CORROSION SCIENCE AND TECHNOLOGY, Vol.31, No.4(2002), pp.287~290

Synthesis and Characteristics of Consolidated Nanocrystalline Two-Phase $Ag_{50}Ni_{50}$ Alloy by Hot Pressing

Jiming Zhao

Room 2106, No.37, the 11th area of Heping Street, Chaoyang District, Beijing, P.R.China 100013

Silver and nickel are mutually only very slightly soluble and have a positive heat of mixing. Powder of $Ag_{50}Ni_{50}$ was prepared by mechanical alloying (MA) for 200 hr and subsquently hot pressing (HP) at 620℃ under 60 MPa. XRD results indicated that ball milling produced a mixture of two-phase mixture of supersaturated, nanocrystalline Ag-rich (αphase) and Ni-rich (βphase)solid solutions with grain sizes of 5 and 4 nm, respectively. Their grain sizes increased to about 40 and 26 nm after hot pressing. The HP $Ag_{50}Ni_{50}$ had a density very close to the theoretical value. The HP alloy consisted of an interconnected network of the α phase and islands of two-nanophase mixture rich in β phase. Accordingly, the stability of the microstructure of the alloy and the effects of mechanical alloying on the supersaturation of the two phases and on the formation of the Ag-rich network were also discussed.

Keywords : *$Ag_{50}Ni_{50}$, MA, HP, nanocrystalline, two-phase alloy*

1. Introduction

It had been recognized that ball milling of crystalline elemental powder mixtures can produce a variety of materials consisted with equilibrium phases as well as metastable phases, including intermetallic compounds, supersaturated solid solutions, and amorphous alloys.[1] As a result, there had been a surge of interest in mechanical alloying (MA) as a non-equilibrium materials processing method to achieve alloying on an atomic level, especially for alloys difficult to synthesize by conventional processing techniques. Generally, the nanometer-sized powders are in a non-equilibrium thermodynamical state and exhibit huge surface area, and considerable internal stress. However, after a heat treatment, the alloyed powder of the immiscible elements present as supersaturated solid solution could decompose and fine grains could form.[2-3] Due to these reasons, there are only few reports on the synthesis solidified nanocrystalline two-phase alloys so far. In the present Ag-Ni system, according to the equilibrium phase diagram, silver and nickel have very small mutual solubilities in both the solid and liquid states. [4] It is impossible to synthesis a homogenous and compact Ag-Ni alloy by traditional processes, e.g. by arc melting. The MA Ag-Ni alloy powder had already prepared by a high-energy ball milling.[5] In the present study, a two-phase $Ag_{50}Ni_{50}$ consolidated alloy with nanometer-sized grains was successfully prepared by means of MA followed by a hot pressing (HP) process. The microstructure and stability of the alloy was studied by means of XRD and TEM.

2. Experimental

Elemental silver and nickel powders (purity >99.9%) with particle size under100 μm were blended into mixtures with the desired overall atomic fraction of the two components. The grinding of the powder was performed in a QM-1SP low-energy planetary ball miller. For each milling run 40 grams of powder mixture were loaded into a stainless steel vial, together with hardened stainless steel balls of 20 mm and 10 mm diameter, at a ball-to-powder weight ratio of about 10 to 1. The powders were stir-mixed in a vial, which was subsequently evacuated to 0.1Pa and sealed in an argon atmosphere. During ball milling a relay was used to allow intermediate stops of 15 minutes every hour to avoid excessive heat effects. The solidification was performed by HP using a graphite model at 620℃ for 10 minutes at 60 MPa under a vacuum of 0.06Pa.

In order to study the microstructure stability, the milled powder was consolidated at room temperature under a pressure of 400MPa in a stainless model and the alloy obtained was annealed at 700℃ for 24 hr under a vacuum of 0.1Pa.

Both the MA and HP alloys were analyzed by X-ray diffraction. The average grain size was calculated using

the Scherrer Formula[6] corrected for instrumental broadening, taking strain effects into account. The grain size of the HP alloy was also determined by a Philipsem 420 TEM. The HP alloy was also examined with a Philips XL30 Scanning Electron Microscope (SEM). The energy-dispersive spectrometer unit (EDS) attached to the SEM was used for the qualitative and quantitative analysis of the different phases.

3. Results

X-ray Diffraction patterns obtained from the MA $Ag_{50}Ni_{50}$ powders are shown in Fig. 1. With increasing the milling time, the diffraction peaks of both Ag and Ni broadened significantly, indicating a decrease of the grain size and the introduction of internal stress.[7] Deducing from the diffraction peak Ag (222) and Ni (311), the average grain size of the α-Ag phase was found to be about 5 nm and that of the β-Ni phase about 4 nm after 200 hr ball milling. Meanwhile, the grain sizes of the α-Ag and β-Ni phases in the HP alloy were about 40 nm and 26 nm, respectively. Based upon TEM results, as illustrated in Fig. 2, the dimensions of the α-Ag and β-Ni phases were about 30-50 nm, which are in good agreement with the results of the XRD analysis.

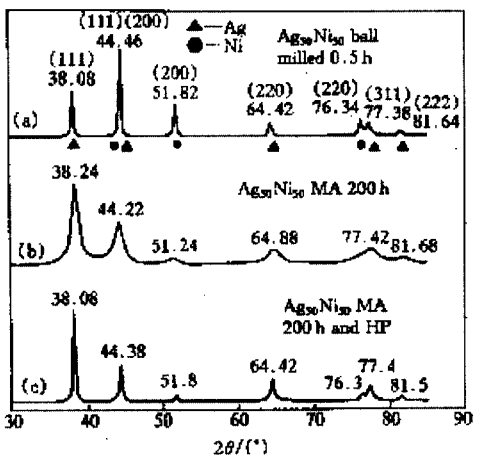

Fig. 1. XRD patterns of ball milled powders and hot pressed $Ag_{50}Ni_{50}$ alloy

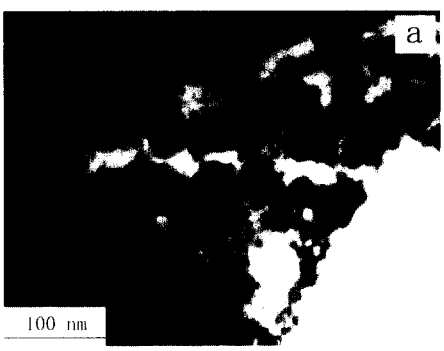

Fig. 2. TEM micrograph of the consolidated HP alloy

The volume fraction of grain boundaries, G_{gb}, could be evaluated by $G_{gb}=3\Delta(d-\Delta)^2/d^3$,[8] where Δ is the average grain boundary thickness which is approximately equaled to 1.2 nm and d is the

Average grain diameter in nm. Using the average grain size (30 nm) of Ag and Ni, the theoretical density of the actual nanocrystalline $Ag_{50}Ni_{50}$ MA was calculated to be 9.60 g/cm^2 (grain boundary possesss about 70 vol.% of the bulk). The HP alloy density was measured to be 9.47g/cm^2 with the

Archimedes Method, which is 98.6% of the theoretical value (with an uncertainty of 1-3%). Therefore, it can be concluded that a very compact nanocrystalline two-phase alloy had been obtained.

The microstructure of the HP alloy is shown in Fig. 3 (a) and Fig. 3 (b). The light α-Ag phase is uniformly distributed in the alloy and shows an interconnected network structure. The average particle size of the network consisting of the α-Ag phase is about 2-3 μm and less than 5 μm, as is shown in Fig. 3 (a). Between the α-Ag phase network, there are gray Ni-rich islands not larger

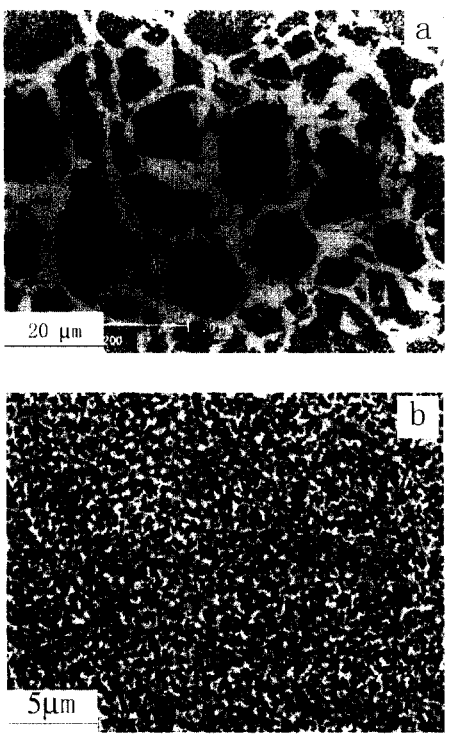

Fig. 3. Microstructures of the HP $Ag_{50}Ni_{50}$ alloy
(a) General view
(b) Expanded view of the mixture phases

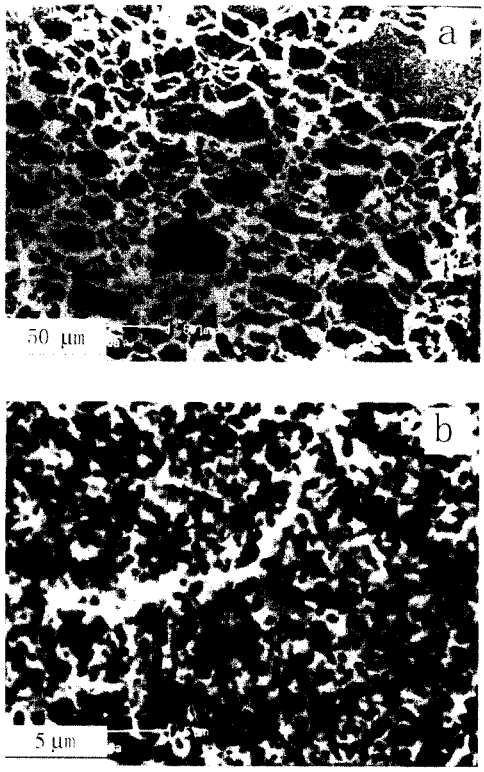

Fig. 4. Microstructures of as-annealed $Ag_{50}Ni_{50}$ alloy (a and b)

than 20μm, which are very fine mixtures of the two nanophases of α-Ag and β-Ni. Fig. 3 (b) is the magnified microstructure of an island rich in β-Ni shown in the Fig. 3 (a). The extremely fine α-Ag and β-Ni particles are dispersed uniformly with an average content of 43 at % Ag and 57 at % Ni. The α-Ag phase displayed also a network structure but much finer than that in Fig. 3 (a).

The microstructure of the HP alloy after annealing at 700℃ is shown in Fig. 4. The α-Ag phase with network structure obviously grew up, as can be observed in Fig. 4 (a). Fig. 4 (b) is the corresponding magnified microstructure of the islands rich in β-Ni in Fig. 4 (a). It was found that the α-Ag and β-Ni particles both grew up in comparison with the particles in Fig. 3 (b). Based on the XRD analysis, the average grain sizes of α-Ag and β-Ni were 93 nm and 90 nm, respectively.

4. Discussion

Models of phase formation in mechanically driven systems have already been developed[9] and have been recently applied to the ball milling process.[10] It was demonstrated that the steady state phase was determined by a competition between mechanically driven alloying and diffusion-controlled decomposition. A random solid solution was found when the shearing rate dominated,

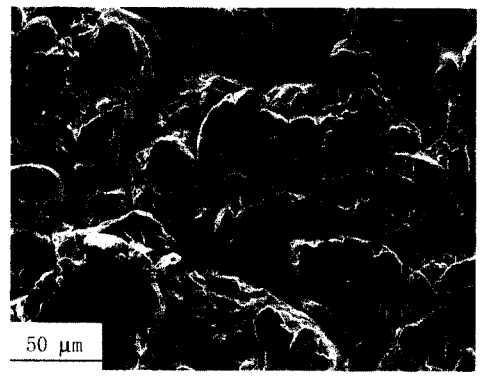

Fig. 5. Morphology of 200 h ball milled powder cold pressed at room temperature

while a decomposed state was observed when the diffusion rate was controlled. After 200 hr ball milling, the 2 θ values of the diffraction peaks of the α-Ag phase increased due to a supersaturation of Ni in silver, as is illustrated in Fig. 1. On the other hand, the 2 θ values of the diffraction peaks of the β-Ni phase decreased when Ag supersaturated into Ni. By using pure silicon powder as internal standard, the accurate lattice constants of α-Ag and β-Ni can be obtained, then the mutual solubilities of Ag and Ni are accurately deduced with Vagards method .[11] The results indicated that the average solid solubility of Ni in Ag was 0.84 ± 0.20 at % and Ag in Ni 4.96 ± 0.15 at %.

As suggested above, considerable mutual solid solubilities were reached during ball milling. However, since the MA powder was in a non-equilibrium state, the solute concentration of the supersaturated solid solutions in the powder should decrease when a heat treatment was performed.[2-3] Accordingly, the powder underwent grain growth during hot pressing, as was shown in Fig. 1. The peaks of both the α-Ag and the β-Ni phases became sharp and narrow. In contrast to the average grain size of several nanometers of the milled powder, the α-Ag and β-Ni particles were about several tens of nanometers. In the meanwhile, the relevant XRD peaks may surely return to their initial positions (When we take the XRD peaks of Ag and Ni of the powder milled for half an hour as the initial ones). Due to the solute decomposition during hot pressing, the solubility of Ag in Ni decreased to 0.45 ± 0.11 at %, which was still higher than the solid solubility of Ni in Ag corresponding to the Ni-Ag phase diagram.[4] However, the solubility of Ni in Ag was almost entirely destroyed during hot pressing.

Since Ag is the lower melting point component in the present alloy and much more ductile than Ni, therefore, when heat treat, the nanocrystalline α-Ag phase could melt in some sense and flow to form a continuous structure.

In fact, the result indicated that a network of the α-Ag phase was formed, as is illustrated in Fig. 2 (a). Special attention was devoted to study how the micron-sized α-Ag network formed that impeded formation of a perfect nanocrystalline material. The SEM/SEI morphology of the milled powder pressed under 400 MPa at room temperature is shown in Fig. 5. The Ag and Ni conglomerated as particles about 50 μm or less, which is slightly a little larger than the Ni-rich islands in Fig. 2 (a). This could be explained by the fact that the particles were impacted during the HP procedure. The EDS results indicate that the chamical composition in the center is the same as that at the edge of any particles. Therefore, this implies that the α-Ag network in the HP alloy had not formed during ball milling. Corresponding to the interconnected α-Ag network in the HP alloy, there exist a large number of interspaces between the particles. It was reported elsewhere that the nanocrystalline Ag could begin to melt at 373K if the grain size was reduced to 5 nm.[12] Due to the relatively low melting point, the α-Ag could melt or flow in some sense when the grain sizes increased during the HP procedure. To release the immense stress introduced by ball milling, the molten α-Ag originating from the non-equilibrium powder filled the interspaces between the particles. Furthermore, in the microstructure of the annealed HP alloy of Fig. 4 (b), an α-Ag strip was found that had formed in the Ni-rich islands, which is an evident that the α-Ag had amassed from the two-phase mixture to form the Ag network.

A possible formation mechanism of the α-Ag network was illustrated in Fig. 6. Before hot pressing, the milled powders had mutual contacted only in very limited parts or points. With the hot pressing performed, the contact areas could grow and develop into the contact surfaces due to the deformation of the elements. Subsequently, an interconnected interspace network is formed between the particle.[13] At the same time, due to the very short migrate distant (less than 50 μm) and the fast deformation rate of the element Ag, the quasi-molten α-Ag particles could move into the interspaces and form the α-Ag network.

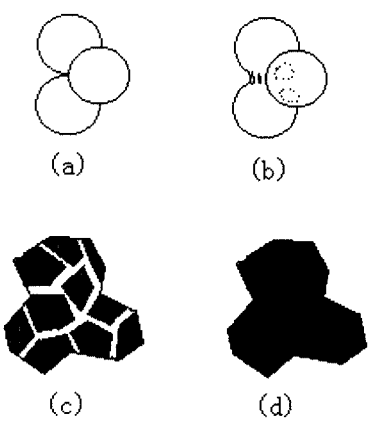

Fig. 6. Schematic representation for the formation mechanism of the α-Ag phase interconnected network

5. Conclusion

1) A two-phase nanocrystalline consolidated $Ag_{50}Ni_{50}$ alloy excellent density was obtained by controlled the hot pressing.

2) An explanation is given to interpret the formation of the micron-sized interconnected α-Ag network in the HP alloy during hot pressing. To release the huge stress resulting from ball milling, the Ag element would amass from the fine MA mixture of nanophases to form a continuous microstructure.

3) The HP alloy obtained was thermodynamically unstable. With the heat treatment, the grain size of each phase increased and the α-Ag network propagated.

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