JOURNAL OF MATERIALS SCIENCE **39** (2004) 4255–4262

Synthesis by ball milling and characterization of Al-Zn alloys

M. IQBAL, M. A. SHAIKH, J. I. AKHTER*, M. AHMAD, M. AKHTAR, M. J. MOUGHAL‡
Nuclear Physics Division and ‡Nuclear Materials Division, Pakistan Institute of Nuclear Science and Technology, P.O. Nilore, Islamabad, Pakistan
E-mail: jiakhter@yahoo.com; akhterji@pinstech.org.pk

Mechanical ball milling is a useful technique for systems with positive enthalpy of mixing. With this technique solubility of a solute in a solid solution can be enhanced. Al-Zn system has positive heat of mixing. High energy ball milling has been employed to produce four alloys of Al with 2.5 to 10 wt% Zn. Powders of Al (1–125 μm) and Zn (0.7–5.0 μm) were mixed together in the desired proportion and milled with a powder to ball weight ratio of 1:20. The size and shape of the particles of as-received and alloy powders were examined in a scanning electron microscope (SEM) while their microanalysis was performed by energy dispersive system (EDS) attached with SEM. It has been observed that 120 h of milling of the powders produced homogeneous alloys. X-ray diffraction (XRD) patterns confirm complete solubility up to 10 wt% Zn in Al. Using the quasi-chemical theory of binary solid solutions, the enthalpy of mixing of 10 wt% Zn in Al has been determined to be 276 cals/mol. It is shown that stress exerted by very high density of dislocations, generated by mechanical milling, plays a major role in the enhancement of solubility. Hardness has been measured and it increases with increasing solute content.

1. Introduction

Over the years high energy ball milling has been used to produce nanocrystalline materials [1, 2], amorphous alloys [3], and ultrafine composite magnetic particles [4] and oxide dispersion strengthened (ODS) superalloys [5] for their superior properties in the nanometer scale range. As this technique overcomes many of the limitations of conventional alloying, it can be employed to produce alloys, which are difficult or impossible to obtain, by other means [6]. Mechanical alloying (MA) is performed in a high energy ball mill with a suitable grinding medium and it is a complex dynamic process involving ball-powder-ball collisions which cause heavy deformation. The particles are flattened because of severe plastic deformation and when clean surfaces come into contact, cold welding takes place. In addition high strain rate deformation leads to particle fracture. These competing fracture and welding events continue till steady state reaches [7, 8]. This process enhances the solubility of a solute in the solvent because of increase in the number of grain boundaries, heavy deformation and very high dislocation density. It means alloys far from thermodynamic equilibrium can be produced by MA. MA of system with positive heat of mixing is not well understood [9]. Al-Zn system has also positive heat of mixing [10] and the solubility of Zn in Al at 20°C is less than 2 wt% [11]. Although the solubility of Zn increases with increase in temperature, enhancement of solubility at lower temperature can be achieved by MA. In the present study, high energy ball milling has been employed to produce alloys of Al with Zn. The techniques of scanning electron microscopy (SEM), energy dispersive system (EDS) and X-ray diffraction (XRD) have been used to characterize the alloys.

2. Experimental

Powders of Al and Zn were prepared locally by gas atomization under nitrogen atmosphere and particle size was measured by SEM. Appropriate weighed quantities of Al and Zn powders were put in the WC containers to obtain alloys of Al with 2.5, 5, 7.5 and 10 wt% Zn. The milling was carried out upto 120 h in a laboratory planetary ball mill having a sun disk and grinding jars rotating opposite to each other. The speed of the sun disk was kept at 160 revolutions per minute and that of the jars was about double. Due to the counter movement of the sun disk and the jars, extremely high centrifugal forces are produced. The WC balls were used for grinding and powder to ball weight ratio 1:20 was used during the experiment. A small amount of hexane was added to the containers in order to overcome the problem of sticking of the powder to the balls and containers. After 60 h of milling some amount of powders was taken for

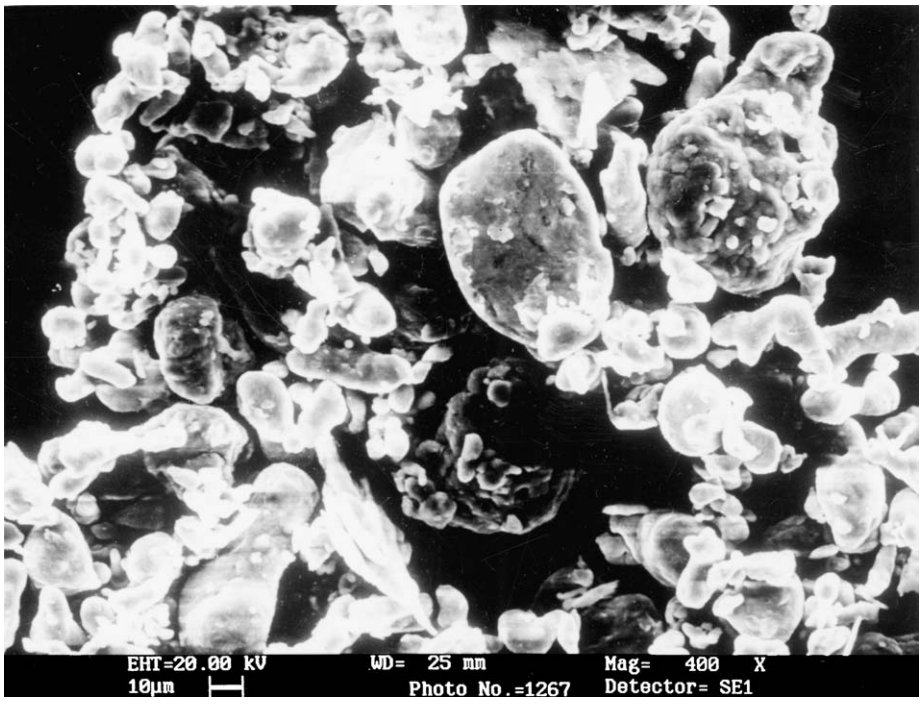
*Author to whom all correspondence should be addressed.

investigations. Pellets of the size 13 mm diameter and 3 mm thickness were prepared by compaction of the powders in a press using a load of 5 tons for 3 min. In certain cases pellets were etched in fresh Keller's reagent to reveal the particle boundaries. For the particle size measurements the powders were dispersed ultrasonically in methanol and then collected on stubs. The elemental powders and the pellets were examined in a scanning electron microscope (SEM) having the attachment of energy dispersive system (EDS). X-ray diffraction patterns of the pellets of Al, Zn, Al-Zn mixtures and Al-Zn alloys after 60 and 120 h milling were taken using Cu K_α X-rays. Vicker's microhardness was measured on a micro indentation tester using a load of 25 p. Average of eight to ten measurements has been taken.

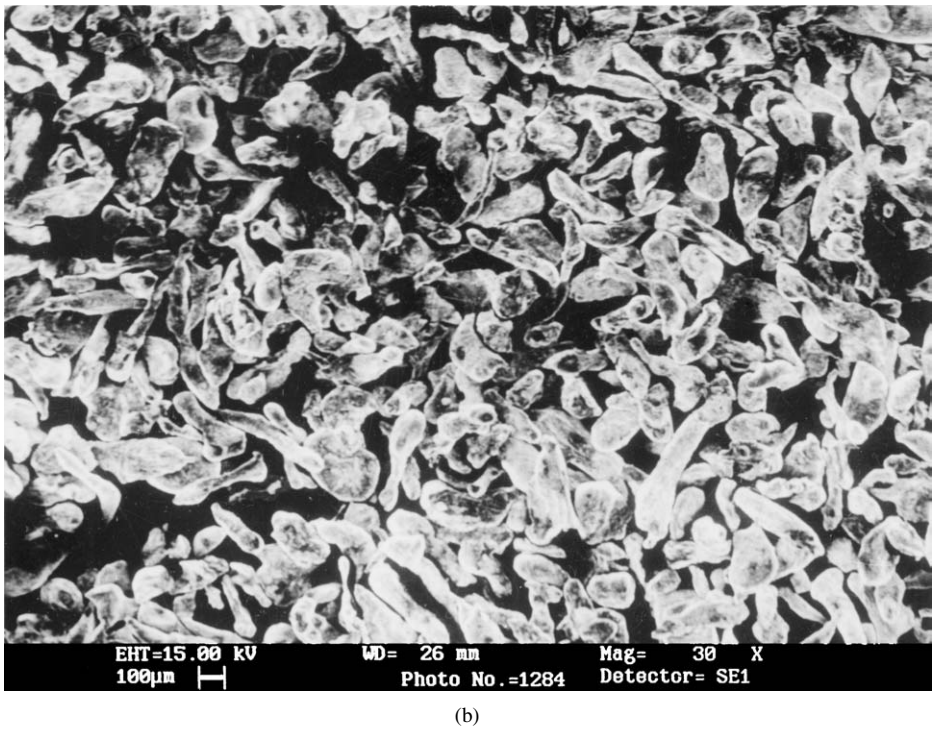
3. Results and discussion

3.1. SEM/EDS investigations

SEM examination of the as-received Al powder showed that the particle size ranges from 1 to 125 μm. Some of the particles were spherical but majority had irregular shape (Fig. 1a). The size of the as-received powder



(a)



(b)

Figure 1 (a) SEM micrograph of as-received powder of Al and (b) SEM micrograph of as-received powder of Zn.

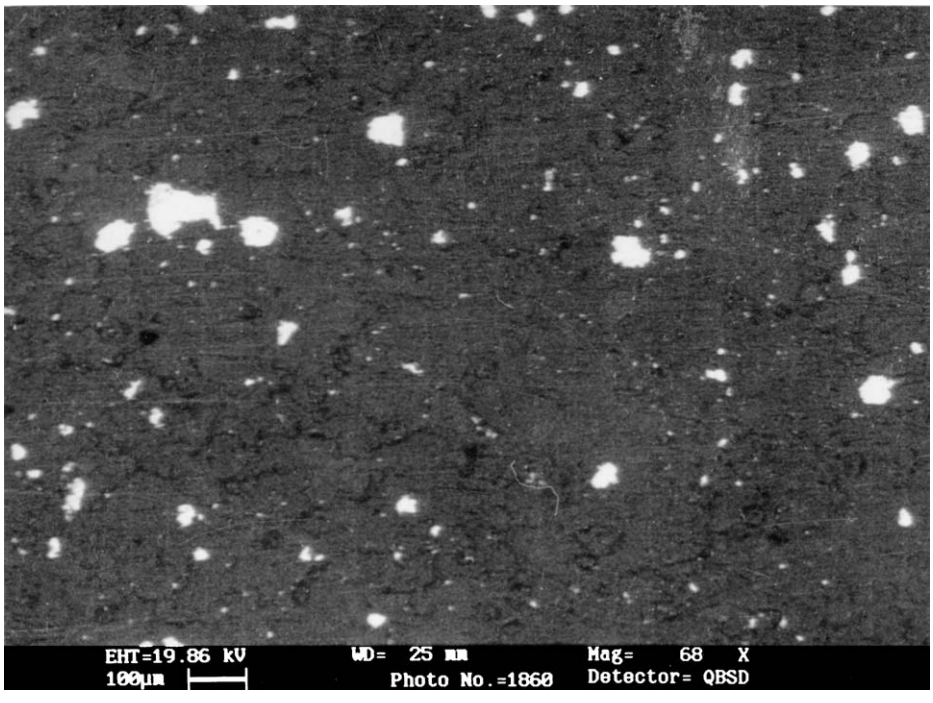


Figure 2 Back scattered electron image of a pellet of Al-10 wt% Zn mixture without milling.

particles of Zn was found to be much bigger. It varied from 50 μm to 850 μm. These particles also had irregular shape (Fig. 1b). This powder of Zn was milled for 60 h to reduce the size, which then was in the range from 0.7 to 5 μm. The two powders were mixed together in the desired proportion. Examination of the pellets made up of the mixtures of the different compositions showed the presence of individual particles of both Al and Zn. Fig. 2 is a back scattered electron image of Al-10 wt% Zn pellet. Particles showing white contrast are of Zn and are randomly distributed in the Al matrix while large particles are agglomerates of Zn particles. Although four alloys were prepared and measurements were done for all the alloys, yet the results of the alloy with maximum solute content are discussed.

Milling of mixtures for 60 h reduced the size of the particles. The minimum particle size of the Al-10 wt% Zn alloy powders was measured with SEM to be 280 nm. Examination of the pellets after etching revealed that some areas gave different contrast (Fig. 3). It was found that such areas were much less in alloys with low solute content. Microanalysis showed that these areas are enriched in Zn. Fig. 4a is a scanning electron micrograph of such an area at higher magnification and EDS

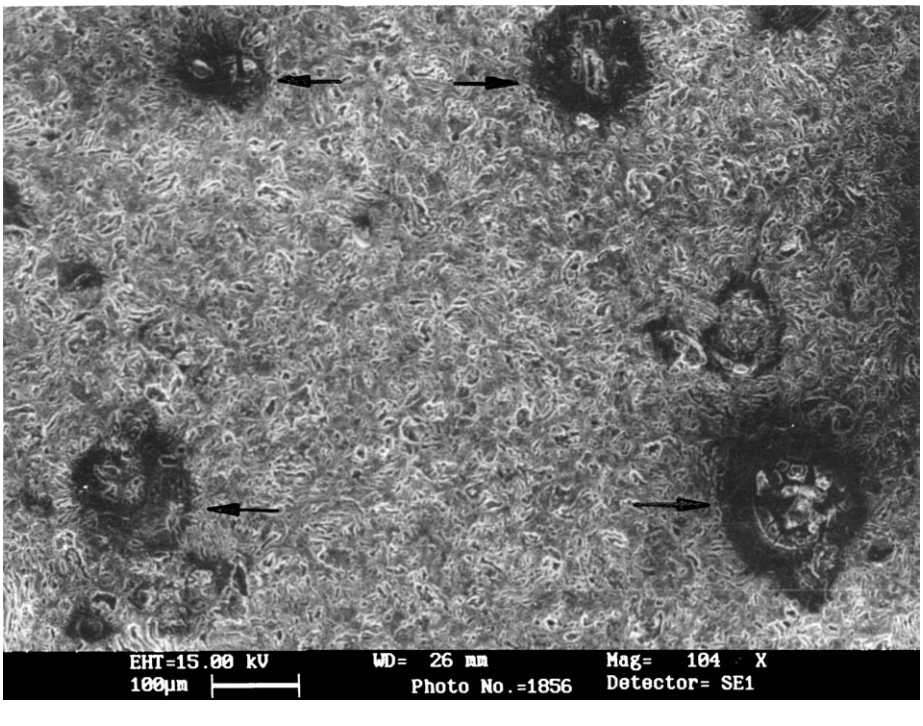
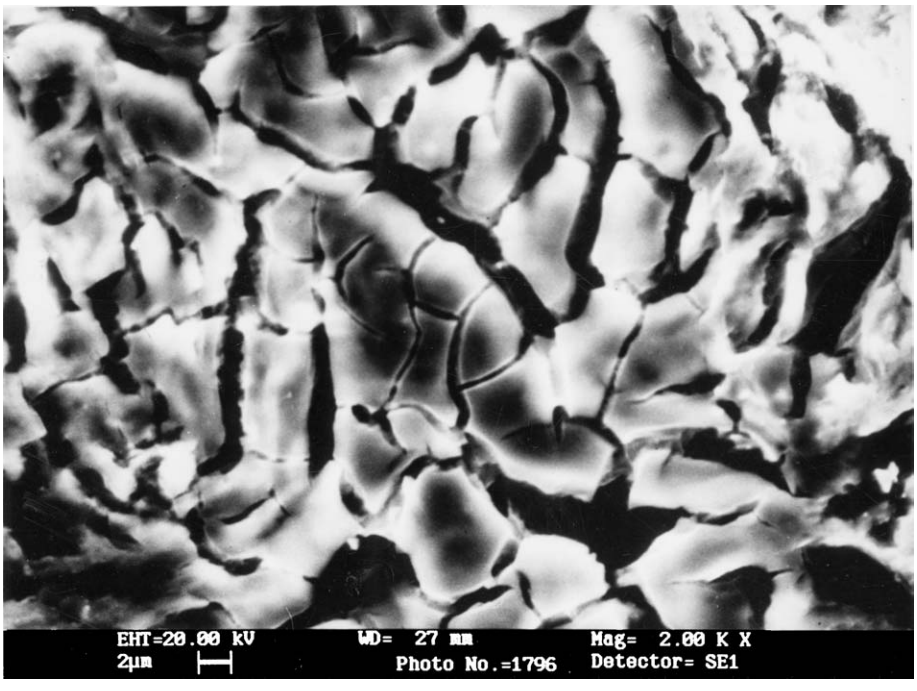
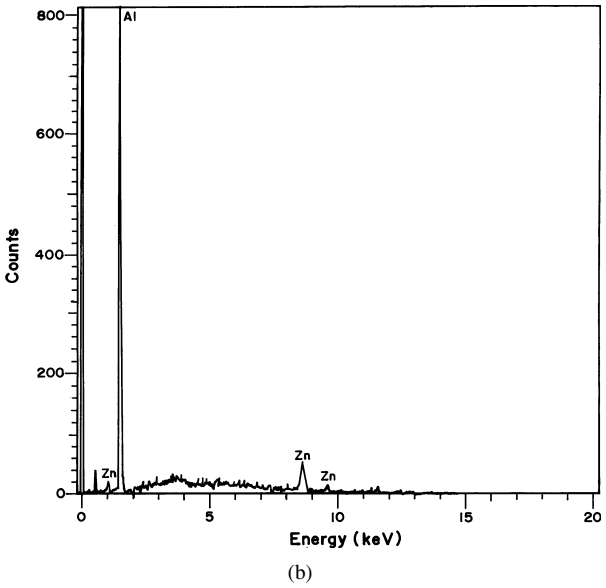


Figure 3 SEM micrograph of area with segregation of Zn in a sample milled for 60 h.



(a)



(b)

Figure 4 (a) Electron micrograph of area of segregation (shown in Fig. 3) at higher magnification and (b) EDS spectrum of the area shown in Fig. 4a.

spectrum of this area is given in Fig. 4b. Enrichment of Zn (Zn varies from 20 to 50 wt%) in some areas of all the alloys showed that alloying was not homogeneous after 60 h of milling. Another type of particles was found to show bright contrast (Fig. 5) and their microanalysis indicated that these are tungsten carbide (WC) particles. The source of these particles is the WC balls and WC containers used for the milling.

After 120 h of milling, morphology of the alloy particles was examined by SEM in detail. It was observed that there were no particles of the original shape. This means that all of the particles were involved in the milling process. The alloy particles were spheroidal in shape as shown in Fig. 6. Such observations have been reported by Gilman and Nix [12] for Al alloy 6061 and Kedzierzawski [13] for Ni-Mo alloys. Examination of one of the smaller particles at higher magnification showed the composite nature of the particles. Fig. 7 shows flake-shaped particles stacked together. This is in agreement with the observations of Aikin and Courtney [14].

Detailed microanalysis by EDS showed that there was no segregation of Zn in any of the alloy particles. Zn was found to be uniformly distributed through out the sample whether in etched, unetched or broken pellets condition. Every particle was found to have almost the same composition within experimental error. Thus EDS results indicate that homogeneous and complete alloying of Al with Zn has been achieved.

3.2. XRD investigations

In order to confirm that alloying of Al and Zn has been achieved, X-ray diffraction patterns of the pellets of unmilled mixtures of Al and Zn and of the pellets of alloy powders milled for 60 and 120 h were taken. Fig. 8 shows the XRD patterns for unmilled mixture and milled (60 and 120 h) samples of Al-10

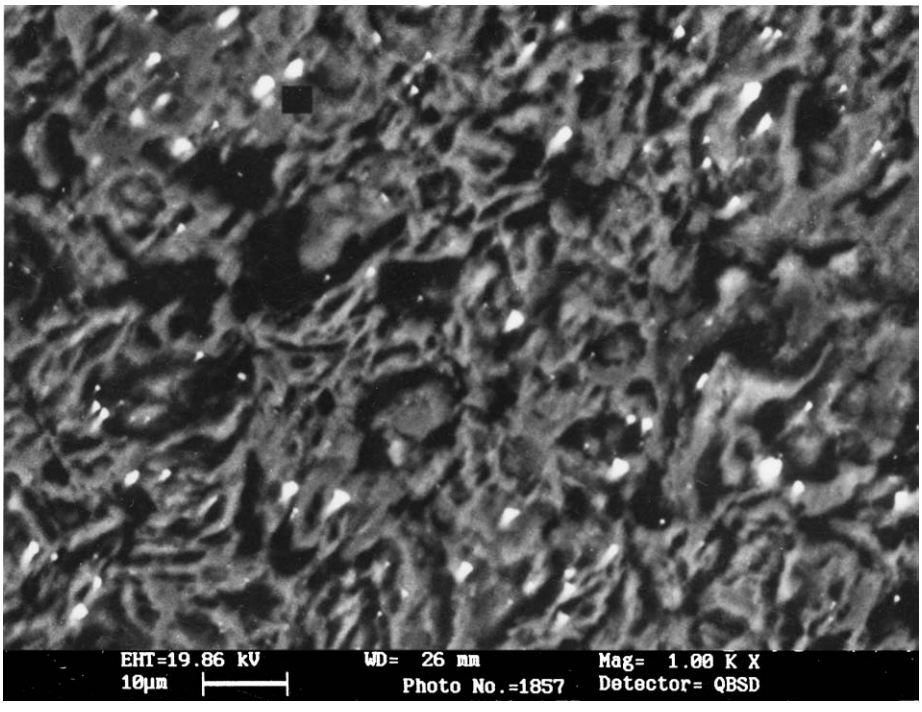


Figure 5 Back scattered electron image of WC particles in Al-10 wt% Zn powder milled for 60 h.

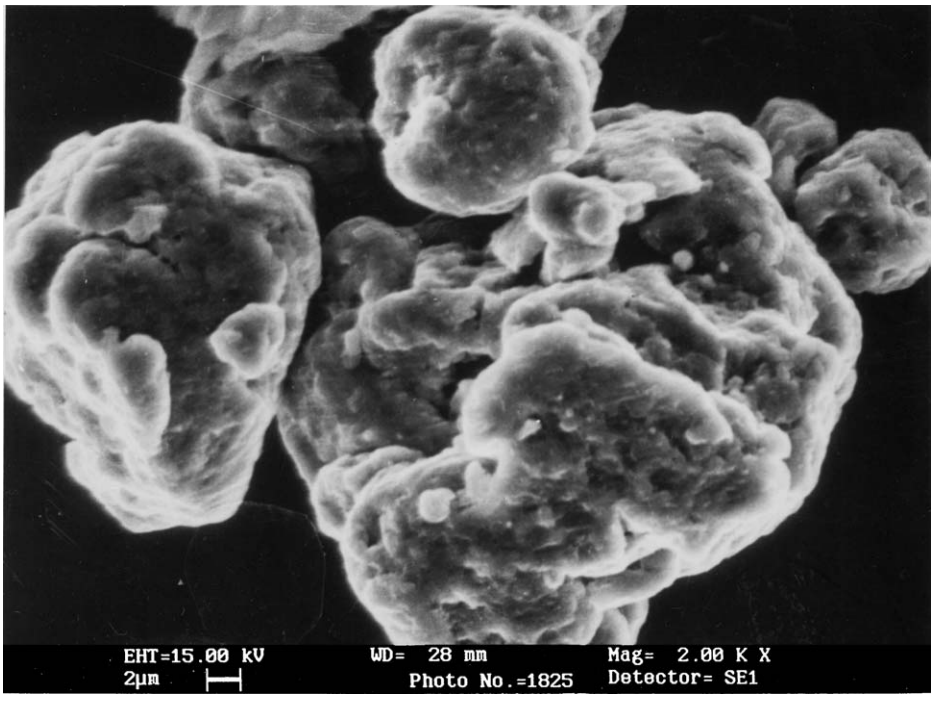


Figure 6 SEI micrograph showing the alloy particles after 120 h milling.

wt% Zn. Comparison shows that there is broadening of diffraction peaks and decrease in the intensity. The observed broadening of the (111) and (200) peaks are given in Table I. This indicates that milling causes reduction in the particle size. Furthermore reduction in the Zn peaks suggests that Zn dissolves into Al. Disappearance of Zn peaks after 120 h of milling is clear cut evidence that complete alloying has been achieved. This corroborates our SEM/EPMA results. The peaks are found to shift towards lower angle side. Table I also gives the d values for mixture and the sample milled for 120 h, which shows an increase in d values after alloying. According to Pearson [15] solid solution of Zn with Al causes reduction of lattice constant. As the atomic size of Zn (1.33 Å) is smaller than that of Al (1.43 Å), the lattice constant is expected to decrease after substitutional solid solution of Zn with Al. However in our case it was found that lattice parameter increases slightly. During milling the powder particles in between the balls experience compressive forces, which cause the distortion of the unit cell, the dimension of which increases slightly due to tensile effect. Therefore, we can conclude that ball milling causes the observed increase in lattice parameter. There are two effects, i.e.,

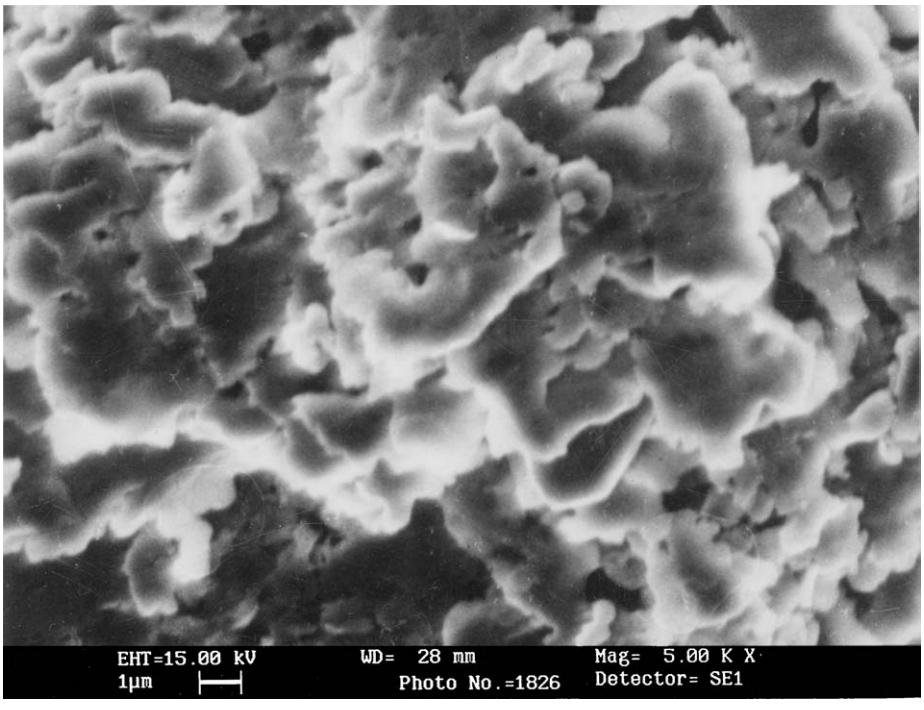


Figure 7 SEI micrograph showing flakes.

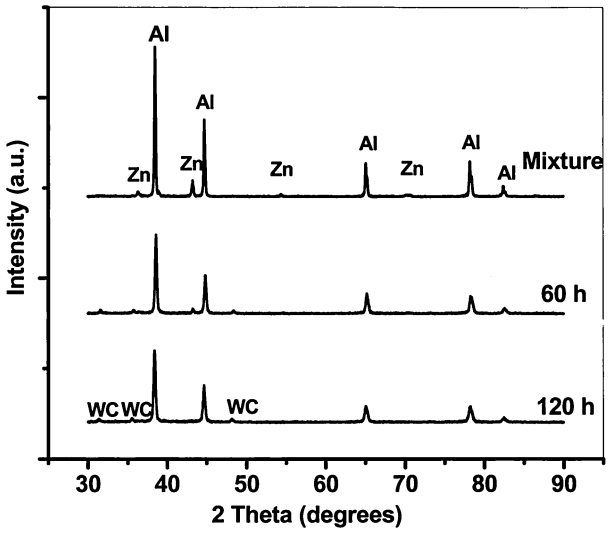


Figure 8 XRD patterns for unmilled mixture and Al-10 wt% Zn samples milled for 60 and 120 h.

decrease in lattice constant due to substitution of Zn in place of Al and increase due to ball milling. The net effect is increase in the lattice constant. It is expected that there would be compression texture, which is known to exclude [111] orientations in Al within 20 degrees of compression axis. This would lead to reduction in the intensity of (111) reflection and increase in the (200)/(111) intensity ratio. As shown in Table I, in our case this ratio is almost 50%, which indicates randomly oriented Al powders [8].

TABLE I Peak width and d values for diffraction peaks

Reflection peak	Parameter	Mixture	Alloy (120 h)
111	Width	0.27°	0.36°
	d	2.3387 Å	2.3422 Å
200	Width	0.27°	0.33°
	d	2.0257 Å	2.0282 Å
Intensity ratio I_{200}/I_{111}		0.48	0.49

3.3. Theoretical calculations

There are some factors which affect the solubility of a solute in a solvent and temperature is an important factor for solubility enhancement. It is assumed that during MA the powder particles trapped between the two colliding balls deformed by localized shear, the normal stress σ developed due to head-on-collision of the two balls is given by [16].

$$\sigma = \rho_b v_s v_r \tag{1}$$

where $\rho_b = 17.2 \times 10^3$ kg m^{-3} is the density of WC balls, $v_s = 5500$ m s^{-1} is the velocity of longitudinal wave in WC and $v_r = 2$ m s^{-1} is the relative velocity of the balls. The normal stress calculated from these values is 189×10^6 kg m^{-1} s^{-2}. The total energy flux F dissipated on the glide plane is given by

$$F = \sigma v_r \tag{2}$$

Substituting the values of σ and v_r, the value of F was found to be 378×10^6 kg s^{-3}. Although it was not possible to measure the localized temperature for the powder in between the balls, however, overall rise in temperature (ΔT) during ball milling was calculated by the following relationship [16].

$$\Delta T = F\left[\frac{\Delta t}{\pi K_o \rho c}\right]^{1/2} \tag{3}$$

F is the total energy flux calculated above, ρ and c are density and specific heat of the powder, K_o is the thermal conductivity and Δt is the time for which stress σ

lasts and calculated to be 7.3 μs. Using the appropriate values for our case, the rise in temperature is estimated to be ~21 K. The temperature of the powder during milling was thus about 320 K. This is in agreement with the value reported by Gaffet [17] for Ni-Zr alloy. At 320 K solubility of Zn in Al is estimated from phase diagram to be about 2 wt% [11]. Therefore the enhancement of solubility from 2 to 10 wt% i.e., by a factor of 5 cannot be due to rise of temperature. It is due to the effect of ball milling in which the factors contributing to the increase in the solubility are (i) reduction in grain size which increases the area of grain boundaries, (ii) heavy deformation and (iii) stress on solute exerted by very high density of dislocations.

For alloying to take place, thermodynamic considerations of mixing of the alloying components are essential. For this purpose enthalpy of mixing is determined. In the case of Al-Zn alloy system, the atomic sizes of Al and Zn are almost identical and the lattice strains arising from the difference in sizes are negligible. Therefore for the determination of enthalpy of mixing quasi-chemical theory of binary solutions can be applied. According to this theory the enthalpy of mixing is given by the relationship [10].

$$\Delta H_{\text{mix}} = X_{\text{A}} X_{\text{B}} Z N_0 \left[\varepsilon_{\text{AB}} - \frac{1}{2}(\varepsilon_{\text{AA}} + \varepsilon_{\text{BB}}) \right] \quad (4)$$

where X_{A} and X_{B} are the mole fractions of atoms A and B respectively, Z is the co-ordination number, N_0 is the Avogadro's number, ε_{AA}, ε_{BB} and ε_{AB}, are bond energies of A-A, B-B and A-B bonds. Al—Al and Zn—Zn bond energies are 0.19 [18] and 0.054 eV [19] respectively and Al-Zn bond energy is calculated to be 0.101 eV by using the relation $\varepsilon_{\text{AB}} = \sqrt{\varepsilon_{\text{AA}} \varepsilon_{\text{BB}}}$ [20]. Putting these values and $X_{\text{A}} = 0.05$, $X_{\text{B}} = 0.95$, Z = 12 and Avogadro's number in Equation 4 positive enthalpy of mixing is determined to be 276 cals/mol. There are three factors contributing to the enthalpy, (i) grain boundaries, (ii) mechanical deformation and (iii) stress on solute atoms by high density of dislocations.

The contribution of grain boundaries has been evaluated using the relationship [21].

$$\Delta G_{\text{b}} = \frac{4\gamma V_{\text{m}}}{D} \quad (5)$$

where grain boundary energy $\gamma = 324$ mJm^{-2}, V_{m} = molar volume = 10^{-5} m^3 of solvent Al and D is the average grain size. The minimum grain size achievable by mechanical milling is given by the minimum dislocation separation in a dislocation pile-up, which is calculated using the relationship [9].

$$L = \frac{3Gb}{\pi(1-\upsilon)h} \quad (6)$$

where G, b, υ and h are respectively the shear modulus, Burger's vector, Poisson's ratio and hardness of Al. Taking the values of these parameters, we obtain $L = 30$ nm. Putting $D = 30$ nm in Equation 5, we get $\Delta G_{\text{b}} = 103$ cals/mol.

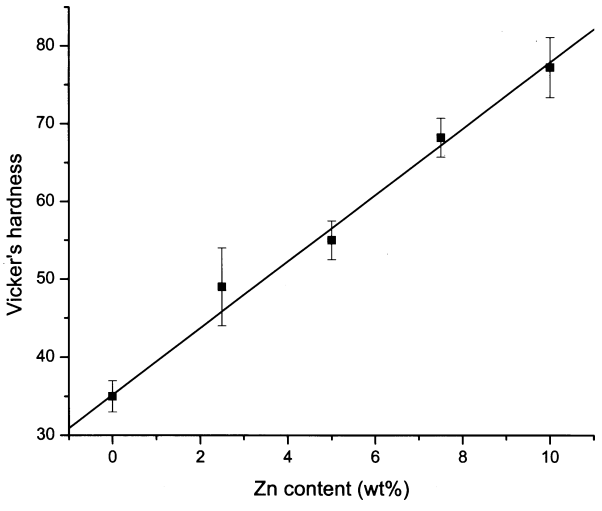


Figure 9 Variation of hardness as a function of Zn content.

The second factor, i.e., stored energy by mechanical deformation is 40 cals/mol, which is the stored energy in Al by multiple impacts [22]. The total contribution of the two factors is 103 + 40 = 143 cals/mol. The remaining enthalpy (133 cals/mol) comes from the stress on solute atoms due to a very high density of dislocations introduced by the mechanical alloying [8]. It thus suggests that although enthalpy stored in the grain boundaries assists in the enhancement of solubility, yet this effect alone cannot account for the observed increase in the solubility of Zn in Al, rather stress exerted by very high density of dislocations on solute atoms plays a major role in this case.

3.4. Hardness

In order to investigate the effect of dissolution of Zn in Al on mechanical properties, microhardness was measured on the compacted powder pellets. Fig. 9 shows the variation of hardness with Zn content. Hardness is found to increase with increasing solute content. Two factors contribute to the enhancement of hardness, one is solid solution hardening and the other is hardening due to reduced particle size. With the present results it is not possible to conclude about the extent of the contribution from each of the two factors. However it is obvious that hardness has increased from the value of pure Al.

4. Conclusions

Mechanical ball milling has been employed to achieve alloying of Zn up to 10 wt% Zn in Al. It is found that in order to obtain homogeneous alloys 120 h of milling is required when the powders of Al and Zn are milled together with a powder to ball weight ratio of 1:20. Enhancement of solubility and homogeneous alloying has been confirmed by SEM/EDS and XRD results. It is shown by calculation through quasi-chemical approach that 276 cals/mol are needed for alloying of 10 wt% Zn with Al. The two main factors contributing to this energy are found to be interfacial energy and stress on the solute atoms due to a very high density of dislocations. Mechanical milling and alloying of Zn with Al enhances the hardness of Al-Zn.

Acknowledgements

The authors are grateful to Mr. M. Akram for providing the powders and to Mr. Liaquat Ali for help in ball milling. Thanks are also to the staff of Radiation Damage Group for help in experimental work.

References

1. C. C. KOCH, *Nano Struct. Mater.* **2** (1993) 109.
2. M. OEHRING and R. BORMANN, *Mater. Sci. Engng.* A **134** (1991) 1330.
3. F. PETZOLDT, B. SCHOLZ and H. D. KUNZE, *Mater. Lett.* **5** (1987) 280.
4. W. GONG, G. C. HADJIPANAYIS and R. F. KRAUSE, *J. Appl. Phys.* **75** (1994) 6694.
5. M. J. FLEETWOOD, *Mater. Sci. Technol.* **2** (1986) 1176.
6. L. SCHULTZ, *Mater. Sci. Engng.* **97** (1988) 15.
7. D. R. MAURICE and T. H. COURTNEY, *Metall. Trans.* **21A** (1990) 289.
8. A. BHADURI, V. GOPINATHAN, P. RAMAKRISHNAN and A. MIODOWNIK, *Metall. Mater. Trans.* **27A** (1996) 3718.
9. J. ECKERT, J. C. HOLZER, C. E. KRILL III and W. L. JOHNSON, *J. Appl. Phys.* **73** (1993) 2794.
10. J. E. HILLIARD, B. L. AVERBACH and M. COHEN, *Acta Metal.* **2** (1954) 621.
11. M. HANSEN, in "Constitution of Binary Alloys" (McGraw- Hill, London, 1958) p.148.
12. P. S. GILMAN and W.D. NIX, *Metall. Trans.* **12A** (1981) 813.
13. P. KEDZIERZAWSKI, D. OLESZAK and M. JANIK-CZACHOR, *Mater. Sci. Engng.* A **300** (2001) 105.
14. B. J. M. AIKIN and T. H. COURTNEY, *Metall. Trans.* **24A** (1993) 647.
15. W. B. PEARSON in "A Handbook of Lattice Spacings and Structures of Metals and Alloys" (Pergamon Press, London, 1967) Vol. 2, p. 603.
16. R. B. SCHWARZ and C. C. KOCH, *Appl. Phys. Lett.* **49** (1986) 146.
17. E. GAFFET, *Mater. Sci. Engng.* A **132** (1991) 181.
18. W. SCHULE and R. SCHOLZ in "Point Defects and Defect Interactions in Metals," edited by J. Takamura, M. Doyma and M. Kiritani, (North Holland Pub. Co., New York, 1982) p. 257.
19. O. TAKAI, M. DOYAMA and HISAMATSU in "Point Defects and Defect Interactions in Metals," edited by J. Takamura, M. Doyma and M. Kiritani (North Holland Pub. Co., New York, 1982) p. 113.
20. J. BROUGHTON, *Phys. Rev. Lett*. **67** (1991) 2990.
21. D. A. PORTER and K. E. EASTERLING, "Phase Transformations in Metals and Alloys" (Van Nostrand Reinhold, England, 1984) p. 46.
22. M. B. BEVER, D. L. HOLT and A. L. TITCHENER, *Prog. Mater. Sci.* **17** (1973) 33.

Received 9 January 2003
and accepted 9 March 2004