PHYSICAL REVIEW B VOLUME 36, NUMBER 15 15 NOVEMBER 1987-II

Enhanced specific-heat-capacity (c_p) measurements (150–300 K) of nanometer-sized crystalline materials

J. Rupp and R. Birringer
Werkstoffwissenschaften, Universität des Saarlandes, Fachbereich 12.1, Bau 2, D-6600 Saarbrücken, West Germany

(Received 26 May 1987)

Nanometer-sized crystalline materials are polycrystals with a crystal size of a few (1–10) nanometers. Because of the small crystallite size, these materials consist of two components with comparable volume fractions: a crystalline component comprising all atoms located in the lattice of the crystallites (grains) and an interfacial component formed by all atoms situated in the interfaces (grain boundaries). In order to test the influence of the interfacial component on the specific heat c_p, nanometer-sized crystalline Pd (6 nm crystal size) and Cu (8 nm crystal size) were measured and the results compared with the c_p values for polycrystalline Pd, Cu, and a corresponding $Pd_{72}Si_{18}Fe_{10}$ metallic glass. Specific-heat measurements in the temperature range between 150 and 300 K revealed that the c_p values of nanometer-sized crystalline Cu were about 10% higher than in the polycrystalline state and that the values for nanometer-sized crystalline Pd were about 40% higher than in crystalline Pd or 30% higher than in the metallic glass $Pd_{12}Si_{18}Fe_{10}$.

INTRODUCTION

As many properties of solids depend primarily on the nearest-neighbor configurations, e.g., interatomic potentials or the exchange energy of 3*d* ferromagnets, it would seem of interest to develop a new category of solid materials which differ from glasses and crystals in the sense that they exhibit little short-range or long-range order (Fig. 1). It has been suggested recently that this new type of solid-state structure exists in nanometer-sized crystalline materials[1-3] for the reasons discussed below.

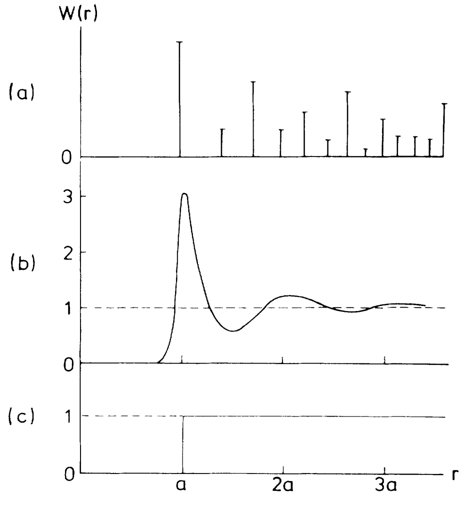

FIG. 1. The probability functions, $W(r)$, for interatomic distances of a one-element system which expressed the probability that the centers of two specified atoms should lie at a distance r apart. (a) Long-range ordered crystalline structure; (b) short-range ordered glassy structure; (c) neither long- nor short-range ordered structure.

Nanometer-sized crystalline materials are polycrystals in which the size of the individual crystallites is on the order of several (1–10) nanometers (Fig. 2). Structural investigations by transmission electron microscopy,[4] x-ray diffraction,[5] positron annihilation,[6,7] hydrogen solubility,[8] and Mössbauer spectroscopy[9] have indicated that nanometer-sized crystalline materials consist of the following two components: a crystalline component formed by all atoms located in the lattice of the crystallites (grains) and an interfacial component comprising all atoms which are situated in the grain (or interphase) boundaries between the crystallites. The volume ratio of

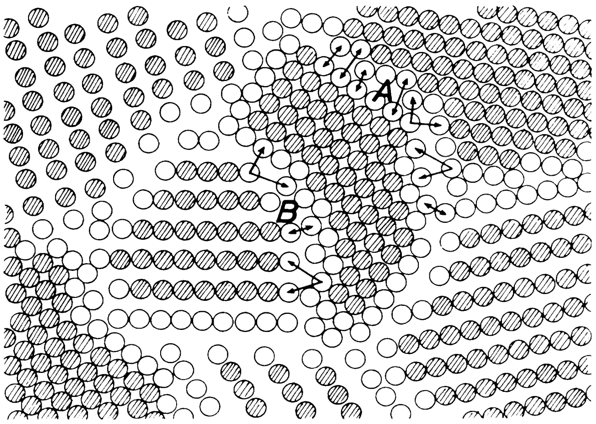

FIG. 2. Schematic cross section through a nanometer-sized crystalline material (hard-sphere model). The different interatomic spacings in the grain boundaries *A* and *B* are indicated by arrows. In reality, the atoms are known to relax from the ideal lattice sites given by a hard-sphere model. The relaxation involves the atoms at the boundary and extends several layers into the lattice of the adjacent crystals (Ref. 2).

the interfacial component to the crystalline component may be estimated by $3\delta/d$ where d is the average size of the crystallites and δ is the average thickness of the interfaces which is known to be on the order of 3 or 4 atomic layers.

The atomic structure of an interface is known[2] to depend on the orientation relationship between adjacent crystals and the boundary inclination. If the crystallites are oriented at random, all of the grain boundaries of a nanometer-sized crystalline material have different atomic structures, characterized by different interatomic spacings, for example. In Fig. 2, for example, the different interatomic spacings are indicated by arrows in the boundaries A and B. A nanometer-sized crystalline material with a crystallite size of 5 nm contains typically about 10^{19} interfaces per cm^3. The interfacial component is the sum of the 10^{19} interfacial structures. If the interatomic spacings in all boundaries are different, the average of 10^{19} different boundaries results in no preferred interatomic spacings except for the one prevented by interatomic penetration (Fig. 1). Hence, it is suggested that the interfacial component represents the solid-state structure without long- or short-range order.

Consequently, the structure-sensitive properties of nanometer-sized crystalline materials are expected to be different from those of the chemically identical substances in the glassy or crystalline state. As the specific heat of a material is directly related to the atomic structure, measurements of the specific heat as a function of temperature of nanometer-sized crystalline materials should reveal differences in comparison to glassy or crystalline materials of comparable chemical composition. In order to test this hypothesis, the specific heat of nanometer-sized crystalline Cu and Pd samples was measured and compared with the values for the polycrystalline elements and for a metallic glass ($Pd_{72}Si_{18}Fe_{10}$) of approximately the same mole mass.

EXPERIMENTAL

Nanometer-sized crystalline Cu and Pd samples were prepared by means of the procedure described in Ref. 3. The average crystallite size of the disk-shaped samples (diameter 8 mm, mass 30–80 mg) was deduced from the (111) peak broadening of the corresponding x-ray diffractometer curves (Mo $K\alpha$ radiation): 6 nm for Pd and 8 nm for Cu. The density of the Cu samples determined from mass and volume measurements was about 90% of the polycrystalline density. The corresponding value for Pd was 80%. The total impurity content of both types of samples was about 1 at. %.

The specific heat c_p as a function of temperature was measured in a differential scanning calorimeter (Perkin Elmer DSC-2C) equipped with a low-temperature stage. The accuracy of the calorimeter was tested by measuring the values of c_p of polycrystalline disk-shaped Cu and Pd samples (99.99% purity) having the same mass and similar dimensions as the nanometer-sized crystalline samples. The results of these measurements are shown in Fig. 3. In comparison to reference data taken from the Refs. 10 and 11, the deviation between both sets of data is less than 2% in the entire temperature range studied.

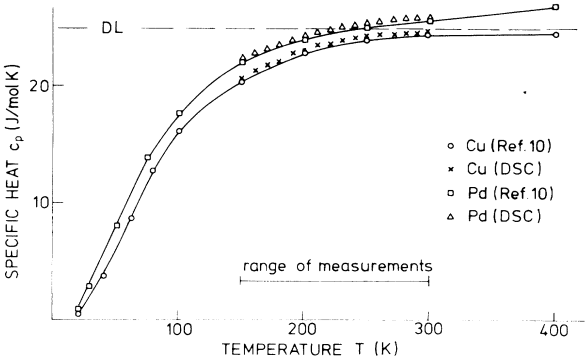

FIG. 3. Comparison of the specific-heat measured (DSC) with the data taken from Refs. 10 and 11.

RESULTS AND DISCUSSION

The curves of the specific heat as a function of temperature measured for nanometer-sized crystalline and polycrystalline Cu or Pd as well as for a metallic glass ($Pd_{72}Si_{18}Fe_{10}$) are summarized in Fig. 4. The enhancement of c_p in going from the polycrystalline to the nanometer-sized crystalline state varies between 29% and 53% for Pd in the temperature range investigated [Fig. 4(a)]. The corresponding values for Cu are 9% and 11% [Fig. 4(b)].

The c_p values of the polycrystalline Pd and glassy state ($Pd_{72}Si_{18}Fe_{10}$) differ by about 8% [Fig. 4(a)]. This deviation may arise from the different atomic structure as well as from the variation of the chemical composition. In order to estimate the significance of the second factor, the metallic glass studied was crystallized (at constant chemical composition) by annealing it for 30 min at 750 K. The decrease of c_p due to the transition from the glassy to the crystalline state was 4%. In other words, about 50% of the enhanced specific heat of the metallic glass [Fig. 4(a)] originates from the different atomic structure and the residual portion is due to the deviating chemical composition. The available copper-based metallic glasses are not suitable for a comparison because the mole mass of these glasses is more than 10% higher than the mole mass of the pure element.

Cu and Pd are diamagnetic and paramagnetic metals. Hence, electronic and magnetic contributions to the specific heat in the temperature range between 150 and 300 K are negligible. The specific heat of nanometer-sized crystalline Cu and Pd is, thus, due to the thermally induced variation of the vibrational and configurational entropy of the materials (i.e., due to lattice vibrations, variation of equilibrium defect concentration, etc.). The vibrational and configurational entropy of the crystalline state (with long-range order), the glassy state (with short-range order), and the nanometer-sized crystalline structure (without short-range order in the interfacial component) should differ to varying degrees as a function of temperature. Hence, the crystalline, glassy, and nanometer-sized crystalline samples could be expected to exhibit different specific heats, as was observed. The de-

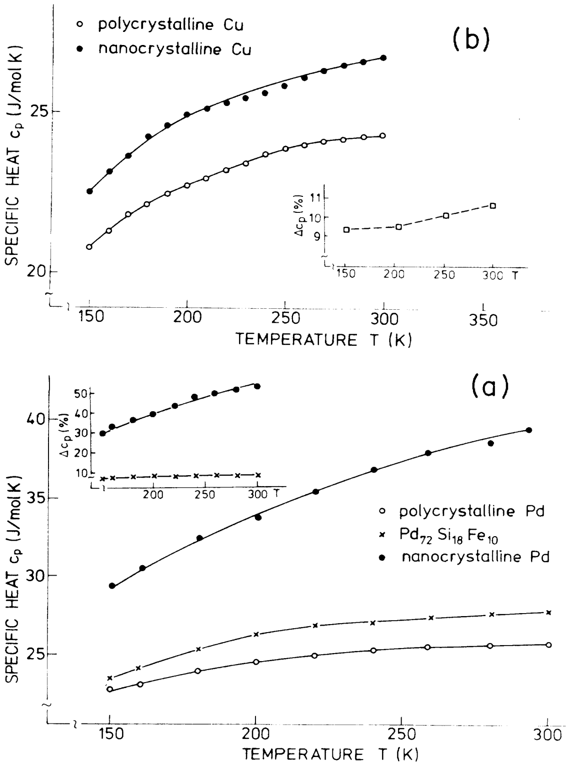

FIG. 4. (a) The specific heat (c_p) of polycrystalline Pd in comparison with nanometer-sized crystalline Pd and a corresponding $Pd_{72}Si_{18}Fe_{10}$ metallic glass. The enhancement Δc_p of the nanometer-sized crystalline Pd (●) and the metallic glass (×) relative to the polycrystalline Pd is shown in the upper left-hand corner. The mole mass of the glass (see ordinate) means the mass of N_A atoms, the type and composition of which is given by the chemical formula of the glass. (b) The specific heat (c_p) of polycrystalline Cu (○) in comparison with nanometer-sized crystalline Cu (●). The enhancement Δc_p of nanometer-sized crystalline Cu (□) relative to the polycrystalline Cu is shown in the lower right-hand corner.

viation of the crystalline and nanometer-sized crystalline states is unlikely to result from internal surfaces because small-angle x-ray diffraction,[12] positron annihilation,[6,7] and hydrogen solubility measurements[8] give little evidence of pores. The different enhancements of c_p of Pd and Cu in the nanometer-sized crystalline state seem to be consistent with the different densities of both substances. In fact, the lower relative density of nanometer-sized crystalline Pd in comparison to nanometer-sized crystalline Cu suggests a more open atomic structure of the grain-boundary component in the case of Pd, and hence weaker interatomic coupling, which should enhance c_p, as was observed. This argument implies that the enhancement of c_p is primarily due to the grain-boundary component. If this is so, grain growth should reduce the specific heat of the nanometer-sized crystalline materials to that of polycrystals. This was, in fact, observed when the nanometer-sized crystalline Cu and Pd samples were annealed in the DSC at 750 K to initiate grain growth. The grain size of the samples after annealing was 20 nm. In the case of Pd it was also observed that during the heat-up cycle an exothermic reaction took place at about 350 K. Subsequent cooling to 200 K revealed that the enhancement of the specific heat was reduced to about 5%. The grain size of the samples was unchanged or increased up to 10 nm. This observation may indicate a type of structural relaxation in the grain-boundary component.

The enhanced specific heat of nanometer-sized crystalline Cu and Pd is also consistent with the experimentally observed[13] increase of the thermal expansion of these materials. In fact, the thermal expansion of 8-nm nanometer-sized crystalline Cu is 31×10^{-6} K^{-1} in comparison to 16×10^{-6} K^{-1} for polycrystalline Cu.[13] Recent low-temperature specific-heat (c_p) measurements (3–20 K) have shown enhanced c_p values for nanometer-sized crystalline Pd.[14]

ACKNOWLEDGMENTS

The authors are indebted to Professor Gleiter and his associates (Universität des Saarlandes) for very helpful discussions. This study has been supported financially by the Bundesministerium für Forschung und Technologie (Contract No. 523/4003/03M0023-4), the Alcoa Foundation, and the Deutsche Forschungsgemeinschaft.

---

[1] H. Gleiter, in *Second Risø International Symposium on Metallurgy and Materials Science*, edited by N. Hansen, A. Horsewell, T. Leffers, and H. Lilholt (Risø National Laboratory, Raskilde, Denmark, 1981), p. 15. In Refs. 2–6, 8, and 9, nanometersized crystalline materials have also been called nanocrystalline materials.

[2] R. Birringer, P. Marquardt, H. P. Klein, and H. Gleiter, Phys. Lett. **102A**, 365 (1984).

[3] R. Birringer, U. Herr, and H. Gleiter, Suppl. Trans. Jpn. Inst. Metals **27**, 43 (1986).

[4] P. Y. Gao (unpublished).

[5] X. Zhu, R. Birringer, U. Herr, and H. Gleiter, Phys. Rev. B **35**, 9085 (1987).

[6] H. E. Schaefer, R. Wuerschum, M. Scheidt, R. Birringer, and H. Gleiter, J. Mater. Sci., Forum **15-18**, 955 (1987).

[7] H. E. Schaefer and R. Wuerschum, Phys. Lett. **119A**, 370 (1987).

[8] T. Muetschele and R. Kirchheim, Scr. Metall. (to be published).

[9] U. Herr, J. Jing, R. Birringer, U. Gonser, and H. Gleiter, Appl. Phys. Lett. (to be published).

[10] K. Clusius and L. Schachinger, Z. Metallforsch. **2A**, 90 (1947).

[11] U. F. Giauque and P. E. Meads, J. Am. Chem. Soc. **63**, 1997 (1941).