Variation of the interfacial energy with grain size in nanocrystalline materials

K. Lu*, R. Lück** and B. Predel
Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaft, Seestr. 75, D-70174 Stuttgart (Germany)

Abstract

The transformation of an amorphous Ni-P alloy was investigated calorimetrically. In particular, the formation of the interfaces in nanocrystalline Ni-P samples with grain sizes ranging from a few nanometers to 60 nm was studied. A linear increase in the interfacial excess energy was found with increasing grain size on a nanometer scale. However, a rather small interfacial excess energy was obtained when the grain size was a few nanometers. The variation of interfacial excess energy with grain size was found to correlate with that of the interfacial excess volume derived from experimental results.

1. Introduction

Nanocrystalline (NC) materials are characterized structurally by ultrafine crystallites. The properties of their grain boundary structure seem to be very interesting. The unusual properties and the special microstructure [1, 2] have been studied extensively. It is assumed that a large fraction of atoms is located at grain boundaries in NC materials. The relatively high thermal stability against grain growth [2-4] and the abnormal Hall-Petch relation [5-7] are attributed to structural and energetic properties of the NC interfaces. Several techniques have been used to study NC interfaces [1, 2], however, no general conclusion on the structure of the interfaces has yet been drawn. From many structural investigations Gleiter and co-workers [1, 8, 9] concluded that the NC boundaries are random and highly disordered without either long- or short-range order. Siegel and co-workers [2, 10] found from high-resolution electron microscopy and measurements of physical properties that the NC boundaries are in rather low energy configurations; the grain boundaries exhibited flat facets with some steps.

These structural properties of the NC interface are related to thermodynamic parameters such as the interfacial excess enthalpy, the interfacial excess entropy, and the interfacial excess free energy. Precise experimental determination of these parameters is difficult because of the porosities of the samples. Usually, the NC specimens are synthesized by evaporating the metal in an inert atmosphere, then collecting and compacting the ultrafine particles in situ into bulk samples (UFP compaction) [11], where the formation of porosities or nanometer-sized voids cannot be avoided [2].

The crystallization process of amorphous solids is being used more frequently as a method for the formation of NC materials [12, 13]. The procedure consists of rapid heating of the amorphous sample to an annealing temperature (usually below the crystallization temperature), maintaining the sample at this temperature for a certain period, so that the amorphous phase is completely crystallized, and then cooling it down. The crystallization method has the great advantage, in addition to the simple experimental procedure, that it can produce NC samples with various grain sizes from a few to a few hundred of nanometers in which only free volumes (less than monovacancies) or microvoids (of a few vacancies) are created, without any porosity or voids [14]. This property makes a more accurate study of the average grain boundary properties possible. Meanwhile, the amorphous-to-NC transformation itself allows experimental investigation of the formation process of the nanometer crystallites and interfaces [15-18].

In this study, the interfacial excess energies of NC samples with different grain sizes were determined by calorimetric measurement of the amorphous-to-NC transformation. The investigations were carried out on an Ni-P alloy. The results have shown that the NC
interfacial excess energy depends clearly on the average grain size.

2. Experimental details

By use of the melt-spinning technique an amorphous ribbon (20 μm thick and 2.1 mm wide) of composition Ni₈₀P₂₀ was prepared. X-ray diffraction and thermal analysis confirmed that the sample was amorphous. The isothermal heat treatments ranged from 627 to 565 K and formed the different grain-sized NC samples. The procedures were monitored and recorded by a differential scanning calorimeter (DSC-2, Perkin-Elmer). Both X-ray diffraction and transmission electron microscopy (TEM) experiments gave evidence that the as-crystallized samples were completely crystalline with ultrafine grains, while the overall composition was not changed. Two crystalline phases were formed in the as-crystallized NC Ni-P samples: nickel solid solution (f.c.c.) and the Ni₃P compound (b.c.t.) [18]. The following relationship of the orientations of the two phases was found: (001)bct∥(110)fcc and (110)bct∥(111)fcc. The crystalline phases and their orientation relationship in the as-crystallized samples did not change at the various annealing temperatures. The only difference between the as-crystallized Ni-P samples formed at different temperatures was the grain size.

The grain size in the as-crystallized Ni-P samples were determined experimentally by both X-ray diffraction (XRD, according to the half-maximum width of the diffraction line) and high-resolution electron microscopy (HREM)[13]. The experimental results for the average grain sizes obtained using both methods coincide closely. In Fig. 1 the Ni₃P grain sizes (determined from the (341) bct line in the XRD diagram) are represented for various annealing temperatures Tₐ. The Ni₃P grain size increases with increasing annealing temperature. The nickel solid solution grains are even smaller than the Ni₃P grains; the average grain size of nickel grains is about 0.63 d_bct, which can also be measured from HREM observations [18].

Calorimetric measurements of the amorphous-to-NC transformation were taken with the DSC-2, for which the temperature (with an accuracy of ±0.02 K) and energy (±0.04 mJ s⁻¹) calibrations were done using pure In and Zn standard samples. Aluminum pans were used for both the sample and the reference.

3. Experimental results

The amorphous Ni-P sample transforms during isothermal heat treatment into an NC sample. The transformation is indicated by a single exothermal peak in the DSC signals. The enthalpy change of the transformation was determined from the exothermal peak area. These data are represented in Fig. 2 for different temperatures of heat treatment. The absolute value of ΔH increases with a rise in annealing temperature, from 3.789 kJ mol⁻¹ at 565.1 K to 4.221 kJ mol⁻¹ at 627.0 K, which is the upper limit of isothermal annealing temperature. To extrapolate the ΔH vs. T relationship the higher temperatures, a linear heating technique with various heating rates ranging from 10 to 160 K min⁻¹ was used to crystallize the amorphous sample. A similar procedure which monitors the magnetic susceptibility with heating rates ranging from 2 to 20 K min⁻¹ is reported in ref. 16. As the crystallization process occurs within a temperature range on linear heating, the peak temperature of the exothermal peak was approximated as an average temperature of the transformation. These data are additionally represented in Fig. 2. The plot shows that the data for linear

Fig. 1. Average grain size of the Ni₃P phase d_bct (measured from the X-ray diffraction spectrum) vs. annealing temperature Tₐ.

Fig. 2. Data of the heat energy released during the amorphous-to-NC transformations vs. annealing temperature Tₐ, and the variation in enthalpy change to the amorphous-to-crystal transformation with temperature.
heating are consistent with the isothermal data, showing a common tendency of continuous variation of $\Delta H$ with $T_r$.  

4. Discussion

The enthalpy change for the amorphous-to-crystalline transformation process may be described by

$$\Delta H^{a \rightarrow b}(T) = \Delta H^{a \rightarrow b}(T_0) + \int_{T_0}^{T} (C_p^a - C_p^c) \, dT$$  \hspace{1cm} (1)

with $\Delta H^{a \rightarrow c}(T_0)$ the enthalpy change as a specific temperature $T_0$, $T_0$ the temperature at which the amorphous phase is transformed into crystals, and $C_p^a$ and $C_p^c$ the molar heat capacities of the amorphous and crystalline phases respectively.

When the amorphous Ni-P sample is heated linearly at a large heating rate, e.g. 160 K min$^{-1}$, the crystallization products formed at higher temperatures are composed of grains so coarse that the transformation can be regarded approximately as an amorphous-to-crystalline process. The molar heat capacities [18] of the amorphous sample and the as-cast crystalline sample with coarse grains were measured experimentally by DSC together with stepwise heating [20].

The evident divergence between the two relations of enthalpy change with annealing temperature of the amorphous-to-NC and the amorphous-to-crystalline transformations is clearly displayed, and the lower the temperature the greater the difference. This significant difference between the two processes stems from the formation of interfaces in the NC samples as the interface is the only difference between the normal crystalline and NC samples.

For an amorphous-to-NC transformation, the products consist of two structures, firstly the Ni and Ni$_3$P crystalline phases and secondly the interfaces separating the crystalline grains. Most interfaces are Ni-Ni$_3$P interphase boundaries [21]. Therefore, the present amorphous-to-NC transformation is actually a eutectic decomposition of the amorphous phase into the two crystalline phases and the interface which might be considered as a separate “phase” [15].

To obtain the excess energy of the interfaces in the NC materials, one must determine the fraction of atoms in the interfaces. The interface structure and the volume fraction of the interfaces in NC Ni-P alloy samples have been studied previously [19, 21]. It is reasonable to suppose from the atomistic structure of the interfaces determined by the orientation relationship, an interface consisting of only four layers of atoms, of which the central two layers have a maximum excess energy $\Delta E_{in}$, and the neighboring layer on each side is approximated as having only half of the maximum excess energy. The volume fraction of the interfaces in the NC Ni-P samples was obtained as a function of the grain size in $1.9/\bar{d}_{\text{nc}}$ [22], in which the average grain size of the Ni$_3$P phase $\bar{d}_{\text{nc}}$ is in nanometers, and the molar fraction $\chi_{in}$ can be estimated from the density of the interfaces [21]. The molar fractions of the interfaces in the as-crystallized NC Ni-P samples are plotted vs. annealing temperature $T_a$ in Fig. 3.

Figure 4 shows the resultant data of the interfacial excess energies with different grain sizes. From this figure we have deduced that the excess energy of the interfaces depends strongly on the average grain size of the NC samples. For $\bar{d}_{\text{nc}} = 60$ nm, the interfacial excess energy is about 8.84 kJ mol$^{-1}$, which is approximately half the melting enthalpy of the Ni crystal; $\Delta E_{in}$ increases approximately linearly with increasing grain size. A steady value of 2.30 kJ mol$^{-1}$ is obtained for $\Delta E_{in}$ when $\bar{d}_{\text{nc}}$ has decreased to approximately 7 nm.
This value of interfacial excess energy, which is very close to the value of interfacial energy in the same sample measured during grain growth [23], is comparable with that of a small angle grain boundary. The small value of NC interfacial excess energy supports the HREM examinations of the grain boundaries in the NC Ni-P samples which revealed rather straight boundaries [19].

The evident decrease in the interfacial excess energy implies a significant change in the microstructure of the interfaces in the NC sample. The excess energy of an interface is regarded as closely related to the structural characteristics of the interface. Theoretical arguments and computer simulations indicate that the excess volume of a grain boundary in comparison with a perfect crystal is the most significant parameter designating the grain boundary energy [24]. The dependence on grain size of the excess energy can be correlated with the excess volume of the interfaces.

Qualitatively, a trend of increasing excess volume in the NC interfaces with an increase in grain size in the Ni-P samples was detected. A positron lifetime spectroscopy study [19] of the interfacial defects in the NC Ni-P alloys with various grain sizes indicated that there are two kinds of defect in the interfaces corresponding to the short- and intermediate-lifetime components: type I is free volume smaller than a monovacancy in size; type II is microvoids. Also, with an increase in the annealing temperature, i.e., an increase in grain size, there are more type II defects and less type I in a unit area of interface. With an increase in the grain size, the density of the interfaces decreases and, consequently, the interfacial excess volume increases. This finding is in agreement with investigations on the mechanical properties (fracture stress and fracture strain) and densities [21, 22].

From the density measurements and structural analysis of the NC Ni-P samples with grain sizes ranging from a few nanometers to 100 nm [21], the density of the interfaces $D_{in}$ was deduced quantitatively as a function of the average grain size of the Ni$_3$P phase in $D_{in} = 8.36 - 0.0189d_{in}$, where $D_{in}$ is in grams per cubic centimeter and $d_{in}$ is in nanometers. From this we can determine the excess volume of the interfaces which is defined as $\Delta V_{in} = (V_{in} - V_c)/V_c$ in which $V_{in}$ and $V_c$ are molar volumes of the interface and the perfect crystal lattice respectively. The variation in $\Delta V_{in}$ with the grain size $d_{in}$ is also plotted in Fig. 4. The excess volume of the interfaces evidently increases with an increase in the grain size, ranging from 8% to 24%, values which are close to the reported value in NC samples prepared by ultrafine particle compaction (about 10%–30% [1, 9]). The variation in $\Delta V_{in}$ with $d_{in}$ derived from the density measurement, an approximate straight line, is quite similar to that of $\Delta E_{in}$ from the calorimetric results. This agreement indicates a good correlation between the excess volume and the excess energy of the interfaces in the NC samples, which is consistent with the theoretical calculation based on the “universal equation of state (EOS)” [25]. Of course, the interfacial excess volume (as well as the interfacial excess energy) will not increase with the grain size without limit. There is a critical excess volume for the interface $\Delta V_{in}$; when $\Delta V_{in} > \Delta V_{in}^c$ the interface will be mechanically unstable [25].

The trend of decreasing interfacial excess energy with a reduction in grain size on a nanometer scale is very significant for interpreting the physical properties of the NC materials. For example, the relative high thermal stability of the NC materials in which grain growth begins at a temperature as high as 0.5 $T_m$ [3, 4], and the abnormal Hall–Petch relation in the NC samples [5–7], could be explained on the basis of the decreasing tendency of the interfacial excess energy with the grain size. The behavior of other properties of NC materials relative to the interfacial energy, such as diffusional creep, boundary diffusion, etc. may also be understood according to the present results of the NC interfacial excess energy.

5. Conclusion

The interfacial excess energy in NC Ni–P was found to increase linearly with increasing grain size at a nanometer scale, and a rather small interfacial excess energy was obtained when the grain size was a few nanometers. The variation of interfacial excess energy with grain size correlates well with that of the interfacial excess volume deduced from experimental results. These results of the NC interfacial excess energy are significant for understanding the nature of the structure and the properties of NC materials.

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References