Curie Transition of NC Nickel by Mechanical Spectroscopy and Magnetization Study *

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Mechanical spectroscopy measurement is performed to study the internal friction of nanocrystalline (NC) nickel with an average grain size of 23 nm from room temperature to 610 K. An internal friction peak is observed at about 550 K, which corresponds to the Curie transition process of the NC nickel according to the result of magnetization test. Moreover, the fact that the Curie temperature of NC nickel is lower than that of coarse-grained nickel is explained by an analytical model based on the weakening of cohesive energy.

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NC materials are the subject of very intensive studies in the last years in viewpoints of basic research and applications.[1,2] Mechanical spectroscopy test, as a sensitive technique, has been widely used to study structures, crystal defects, dislocations, atomic diffusion and phase transitions of bulk materials.[3−7] In the past decades, mechanical spectroscopy has also been employed to investigate the structure, relaxation of grain boundaries and dislocations of NC materials.[8−13] However, litter attention has been paid to the phase transition of NC materials by mechanical spectroscopy measurement. In this Letter, we report the experimental results on the phase transition of NC nickel combined with magnetization test.

Thin bar-shaped NC nickel foil for mechanical spectroscopy measurements were purchased from Goodfellow Corp. The average grain size of the as-received NC nickel 150-μm-foil is determined to be about 23 nm by transmission electron microscopy (TEM) observation, as shown in Fig. 1. The chemical composition of the as-received Ni was analysed by x-ray fluorescence spectroscopy and was listed below in atomic contents: Ni 98.8%, Al 0.52%, Na 0.30%, Si 0.155%, S 0.09%, Fe 0.025%, Co 0.04%, Cl 0.04%, and K 0.03%. The internal friction and resonant frequency of the material were measured by vibrating reed method. Three samples were used, sample 1 was cut from the as-received thin foil; samples 2 and 3 were cut from the thin foil, heated up to 393 and 423 K, kept for 3 min and then cooled down to room temperature, respectively. It has been reported that the change of the grain size of NC nickel was very small when the material was annealed at temperature below 423 K for 1 h.[14] Thus, the variations of grain sizes for samples 1, 2 and 3 can be neglected as a first-order approximation. The sample was mounted in clamped-free (cantilever) arrangement and then heated up to 610 K with the heating rate of about 1-1.5 K/min.

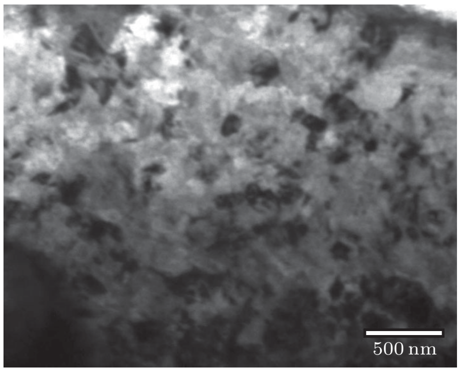

Fig. 1. Microstructure image of the NC nickel.

Figure 2 shows the internal friction and normalized dynamic Young's modulus of these three samples. It is noted that the dynamic Young's modulus is proportional to the square of the resonant frequency and is normalized to the value of room temperature. The reliability of data above 560 K during the measurement of sample 3 is questionable because the vibration signals above this temperature are irregular. Thus, only the data below 560 K are given, as shown in Fig. 2(c). It can be seen from Fig. 2 that the internal friction increases with temperature up to about 550 K and then a sharp decreasing appears at higher temperatures. The occurrence of this internal friction peak of NC nickel is similar to the results of the mechanical spectroscopy study of coarse-grained nickel

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where the appearance of an internal friction peak is attributed to the Curie transition process.[15] Therefore, the internal friction peak shown in Fig. 2 may also correspond to the Curie transition of NC nickel noted that the Curie temperatures of ferromagnetic NC materials have been found experimentally and theoretically to be lower than those of their coarse-grained counterparts.[16,17] In order to confirm this expectation, the magnetization test of a specimen cut from the as-received foil was performed at vibrating sample magnetometer (VSM) from room temperature to 610 K with the magnetic field being 2000 Oe and the heating speed being 5 K/min. Figure 3 shows the $M-T$ and $M^{-1}-T$ curves of the sample where the magnetization of the as-received nickel decreases markedly with increasing temperature up to 577 K and only a slight decrement of the magnetization takes place at higher temperatures. The Curie temperature of the NC nickel determined from $M^{-1}-T$ curve is 577 K, which is in agreement with the peak temperature obtained from mechanical spectroscopy measurement. This correspondence indicates that the internal friction peak of the NC nickel shown in Fig. 2 is caused by the Curie transition process. Moreover, the peak temperature obtained from mechanical spectroscopy measurement is 27 K lower than the Curie temperature determined by magnetization test, which results from the effect of stresses on the magnetic ordering processes and related fluctuation processes.[18]

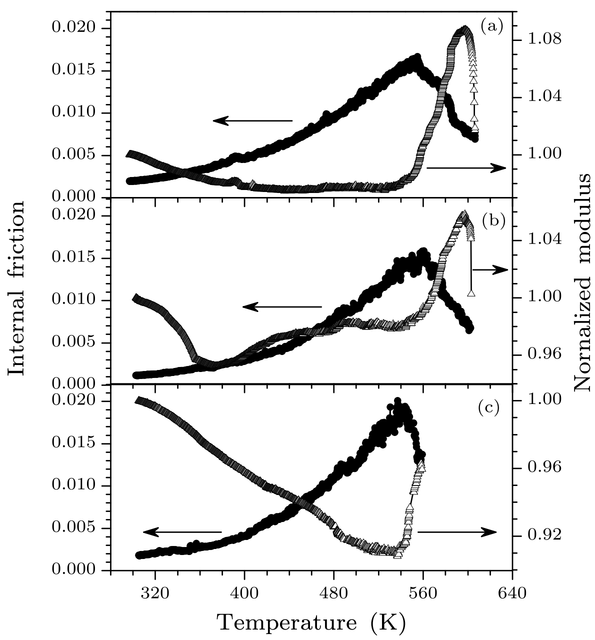

Fig. 2. Temperature dependence of the internal friction and normalized Young's modulus of (a) sample 1, (b) sample 2, (c) sample 3.

The Curie temperature is one of the most important magnetic parameters to describe the phase stability of NC Nickel. It is well known that the Curie temperature of coarse-grained nickel is 631 K.[19] However, the Curie temperature of the NC nickel is lower than that of coarse-grained nickel, as shown in Figs. 2 and 3. A number of theoretical models have been developed to explain the decreasing of Curie temperature.[20−22] Recently, the decrease of Curie temperature has been found to be originated from the weakening of cohesive energy in terms of the bond order-length-strength correlation mechanism and the Ising premise.[16,23] Combining the size-dependent melting temperature model, we have developed an analytic expression to model the size-dependent Curie temperature $T_c(D)$ of ferromagnetic nanocrystals,[16,23]

$$\frac{T_c(D)}{T_{c0}} \approx \exp\Big(-\frac{2S_{\rm vib}}{3R}\frac{1}{D/6h-1}\Big), \qquad (1)$$

where T_{c0}, h and R denote the bulk Curie temperature, atomic diameter, and the ideal gas constant, respectively. $S_{\rm vib}$ is the vibrational component of the melting entropy S_m at the bulk melting temperature, and $S_{\rm vib} \approx S_m$ can be employed for metals.[24,25] Figure 4 shows the comparison among the model predictions of Eq. (1) and our measured results where good agreement can be observed.

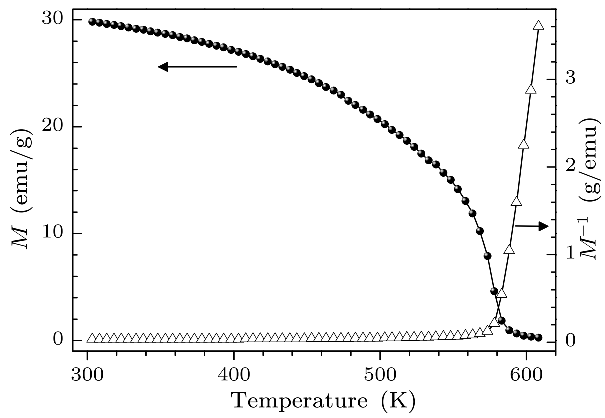

Fig. 3. Magnetization-temperature curves of the NC nickel.

As shown in Fig. 2, Young's modulus below 550 K is dependent on thermal treatments. In Figs. 2(a) and 2(b), slight increment of Young's modulus is observed in the temperature range 380–550 K. These are consistent with the mechanical spectroscopy studies of NC Pd[26] and Fe,[27] where the increasing Young's modulus is considered to be caused by the atomic rearrangement at grain boundaries.[27,28] However, the monotone decreasing of Young's modulus is observed from room temperature to 550 K in Fig. 2(c). This behaviour is very surprising because atomic rearrangement at grain boundaries should occur in this temperature range and the reason needs further study. It is found in Figs. 2(a) and 2(b) that Young's modulus increases dramatically from 550 to 600 K and then decreases above 600 K, which are similar to the behaviour of coarse-grained nickel.[28] These phenomena are caused by the behaviour of magnetoelastic strain induced by magnetostriction.[29,30] A minimum and then sharp decreasing of the magnetoelastic strain appear at a certain temperature.[15,29,30] Thus the sharp increasing of Young's modulus occurs at this temperature because Young's modulus is determined by the ratio of the applied stress to the total strain where the total strain is the sum of elastic strain and magnetoelastic strain.[29,30] When the magnetoelastic strain reaches zero, the largest Young's modulus should appear and then the decreasing of Young's modulus can be observed at higher temperatures because only the elastic strain comes into play at these temperatures. It is well known that the largest Young's modulus of coarse-grained nickel situates at the Curie temperature (631 K). However, the largest Young's modulus of NC nickel locates at 600 K, 23 K higher than the Curie temperature (577 K) of the NC nickel. The reason for this difference is uncertain and the interpretation of the increasing of Young's modulus above Curie temperature of the NC nickel awaits the development of a theoretical model in ferromagnetic nanocrystals.

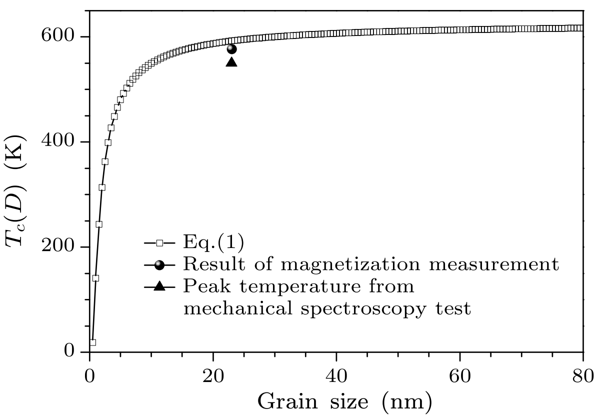

Fig. 4. Curie temperature as a function of average grain size where $T_{c0} = 631\,\mathrm{K}$, $h = 0.2492\,\mathrm{nm}$ and $S_m = H_m/T_m \approx 9.95\,\mathrm{J{\cdot}mol^{-1}K^{-1}}$ with melting enthalpy $H_m = 17.2\,\mathrm{kJ{\cdot}mol^{-1}}$ and melting temperature $T_m = 1728\,\mathrm{K}$.[31]

In summary, the mechanical spectroscopy and magnetization studies of NC nickel with an average grain size of about 23 nm have been performed from room temperature to 610 K. An internal friction peak is observed at about 550 K, which corresponds to Curie transition process of NC nickel according to the magnetization measurement. The Curie temperature of NC nickel is lower than that of coarse-grained nickel, which can be explained by an analytical model. Moreover, the behaviour of Young's modulus below 550 K is dependent on the thermal treatment of the NC nickel while the abrupt increasing of Young's modulus at 550 K is considered to be resulted from magnetoelastic strain.

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