

Mechanical alloying in immiscible alloy systems*

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Abstract In recent years, mechanical alloying (MA) of immiscible alloy systems characterized by positive heat of mixing has been extensively investigated. The present article reviews the latest progress in MA of immiscible alloy systems including the mechanisms of non-equilibrium phase transformation and metastable phase formation of the MA-driven supersaturated solid solutions, amorphous phases and nanophase composites as well as their mechanical and physical properties related to those metastable phases.

Keywords: mechanical alloying, immiscible alloy system, non-equilibrium phase transformation, metastable phase.

Immiscible alloy systems are characterized by positive heat of mixing ($\Delta H_{\text{mix}} \geq 0$), and the miscibility of components in such systems is very low or even virtually absent in both solid and liquid states except at very high temperatures. Therefore, inter-metallic phases and solid solutions can hardly be formed in such alloy systems. Some immiscible alloy systems, such as Ag-Cu, Fe-Cu, Cu-Ta and Al-Bi, have strong sedimentary tendency due to mutual immiscibility and great differences in density between the components, which makes it difficult for them to form homogeneous mixtures of component phases.

About 20 years ago, mechanical alloying (MA) was developed as a way to surmount the limitation of the conventional alloying^[1]. One of the most unusual effects observed in MA is the extensive enhancement of solid solubility of solid solutions and phases, e. g. AlCo intermetallic compound^[2], and the formation of nanocrystalline supersaturated solid solutions in systems, e. g. Fe-Cu^[3-5], which is virtually immiscible under thermodynamic equilibrium conditions due to their positive enthalpy of mixing. Till now, different metastable phases such as supersaturated solid solutions, amorphous phases and nano-phase composites have been synthesized by MA in immiscible alloy systems. Investigations on the properties of those metastable phases revealed some interesting phenomena, such as the softening effect of the Fe-Cu nanocrystallized supersaturated solid solution^[6], giant magnetoresistance (GMR) shown in the Cu-Co nanophase composite^[7], and the evidently improved wear properties of the Al-Pb alloy^[8]. Those unique

properties highlight the technological importance of the non-equilibrium alloys of the immiscible systems. An understanding of the non-equilibrium phase transformation of immiscible systems in MA and the correlation between metastable phases in immiscible alloy systems and their properties will facilitate future development of such alloy systems.

In this paper, the experimental and theoretical progress on the mechanisms of phase transformation and metastable phase formation under highly non-equilibrium conditions together with their abnormal properties of the alloy systems with positive heat of mixing are reviewed.

1 Mechanisms of the formation of metastable phases

1.1 Supersaturated solid solutions

The formation of supersaturated solid solutions prepared by MA was observed in several alloy systems with positive heat of mixing, such as Fe-Cu^[4,5], Cu-Co^[7], Ag-Ni^[9] and Cu-W^[10], in which supersaturated solid solutions could not be formed in equilibrium states.

Uenishi et al.^[3] ball-milled the mixed powders of Fe and Cu, and obtained bcc and fcc supersaturated solid solutions on Fe-rich and Cu-rich sides respectively. Other researchers also demonstrated that the solubility of Fe-Cu binary immiscible alloy systems can be extended through MA, and nanocrystalline supersaturated solid solutions can be achieved in a wider range

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of components with prolonged milling time^[11,12]. A simulation with the Monte Carlo^[13] method suggested that a moderate atomic mixing could be realized and solid solutions could be formed in systems with positive heat of mixing.

The mechanism by which a supersaturated solid solution formed by MA in immiscible systems has been extensively studied in the last few years. Several different mechanisms were proposed. It was proposed that the stress field of dense dislocations induced by severe deformation of MA is responsible for the formation of supersaturated solid solution and the extended solubility^[14]. The solubility enhancement x/x_0 is given by^[14]

$$x/x_0 = \exp(-\Delta\mu/RT) = \exp(-\sigma V_m/RT),$$

where x_0 is the equilibrium solubility, x the extended solubility, σ the stress acting on a solute located at a distance r from a dislocation, R the gas constant and T the temperature. For a typical dislocation density of 10^{12}cm^{-2} , there is approximately one dislocation within a grain of 10 nm diameter. Experimental results showed that the solubility enhancement depends strongly on r —i.e. with a decrease in r , and solubility enhancement x/x_0 will increase. This suggests that the high dislocation density of ball-milled powders causes a drastic increase in the mutual solubility.

Veltl et al.^[15] suggested that the energy stored in grain boundaries during MA serves as a driving force for the formation of a solid solution. Gente et al. studied the phase formation of the Cu-Co immiscible alloy system during MA and deemed that the driving force for alloy formation was provided by the contribution of the Cu/Co interface enthalpy and the high configurational enthalpy of the randomly distributed atoms in the solid solution^[16]. Yavari et al.^[17] put forward an alternative alloying mechanism that the capillary pressure from constituent phase fragments with tip radii of the order of 1 nm forces the atoms at the tips of the fragments to dissolve. This process will continue until full dissolution is reached due to the generation of such small particles by necking at tips of larger ones during continuous milling.

Actually, the accumulation of dislocation, increase of grain boundary energy and fragmentation of components all take place during MA. It is likely that the formation of supersaturated solid solutions is due to the combination of the above mechanisms.

1.2 Amorphous phases

Since Koch et al.^[18] first produced amorphous $\text{Ni}_{60}\text{Nb}_{40}$ powder by MA, amorphous alloys have been synthesized by MA in a large number of alloy systems, particularly those with negative heat of mixing. This is because such systems possess potentially a chemical driving force, which is believed to assist inter-diffusion of the constituent elements across the interface between two metals^[19]. However, the formation of amorphous phases by MA was reported in Cu-W^[10] and Cu-Ta^[16,20] systems, which are characterized by a positive heat of mixing. Here the chemical driving force is no longer functioning and, instead, an energizing process is thought to be involved in the formation of the amorphous phases^[20]. Further evidence for the formation of amorphous phases in immiscible alloy systems demonstrates that negative heat of mixing is not the prerequisite for amorphization by MA.

A lot of work has been performed on the mechanism of amorphization induced by MA in binary systems^[15,21,22]. Schwarz et al.^[21] argued that the amorphization by MA resulted from a solid-state reaction between ultrafine crystalline particles and fresh surfaces created by MA of appropriate duration. In the case of amorphization in the Zr-Al binary system by MA, Fecht et al.^[22] suggested that the amorphization process of α -Zr should be viewed as a compositionally induced melting transition when the crystal is driven out of its own stability range. Veltl et al.^[15] indicated that the large interface percentage and the high stress field of dense dislocations produced by severe deformation of MA is responsible for the formation of amorphous phases. For the latter two mechanisms, negative mixing heat is not a basic condition for amorphization, which explains the amorphization transition caused by MA in immiscible alloy systems.

1.3 Nano-phase composites

In recent years the synthesis of nanophase composites, or nanocrystalline composites have been studied extensively^[5]. The main way to synthesize nanophase composites by MA is to alloy metal powder and ceramic powder together to form homogeneously distributed nanocrystalline metal/ceramic composites or milling element powder under the atmosphere or a medium to form metal/ceramic composites via reaction between elements and medium^[23]. Actually,

MA of an immiscible alloy system may lead to the formation of a nanophase composite if two components can hardly dissolve into each other, such as Ag-Fe^[24] and Al-Pb^[25-27]. Fig. 1 shows the homogeneously distributed fine nanophase composite synthesized in the Al-Pb alloy system by milling for 15 h. The grain size of Al decreased to about 30 nm and the Pb phase existed on two-dimensional levels. On a larger scale, the Pb grains of less than 0.5 μm are mixed homogeneously with Al grains. For smaller ones, very fine Pb particles of less than 10 nm are distributed inside the Al grains. It is obvious that the microstructure obtained is strongly dependent on synthetic conditions. For instance, the nano-phase composite obtained by Zhou et al.^[27] in Al-Pb system after 10-h milling consists of homogeneously distributed Al grains of 24 nm and Pb grains of 6.5 nm in size.

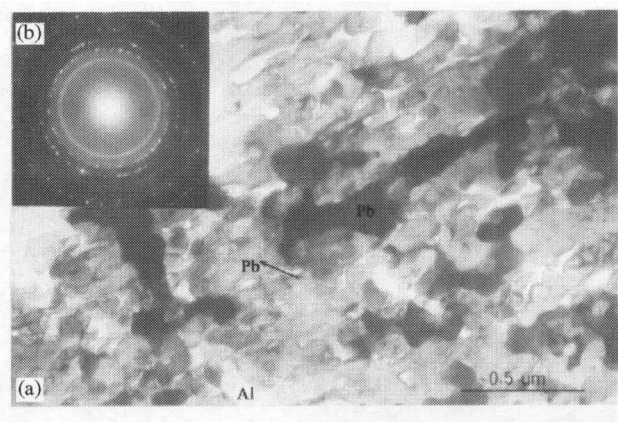


Fig. 1. Morphology (a) and corresponding electron diffraction pattern (b) of the Al-50at. % Pb sample obtained by milling for 15 h.

Moreover, nano-phase composites can also be formed by annealing supersaturated solid solutions obtained by MA in immiscible systems. For instance, the nano-phase composite with phase size less than 100 nm was obtained after 1 h annealing the Fe-20at. % Cu nanocrystalline supersaturated solid solution prepared by MA at a temperature lower than 773 K. The average grain size of Cu and Fe phases increased to 250 and 180 nm respectively when annealing temperature was 873 K. Since the grain size of Fe and Cu phases remains smaller than 100 nm when annealing temperature does not exceed 773 K, it is possible to consolidate a bulk nano-phase composite of Fe and Cu by sintering. Considering that the sintering temperature of nanocrystalline materials is much lower than that of the conventional materials^[5], the density of the bulk nano-phase composite can be high even though low sintering temperature is

applied.

2 Properties of alloys prepared by MA of immiscible systems

The alloys with metastable microstructures synthesized by MA in immiscible alloy systems often exhibit unique mechanical and physical properties. These unique properties are not only challenges to the theory of microstructure-dependence for properties of the traditional materials, but also of vital importance in the field of technical application.

2.1 Mechanical properties

For alloys of conventional grain sizes, the dependence of strength or hardness on grain size obeys the Hall-Petch relation. However, the relationship between strength and grain size deviates from the Hall-Petch relation for many nanocrystalline metals^[28]. Softening and hardening may take place in the case where the grain size is decreased to a level of several nanometers in different nanocrystalline alloys prepared by MA. In nanocrystalline-supersaturated solid solutions, another kind of softening and hardening effect was observed^[29]. In these cases, softening and hardening take place corresponding to the increase of solute concentrations. For instance, in nanocrystalline supersaturated Fe(Cu) (denoting solid solution of Cu in Fe) prepared by MA, although the hardness of Fe(Cu) nanocrystalline alloy increases with the reduction in grain size, it decreases with increasing solute concentrations, which is in contradiction to the general solid solution hardening effect. By comparison, the hardness of Fe-Cr alloys characterized by a negative enthalpy of mixing increases with increasing solute concentrations. Fig. 2 shows the effect of composition on the hardness of Fe base nanocrystalline alloys prepared through 20 h ball milling. It can be found that the Fe-Al, Fe-Cr and Fe-Ni alloy systems with negative heats of mixing show strong solution hardening effect. On the other hand, solution softening effect occurs in Fe-Cu and Fe-Ag nanocrystalline supersaturated solid solutions. No obvious softening and hardening effects were found in the Fe-Mn nanocrystalline supersaturated solid solution, i. e. the hardness of Fe(Mn) is almost the same as that of Fe.

Strong refinement strengthening effects are demonstrated in MA alloys of immiscible systems. Sheng et al.^[30] found that a small amount of Pb

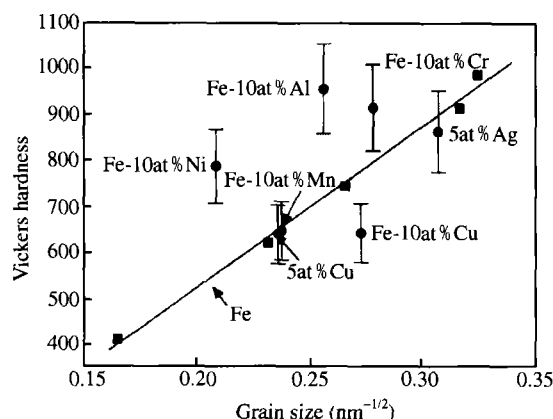


Fig. 2. Effect of composition on the hardness of Fe base nanocrystalline alloys prepared through 20 h ball milling.

nanoparticles may strengthen the Al matrix. The microhardness of ball-milled Al-Pb samples increases with increasing milling time, following the Hall-Petch relation. Experiments by Zhu et al.^[8] showed that the hardness of Al-Pb alloys obtained by ball milling was nearly Hv100. It reduced to Hv50 ~ 70 after sintering, but was still about two to three times harder than the cast Al-Pb alloys.

2.2 Giant magnetoresistance effect

In 1988 Baibich et al.^[31] first reported the giant magnetoresistance (GMR) in Fe/Cr multilayers. Similar effect was observed in immiscible alloy systems such as Cu-Co and Co-Ag systems^[32]. GMR refers to the drastic drop in resistance when an applied field progressively overcomes an antiferromagnetic coupling and aligns the magnetizations of the magnetic layers. It was subsequently found that GMR is not associated exclusively with multilayers but can be exhibited by heterogeneous alloy systems if single domain particles are embedded in a non-magnetic metallic matrix in which the electron mean free path is larger than the size of the magnetic particles and their spacing^[33,34].

Mahon et al.^[7] prepared a Cu₉₀Co₁₀ supersaturated solid solution, with the grain size of 3 ~ 4 nm by ball milling. The supersaturated solid solution was metastable and decomposed at around 400 °C. During the early stage of the decomposition the samples contained extremely small Co clusters with very large GMR values. Fig. 3 shows the percentage change of resistance in a field of 5 T as a function of annealing temperature (T_A), which presents a sharp peak at $T_A = 390$ °C, with a GMR value about 22 %. The increase in GMR is presumably associated with the for-

mation of very fine Co precipitates during the early stage of phase separation at $T_A > 390$ °C. It was found that GMR relates to grain size, small grain size favors GMR, and the largest GMR appears at an optimal grain size.

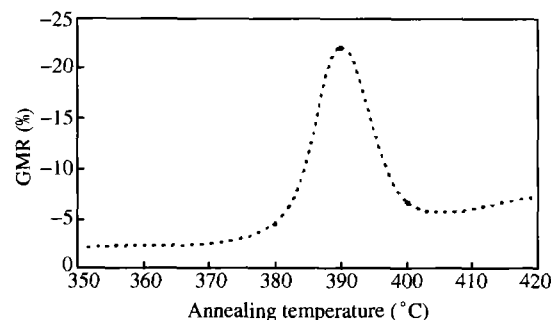


Fig. 3. Variation of GMR at 4 K as a function of annealing temperature^[7].

2.3 Melting point depression

The melting point of nano-particles would be depressed when one of the components is embedded in the other component matrix after MA of an immiscible binary alloy system. Sheng et al.^[35] studied the melting and freezing behavior of embedded nanoparticles in ball-milled Al-10wt. % M (M = In, Si, Bi, Cd, Pb) mixtures. It was observed that the melting temperature as well as the latent heat of fusion of the embedded particles decreased due to the size effect of particles. Unruh et al.^[36] indicated that the melting point of nanoparticles would decrease significantly if the system has a large positive heat of mixing.

Zhou et al.^[37] found that Al-Pb nanocomposite bulk samples with a full density could be prepared by consolidating ball-milled powder at a temperature as low as 280 °C and a pressure above 1.5 GPa. It was pointed out that the melting point depression of nanometer sized Pb particles may play a dominant role in such an achievement of full density with no grain coarsening during the hot densification process. Such an observation provides a unique approach to the stability of nanophase composites.

2.4 Wear properties

The previous work on casting Al-Pb alloys proved that homogeneously distributed fine Pb particles in Al matrix are beneficial to the wear property of Al-Pb alloys^[38]. Compared with other techniques, MA overcomes the strong sedimentary tendency of Al-Pb alloys and produces Al-Pb alloys with the mi-

microstructure of very fine Pb particles distributed homogeneously in the Al matrix. It is reported that the ability of MA Al-Pb alloys against wearing is much better than those prepared by other methods^[8]. The improvement is more obvious under dry wear conditions. The homogeneous dispersion of Pb in Al matrix after MA is thought to contribute to the improvement of wear properties.

3 Conclusions

The unique properties of alloys with metastable microstructures formed by MA in immiscible alloy systems show important potential applications. Studies on the non-equilibrium transformation driven by MA will facilitate the development and application of this kind of materials. Further researches, both experimental and theoretical, are required in order to get a better understanding of the mechanisms of MA in immiscible alloy systems.

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