SUPERHEATING OF Ag NANOPARTICLES EMBEDDED IN Ni MATRIX

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Abstract—Nanometer-sized Ag particles embedded in a Ni matrix were prepared by using melt spinning. The uniformly distributed Ag nanoparticles with a mean size of 30 nm exhibit a cube–cube orientation relationship with the Ni matrix, and some Ag nanoparticles are surrounded by {111} and {100} low-energy interfaces. Differential scanning calorimetry (DSC) and in situ X-ray diffraction (XRD) analysis results indicate that the Ag nanoparticles can be substantially superheated above the equilibrium melting point \( T_0 \) of the bulk Ag, as much as about 70 K above \( T_0 \) in the DSC measurement at a heating rate of 20 K/min. The superheating phenomenon is reproducible upon several heating/cooling cycles. In situ XRD results also indicate that the smaller the Ag particle, the higher the superheating. Our observations can be qualitatively interpreted with thermodynamic considerations.

Keywords: Melt spinning; Superheating

1. INTRODUCTION

The melting behavior of low-dimensional solids has drawn increasing attention in the past decades owing to a fundamental understanding of the melting mechanisms and practical concerns of their technological applications. Numerous experimental evidences showed that the melting point of a free-standing ultrafine particle can be much depressed relative to the equilibrium melting point \( T_0 \) for the bulk solid. However, when the particles are coated by (or embedded in) a high-\( T_0 \) solid with proper low-energy particle/matrix interfaces, their thermal stability against melting would be enhanced, so that the melting point can be even higher than \( T_0 \). In 1986, Daeges et al. [1] demonstrated that Ag particles coated by Au could be heated up to 25 K above \( T_0 \) for 1 min without melting.

Since then, the superheating phenomenon has been observed in a number of low-\( T_0 \) metals, such as In, Pb, Cd, Tl embedded in Al or Pb in Zn, Cu, respectively [2–11]. In those cases with a substantial superheating of the metal particles, some common features are found: (i) the binary system is immiscible or has very limited solubility; (ii) the interfaces between precipitates and the host matrix must be low index or low energy; and (iii) the size of embedded single crystal particles is small enough, normally in the nanometer scale. The first feature guarantees that the melting behavior of the embedded particles is not influenced by mixing with the matrix element. The low-energy interface between precipitates and the matrix normally suggests that a coherent or semi-coherent particle/matrix interface is developed in the nanogranular structure during the non-equilibrium processing such as melting quenching or ion implantation. Such a special interface was considered to be responsible for the achievement of superheating as the heterogeneous nucleation of melting at the particle surface might be significantly suppressed by the low-energy coherent interface [12]. This point has been experimentally approved by a comparative study of two nanogranular Pb/Al samples with the same Pb particle size but different Pb/Al interfaces [9]. For the sample with a randomly orientated Pb/Al interface, the melting temperature of the Pb particles is much lower than the bulk \( T_0 \), while for a semi-coherent Pb/Al interface, a substantial superheating was observed for Pb particles. Furthermore, Zhang et al. [13] succeeded in observing a superheating phenomenon in Pb/Al films due to suppression of growth of the molten droplets by the epitaxial Al/Pb/Al confinement, which again indicates that the low-energy interfaces play an important role in superheating. As for the third fea-

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ture, there are two implications. First, for particles the small size favors for the development of single crystal structure during preparation, which rules out the possibility that melting initiates at grain boundary around $T_m$. And second, the small particle size in the nanometer scale facilitates achieving substantial superheating phenomenon due to the size effect on superheating [2, 4, 11].

In order to extend the understanding of the intrinsic mechanism for melting of solid and to explore new possibilities for technological applications of superheated materials, the seeking of new systems capable of superheating is still underway in recent years. Based on those common features for achieving the superheating state, we found that the Ag/Ni system might be one of the candidates. Both Ag and Ni are of fcc structure and the solubility of Ni in Ag is very small, only about 0.2 at % even at the thermodynamic equilibrium melting point of Ag [14]. The melting point difference is as large as 493 K. The lattice mismatch between Ag and Ni is only 16%, which is smaller than those superheated systems (normally greater than 22%) reported in the literature. This means the dislocation density might be smaller in the semi-coherent Ag/Ni interfaces than in any other systems studied before. Therefore, Ag nanoparticles embedded in a Ni matrix might be superheated provided that low energy semi-coherent Ag/Ni interfaces are constructed experimentally. Actually, stable superheating phenomenon has not been observed for high-$T_m$ metals like Ag. Previous studies only dealt with low-$T_m$ metals (below 600 K), such as In, Pb, Cd and Tl.

In this paper, we prepared a nanogranular Ag/Ni sample by means of melt spinning. The melting of Ag nanoparticles embedded in Ni was investigated by using high-temperature differential scanning calorimetry (DSC) and in situ X-ray diffraction (XRD) analysis. A significant superheating in the embedded Ag particles has been observed in these two measurements. The melting process and the superheating phenomenon are clearly demonstrated that will facilitate understanding of the intrinsic mechanism of melting and superheating of the nanogranular structure.

2. EXPERIMENTAL

Alloy ingots with a composition of Ni–10 wt %Ag were prepared by arc melting of 99.95% pure Ni and 99.99% pure Ag in a water-cooled copper crucible under Ar atmosphere. The Ag/Ni thin ribbons with a width of 2–3 mm and a thickness of 30–40 μm were obtained by using a single roller melt spinning apparatus with a wheel speed of 25 m/s under Ar atmosphere.

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HREM) experiments were conducted on a JEM-2010 microscope with the accelerating voltage of 200 kV. Specimens for TEM and HREM observations were prepared by ion thinning of the melt-spun ribbons.

Thermal analysis was conducted on a Netzsch high-temperature differential scanning calorimeter (DSC 404 C). The sample was measured in a dynamic Ar atmosphere with the gas flow rate of 50 ml/min. The temperature range for measurements is between 1073 and 1343 K with the scanning rate of 20 K/min. The temperature was calibrated using pure In, pure Au and pure Ni. The sample weight is 322.83 mg for the DSC measurements.

XRD experiments at ambient temperature for Ni–10 wt %Ag were carried out on a Rigaku D/MAX 2400 X-ray diffractometer with a wide angle goniometer operated at 150 mA, 50 kV with Cu Kα radiation. The divergence slit, the scattering slit and the receiving slit were chosen with the width of 1°, 1° and 0.15 mm respectively. Measurements of 0–2θ scans were made in the reflection mode. A small angular step of 2θ (0.02°) and a scan speed of 5°/min in the range of 20–144° were taken to measure the intensity of Bragg reflections. A standard SiO₂ sample provided a measurement of the instrumental broadening.

In situ XRD experiments were conducted on the same diffractometer equipped with a high-temperature attachment which allows the measurements at high temperatures up to 1573 K. The current of 170 mA and a scan speed of 0.2°/min were employed. A platinum thermocouple was used to monitor the temperature. The temperature with an accuracy of ±1 K was calibrated by means of pure Pb (melting at 600 K) and pure Fe (a phase transformation from $α$-Fe to $γ$-Fe at 1183 K). All experiments at high temperatures were carried out under He atmosphere. Only one Bragg reflection peak (111) of Ag nanoparticles was monitored at high temperatures in this work, because (200) and (311) peaks of Ag overlap with (111) and (220) peaks of Ni respectively, and the intensities of other peaks of the embedded Ag particles are very weak around the melting point 1234 K.

3. RESULTS AND DISCUSSION

3.1. Structure characterization

The structure of the melt-spun Ni–Ag ribbons was firstly characterized by using XRD in the 2θ range of 20–144° at ambient temperature (Fig. 1). Only the Bragg diffraction peaks of Ag and Ni elements were detected. The lattice parameters calculated from the XRD profiles indicated that no solution was formed between the two elements in the present sample, underlying the two elements are immiscible in the as-quenched Ag–Ni sample.

Figure 2(a) shows a typical bright-field TEM observation of the melt-spun Ni–Ag ribbon. It can be seen that Ag particles are uniformly distributed throughout the Ni matrix. The Ag particle sizes are in the range 10–45 nm with a mean diameter of 30.
nm, as shown in Fig. 2(b). A close observation indicates the shapes or morphologies of the embedded Ag particles are not entirely identical. Some Ag particles are faceted while others are spherical. Most Ag particles are single crystals while few particles consist of two crystallites. Figures 3(a) and (b) show the typical electron diffraction patterns along Ni [011] and Ni [001] zones for the faceted granules in the Ni–Ag sample. The Ag particles exhibit an obvious cube–cube orientation relationship with Ni matrix, with close-packed planes and directions parallel: (111)$_{Ag}$$\parallel$(111)$_{Ni}$ and [001]$_{Ag}$$\parallel$[001]$_{Ni}$. Figure 4 shows a HREM image of an Ag particle corresponding to Fig. 3(a). The Moiré fringes inside the Ag particle confirm the orientation relationship between Ag and Ni. The atomic image clearly indicates the coherency across the Ag/Ni interface. In addition, the hexagonal shape of Ag particles perpendicular to the Ni [011] zone axis indicates that the particle shape takes the shape of a truncated octahedron bounded by [111] and [001] planes. This morphology of Ag particles in the Ag–Ni system is very similar to that of the Pb particles in the Pb–Al system [6, 8, 9].

3.2. Measurement of melting and superheating

Figure 5 shows typical DSC melting curves for the Ni–Ag sample measured by means of high-temperature DSC in five heating/cooling cycles. In the 1st heating curve multistep endotherms corresponding to melting of Ag were seen at 1230–1320 K, with peak temperatures at 1239 K ($T_{p1}$), 1280 K ($T_{p2}$) and 1304 K ($T_{p3}$), respectively. The onset temperature of 1230 K for the first peak indicates that most Ag nanoparticles melt at a temperature below its equilibrium melt-
Fig. 4. A HREM image corresponding to the [011]_{Ni} zone axis, showing the hexagonal-shaped Ag particles and the semi-coherent Ag–Ni interface.

The melting point \(T_0\) 1234 K. The melting point depression might originate from those spherical particles. The endothermal processes continued up to 1304 K, which means that some Ag nanoparticles has been superheated, 70 K higher than the \(T_0\) of Ag. The multistep melting processes imply different melting behaviors among the Ag particles due to probably the morphology differences of the Ag particles. The integrated area of the third peak \((T_{p3})\) is only about 3.2% of total area of endothermal peaks in the first heating DSC curve, which indicates only a very small part of particles can be substantially superheated to 70 K. In the following four DSC heating/cooling cycles, as shown in the insert of Fig. 5, the second peak disappeared and the third peak is weakened gradually. The endothermal enthalpy of the third peak, respectively, in the second, third, forth and fifth heating DSC curves, dropped down to about 1.1%, 0.7%, 0.4% and 0.3% of total area of melting peaks. That is to say, about 90% of formerly superheated Ag particles have been destroyed and lost their original structures after undergoing five heating/cooling circles. However, even so, an obvious superheating peak around 1304 K is still visible in the fifth heating curve, indicating that the superheating of some Ag particles can be repeated in the sample. Such a reversible behavior confirmed that the Ag particles underwent a melting-freezing reversible transformation around \(T_0\), i.e., the existence of the superheated Ag particles. Similar observations were also repeated experimentally for other samples at different heating rates.

Figure 6 collects \textit{in situ} XRD profiles of peak (111) of the embedded Ag particles at different heating stages. Heating from ambient temperature to 1173 K, we have seen a substantial change in peak position (due to the lattice expansion), but with almost no change for the peak intensity as in Fig. 6. The diffraction intensity of peak (111) reduced gradually when the temperature was elevated above 1173 K. Since the \(T_0\) of Ag is 1234 K, it was expected that the Ag diffraction line would disappear around this temperature. However, we found that an evident Ag (111) line with a rather high intensity still exists at 1233 K. Even at 1263 K, which is 29 K higher than the \(T_0\), the diffraction peak is still clearly visible. This phenomenon indicated that some Ag crystals exist in the sample at this temperature well above \(T_0\), i.e., the
Ag crystals are superheated. At 1273 K, the (111) line tends to disappear. The sample was then cooled down from 1273 to 1193 K in the diffractometer, and heated again. A similar superheating phenomenon was observed up to 1268 K.

Figure 7(a) shows the variation of the integrated intensity of the Ag (111) peak with temperature for the 1st and 2nd heating runs (denoted as A1 and A2 respectively). The smoothing, background elimination and $K\alpha_2$ elimination processes were performed for the diffraction peaks in calculation of the integrated intensity. From Fig. 7(a) one can see the superheated Ag particles can survive up to 39 K above the $T_0$. The integrated intensity in the 2nd heating run is much smaller than that in the 1st run. This can be explained by the result of DSC. The solidification process of embedded Ag particles took place in the temperature range of 1163–1231 K in the DSC measurement. When the sample was cooled to 1193 K and heated again in the 2nd XRD experiment, parts of Ag particles were still liquid, which would not contribute to the diffraction intensity. The reduced intensity of Ag (111) peak in the 2nd XRD heating run also results from the disappearance of many formerly superheated Ag nanoparticles, as hinted in the DSC results.

Three other samples (denoted as B, C, D) from different parts of the ribbon were used to check reproducibility of the superheating phenomenon. The variations of integrated intensity of the peak (111) with the increasing temperature for these samples are plotted in Fig. 7(b) together with that for the first sample (sample A). It is clear that a good reproducibility of superheating phenomenon was obtained for the embedded Ag particles. Below 1233 K, a moderate decrement of the integrated intensity with the increasing temperature can be seen, which originates mainly from the increased scattering at higher temperatures. A prompt reduction of the intensity occurs above 1233 K indicating that a considerable amount of Ag particles melt within a narrow temperature range (about 20 K). This observation is in agreement with the DSC result that an evident endothermal peak appears around the $T_0$. Further heating will eventually result in a complete disappearance of the Ag (111) peak, up to 1273 K (which is 39 K higher than the $T_0$).

The degree of superheating detected from DSC is as large as 70 K in the Ag/Ni sample, while the in situ XRD results show that all Ag particles with crystalline structure melt at 39 K higher than the $T_0$. The difference between the DSC and XRD results may be attributed to the different experimental conditions. In the DSC experiments, the sample was heated continuously at a heating rate of 20 K/min. But in the in situ XRD tests the XRD patterns were collected at a cer-
Fig. 7. The variation of the integrated intensity of Ag (111) peak for the embedded Ag particles with temperature, showing the reversibility for sample A (a), A1 for the 1st heating, A2 for the 2nd heating) and the reproducibility for samples A, B, C, D (b).

Fig. 8. The FWHM of Ag (111) diffraction peak and the estimated mean particle size as a function of temperature for sample A (open square for the 1st heating and solid square for the 2nd heating) and sample B (open up triangle). The insert shows the variation of the superheating $\Delta T$ with the estimated mean particle size $d$. The lattice microstrain and/or a decrease of the crystallite size. By means of the Scherrer equation [15], the crystallite size was estimated by neglecting the microstrain effect. In Fig. 8, the variation of the estimated mean grain size with temperature is also plotted for sample A and B. The grain size of Ag above 1258 K was not given because the diffraction peaks are too weak. The calculated crystallite size can be considered as the superheated Ag particle size for the Ag particles are single crystals. From Fig. 8, one can see that with an increase of temperature above $T_p$, the remaining superheated particles are smaller. The variation of the superheating with the particle size is plotted in the insert of Fig. 8. It indicates a pronounced size effect of superheating of particles, although the data are scattering and approximate, that smaller particles can be superheated to higher temperatures. This behavior is in agreement with that observed in other nanogranular systems [2, 4, 11].

By using the Scherrer equation, the mean grain size at 298 K was also estimated from peak (111). The value is about 30 nm for sample A and B, which is in accordance with the TEM result (30 nm). When the temperature was elevated to 1173 K, the grain size was enlarged to about 60 nm. That may originate from coarsening of the neighboring particles at high temperatures, which may be one of the reasons that account for the weakened superheating peak of DSC curves and reduced integrated intensity of XRD peak.

3.3. Thermodynamic analysis of superheating of Ag particles

In the literature, the superheating of confined metal particles was interpreted in terms of two effects: (i) the epitaxial particle/matrix interfaces and (ii) the elastic constraint of the particle. Due to the existence of the coherent or semi-coherent particle/matrix interface, heterogeneous nucleation of melting at the interfaces will be suppressed, as the interfacial energy is low. The elastic constraint from the matrix will make
the solid-to-liquid transformation of the particle more difficult due to the thermodynamic reasons. Taking these two effects into account, Allen et al. [16] proposed a thermodynamic model and derived a relationship between the melting temperature and the embedded particle size:

$$T_m = T_0 \left[ 1 + \frac{3}{L} \left( \frac{\Delta E}{r} + \frac{2(\sigma_{ml} - \sigma_{ms})}{\Delta E} \right) \right]$$  \hspace{1cm} (1)$$

where $\Delta E$ is the change in strain energy density on melting, $L$, the melting latent heat per unit volume, $\sigma_{ms}$, the solid–matrix interface energy, and $\sigma_{ml}$ the liquid–matrix interface energy. $\Delta E$ can be expressed as

$$\Delta E = \frac{18K\mu(\delta_1^2 - \delta_2^2)}{3K + 4\mu} k,$$  \hspace{1cm} (embedded model) (2)$$

where $k$ is a factor to account for the effect of a free surface on the strain energy density, $\mu$ is the shear modulus of the matrix, $K$ is the bulk modulus of the particle, $\delta_1$ and $\delta_2$ are misfit parameters for the liquid and solid spheres respectively.

In contrast, for free-standing small particles, the melting temperature is correlated with the particle size by

$$T_m = T_0 \left[ 1 - \frac{3}{L_0} \left( \frac{\Delta E}{r} - \frac{\Delta E}{r} \right) \right]$$  \hspace{1cm} (3)$$

where $r$ is the particle radius, $L_0$ is the melting latent heat per atom, $\sigma$ is the areal surface work, $v$ is the atomic volume. Subscript s and l denote solid and liquid, respectively.

From equation (1), one can see that the superheating of embedded particles is influenced by both the interface energy $\sigma_{ml}$, $\sigma_{ms}$ and the strain energy change $\Delta E$. If the interface energy $\sigma_{ms}$ is smaller than $\sigma_{ml}$, the value of $(\sigma_{ml} - \sigma_{ms})$ will be positive, then the melting temperature will be elevated. If the valid constraint between particles and matrix exists, the change of strain energy will also enhance the melting point of the particles. For the faceted granules in our sample, due to the construction of low-energy interfaces of {111} and {100} and the small mismatch across the interface between Ag and Ni, $\sigma_{ms}$ may be smaller than $\sigma_{ml}$ on the other hand, due to Ag particles are constrained by Ni with the epitaxial interface, $\Delta E$ effect also exists. Both effects may contribute to the observed superheating of Ag particles embedded in Ni matrix. For those spherical granules, due to the randomly orientated interface, $\sigma_{ms}$ may be larger than $\sigma_{ml}$ and $\Delta E$ effect is also very faint, which may result in the depression of melting point observed in DSC measurements.

Furthermore, from equation (1), the superheating of embedded small particles is related to the particle size. The superheating increases with a decrease of particle size. This trend is observed in our in situ XRD results, i.e., small Ag particles can be superheated to higher temperatures. Recently, the above experimental result has been well interpreted by a thermodynamic model developed from a model for size-dependent melting and the Lindemann criterion [17].

Although the thermodynamic model may qualitatively or semi-quantitatively explain our experimental observation of the superheating phenomenon in the Ag nanoparticles embedded in Ni matrix, the intrinsic melting kinetic mechanism of the nanogranular particles is still under exploration. Sasaki et al. [18] observed that the liquid droplet for the In particle embedded in Al matrix nucleated at a {100} facet at the very beginning of the melting process by using an in situ HREM. Xu et al. [19] found that melting of an Ag cluster with a Ni coating initiated at a defective interfacial region and then propagated inwards by molecular dynamic (MD) simulation. In order to further clarify the melting kinetic process, more quantitative experiments and theoretical analysis as well as MD study on the melting and superheating behavior of the embedded particles are urgently needed and are in progress.

4. SUMMARY AND CONCLUSIONS

In summary, we succeeded in preparing a nanogranular Ag/Ni sample by using the melt spinning technique, in which Ag nanoparticles with a truncated octahedral shape are embedded uniformly in the Ni matrix. A cube–cube orientation relationship was constructed between the Ag nanoparticle and Ni. A substantial superheating for the Ag nanoparticles was detected by means of DSC and in situ XRD experiments. It was also noticed that the smaller the Ag particles, the higher the degree of superheating which could be achieved. Such a superheating phenomenon for Ag nanoparticles might be qualitatively understood in terms of the thermodynamic model reported in the literature.

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