Thermal stability of electrical and magnetic properties of a nanocrystalline Hf–Ni alloy

By Z. F. D. ONG†‡, L.-M. PENG†, R. L. Buck§ and K. L.†‡
† Beijing Laboratory of Electron Microscopy, Institute of Physics and Center for Condensed Matter Physics, Chinese Academy of Sciences, PO Box 2724, Beijing 100080, PR China
‡ State Key Laboratory for RSA, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110015, PR China
§ Max-Planck-Institut für Metallforschung, D-70174, Stuttgart, Germany

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Abstract

The thermal stability of a nanocrystalline (NC) Hf_{11}Ni_{89} alloy was studied using X-ray diffraction, transmission electron microscopy, resistivity measurements and magnetothermal analysis. Microstructure and composition evolution in the grain boundaries and nanograins prior to evident grain growth was detected, and it was shown that this evolution may have a significant influence on the electrical resistivity and magnetic properties of the sample. Our findings demonstrated that the thermal stability of properties of NC materials is not necessarily equivalent to the grain-size stability of the same materials.

§ 1. Introduction

Nanocrystalline (NC) materials are structurally characterized by their ultrafine grains (Siegel et al. 1988, Gleiter 1989), and their thermal stability is usually characterized by grain growth temperature during an isochronal heating process. In recent years the problem of the thermal stability of NC materials has attracted considerable attention among materials scientists (Ganapathi et al. 1991, Siegel 1992, Lu 1993, Gertsman and Birringer 1994, Klement et al. 1995, Lu et al. 1995, Suryanarayana 1995, Malow and Koch 1996, 1997, Wang et al. 1997). On the one hand, abnormal grain growth has been experimentally observed at ambient temperature or at temperatures lower than 100°C in some pure elemental NC samples (Ganapathi et al. 1991, Gertsman and Birringer 1994, Klement et al. 1995). On the other hand, most NC alloys exhibit high grain-size stability even at elevated temperatures, regardless of the synthesizing methods (Siegel 1992, Lu 1993, Lu et al. 1995, Suryanarayana 1995, Malow and Koch 1996). Although the grain-size stability in NC alloy systems is rather high, one may ask whether or not the grain-size stability is equivalent to the thermal stability of physical properties against microstructure evolution, and the latter is of crucial importance for designing new NC materials for industrial applications. Physical property change has been rarely reported before the detectable grain growth process in NC materials. It is the aim of this work to investigate the microstructure evolution prior to any observable grain growth in a NC Hf_{11}Ni_{89} alloy, as well as its influence on the electrical and magnetic properties of the alloy.

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§ 2. Experimental details

A NC Hf$_{11}$Ni$_{89}$ alloy was prepared by the melt-spinning technique, and experimental details have been described previously (Bakonyi et al. 1995). X-ray diffraction (XRD) spectra were recorded with a Rigaku X-ray diffractometer (max-rA; 12kW) using copper K$_\alpha$ radiation as the X-ray source. Transmission electron microscopy (TEM) observation was carried out on a Philips CM12 microscope. A traditional dc four-probe technique was used to measure the electrical resistivity of a certain sample corresponding to different heat-treatment conditions. The geometrical constant of this arrangement was calibrated using a copper foil. The isothermal heat treatment of the sample was performed in a differential scanning calorimeter (Perkin-Elmer DSC-7), and the temperature measurement was calibrated using standard pure indium and zinc samples. Magnetic properties were measured using a magnetothermal analysis (MTA) method via a Faraday-type magnetic balance (Beisswenger and Wachtel 1955). The temperature accuracy of the device was calibrated to be ±2°C. An alumina crucible was used as sample holder.

§ 3. Results and discussion

A HfNi$_5$ nanophase compound with randomly oriented grains has been identified in the as-quenched sample, and the grains have an average size of about 10 nm (Lu et al. 1995). Figure 1, curve a, shows the XRD spectrum obtained from an as-quenched sample. The average grain size was estimated to be 7.4 nm from the peak broadening using the Scherrer equation and neglecting the microstrain contribution. It is also seen that each diffraction peak can be indexed as resulting from the

![Figure 1. XRD spectrum for the as-quenched sample (curve a) and the sample isothermally annealed at 340°C for 100 min (curve b) and 510 min (curve c).](image-url)
HfNi$_5$ compound. It should be noted, however, that the (311) peak in this figure is asymmetric. This asymmetry may be attributed to the overlap between the (111) peak of nickel and the (311) peak of HfNi$_5$, suggesting the existence of a Ni(Hf) solid solution in the as-quenched state together with the HfNi$_5$ nanophase. The existence of the Ni(Hf) solid solution phase has also been confirmed by the field dependence of magnetization and MTA measurements, although its volume fraction and dimensionality are very small (Lück et al. 1998). Figure 1, curve b, shows the XRD spectrum obtained from a sample which was isothermally annealed at 340°C for 100 min. The onset temperature for grain growth of the HfNi$_5$ phase is 401.5°C at a constant heating rate of 10°C min$^{-1}$ (Lu et al. 1995). Since the annealing temperature used here is well below the grain-growth temperature, the grain size is expected to remain unchanged during the annealing process and this point will be further discussed in view of our TEM observations in the next paragraph. Figure 1, curve b, shows distinct (111) and (200) diffraction peaks of the Ni(Hf) phase. This suggests that a second precipitation process of the Ni(Hf) phase may exist during the isothermal annealing process. When the annealing time reaches 510 min, the diffraction feature resulting from the Ni(Hf) phase becomes more evident (figure 1, curve c), indicating that more precipitation has occurred. The essential deviation of the (111)$_{\text{Ni}}$ peak position towards the lower 2$\theta$ side is evidence for the substitution of the larger hafnium atoms on some sites of the smaller nickel atoms (refer to the standard diffraction position as indicated by the vertical broken line in figure 1). A shift in the (111)$_{\text{Ni}}$ diffraction position towards a larger value 2$\theta$ with increasing annealing time may also be identified in the figure, suggesting a depletion process of hafnium atoms in the Ni(Hf) phase.

The dark-field (DF) TEM image taken from the as-quenched sample is shown in figure 2(a). The average grain size is measured to be about 10 nm, slightly larger than

![Figure 2. DF TEM images for (a) the as-quenched sample and (b) the sample annealed at 340°C for 510 min.](image)
that estimated from the XRD result. This result is indeed consistent with the XRD result when taking into consideration the fact that microstrain exists in the as-quenched sample owing to the rapid quenching rate in the preparation of the sample. Figure 2(b) is a DF image for the sample annealed at 340°C for 510 min. No evident difference in the grain size of the NC alloy can be identified from the two DF images. We therefore conclude that the microstructure evolution of the Ni(Hf) phase (including its volume fraction and composition) takes place prior to grain growth during an isothermal annealing process. A similar phenomenon has also been observed during a non-isothermal annealing process.

To investigate the influence of the microstructure evolution prior to the grain growth on the physical properties of the material, the variation in electrical resistivity and magnetic properties with isothermal annealing time was measured. Figure 3(a) shows the electrical resistivity of a sample with the cumulative isothermal annealing time at 340°C. It is seen that the resistivity decreases dramatically from 90 to 75 µΩ cm after the sample had been annealed at 340°C for 510 min. This observation is consistent with the formation of a second precipitation and hafnium depletion process of the Ni(Hf) phase, since the resistivity of the Ni(Hf) phase is much lower than that of the HfNi$_5$ compound phase. The variation in the electrical resistivity with the annealing time indicates that the electrical resistivity of NC materials is not stable although the grain size of the NC material remains roughly the same for different annealing treatments.

Based on the MTA measurements, the two characteristic parameters of the effective paramagnetic Curie temperature $T_C$ and the Curie–Weiss slope $\partial(1/\chi)/\partial T$ may be determined from the relationship between the susceptibility and temperature. In general, $T_C$ increases with decreasing hafnium concentration in the Ni(Hf) phase, and the Curie–Weiss slope increases with increasing $T_C$ and decreases with increasing volume fraction of the Ni(Hf) phase (Lück et al. 1998). Figure 3(b) shows the variations in these two parameters with the annealing time at 313°C. The effective paramagnetic Curie temperature $T_C$ increases (by about 100%) quickly during the initial stage and then approaches an approximate saturation, suggesting a significant depletion process of the hafnium concentration in the Ni(Hf) phase. This observation is consistent with the XRD measurement results that the (111)$_{Ni}$ peak shifts to a larger 2θ value during the isothermal annealing process. This may result from the diffusion of hafnium atoms in the Ni(Hf) phase as well as the precipitation of a Ni(Hf) phase with a lower hafnium concentration. As for the Curie–Weiss slope, it decreases initially and then increases with increasing annealing time for about 100 min. This is because the decreasing Curie–Weiss slope is compensated by the increase in $T_C$ value (there is a correlation between them (Lück et al. 1998)). After passing through a maximum, the Curie–Weiss slope decreases again with increasing annealing time when $T_C$ remains nearly unchanged. The decrease in the Curie–Weiss slope provides further evidence for the second precipitation process of the Ni(Hf) phase during the isothermal annealing treatment even at 313°C, which is well below the onset temperature for grain growth of the HfNi$_5$ phase.

On the basis of our experimental results, we may conclude that the observed high grain-growth temperature of the NC materials may not necessarily mean that they have an inherent thermal stability against microstructure and composition change. Some properties of the NC materials may be unstable well below the detectable grain-growth temperature.
§ 4. CONCLUDING REMARKS

In this letter we have shown that microstructure evolution takes place prior to any evident grain growth process in a NC Hf\textsubscript{11}Ni\textsubscript{89} alloy, and this microstructure evolution significantly affects the electrical and magnetic properties of the NC alloy. Our findings have demonstrated that certain properties of NC materials may be unstable before the onset of grain growth, indicating that property stability may not necessarily be equivalent to grain-size stability in NC materials.

Figure 3. (a) Variation in the room-temperature resistivity with the annealing time at 340°C. (b) Variations in the effective paramagnetic Curie temperature and the Curie–Weiss slope with the annealing time at 313°C.
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