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Low temperature heat capacity and thermal stability of nanocrystalline nickel

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Abstract

The heat capacity (C_p) of nanocrystalline nickel (nc-Ni, 40 nm crystallite size) has been measured over the temperature range of 78–370 K with a high-resolution automated adiabatic calorimeter. The measured results are compared with the C_p values of the corresponding coarse-grained crystal, and an enhancement of heat capacity of the nanocrystalline nickel was observed to be 2–4% in the temperature range between 100 and 370 K. The thermal stability of the nanocrystalline nickel sample was determined by a differential scanning calorimeter and a thermogravimetric system. The melting point of nc-Ni is the same as that of the corresponding coarse-grained crystalline nickel and the sample is stable at temperature lower than 500 K.

Keywords: Nanocrystalline nickel; Phonon specific heat; Adiabatic calorimeter

1. Introduction

Nanometer-sized crystalline (nanocrystalline) materials are polycrystals in which the particle size is in the order of 1∼100 nm. Those materials differ from glasses and crystals in the sense that they exhibit little short-range or long-range order. A series of novel physical and chemical properties of the nanocrystals, such as high diffusivity and reactivity, great ductibility, large thermal expansion, enhanced phonon specific heat, and a significant change in the magnetic susceptibility, relative to the corresponding coarse-grained ploycrystals, have captured the attention of the scientists and engineers because of their potential application [1]. Although a variety of physical properties of nanocrystalline materials were extensively studied with an eye to engineering applications, the thermodynamic properties have received less attention. Rupp and Birringer [2] studied the heat capacity of nanocrystalline Cu and Pd, and enhanced heat capacities were observed in the temperature range of 150–300 K. Similar results have been reported by Korn et al. [3], Hellstern et al. [4], Lu et al. [5], Chen et al. [6], Wanger [7] and Bai et al. [8].

Nanocrystalline nickel is an important catalyst in the chemical industry, and possesses application perspective as magnetic material. Heat capacity is an important thermodynamic property and is directly related to the structure and energy of substances. Nanocrystalline state materials have unique properties different from those of the conventional state materials. In order to understand the special properties and develop the application of type of this nanocrystal, it is of interest to investigate its heat capacity and thermal stability.

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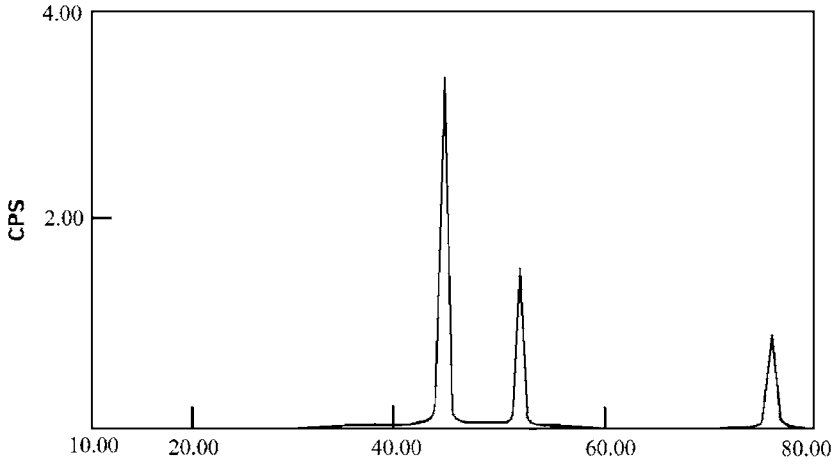

Fig. 1. X-ray diffraction pattern of nanocrystalline nickel.

2. Experimental

The powder sample of nanocrystalline nickel (nc-Ni) was produced by Zhengyuan Nano-materials Engineering Corp. (Shandong, China). The labelled chemical purity is not less than 99 at.%. The average crystallite size is 40 nm which was deduced from the Ni (111) peak broadening of the corresponding X-ray diffractometer curve (Fig. 1) (Cu Kα radiation). The density of the nc-Ni sample determined from mass and volume measurements is 7.68 g cm^{-3}, which is about 86% of the coarse-grained crystalline density (8.90 g cm^{-3}).

Heat capacity measurement was carried out by an automated adiabatic calorimeter for small samples. The construction of the calorimeter has been described previously in detail [9]. Briefly, the construction of the calorimeter included a sample cell, a thermometer, a heater, two adiabatic shields, two sets of 8-junction chromel-copel thermocouples, and a high vacuum system. The calorimeter cell was made of gold-plated copper with internal capacity of 6 cm^3. A miniature platinum resistance thermometer made by Shanghai Institute of Industrial Automatic Meters, China, was used to measure the temperature of the calorimeter cell. The thermometer with an uncertainty of about 1 mK (in absolute) was calibrated on the basis of ITS-90 by the station of low temperature metrology, Chinese Academy of Sciences. The thermometer was placed in the copper sheath at the bottom of sample cell. After loading the sample into the cell, the up-cover and body was sealed with a special kind of cycleweld. The cell was evacuated, and then a small amount of helium gas introduced through a copper capillary on the up-cover to promote the heat transfer. Finally, the cell was sealed by pinching off the tube. Two adiabatic shields surrounded the cell and controlled its temperature. The whole calorimetric system was kept in a high vacuum with residual pressure of 10^{-3} Pa to obtain good adiabatic conditions. In order to verify the reliability of the calorimeter, the molar heat capacity of α-Al_2O_3 was measured in the temperature range 60–350 K. Deviations of the experimental results from the smoothed curve lie within ±0.2%, and the inaccuracy is within ±0.5%, as compared with those of the National Bureau of Standards [10] over the investigated temperature range. The amount of nc-Ni sample used for heat capacity measurement is 3.0277 g.

A differential scanning calorimeter (DSC, NETZSCH STA409) and a thermogravimetric system (Amp TG-20, Shimadzu) were employed to determine the thermal stability of the sample.

3. Results and discussion

Heat capacity of nc-Ni was measured over the temperature range from 78 to 370 K. The curve of C_p as a function of temperature is plotted in Fig. 2. No thermal anomaly is observed over the investigated temperature range. The experimental heat capacity

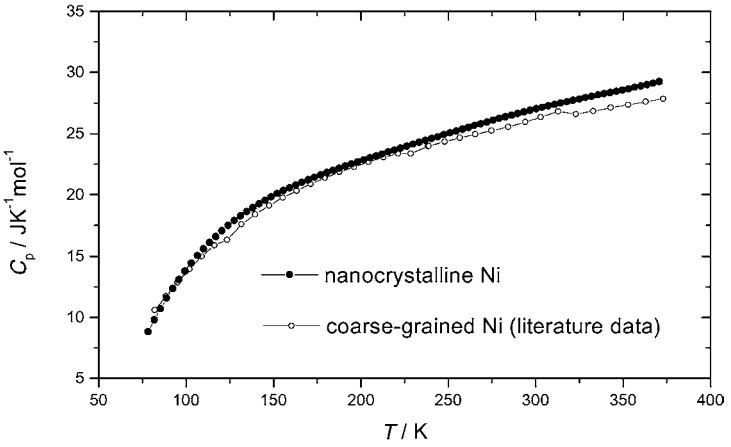

Fig. 2. Experimental molar heat capacity of nanocrystalline nickel as a function of temperature, and the literature molar heat capacity of conventional nickel as contrast.

$JK^{-1}mol^{-1}$ data was fitted to the polynomial in reduced temperature (X) by the least-squares fitting.

$$C_p = 23.8580 + 6.4801X - 0.6285X^2 + 0.2420X^3 - 4.3141X^4 + 3.3587X^5$$

where $X = (T-224.5)/145.5$, $T = 79$ K to $T = 370$ K.

The deviation of experiment heat capacity data from the polynomial is less than 0.3% in investigated temperature range.

The enhancement of C_p in going from the coarse-grained crystalline [11] to the nanocrystalline state varies between 2 and 4% for Ni in the temperature from 100 to 370 K (Fig. 2). Nanocrystalline samples can be generally described as a two-component system [12] consisting of the nanocrystallines and the grain or interphase boundary components. The heat-capacity enhancements in the nc-materials are usually associated with an increase in the configurational and vibrational entropy of the grain boundaries, which constitute a large volume fraction of the material. The atomic fraction of the grain-boundary component can be approximately estimated to be $3\delta/d$, where d is the average size of crystalline and δ is the average thickness of interfaces which is known to be on the order of three or four atomic layers. For the nc-Ni with $d = 40$ nm, about 10% atoms are on the grain boundaries. Hence, the grain-boundary configurations or the grain-boundary energy should be responsible for the C_p enhancements. In fact, the relative density of nc-Ni is 87% indicting a more open atomic structure of the grain-boundary component than coarse-grained polycrystalline Ni, and hence weaker interatomic coupling, which should enhance C_p, as observed.

DSC was used to investigate the thermal stability and melting of nc-Ni. Pure argon (99.999%) was used to purge the sample cell in the DSC with flowing rate of 100 ml/min. Each sample of about 15 mg was measured with a heating rate of 20 K/min. The result shown in Fig. 3 indicating that the melting temperature is 1725.8 ± 0.5 K, which has no significant difference with that of coarse-grained polycrystalline Ni. This does not agree with previous works [13] which reported a notable lower melting temperature of nc-materials. It is interesting to investigate this further to understand the underlying mechanism.

In order to determine oxygenation of nc-Ni, a thermogravimetric system was used at the condition of static state air and argon atmosphere. The TG curves were shown in Fig. 4 indicating that a slight increase on the weight in the air atmosphere due to the formation of a light oxygenation layer even at temperature of 323 K. Thus, the sample has been stable, and the deep oxygenation took place at a temperature higher than 500 K. Based on the calculation of weight increase, the last production for nc-Ni should be Ni → NiO. In argon atmosphere, significant weight increase was observed at a temperature higher than 800 K.

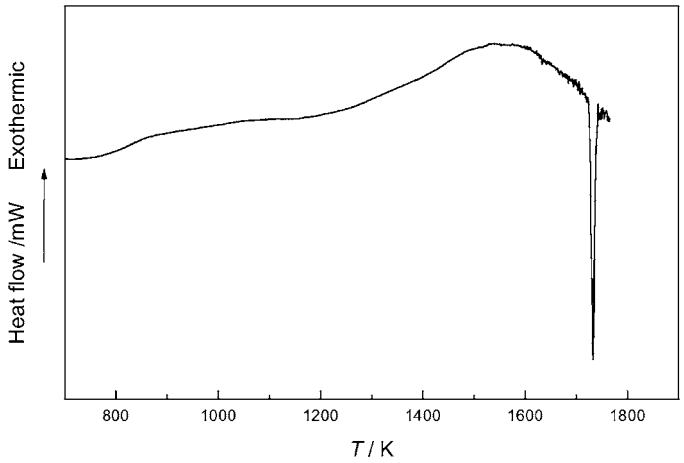

Fig. 3. DSC curve as a function of temperature of nanocrystalline nickel.

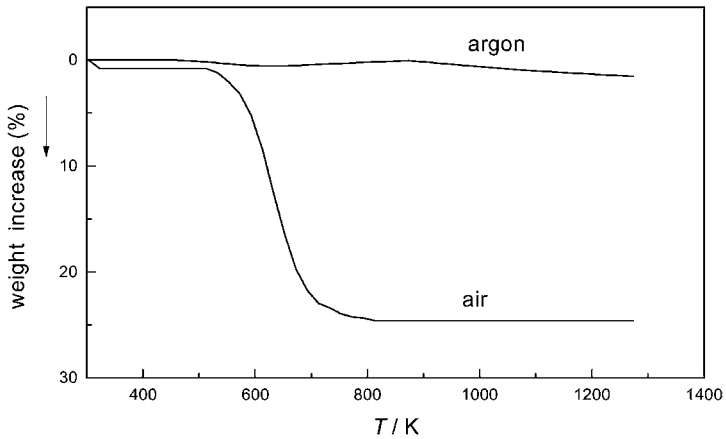

Fig. 4. TG curves as a function of temperature under the condition of air and argon.

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