau (FRG), Informationsgesellschaft Verlag, 354
- 22 Yermakov, A. Y., Yurchikov, Y. Y. and Barinow, V. A. Phys. Met. Metall. 1981, 52, 50
- 23 Gilman, P. S. and Nix, W. D. The structure and properties of aluminium alloys produced by mechanical alloying: powder processing and resultant powder structure. *Metall. Trans. A* 1981, 12A, 813-823
- 24 Davis, R. M. and Koch, C. C. Mechanical alloying of brittle components: silicon and germanium. Scripta Metall. 1987, 21, 305-310
- 25 Davis, R. M., McDermott, B. and Koch, C. C. Mechanical alloying of brittle materials. *Metall. Trans. A* 1988, 19A, pp. 2867-2874
- 26 Zhang, S., Khor, K. A. and Lu, L. Preparation of Ti (C,N)-WC-TaC solid solution by mechanical alloying technique. J. Mat. Proc. Tech. 1995, 48, 779-784
- 27 Lu, L., Lai, M. O. and Zhang, S. "Thermodynamic properties of mechanically alloyed nickel and aluminium powders. J. Mat. Res. Bull. 1994, 29, 8, 889-894
- 28 Metals, Alloys, Compounds, Ceramics, Polymers and Composites-Catalogue 1994/1995, Goodfellow Cambridge Limited, Cambridge Science Park, Cambridge, CB4 4DJ, England (1994), p. 33
- 29 Carslaw, H. S. and Jaeger, J. C. Heat Conduction in Solids, Oxford University Press, New York, 1959, p. 255
- 30 Schaffer, G. B. and McCormick, P. G. Displacement reaction during mechanical alloying. *Metall. Trans. A.* 1990, 21A 2789-2794
- 31 Smith, W. F. Foundations of Materials Science and Engineering, 2nd edition, McGraw-Hill, New York, 1993, p. 172
- 32 Frost, H. J. and Ashby, M. F. Deformation-Mechanism Maps-The plasticity and creep of metals and ceramics, Pergamon Press, New York, 1982, p. 21
- 33 Bhattacharya, A. K. and Arzt, E. Diffusive reaction during mechanical alloying of intermetallics. *Scripta Metall.* 1992, 27, 635–639
- 34 Atkinson, H. V. and Rickinson, B. A. In *Hot Isostatic Processing*, The Adam Hilger Series on New Manufacturing Processes and Materials, Wood, J., Adam Hilger, Bristol, 1991, pp. 34-38
- 35 Porter, D. A. and Easterling, K. E. *Phase Transformation in Metals and Alloys*, Van Nostrand Renhold, London, 1980, pp. 66–68
- 36 Hilda, G. T. and Lin, I. L. Elementary processes in SiO₂-Al thermite reaction activated or induced by mechanochemical treatment. Combustion and Plasma Synthesis of High Temperature Materials, Eds Holt, J. B. and Munir, Z. A., American Ceramic Society, 1988, pp. 246-261
- 37 Gleiter, H, Eds Weidershich, H. and Mechii, M. Structure and properties of nanocrystalline materials. In Science of Advanced Materials, ASM Mat. Sci. Semi., 26-29 September 1988, ASM International, Materials Park, OH, 1988, pp. 203-223
 38 Suryanarayana, C. and Froes, F. H. Nanocrystalline tita-
- 38 Suryanarayana, C. and Froes, F. H. Nanocrystalline titanium-magnesium alloys through mechanical alloying. J. Mat. Res. 1990, 5, 1880-1886
- 39 Schumacher, S., Birringer, R., Straub, R. and Gleiter, H. Diffusion of silver in nanocrystalline copper between 303 and 373 K. Acta Metall. 1989, 37, 2485–2488
- 40 Zhang, S., Lu, L. and Lai, M.O. Cu-base shape memeory powder preparation using the mechanical alloying technique. *Mat. Sci & Eng.* 1993, 171A, 257-261