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by Mechanical Alloying**

M.R. Paruchuri
D.L. Zhang
T.B. Massalski

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On the Formation of μ - and ζ - Phases in Ag-Al System

by Mechanical Alloying

M. R. Paruchuri, D. L. Zhang and T. B. Massalski
Department of Materials Science and Engineering
Carnegie Mellon University, Pittsburgh, USA

Abstract

Pure silver and aluminum powders have been mechanically alloyed in a Spex mill. Four selected nominal compositions $\text{Ag}_{1-x}\text{Al}_x$ ($x = 0.20, 0.23, 0.26$ and 0.37) were investigated by x-ray diffraction and differential scanning calorimetry, after being subjected to different times of ball milling. In all four selected compositions, the close packed hexagonal intermediate ζ -phase and the fcc α -phase (Ag-based solid solution) formed together during the first hour of milling, but subsequently the ζ -phase disappeared during continued milling except in the two alloys corresponding to 26 at.%Al and 37 at.%Al where the ζ -phase is the equilibrium phase. With continued milling, the complex cubic μ -phase formed in the alloys of nominal composition 20, 23 and 26 at.%Al where it is expected in equilibrium alloys. No amorphous phases have been observed in the mechanically alloyed powders in this system.

1. Introduction

Mechanical alloying is a solid state method which can be used to produce composite metal powders with controlled microstructures by repeated cold welding and fracture of powder particles [1]. Mechanical alloying by high energy ball milling has received increasing attention in recent years as a method for synthesizing a number of equilibrium or metastable intermetallic phases, nanocrystalline materials and amorphous alloys [2-5]. The main objective of many recent investigations has been to define both the kinetic and thermodynamic criteria that must be fulfilled in order to form an amorphous phase mechanically in an alloy system. A large thermodynamic driving force, which is generally supplied by the highly negative heat of reaction between the starting elements is one of the major requirements, the other being the presence of the so-called "fast diffusing component". Amorphous alloys have been produced by mechanical alloying in a number of binary systems involving either two transition metals, or a combination of a transition metal and a non-transition metal [6,7,8], but amorphization does not occur in other systems, such as Cu-Zn and Cu-Al [9,10], where it also cannot be achieved by other means. In some cases, amorphization could be produced by prolonged milling of previously prepared equilibrium intermetallic phases [11,12].

In the present study, we explored the amorphization possibilities and the formation of intermediate phases in the Ag-Al binary system, which exhibits a negative heat of mixing [13]. The four nominal compositions for this study were chosen to fall in the μ and ζ single phase fields, and in the $\alpha + \mu$ and $\mu + \zeta$ two-phase fields. They are 23, 37 and 20, 26 at.%Al respectively, and are shown by vertical lines in Fig.1.

2. Experimental details

Elemental powders of Ag and Al with a purity of 99.9% and a particle size of -270 mesh for Ag and -325 mesh for Al were used. Mechanical alloying was carried out in a Spex mixer/mill model 8000 using carefully weighed and mixed starting powders of the desired proportions. A hardened tool steel vial ($2\frac{3}{8}$ " d x 3") and steel balls ($2\frac{1}{5}$ " d) were used. Ball to powder weight ratio of 5:1 was used.

The milling and handling of the powder was carried out in a glove box in an atmosphere of helium. Powder diffraction x-ray measurements were made following various times of milling, using Cu K α radiation. The apparent particle size, D was calculated from the broadness of the most intense diffraction peak, using the Scherrer relation, $D = 0.9 \lambda / \beta \cos\theta$, where λ is the wavelength of the x-ray radiation, β is the full width at half maximum of the diffraction peak and θ is the diffraction angle [14]. Differential scanning calorimetry (DSC) was used to monitor the reactions among different phases formed in the mechanically alloyed powders, during heating. The powders of composition 37 at.%Al obtained after 1hr and after 20 hrs of milling were studied at a heating rate of 20°C/min.

3. Results

The results obtained from the x-ray diffraction analysis of the powders of different compositions are shown in Figs. 2 to 5, in the form of diffractometer scans. After milling for 1 hr, diffraction peaks corresponding to the close packed hexagonal ζ -phase appeared in the patterns of all alloys in addition to the diffraction peaks of the α -phase (Ag-rich solid solution). Continued milling of the 20 at.%Al nominal composition powders resulted in an extended metastable fcc Ag-rich solid solution after 4hrs, (and the corresponding disappearance of the lines of the

hcp ζ -phase). However, after 8 hrs, a mixture of the equilibrium intermetallic μ -phase and α -phase was produced. In milled powders of nominal composition 23 at.%Al, the μ -phase was observed after 2 hrs of milling in addition to the α -phase and ζ -phase. The volume fraction of the μ -phase increased with time until finally the entire powder transformed to the μ -phase after 8 hrs. Similar milling conditions applied to the powder of nominal composition 26 at.%Al produced the μ -phase in addition to the α - and ζ -phases after 4 hrs, and the disappearance of the α -phase after 8 hrs. In the powder of nominal composition 37 at.%Al, the volume fraction of the initially observed α -phase decreased after 2 hrs, and completely disappeared after 4 hrs, leaving only the ζ -phase present.

In all four samples continued milling up to 20 hrs., produced no further significant changes in the observed phases. The apparent particle size in these phases was calculated using the Sherrer formula neglecting the internal strain. The apparent particle size derived from the broad (111) peak in the metastable fcc solid solution obtained from the powder of composition 20 at.%Al, from (003) peak in the μ -phase obtained from composition 23 at.%Al, and from (101) peak in the ζ -phase obtained from composition 37 at.%Al were approximately 13 nm, 21 nm and 18 nm respectively.

A DSC scan of the composition 37 at.%Al mechanically alloyed for 20 hrs, is shown in Fig. 6. Two exothermic peaks were observed at 105 and 320°C, respectively. In further experiments, the milled powder of composition 37 at.%Al was heated in the DSC up to temperatures of 200°C and 400°C, which are higher than the first and second peaks respectively, and cooled down. The respective x-ray diffractograms taken from these cooled powders are shown in Figs. 7 and 8. The x-ray pattern in Fig.

8 shows sharp peaks while the one in Fig. 7 shows broad peaks, similar to the diffractograms obtained after 8 hrs and 20 hrs of milling (Fig. 5). It appears that the first peak in the DSC corresponds to the reaction between a small amount of the remaining unreacted elemental powders, Ag and Al and the second peak corresponds to the thermal recovery of the deformed ζ -phase. In order to verify this, the powder of composition 37 at.%Al mechanically alloyed for 1 hr, was subjected to a DSC run, which is shown in Fig. 9. The development of the exothermic peak at 105°C for this sample, begins at the same temperature as the first peak in Fig. 5, which corresponds to the reaction between unreacted elemental powders forming the ζ -phase.

4. Discussion

4.1 Equilibrium phase diagram and the free energy relationships at appropriate ball milling temperature:

The sequence of phase formations and transformations observed in this work may be discussed in reference to the equilibrium phase diagram of the Ag-Al system, shown in Fig. 1. The equilibrium ζ -phase forms peritectically at high temperatures and is stable over a wide composition range between approximately 24 to 40 at.% Al. The μ -phase forms by a peritectoid reaction and is stable over a very narrow composition range approximately between 21 to 24 at.% Al at room temperature. In order to interpret the formation of the various phases during milling, it is of interest to consider the free energy relationships appropriate to the average ball milling temperature (assumed to be 100°C) in this binary system. The free energies of formation of the phases present in the Ag-Al system have been calculated using the reported experimental thermodynamic data by Hultgren et al. [13]. The amorphous phase is

treated as a projection of the liquid phase to the undercooled temperature range. The temperature rise during collisions and impacts in mechanical alloying is not well determined. A temperature rise of 112-350°C involved in individual collisions was estimated by Davis et al. [15]. It has also been calculated to be only 38°C for the milling of Ni and Ti powders [16]. In the case of Ag and Al powders, the temperature rise should be below 105°C because unreacted powders of Ag and Al were observed even after prolonged milling, and they would have reacted to form the ζ -phase at and above 105°C. An attached thermocouple has indicated that the temperature on the outer surface of the vial increases up to 50°C, but the actual temperature of the powder inside the vial is likely to be even higher. The free energy relationships at 100°C in the Ag-Al system are shown in Fig. 10.

4.2 Phase formation during early stages of milling:

In the early stages of milling, the ζ -phase forms at all four compositions, but no amorphous phase formation was observed. In other ball milling experiments [17,18], amorphous phase formation during ball milling was attributed to a solid-state interdiffusion reaction analogous to that occurring in thin-film diffusion couples. In the case of a Ag-Al diffusion couple studied by Weaver and Brown [19], only the ζ -phase was observed to form during annealing of thin-film samples at temperatures up to 240°C; a similar result was obtained during bonding by diffusion welding of Al, using Ag as intermediate coatings [20]. The nucleation of the close packed hexagonal ζ -phase requires a collective atomic rearrangement of both Ag and Al atoms. In the process of multilayer formation and diffusional activity typical of mechanical alloying, the average composition necessary for ζ -phase formation must have been reached at the mechanically created interfaces between the Ag and Al particles in the early

stages of milling. Even though the μ -phase is stable in equilibrium in the 23 - 26 at.%Al composition range, and has a lower free energy than that of the ζ -phase, it is not produced during the early stages of milling. It appears therefore that the critical activation energy associated with the nucleation of the hexagonal ζ -phase must be lower than that of the complex cubic μ -phase. Crystal structure also plays an important role in the process of nucleation because it determines to a large extent the interface energy for compound nucleation. The hcp crystal structure of the ζ -phase is closely related to the close packed face-centered cubic structure of both parent components Ag and Al. The stacking of {111} planes of atoms in the ABCABCABCA..... sequence results in the formation of an fcc structure, while stacking of {0001} planes in the ABABABA..... sequence results in the hcp structure. Thus, the α to ζ transition becomes localized close to the layer interfaces in the early stage of the transformation and is enhanced by milling induced high density of defects. In most commonly observed fcc-hcp transitions induced by changes of temperature, the transition begins near defect regions such as small preexisting aggregates of hcp stacking [21]. The structural transition between the metastable fcc and hcp crystalline solid solutions in the Ni-Ru system was also achieved by mechanical alloying [22], and it is well established that the fcc structure can be easily be converted to an ABABAB close-packing arrangement by the creation and accumulation of stacking faults. In the case of Ag-Al alloys it is possible that the forming ζ -phase is actually metastable and has the ideal rather than the equilibrium axial ratio. The axial ratio in the equilibrium ζ -phase decreases from 1.625 at 26 at.%Al to 1.590 at 39 at.%Al at room temperature [23]. The extrapolation of this axial ratio value to 23 at.%Al gives the ideal close packing value of 1.633. The equilibrium ζ -phase is stable at this composition only above the peritectoid

temperature of 450°C. At the ball milling temperature of about 100°C, this metastable ζ -phase formation with ideal axial ratio is possible because of the nucleation difficulties of the competing equilibrium μ -phase.

4.3 Deformation and temperature induced effects on prolonged milling:

Mechanical alloying of powders is known to be a high energy deformation process and has been shown to result in the formation of solid solutions, equilibrium intermediate phases and amorphous alloys. Since Ag and Al are ductile components, it is expected that a multilayer structure is easily formed on milling. As indicated by x-ray diffraction spectra, the Al layers dissolve during MA, and Al atoms are incorporated into the Ag due to the negative enthalpy of mixing, in addition to the formation of the ζ -phase at all compositions. However, continuous milling of the powders of the composition 20 at.%Al up to 4hrs resulted in the formation of a metastable fcc solid solution of aluminum in silver, by milling-induced high density of defects. No detectable amounts of the μ -phase or ζ -phase are observed at this stage. However, continued milling of the 20 at.%Al powders up to 8hrs resulted in the formation of a large volume fraction of the μ -phase. In equilibrium, the solid solubility of Al in Ag is about 21at.% above the peritectoid temperature of 450°C, but it is less than 10 at.% below 200°C. Since the milling temperature may be near 100°C, the alloy powder is affectively in a two-phase region and the formation of the μ -phase may be expected. The process may involve a phase transformation from the metastable α -phase. In powders of compositions 23 at.%Al and 26 at.%Al, when all the Al is consumed on milling beyond 1 hr, the ζ -phase begins to react with the α -phase to form the μ -phase. In the powder of composition 23 at.%Al, this process of low temperature

peritectoid formation continues until all the ζ -phase and α -phase are converted to the μ -phase which is the only stable equilibrium phase. Continued milling of the 37 at.%Al powders produces the ζ -phase at the expense of the remaining α -phase, because ζ is the only the equilibrium phase present at this composition.

4.4 Formation of nanocrystalline phases and question of amorphous phase formation:

All the phases observed after 8hrs of milling at all the compositions were found to be nanocrystalline. Nanocrystalline alloys can be prepared by mechanical alloying of the elemental powders as well as by ball milling of the intermetallic compounds, when the intermetallic compounds exhibit a large difference in the free energy with respect to the amorphous phase [24]. The difference of the free energy between the ζ -phase and the amorphous phase is about 7 kJ/mole. This value may be attainable if chemical disorder increases on further milling (grinding of the ζ -phase). On further milling beyond 8 hrs, defect concentration could become sufficiently high to allow atomic mobility leading to structural disorder. However, the x-ray diffraction spectra obtained from powders of all the compositions after 20hrs of milling do not show any further increase in the broadening of the Bragg peaks as an indication of any considerable change in the strain, deformation or chemical disorder in either μ - or ζ -phases. The μ -phase could transform into a mixture of α and ζ -phases before it reaches the amorphous phase, since increase in free energy at the composition 23 at.%Al leads to α and ζ -phases consecutively. The stored energy by ball milling in the ζ -phase appears to be not sufficient to transform into amorphous phase. Any further crystal size refinement or increase in lattice strain appears to be not possible because

of the saturation of the dislocation density in this phase. Clearly no more energy can be stored in the μ - or ζ -phases upon further grinding. The formation of amorphous phase in early stages of milling may be hindered by the nucleation of the close packed hexagonal ζ -phase. It appears to be rather unlikely to form an amorphous phase in Ag-Al system by mechanical alloying of the pure elements or the transformation to an amorphous phase from the intermediate phases μ or ζ on grinding for longer times.

5. Conclusions

The equilibrium phases μ and ζ in Ag-Al system are formed by mechanical alloying of pure elemental crystalline powders. In all the compositions studied, the close packed hexagonal ζ -phase forms initially during the first one hour, in addition to the Ag-rich solid solution (α -phase) and remains present only where it is stable in equilibrium. On further milling, the μ -phase which has complex cubic structure forms by solid state reaction between α - and ζ - phases only in compositions where it is stable in equilibrium. A temperature rise of 100°C is estimated during ball milling of Ag-Al powders. The formation of the μ -phase or an amorphous phase during initial stages of milling is presumably hindered by the nucleation of the close packed hexagonal ζ -phase, which has low interfacial energy with the parent Ag and Al close packed cubic structures. No amorphous phases have been observed in the mechanically alloyed powders, although μ - and ζ -phases transformed into nanocrystalline phases on longer milling beyond 8 hrs, in the Ag-Al system.

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Figure captions

Fig. 1. The Ag-rich end of the Ag-Al phase diagram.

Fig. 2. X-ray diffractogram from MA powders of composition 20 at.%Al, showing the formation of fcc primary solid solution and the μ -phase.

Fig. 3. X-ray diffractogram from MA powders of composition 23 at.%Al, showing the formation of the μ -phase.

Fig. 4. X-ray diffractogram from MA powders of composition 26 at.%Al, showing the formation of the μ -phase and the ζ -phase.

Fig. 5. X-ray diffractogram from MA powders of composition 37 at.%Al, showing the formation of the ζ -phase.

Fig. 6. DSC thermogram of a sample of composition 37 at.%Al mechanically alloyed for 20hrs. Heating rate was 20°C/min.

Fig. 7. X-ray diffractogram taken from the powder of composition 37 at.%Al (MA for 20 hrs.) cooled from 200°C in the DSC, after the appearance of the first peak.

Fig. 8. X-ray diffractogram taken from the powder of composition 37 at.%Al (MA for 20 hrs.) cooled from 400°C in the DSC, after the appearance of the second peak.

Fig. 9. DSC thermogram of a sample of composition 37 at.%Al mechanically alloyed for 1hr. Heating rate was 20°C/min.

Fig. 10. Gibbs free-energy curves for the different phases at 100°C in the Ag-Al system.

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