Volume 2, Number 8 ACTA PHYSICA SINICA August, 1993
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THERMAL STABILITY AND GRAIN GROWTH OF NANOCRYSTALLINE METAL SILVER*

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(Received 23 August 1992)

The nanocrystalline metal silver (n-Ag) with average grain size of 10 nm was synthesized by using an inert gas evaporation and in situ compacting technique. The thermal stability of grain size and grain growth caused by isothermally annealing heat treatment, as well as the thermal behavior during grain growth, have been studied. The results indicated that the thermal stability temperature of grain size is about 200 °C. The grain growth depends upon the annealing temperature and exhibits three different stages, i.e., slow, fast, and rapid growth stages, corresponding to the temperature ranges from 200 °C to 300 °C, from 300 °C to 400 °C and above 400 °C, respectively. An exothermal peak and an endothermal peak occur on the *differential scanning calorimetriy (DSC)* curve of n-Ag. The exothermal peak and the endothermal peak appear in the temperature range from 200 °C to 400 °C, and from 400 °C to 660 °C, respectively. The enthalpies calculated from the above two peaks depend on the compacting pressure. Further analyses indicated that the grain growth of n-Ag is related to the release of the surface energy of grains and the interfacial energy, as well as the strain energy stored in the bulk samples induced by compacting process.

PACC: 6825; 6540; 6170N

I. INTRODUCTION

I. INTRODUCTION

The nanocrystalline materials (n-materials) are a new kind of artificial polycrystalline materials, in which the size of individual ultrafine particles (grains) is in the range from 1 to 100 nanometers[1-4]. When particle size of nanocrystalline materials is in the range of a few nanometers, the volume fraction of intercrystalline interfaces becomes comparable to the volume fraction of the residual crystals. As a consequence, nanocrystalline materials exhibit properties different from those of conventional polycrystalline materials with grain size larger than 0.1 μm, single crystals and amorphous materials[4]. The n-materials were widely synthesized by using the inert gas evaporation and in situ compacting method[3]. The ultrafine particles were first prepared by evaporating the highly purified raw materials in the high purity inert gas atomosphere, and then collected and compacted into bulk materials

*Project supported by the National Natural Science Foundation of China and the National Advanced Materials Committee of China under Grant No. 59291006.

under high pressure in an ultrahigh vacuum (UHV) device[1-4]. The bulk n-materials prepared by such a method often have clean interfaces, because very few impurities distribute in the large volume fraction of interfaces[1,3,4]. They are different from those n-materials synthesized by chemical method, by which the surfaces of particles, and hence the interfaces of the bulk n-materials, are polluted to various degrees. The n-materials in as-prepared state are metastable, owing to their high interfacial energy. The grains of n-materials will grow when environmental temperature is higher than a certain critical value. Thus, the interfacial structure and physical properties of n-materials will be subject to variation. For this reason, the study of thermal stability and grain growth is very important for controlling the interfacial structure and physical properties of n-materials, as well as their applications in high technology. Gleiter[4] described the thermal stability of n-materials in terms of the temperature, at which significant grain growth (the particle size doubled in about 24h) was observed, and studied the thermal stability of some nanocrystalline metals, such as Fe, Pd and Cu. The results indicated that the thermal stability of n-materials is related to the melting point of materials. But other effective factors are still unknown at present. Concerning the thermal stability of n-materials, it is necessary to study not only the thermal stability, but also the thermal behavior during grain growth and its relation to the microstructure of the n-materials as well. There is no such work at present. The aim of this work is to study the thermal stability and thermal behavior during grain growth for n-metal silver (n-Ag), as well as the influence of the synthesizing process upon the grain growth and thermal behavior.

II. EXPERIMENTAL PROCEDURE

The n-Ag was synthesized by means of the inert gas condensation and in situ compacting technique, using an equipment designed and manufactured by the present authors. The design principle and technical data of the equipment were similar to that reported in Ref.[3]. The chamber was first evacuated to ultra-high vacuum (UHV) of 7.6×10^{-6} Pa and then filled with high purity (5N) helium gas to a pressure of 5 kPa. The silver raw material with 99.999% purity was evaporated from a tungsten boat, resistance-heated by a large electric current. The evaporated ultrafine particles were transported via convection within the chamber, and deposited on a liquid-N_2-cooled finger, which was rotated at a rate of 0.27 cycle per minute, in the UHV chamber. The convection was caused by temperature difference between the tungsten boat and cold finger. The size of particles deposited on the cold finger remained unchanged owing to the reduction of kinetic energy, caused by collision between particles and helium atoms during convection. The particles were scraped down from the cold finger by using a scraper, collected in a compaction unit with UHV of 10^{-6} Pa and then compacted into bulk samples under different uniaxial pressures from 0.2 to 1.5 GPa. The disk-shaped samples with 6 mm in diameter and 0.2–0.5 mm in thickness were

then obtained. The average grain size of the samples was determined by X-ray diffraction (XRD) and transmission electron microscope (TEM). They gave almost the same result. The density of samples compacted at the pressure of 1.5 GPa was about 86% of that of the coarse-grained polycrystalline silver. In order to investigate the thermal stability and grain growth, the samples were isothermally annealed at the temperatures of 100, 200, 250, 300, 400 and 500 °C for 6h in vacuo (7.06×10^{-3} Pa). The variation of average grain size was again measured by XRD and TEM. The thermal behavior was studied by using a differential scanning calorimeter (DSC-2, Perkin-Elmer). The Vickers microhardness, H_v, of the samples was measured by using a HX-200 type microhardness apparatus.

III. RESULTS AND DISCUSSION

The influence of isothermal annealing temperature (IAT) upon the average grain size (d) and microhardness has been studied for samples compacted at a pressure of 1.5 GPa, as shown in Fig.1. The result indicated that the grain size remains unchanged at IAT below 200 °C, grows fast between 200 and 300 °C, varies slowly from 300 to 400 °C, and then increases rapidly at IAT higher than 400 °C. The highest IAT, at which the grain size remains unchanged, was taken for characterizing the thermal stability of n-Ag. The result shown in Fig.1 is 200 °C.

A similar result of variation of grain size with IAT for n-Fe was reported by Gleiter[4], but the micoprocess has not been considered.

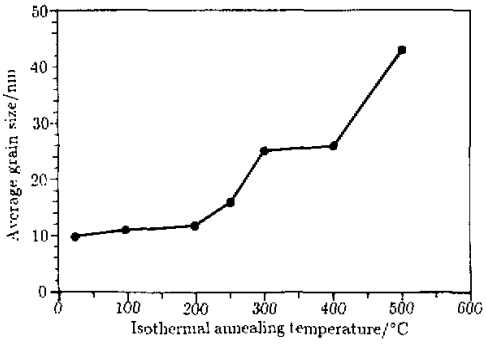

Fig. 1. Variation of average grain size with isothermal annealing temperature for nanocrystalline metal silver synthesized under the pressure of 1.5 GPa.

The variation of Vickers microhardness with IAT is shown in Fig.2. The microhardness, H_V, decreases with increasing IAT, but in a nonlinear way. The result indicated that the grain growth has an obvious effect on the mechanical property of n-Ag.

The thermal behavior in the DSC experiment, at a heating rate of 80 K/min, is shown in Fig.3 for the sample prepared under the pressure of 1.5 GPa. An exothermal peak and an

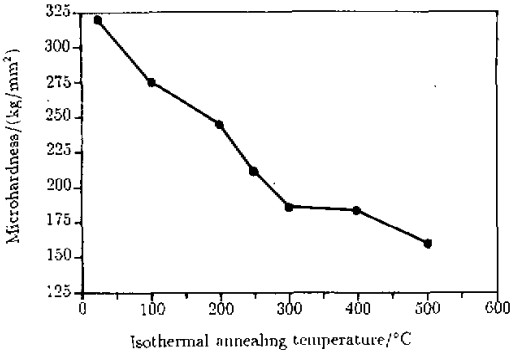

Fig. 2. Variation of Vickers microhardness with isothermal annealing temperature for nanocrystalline metal silver synthesized under the pressure of 1.5 GPa.

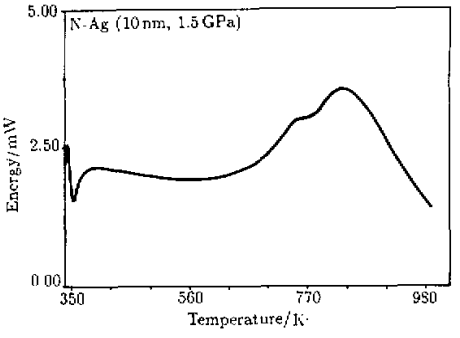

Fig. 3. Differential scanning calorimetric (DSC) curve for nanocrystalline metal Ag, with an average grain size of 10 nm, synthesized under the pressure of 1.5 GPa.

endothermal peak appear in the temperature range from 402 to 664 K (about 130 to 390 °C) with a minimum at 559 K (286 °C), and in the temperature range from 664 to 935 K (about 390 to 660 °C) with a maximum at 828 K (555 °C), respectively. Similar exothermal and endothermal phenomena have been observed in n-Al[5] and n-NiP[6], as well as in n-ceramics and other n-materials, but never been observed in the as-prepared coarse-grained polycrys-

talline and single crystalline materials. This means that this kind of thermal phenomena is a general characteristic thermal behaviour of the nanocrystalline materials. Therefore, the study of exothermal and endothermal phenomena is very important in understanding the variation of microstructure of n-materials during heating process, as well as its relation to the thermal stability and grain growth.

In order to study the variation of grain size in the DSC experiment, the samples were heated up to 402, 466, 558 and 828 K at a rate of 80 K/min and then rapidly cooled to room temperature at a rate of 320 K/min. The results showed that the variation of grain size with the temperature (Fig.4) is similar to that of Fig.1, i.e., the grain size remains stable at the temperature lower than 466 K, increases obviously from 466 to 558 K, then increases slowly from 558 to 664 K, and rapid grain growth occurs at temperatures higher than 664 K. Although the amount of grain growth in the DSC experiment (Fig.4) is less than that in the isothermal-annealing experiment (Fig.1), they have similar variation tendency. This result indicated that the grain growth depends not only on the heating temperature, but also on the heating duration. Comparing Fig.3 with Figs.1 and 4, it can be seen that the temperature range of the exothermal peak covers approximately the temperature range in which the grain size remains stable, and then grains grow rapidly as well as slowly, while the temperature range of the endothermal peak corresponds to that for very rapid grain growth.

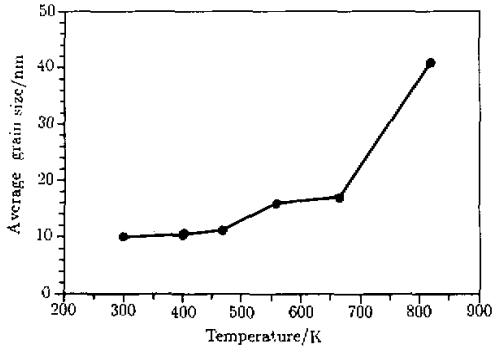

Fig. 4. Variation of average grain size with DSC scanning temperature for nanocrystalline metal Ag, in the DSC experiment at the heating rate of 80 K/min and cooling rate of 320 K/min.

For understanding the origin of the exothermal and endothermal peaks, the influence of compacting pressure on the peaks has been studied. The variation of enthalpy obtained from the exothermal peak with compacting pressure is shown in Fig.5. It is obvious that the exothermal peak is dependent upon the compacting pressure. This means that the exothermal peak is dependent upon the release of the strain energy caused by compacting

process. This is similar to the exothermal peak observed on the DSC curves of the strained coarse-grained polycrystalline metals Cu and Ni[7]. Moreover, the atomic structure and defects in the bulk n-materials are dependent upon the compacting pressure and annealing temperature[4]. So the exothermal peak is also related to the release of the interfacial energy of the bulk n-materials. The 0.02 %–0.3 % lattice strain in the nanocrystalline metals Cu and Pd synthesized under 1.4 GPa has recently been measured by Nieman *et al.*[8] in the X-ray experiment. The 0.6 % lattice strain in n-Pd synthesized under 1.4 GPa has also been determined by Fitzsimmons *et al.*[9] in the EXAFS experiment. The maximum pressure of the n-Ag in this work is 1.5 GPa, which is similar to that in Refs.[8] and [9]. This implies that the lattice strain should exist in the present bulk samples of n-Ag. Therefore, the exothermal peak of bulk n-Ag is related to the release of the lattice strain energy stored in the bulk samples.

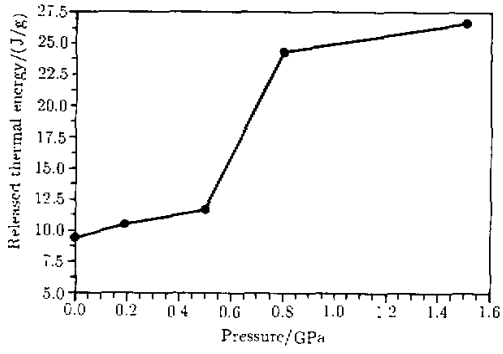

Fig. 5. Variation of enthalpy of the exothermal peak on DSC curve with compacting pressure for nanocrystalline metal Ag.

For comparison, the thermal behavior for nanometer-sized silver particles in the DSC experiment was also studied. The result is shown in Fig.6. An exothermal peak and an endothermal peak occur in the temperature range from 505 to 706 K with a minimum at 648 K, and from 706 to 780 K with a maximum at 729 K (see curve 1 of Fig.6), respectively. It is noted that the average grain size of silver particles increases from 6 to 27 nm in the DSC experiment from 505 to 706 K, indicating that the grain growth takes place also in the temperature range of the exothermal peak for silver particles. During the second scan, the exothermal and endothermal peaks disappear (see curve 2 of Fig.6). Because the surface energy of ultrafine particles is inversely proportional to the particle size, it can be estimated that about 78 % of the surface energy is released when the average particle size increases from 6 to 27 nm. Hence, the exothermal peak on the DSC curve of n-Ag is related to the release

of surface energy of silver particles. Comparing Fig.3 with Fig.1, it is noted that the grain growth takes place in the temperature range of the exothermal peak. So the exothermal peak originates not only from the strain energy and interfacial energy as metioned above, but also from the surface energy released during grain growth.

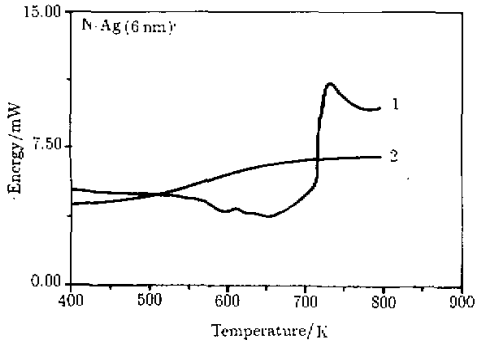

Fig. 6. DSC curve of first scan (1) and second scan (2), for metal Ag particles with average particle size of 6 nm.

In summary, there are various microprocesses for generating the exothermal and endothermal peaks. In the temperature range in which the grains of the bulk n-Ag remain stable, the exothermal peak originates from the release of the interfacial energy and the strain energy stored. When the temperature is higher than the thermal stability temperature of n-Ag, the release of the surface energy in the grain growth process contributes to the exothermal peak as well. The endothermal peak is mainly related to the rapid growth of grains. Its micro-process is still unclear.

IV. CONCLUSIONS

The following conclusions could be drawn from the above results:

1. The variation of average grain size of nanocrystalline metal silver (n-Ag), caused by isothermal annealing for 6 h, displays four different stages: (1) Grains remain stable when isothermal annealing temperature is below 200 °C. This means that the thermal stability temperature of n-Ag is 200 °C. (2) Grains grow faster in the temperature range from 200 to 300 °C. (3) Grain growth becomes slow from 300 to 400 °C; and (4) rapid grain growth takes place at temperature higher than 400 °C.

2. A characteristic exothermal peak and an endothermal peak occur on the DSC curve of n-Ag. The exothermal peak covers the temperature ranges for the thermal stable region of n-Ag, and fast as well as slow growth of grains, while that of the endothermal peak

corresponds to the temperature range of rapid growth of grains.

3. The enthalpy calculated from the exothermal peak is dependent on the compacting pressure. The higher the pressure, the higher the enthalpy of the exothermal peak, but they are related in a nonlinear way.

ACKNOWLEDGEMENTS

The authors wish to thank associate professor Shui Jia-peng, engineers Cheng Li-fang and Kong Jie for technical assistance in the mircrohardness measurements, DSC and X-ray experiments.

REFERENCES

[1] H. Gleiter and P. Marquardt, *Z. Metallk*, **75**(1984), 263.
[2] R. Birringer, H. Gleiter, H. P. Klein and P. Marquardt, *Phys. Lett.*, **102A**(1984), 365.
[3] R. Birringer, U. Herr and H. Gleiter, *Suppl. Tran. Japan Inst. Metals*, **27**(1986), 43.
[4] H. Gleiter, *Prog. Mater. Sci.*, **33**(1989), 223.
[5] Xijin Wu, *Chinese J. Adv. Mech.*, **21**(1991), 63 (in Chinese).
[6] Shui Jia-peng, Cheng Li-fang, Liu Jun-ming and Chu Zhao-qing, *Acta Metallurgica Sinica*, **28**(1992), B405 (in Chinese).
[7] L. W. Clarebrough, M. E. Hargreaves and G. W. West, *Proc. Roy. Soc.*, **A332**(1955), 252.
[8] G. W. Nieman, J. R. Weertman and R. W. Siegel, *J. Mater. Res.*, **6**(1991), 1012.
[9] M. R. Fitzsimmons, J. A. Eastman, M. Maeller-Stach and G. Wallner, *Phys. Rev.*, **44B**(1991), 2452.