SUPERSATURATION OF PHOSPHORUS IN NANOPHASE NICKEL CRYSTALLIZED FROM AN AMORPHOUS Ni-P ALLOY

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Abstract—Nanocrystalline (NC) Ni-P materials, consisting of two phases of a Ni solute and a Ni₃P compound, were synthesized by crystallizing the amorphous binary Ni-P alloy. The lattice parameters of the Ni nanophases with the average grain sizes ranging from 3.8 to 50 nm were determined quantitatively by using the x-ray diffraction technique. The P concentration in the Ni(P) solution nanophase, which was determined according to the Vegard's law, was found to be 10 ~ 15 times the equilibrium solubility. The measured P concentrations in the Ni nanophases are even much larger than the calculated values from the Gibbs-Thomson equation for the nanometer-sized grains. The highly supersaturated nanophase structure may be originated from the crystallization process of the amorphous alloy.

1. INTRODUCTION

Extended solubility in a solid solution can be achieved by several different methods involving non-equilibrium processes such as rapid quenching (1) and ball-milling (2). Another way of enhancing solid solubility is possible when the grain size of a polycrystalline sample is reduced, as expected from the well-known Gibbs-Thomson equation which can be expressed as (3):

\[ \Delta C = \frac{4\Omega\gamma}{kd}C_0 \]  

where \( C_0 \) is the equilibrium solute solubility in the coarse crystal, the increment of solubility \( \Delta C = (C - C_0) \), \( k \) is the Boltzmann constant, \( \gamma \) is the interfacial energy, \( \Omega \) is the atomic volume of the crystal, and \( d \) is the grain size of the polycrystal.
The intrinsic reason for the enhancement in the solubility during grain refinement is the increase of Gibbs free energy resulting from an introduction of high-energy grain boundaries. The nanocrystalline (NC) material, which is defined as a polycrystal consisting of nanometer-sized crystallites (4), is an extreme case for grain refinement in polycrystals. The large volume fraction of grain boundaries and/or internal interfaces in the nanocrystalline sample provides a great potential for the solubility enhancement. According to the Gibbs-Thomson equation, one may expect a significant enhancement of the solid solubility in the nm-crystallites, in comparison with that in the single crystal.

In fact, enhanced solute solubility has been experimentally observed in several nanocrystalline systems. Mütschele et al. (5) found that the solubility of H in a Pd nanocrystalline sample (at concentration of \( \leq 10^{-3} \)) is increased by a factor of 10 to 100 relative to a Pd single crystal. A similar effect was reported by Hahn et al. (6) that the solubility of Bi in the nanocrystalline Cu reaches about 4% at 100°C, while the equilibrium solubility of Bi in a Cu single crystal is less than \( 10^{-4} \). Other experimental evidence, such as formation of Cu/Fe and Cu/W solid solutions in the nanocrystalline state (7), implies that an intrinsic enhancement of the solid solubility is available in the nanocrystalline samples.

In this work, we carry out an investigation on the supersaturation of phosphorus in the nickel nanophases crystallized from an amorphous Ni-P alloy. The P concentration in the Ni nanophases was determined and analyzed in a correlation with other experimental measurements.

2. EXPERIMENTS

The NC Ni-P samples with various average grain sizes used in the present work were prepared by means of the crystallization method from the amorphous alloy (8). An amorphous alloy with a chemical composition of Ni_{80}P_{20} (at.%) was made by melt-quenching, using a single roller melt-spinning apparatus. The amorphous alloy ribbon is about 2.1 mm wide and 20 \( \mu \)m thick, the amorphous structure of which was verified by X-ray diffraction (XRD) and transmission electron microscopy (TEM) observation.

The NC samples were synthesized by an isothermal annealing treatment given to the amorphous ribbon below the usual crystallization temperature. In our previous works (8, 9) we have reported the details of the sample preparation and the microstructures of the NC Ni-P samples. Two crystalline phases have been formed in the as-crystallized NC Ni-P samples: an Ni solid solution (with an fcc structure) and an Ni_{13}P compound (a body-centered tetragonal structure, bct). In the present work, eight different annealing conditions (with temperature \( T_a \) for time \( t_a \) ) were chosen, ranging from 648 to 570 K. These annealing treatments resulted in the formation of NC samples with different grain sizes, ranging from about 50 to 3.8 nm for the average grain size of the Ni phase, \( d \), as listed in Table 1. The grain size of the Ni solid solution was determined by means of TEM observations, combined with x-ray diffraction techniques (8,9).

The isothermal annealing procedures were carried out by a differential scanning calorimeter (DSC-II, Perkin-Elmer) so that the annealing process stopped after the exothermal crystallization peak. Both the XRD and the TEM experiments have shown that the as-crystallized samples were completely crystalline with ultrafine grains. Wet chemical compositional analyses, as well as the electron probe compositional analyses of the amorphous and the crystallized samples, indicated that the overall compositions was unchanged at Ni_{80}P_{20} (at.%) before and after the crystallization process. No evidence of oxidation was detected in the NC Ni-P samples.
Lattice parameter measurements were carried out using an X-ray diffractometer (Rigaku D/max-8A, 12kW) with a Cu Kα radiation. Values of the lattice parameter, \(a\), of the Ni phase were determined according to (200) diffraction lines. Quantitative results were obtained after instrument calibration by using a pure Si standard specimen. Repeated measurements of the diffraction line positions resulted in an error of \(\pm 0.05°\) for the 2θ values.

3. RESULTS AND DISCUSSION

According to the diffraction theory, one can derive the plane spacing \((d_{hkl})\) from Bragg's equation \(\lambda = 2 d_{hkl} \sin \theta_{hkl}\), where \(\lambda\) is the wave length of the Cu Kα radiation. Figure 1 shows the (200) XRD lines for different grain-sized Ni-P samples. It can be found that the line positions (2θ) deviate from the equilibrium value for the pure Ni crystal lattice. This deviation increases with increasing annealing temperature, or of the average grain size. The lattice parameter of the Ni solid solution, \(a\), may be obtained by using these diffraction lines. Figure 2 is a plot of the resultant lattice constant \((a)\) for the Ni nanophases with different grain sizes. All the \(a\) values for the nanophases are far below the equilibrium lattice constant for pure Ni, \(a_0 = 0.3524\) nm (10). The lattice parameter exhibits an increasing tendency with a reduction of the average grain size, from 0.35092 ± 0.00011 nm (for the sample N80) to 0.35142 ± 0.00011 nm (for sample N6).

The reduction of the lattice parameter of the Ni crystallites might be reasonably attributed to the solution of P atoms in the Ni lattice. A substitutional solid solution may be formed when a P atom is in solution in the Ni lattice, as the atomic radius of phosphorus is 0.106 nm. However, Dietz et al. (11) reported that the diffraction line positions in electrodeposited Ni-P alloys with up to 15 at.% were independent of composition, which is different from the observations by Cargill (12) and Graham et al. (13). The reason for these controversies might originate from measurement errors of the diffraction line positions. The measurement error in the case of Dietz et al. (11) is about \(± 0.15°\), which is much larger than that in the measurements using an X-ray diffractometer (as in the present study).

Supposing the Vegard's law is valid in the case of Ni(P) solid solution, we may calculate the P concentration in an Ni crystallite from the measured lattice parameter. The resultant data are listed in Table 1. The deduced values of the P concentration from the lattice parameters, \(C\), in the Ni nanophases, are in a range of 1.86 ~ 2.81 at.%, which are much larger than the equilibrium solubility of P in the Ni lattice, \(C_0\). This means the solubility of P in the Ni nanophases is enhanced by a factor of about 10 ~ 15, relative to the equilibrium solubility in a single Ni crystal.

It should be noted that the above calculation of the P concentration in the Ni nanophase is based on an assumption that the reduction of the lattice parameters of Ni solutes completely resulted from the substitutional solution of P. Actually, several other effects will influence the lattice structure of a nanophase, among these the lattice distortion and/or expansion of nanometer-sized crystallites might play a significant role in variation of the lattice parameters (14). Owing to a supersaturation of vacancies, the lattice cell unit of nanocrystallites will expand with an evident increment of the lattice parameters in intermetallic compounds (Ni3P and Fe2B) (14,15) and the metal element (Ni) (16). If the effect of the supersaturation of vacancies in the Ni nanophase in the present Ni-P alloy is taken into account, the actual P concentrations in Ni nanophases might be more or less higher than the calculated values presented above.
Figure 1. X-ray diffraction line (200) for the Ni nanophases in different samples. The dashed line indicates the (200) position for the perfect Ni lattice.

According to the magnetic transformation and the Curie temperature \( T_c \) of the Ni-P alloy, one may get an estimated value of the P concentration in the Ni crystallites. A set of accurate specific heat capacity \( (C_p) \) measurements in the nanocrystalline and normal polycrystalline Ni-P alloys indicated that the Curie temperature of the nanocrystalline Ni-P sample is much depressed relative to that of the conventional polycrystal. The reason for that is due to the supersaturation of P in the Ni nanophase. It was estimated from the decrease of the \( T_c \) that the P concentration in the nanophase Ni crystallites with an average grain size of about 5 nm is around 2.5 at.% (17). This value is in good agreement with the value obtained from the lattice parameter measurements in the present work.
Figure 2. Variation of the lattice parameter of the Ni nanophase, $a$, with the average grain size. The equilibrium lattice constant for the perfect Ni phase is also indicated.

The $P$ concentration in the Ni nanophases with various grain sizes (calculated from the lattice parameter measurement results based on the Vegard's law) exhibits an increasing tendency with an increase of the annealing temperature, or of the average grain size, as seen in Table 1. Such an increasing tendency agrees well with the magnetic measurement results of the nanocrystalline Ni-P samples with different average grain sizes. The susceptibilities ($\chi$) were measured of the as-transformed nanocrystalline Ni-P (from the amorphous state) samples at various annealing temperatures (18). The details of the experimental procedures of the susceptibility measurement were described in (18). The data of $\chi$ for the as-crystallized NC samples were determined as the susceptibility values when the amorphous sample was completely crystallized, i.e., at the time $t_f$ (the finishing time of the transformation). Figure 3 is a plot of the measured susceptibility of the as-transformed Ni-P nanocrystalline samples versus annealing temperature. Such measurements showed that the susceptibility decreases significantly with increasing annealing temperature, i.e.,

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>N6</th>
<th>N6.5</th>
<th>N7.5</th>
<th>N8</th>
<th>N16</th>
<th>N25</th>
<th>N44</th>
<th>N80</th>
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<tbody>
<tr>
<td>$T_a$ (K)</td>
<td>570.0</td>
<td>578.0</td>
<td>585.9</td>
<td>592.9</td>
<td>603.1</td>
<td>609.6</td>
<td>617.5</td>
<td>648.0</td>
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<tr>
<td>$t_a$ (min)</td>
<td>255</td>
<td>120</td>
<td>70</td>
<td>40</td>
<td>17</td>
<td>10</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>$d$(nm)</td>
<td>3.8</td>
<td>4.0</td>
<td>4.7</td>
<td>5.0</td>
<td>10</td>
<td>16</td>
<td>28</td>
<td>50</td>
</tr>
<tr>
<td>$C_0$(at.%)</td>
<td>0.160</td>
<td>0.162</td>
<td>0.164</td>
<td>0.166</td>
<td>0.169</td>
<td>0.171</td>
<td>0.173</td>
<td>0.181</td>
</tr>
<tr>
<td>$C$(at.%)</td>
<td>1.86</td>
<td>2.24</td>
<td>2.11</td>
<td>2.47</td>
<td>2.11</td>
<td>2.72</td>
<td>2.47</td>
<td>2.81</td>
</tr>
<tr>
<td>$\Delta C/C_0$</td>
<td>10.6</td>
<td>13.0</td>
<td>12.2</td>
<td>14.0</td>
<td>11.8</td>
<td>15.0</td>
<td>13.5</td>
<td>14.6</td>
</tr>
</tbody>
</table>
increasing average grain size. The decreasing tendency of the susceptibility implies an enhancement in the P concentration in the Ni lattice. Therefore, it can be seen that the same variation tendency of the P concentration in the Ni nanophase was detected from both measurements. Enhanced solubility of P in ultrafine grained Ni has been observed in several cases. For example, electrodeposition can produce metastable nanocrystalline structures in the Ni(P) solid solution systems (19). Bakonyi et al. (20) reported that in the electrodeposited Ni(P) samples, the amount of P that can be co-deposited with Ni solid solution is as high as about 12 at.%, while Dietz et al. (11) obtained a solubility of 15 at.% P in the Ni solution. Boylan et al. (21) obtained nanocrystalline Ni-P with a grain size range of 5 to 10 nm by electrodeposition, in which the P concentration is approximately 1.2 wt.%. Such a supersaturated P in the Ni nanophase was found to be stable at 473 K for 180 mins. These evidences indicate the solubility of P may be considerably enhanced in the nanocrystalline Ni solution, which, to some extent, support our findings in the present system.

According to the Gibbs-Thomson equation [1], one may expect an enhancement of the solubility in the nanocrystalline phases. Taking the Ni nanophase in the Ni-P system as an example, and assuming constant interfacial energy of 0.35 Jm$^{-2}$ (22), one may gain an enhancement of the equilibrium solubility of P atoms by a factor of about 40% in the 5 nm Ni phase. With increasing grain size, the enhanced solubility should decrease. The calculated results of the P solubility are shown in Figure 4 (represented by open squares, $C_1$), which apparently disagree with the tendency of measurement results.

In our previous work (22), it was reported that the interfacial energy decreases linearly with a reduction of the grain sizes in the Ni-P nanocrystalline materials. Supposing the ratio of $\gamma/d$ in equation [1] to be a constant of about $7.0 \times 10^9$ Jm$^{-2}$, we get a higher enhancement of the P solubility compared with the values of $C_1$. Also, a different enhancement tendency of the P solubility in the Ni nanophase was obtained, as plotted in Figure 4 (open circles, $C_2$). It can be seen that the
solubility of P in the Ni nanophase is increasing with temperature, which shows a similar tendency with the equilibrium data, as well as the measured results.

It is evident that both the calculated results (C₁ and C₂) from the above two different cases of the interfacial energies are still far below the measured results of P concentrations in the Ni nanophases. This means the P atoms are highly supersaturated in the Ni nanophases and in a non-equilibrium state even relative to the nanocrystalline state. Then, one may suppose that the supersaturated P atoms will dissolve from the Ni nanophase under proper conditions such as annealing, to establish a thermodynamic equilibrium. This deduction, in fact, has been proven by a magnetothermal analysis of the isothermal annealing process of the nanocrystalline Ni-P samples. It was found from the magnetothermal measurements that the susceptibility of the NC Ni-P sample clearly increases during isothermal annealing, while the grain size remains unchanged. The Johnson-Mehl-Avrami analysis of this process revealed that its Avrami exponent is about \( n = 0.7 \) at variant annealing temperatures (18). Such an Avrami exponent, according to the classical phase transformation theory, may correspond to a process of solute dissolving from the solution and segregating on the grain boundaries. In the Ni-P system, the segregation process is actually a dissolving process of P atoms and/or vacancies from the Ni lattice susceptibility of the sample,
as observed in experiments (18). To reveal the nature of such a dissolving process in the Ni nanophase, a systematic investigation on the process kinetics is needed, which is in progress.

From above results we may find that the supersaturation of P in the Ni nanophase is far from the thermodynamic equilibrium state. The origin of such a high supersaturation may result from the crystallization process of the amorphous alloy. A crystallization process of an amorphous alloy is actually a process of nucleation and growth of crystals in a highly undercooled state. The crystal growth rate during crystallization of amorphous alloys increases significantly with an increasing annealing temperature. The transformation from an amorphous phase into nanophases takes place much more rapidly at higher annealing temperatures, which can also be seen from Table 1. The greater value of P concentrations in the Ni nanophase formed at higher temperatures may suggest that during the crystallization at higher annealing temperatures, more solute atoms (P) might be kept in the crystallites in forming the nanocrystalline lattice. A detailed quantitative study is needed for understanding the micromechanism.

Therefore, we believe from the above results that the supersaturated nanophase structure is not only a result of the ultrafine grain size as expected from the Gibbs-Thomson equation, but it is also dependent on the formation history of the samples.

4. CONCLUSIONS

Supersaturation of P in the Ni nanophase in nanocrystalline Ni-P alloys was found from lattice parameter measurements. The P concentrations in the different grain-sized Ni nanophases are found to be about 10 to 15 times that of the equilibrium value, and increasing with an increment of the annealing temperature. The values of the measured P concentration in the Ni nanophases are even greater than the calculated results for the nanocrystalline state, according to the Gibbs-Thomson equation. The supersaturated nanophase structure is not only an effect of ultrafine grains, but it is also closely related to the formation history of the nanophase.

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