THE INTERFACIAL EXCESS ENERGY IN
NANOCRYSTALLINE Ni-P MATERIALS WITH DIFFERENT GRAIN SIZES

K. Lu*, R. Lück, and B. Predel
Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaft,
Seestrasse 92, D-7000 Stuttgart 1, Germany
*Also with National Key Laboratory for RSA, Institute of Metal Research,
Academia Sinica, Shenyang 110015, P.R. China
(Received February 23, 1993)
(Revised March 22, 1993)

Introduction

Nanocrystalline (NC) materials, which are structurally characterized by ultrafine crystallite grains, have received much interest recently because of their unusual properties and special microstructure [1,2]. Structure and properties of the interfaces, on which a large fraction of atoms are located in NC materials, have been an important research subject. Many experimental evidences of NC materials, which are difficult to understand following the existing theories suitable to the conventional polycrystals, such as the relative large thermal stability against grain growth [2-4] and the abnormal Hall-Petch relation [5-7], should be closely related to the structure and the energetical state of the NC interfaces. Various structural analysis techniques have been applied in the study of the NC interfaces [1,2], however, no satisfactory conclusion has been reached up to now. Gleiter et al. [1,8,9] claimed from their many structural investigations that the NC boundaries may be random and highly disordered without either long- or short-range order; while from the high-resolution microscopy observation and property measurements Thomas et al. [10,2] found the NC boundaries to be in rather low energy configurations exhibiting flat facets interspersed with steps.

From a thermodynamic point of view, the structural characteristics of the NC interface can be reflected by its average thermodynamic parameters, such as the interfacial excess energy, the interfacial excess entropy, and the interfacial excess free energy, if they are available. Nevertheless, an accurate experimental measurement of these thermodynamic parameters of the interfaces in the NC samples seems difficult because of the sample porosities. The NC materials are normally synthesized by evaporating the metal in an inert atmosphere, collecting and compacting the ultrafine particles in situ into bulk samples (UFP compaction) [11]. Because an artificial compaction process is introduced, porosities or nanometer-sized voids in the bulk NC samples cannot be avoided, which create a difficulty in the study of the average properties of the NC interfaces [2].

Recently, a new synthesizing method for NC materials was developed by means of the crystallization process of amorphous solids, called the "crystallization method" [12]. The procedure of this method is: rapid heating of the amorphous sample to an annealing temperature (usually below the crystallization temperature), and maintaining at the temperature for a certain period, such that the amorphous phase is completely crystallized before cooling it down. The crystallization method has the great advantage, besides its simple experimental procedure, that it can produce NC samples with various grain sizes from a few to a few hundreds of nm in which only free volumes (less than monovacancies) or microvoids (of a few vacancies) are created, but without any porosity or voids [13]. This serves excellently for studying the average grain boundary properties more accurately. Meanwhile, the amorphous-to-NC transformation itself enables someone to investigate the formation processes of the nm-crystallites and the interfaces experimentally [14,15].

In this work, we present an investigation of the interfacial excess energy of a NC Ni-P alloy. The interfacial excess energies of the NC samples with different grain sizes have been determined by means of the calorimetrical measurement of the amorphous-to-NC transformation. The experimental results showed an evident dependence of the NC interfacial excess energy on the average grain size.
Experiments

An amorphous alloy with the composition of Ni₈₀P₂₀ (at.%) was prepared by the melt-spinning technique. The amorphism of the ribbon sample about 20 μm thick and 2.1 mm wide was confirmed by X-ray diffraction and thermal analysis. The isothermal annealing procedures at various annealing temperatures (from 627 to 565 K) to form the different grain-sized NC samples were monitored and recorded by a differential scanning calorimeter (DSC-2, Perkin-Elmer). Both X-ray diffraction and transition electron microscopy (TEM) experiments have shown that the as-crystallized samples were completely crystalline with ultrafine grains, while the overall composition stayed the same as that of the glassy sample. Two crystalline phases have been formed in the as-crystallized NC Ni-P samples: Ni austenite (fcc) and Ni₃P compound (bct) [17], between which the orientation relationship was found to be:

\[ <001>_{\text{bct}}//<110>_{\text{fcc}} \quad \text{and} \quad <110>_{\text{bct}}//<111>_{\text{fcc}} \]

The crystalline phases and their orientation relationship in the as-crystallized samples were found to stay unchanged at various annealing temperatures. The only difference among the as-crystallized Ni-P samples formed at different annealing temperatures was in the grain sizes of the crystalline phases.

The grain sizes in the as-crystallized Ni-P samples were measured experimentally by both X-ray diffraction (XRD, according to the half-maximum width of the diffraction line) and high-resolution electron microscopy observation (HREM) [12]. The experimental results of the average grain sizes obtained from the both methods coincide closely. Figure 1 shows the resultant data of the Ni₃P grain size (measured from the (341)_{bct} line in the X-ray diffraction spectrum) at various annealing temperatures, \( T_a \). Clearly, the Ni₃P grain size decreases with a reduction of annealing temperature. Ni fcc phase grains are even smaller than the Ni₃P grains, the average size of the Ni phase is about 0.63d_{bct}, which can also be identified through the HREM observations [17].

Calorimetrical measurements of the amorphous-to-NC transformation were carried out in the DSC-2, of which the temperature (with an accuracy of ±0.02 K) and energy (±0.04 mJ s⁻¹) calibrations were done by use of pure indium (In) and zinc (Zn) standard samples. Aluminium pans were used for both the sample and the reference.

Experimental Results and Discussion

Upon isothermal annealing, the glassy Ni-P sample transfers into a NC sample, exhibiting a single exothermic peak in the DSC signals. The enthalpy change or heat energy released during the transformation can be obtained by integrating the exothermal peak area from the beginning to the end of the process. Figure 2 shows the measured data of the heat energy released during the amorphous-to-NC transformations at different annealing temperatures. The absolute value of \( \Delta H \) increases evidently with annealing temperature raising, 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 the isothermal annealing temperature. To extrapolate the \( \Delta H \) vs. \( T \) relationship to higher temperatures, a linear heating technique with various heating rates ranging from 10 to 160 K min⁻¹ was applied to crystallize the glassy sample. As the crystallization process occurs within a temperature range upon linear heating, the peak temperature of the exothermal peak was approximated as an average temperature at which the transformation takes place. The data are plotted in Fig. 2, too. The plot reveals that the linear heating data are consistent with the isothermal ones, showing a common continuous variation tendency of \( \Delta H \) with \( T_a \).

The usual crystallization process, a transformation from the amorphous phase to normal crystals, can be considered as a solid state phase transformation following the classical thermodynamic theory of crystallization from the supercooled liquid. The enthalpy change for the amorphous-to-crystal process can be given by:

\[
\Delta H^{am\rightarrow c}(T) = \Delta H^{am\rightarrow c}(T_0) + \int_T^{T_0} (C_p^a - C_p^c) dT
\]

where \( \Delta H^{am\rightarrow c}(T_0) \) is the enthalpy change at a specific temperature \( T_0 \) at which the amorphous phase is transformed into the crystals. \( C_p^a \) and \( C_p^c \) are molar heat capacities of the amorphous and the crystal, respectively.

When the glassy Ni-P sample is heated linearly at a larger heating rate (say 160 K min⁻¹), the crystallization products (which are formed at higher temperature) are composed of so coarse grains (up to a few micrometers) that the transformation can be regarded approximately as an amorphous-to-crystal process. The molar heat capacities [15] of the amorphous sample and the as-cast crystalline sample with coarse grains are measured experimentally by using the DSC together with stepwise heating [16]. Their molar heats can be formulated by...
FIG. 1. Plots of the average grain size of the Ni$_3$P phase, $d_{Bct}$ (measured from X-ray diffraction spectrum) and the molar fraction of the interfaces, $x_{in}$, in the NC Ni-P samples verse the annealing temperature, $T_a$.

FIG. 2. Measured data of heat energy released during the amorphous-to-NC transformations versus annealing temperature, and the variation of the enthalpy change of the amorphous-to-crystal transformation with temperature.

$$C_p^a(T) = 22.994 + 1.01 \times 10^{-2}T - 1.605 \times 10^5T^{-2}(\text{J mol}^{-1}\text{K}^{-1})$$ (2)

and

$$C_p^c(T) = 23.585 + 0.781 \times 10^{-2}T - 1.835 \times 10^5T^{-2}(\text{J mol}^{-1}\text{K}^{-1})$$ (3)

Then, the enthalpy change for the amorphous-to-crystal transformation in the temperature range can be calculated, as plotted in Fig. 2.

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

For an amorphous-to-NC transformation, the products consist of the two structures of (i) crystalline phases, here Ni and Ni$_3$P, and (ii) the interfaces separating the crystalline grains, in this case, most interfaces are Ni/Ni$_3$P inter-phase boundaries [19]. Therefore, the amorphous-to-NC transformation is actually a decomposition process of the amorphous phase into the two crystalline phases and the interface which might be considered as a separate "phase". The enthalpy change can be expressed as:

$$\Delta H^{a\rightarrow nc}(T) = (1 - x_{in})\Delta H^{a\rightarrow c}(T) + x_{in}\Delta H^{a\rightarrow in}(T)$$ (4)

where $x_{in}$ is the fraction of atoms located in the interfaces. Then the difference between the enthalpy changes for the amorphous-to-NC and the amorphous-to-crystal should be the excess energy stored in the NC materials relative to the perfect crystal, which can be written as:

$$\Delta H^*(T) = \Delta H^{a\rightarrow nc}(T) - \Delta H^{a\rightarrow c}(T) = x_{in}\Delta E_{in}(T)$$ (5)

$\Delta E_{in}$ is the molar excess energy for the interfaces relative to the perfect crystal.

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 the NC Ni-P alloy samples have been studied previously [17, 19]. It is reasonable to suppose from the atomistic structure of the interfaces...
determined by the orientation relationship the interface consisting of only four layers of atoms, of which the central
two layers have a maximum excess energy, $\Delta E_{in}$, and the neighbouring layer on each side is approximated to have
only a half of the maximum excess energy. The volume fraction of the interfaces in the NC Ni-P samples was
obtained to be a function of the grain size in $1.9/d_{bct}$ [18], in which the average grain size of Ni$_3$P phase $d_{bct}$ is
nanometers, and the molar fraction $x_{in}$ can be estimated from the density of the interfaces [19]. The molar fractions
of the interfaces in the as-crystallized NC Ni-P samples are plotted versus annealing temperature, as shown in
Fig. 1.

Figure 3 shows the resultant data of the interfacial excess energies with different grain sizes, from which we
have found that the excess energy of the interfaces is strongly dependent on the average grain size of the NC
samples. In the sample with $d_{bct} = 60$ nm, the interfacial excess energy is about 8.84 kJ mol$^{-1}$, which is about half
the melting enthalpy of the Ni crystal; with the decreasing grain size, $\Delta E_{in}$ decreases approximately in an linear
relation with the grain size. When $d_{bct}$ is about 7 nm, a steady value as small as 2.30 kJ mol$^{-1}$ is obtained for
$\Delta E_{in}$. This value of the interfacial excess energy, which is very close to the value of interfacial energy in the same
sample measured during grain growth process [20], is comparable to that of the 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 that rather straight boundaries were observed [17].

The evident decrease of the interfacial excess energy implies a significant change in the microstructure of the
interfaces in the NC samples. The excess energy of an interface is regarded to be closely related to the structural
characteristics of the interface, for example, the atomic coordination, the defect concentration, and so on. The-
eoretical arguments and computer simulations indicate that the excess volume of a grain boundary in comparison
to a perfect crystal is the most significant parameter designating the grain boundary energy [21]. The grain size
dependence of the excess energy may be correlated to the excess volume of the interfaces.

Qualitatively, an increasing tendency of the excess volume in the NC interfaces with an increase of grain size
in the Ni-P samples was detected. A positron lifetime spectroscopy study [18] on the interfacial defects in the NC
Ni-P alloys with various grain sizes has indicated that there are two kinds of defects in the interfaces corresponding
to the short- and the intermediate-lifetime components: type-I of free volumes for which the size is smaller than a
monovacancy; and type-II of microvoids. Also, with an increase in the annealing temperature, i.e., an increase of
grain size, there are more type-II defects and less type-I in a unit area of the interfaces. Or in other words, with
an increase in the grain size, the density of the interfaces decreases, and then the interfacial excess volume increas-

![Graph](image-url)  
**FIG. 3.** Interfacial excess energies, $\Delta E_{in}$, and the excess volume in the interfaces, $\Delta V_{in}$, vs. the average grain size
of Ni$_3$P phase. The linearly increasing tendency of the interfacial excess energy with the grain size correlated well
with the increasing of excess volume of the interfaces in the NC Ni-P samples.
es. This conclusion agrees well with those in mechanical properties testing (fracture stress and fracture strain) and density measurement results, as reported in refs. [18] and [19].

From the density measurements and structural analysis of the NC Ni-P samples with grain sizes ranging from a few to one hundred nanometers [19], the density of the interfaces ($D_{in}$) was deduced quantitatively as a function of the average grain size of Ni$_3$P phase in $D_{in} = 8.36 - 0.0189d_{bct}$, where $D_{in}$ is in a unit of g cm$^{-3}$ and $d_{bct}$ in nm. 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 $\Delta V_{in}$ variation with the grain size $d_{bct}$ is also plotted in Fig. 3. The excess volume of the interfaces evidently increases with an increase of the grain size, ranging from 8 to 24 %, values which are close to the reported one in the NC samples prepared by ultrafine particle compaction (about 10 to 30 % [1,9]). The variation of $\Delta V_{in}$ with $d_{bct}$ derived from the density measurement, an approximate straight line, is quite similar to that of the $\Delta E_{in}$ from the calorimetical results. Such an agreement indicates there is 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)" [22]. 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, $\Delta V_{in}^c$, when $\Delta V_{in} > \Delta V_{in}^c$, the interface will be mechanically unstable [22].

Denser interfaces with a low excess energy were formed in the NC Ni-P samples with smaller nanometer-sized grains during annealing at lower temperature. Densification of the interfaces accompanied by a decrease of the interfacial energy in the NC samples with grain size decreasing might be understood as a common feature for the NC materials rather than a special case caused by thermal-induced process in which activated atomic diffusion dominates. It is known that atomic diffusion will be much enhanced at an elevated temperature, and then the atoms should have larger mobility and may accommodate themselves to the relative low energy configurations during the interface formation process. However, an opposite result is obtained experimentally, indicating that the atomic diffusion does not play a dominant role in the interface formation process. On the other hand, a decrease of the grain size in a nanometer scale would enhance the activity of the grain. Any movement or rearrangement of the nanometer-sized crystallites to form an interface with a low energy configuration would be facilitated by smaller grains.

The decreasing tendency of the interfacial excess energy with a reduction of grain size in nanometer scale is very significant in 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 [5,6,7], could be explained on the basis of the decreasing tendency of the interfacial excess energy with the grain size. Other property behaviours of the NC materials relative to the interfacial energy, such as diffusional creep, boundary diffusion, and so on, may also be understood according to the present results of the NC interfacial excess energy.

**Conclusions**

The excess energies of the interfaces in NC Ni-P samples with grain sizes ranging from a few to 60 nm were measured calorimetrically by means of an amorphous-to-NC transformation. The interfacial excess energy was found to decrease linearly with a reduction of the grain size in the nanometer scale, and 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 on the NC interfacial excess energy are significant for understanding the nature of the structure and the properties of NC materials.

**Acknowledgement**

One of the authors (K.L.) is grateful for a fellowship from the Max-Planck Society during his visit in Germany. The authors are grateful to David H. Warrington for helpful discussions.

**References**

15. K. Lu, R. Lück, and B. Predel, to be published.