JMA ANALYSIS OF THE TRANSFORMATION KINETICS FROM THE AMORPHOUS TO THE NANOCRYSTALLINE STATE

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Introduction

Nanocrystalline (NC) materials, which are polycrystals with nanometer-sized crystallites [1], have drawn much attention in recent years for both scientific and the technological interest. Recently, a novel method for synthesizing NC materials was developed by means of crystallizing amorphous solids [2]. Nanometer-sized crystalline grains are formed during the crystallization of a Ni-P glass when it is annealed isothermally below the usual crystallization temperature. Similar effects have been detected in other systems, such as Fe-Co-Zr [3], Co-Zr [4], and so on. This method for synthesizing NC samples not only provides a unique way to study the formation process of the nm-sized crystallites and the interfaces, but also makes it possible to compare the properties of the NC, the amorphous, and the usual crystalline materials with the same chemical compositions [5].

In the theory of solid state phase transformation, the Johnson-Mehl-Avrami (JMA) equation is widely used in modelling the isothermal phase transformation mechanism [6]. The JMA equation relates the transformed volume fraction x at a constant annealing temperature T and time t [6]:

\[ x(t) = 1 - \exp\left[-K_T(t - t_0)^n\right] \]  (1)

where \( K_T \) is a temperature dependent kinetic constant, \( t_0 \) the incubation time for the process, and \( n \) is an exponent which represents the transformation behavior; the "Avrami exponent". This kinetic parameter has proved to be significant in describing the transformation mechanism, such as nucleation and growth behavior [7].

The Avrami exponent for crystallization of an amorphous Ni–P alloy has been studied by means of differential scanning calorimetry measurements [8, 9]. In this work, the transformation kinetics of the amorphous-to-NC process was studied in a Ni–P alloy system using a magnetothermal analysis method. The JMA analysis of the measured data for the transformation revealed some new phenomena which were not found previously.

Experiments

A Ni$_{80}$P$_{20}$ (at.%) alloy was prepared by melting pure nickel (99.99%) and phosphorous in an argon atmosphere. A single roller rapidly quenching equipment was used to spin the alloy melt into an amorphous ribbon, which was 20 \( \mu \)m thick and 2.1 mm wide. The amorphism of the ribbon was proved by X-ray diffraction and thermal analysis.

Magnetothermal measurements were performed using a Faraday-type magnetic balance [10]. The temperature was controlled by an electronic device (Linseis and Heinzinger TNs 125-1500) and the data were recorded by a data acquisition system (Hewlett Packard 3497A Data acquisition/Control unit and 9915A). The temperature calibration was done using pure metal standard samples and the accuracy is ±2 K. Samples of about 18.0 mg were cut from the glassy ribbon, rolled up in a cylindrical shape and inserted into the aluminium oxide sample holder.

Experimental Results and Discussion

Structural investigations have shown that the crystallization of the amorphous Ni$_{80}$P$_{20}$ alloy is a typical eutectic crystallization process resulting in formation of two crystalline phases simultaneously: a Ni austenite (face-centered...
cubic, fcc) and a Ni$_3$P compound (body-centered tetragonal, bct) \[11\]. Detailed morphologies of the two phases have been reported in Refs. \[2, 11\]. Grain sizes of the two crystalline phases, which are dependent on the annealing temperature, range from a few to a few hundred nanometers when the amorphous sample is annealed below the crystallization temperature \[2\].

Figure 1 shows the measurement results of the transformation process at four annealing temperatures. It can be seen that on isothermal annealing of the amorphous Ni–P alloy, the transformation set in after a certain period of time (or incubation time), and a significant increase in the susceptibility was detected during the transformation. The signals of the enhanced susceptibility resulted from the formation of the (nanometer-sized) magnetic phase of Ni solid solution.

Starting times for the amorphous-to-NC transformation at different annealing temperatures were measured and are listed in Table 1. At a higher annealing temperature, the starting time becomes shorter. Taking the starting time as the incubation time of the transformation, and supposing the normalized susceptibility is approximately proportional to the volume fraction of the crystalline phases, we can carry out the JMA analysis of the measured data following equation (1).

![FIG. 1. Measurement results of susceptibility variation during the transformation from the amorphous to the NC state in Ni–P samples annealed at four different temperatures: a: 598 K, b: 587 K, c: 579 K, and d: 564 K.](image)

![FIG. 2. A JMA plot of the measurement data at an annealing temperature of 579 K.](image)

![FIG. 3a. Annealing time 1300 s.](image)

![FIG. 3b. Annealing time 2400 s.](image)

![FIG. 3c. Annealing time 3900 s.](image)

![FIG. 3. Microscopic observation of the cross-section of the Ni–P samples isothermally annealed at 579 K.](image)
Figure 2 shows a JMA plot of the data measured at 579 K, ln(t - t₀) vs. ln ln(1/z). It can be seen from the plot that in the whole transformation, there are apparently three distinct stages with different Avrami exponents: at the beginning of the transformation, the average value of the Avrami exponent is about 1.3; in the middle stage, the Avrami exponent is about 3.5; and then in the final stage, it decreases and tends to be a constant of about 0.7. The evident variation in the value of the Avrami exponent during the transformation indicates that there are different dominating mechanisms at the different transformation stages. With the theory of kinetics, one can deduce the transformation mechanism from the of n values.

According to classical phase transformation theory, a one-dimensional, interface-controlled grain growth process leads to n = 1.0, and a one-dimensional nucleation and subsequent growth process results in n = 2.0. Combination of both the growth (of pre-existing nuclei) process and the nucleation (and subsequent growth) process would result in an Avrami exponent between 1.0 to 2.0. At the beginning of the transformation in the amorphous ribbon sample, such a surface crystallization process frequently occurs in amorphous alloys [9, 12], so it is reasonable to deduce that the surface nanocrystallization might dominate the kinetics at the early stage.

With the crystallization proceeding, the value of n increases and tends to an average value of about 3.5, indicating that a 3-dimensional nucleation and growth process becomes dominating, of which the theoretical value of n should be within 3.0 - 4.0. We suggest that in this stage of transformation, 3-dimensional nucleation and growth of the spherical crystals inside the bulk of the sample might be occurring.

Finally, the n value decreases and tends to about 0.7. According to kinetic theory, an n value below 1.0 implies the reaction might be a precipitation of solutions on dislocations, or a diffusion flow of solute atoms to grain boundaries [7]. It has been found that in the very early stage of segregation of solute atoms to dislocations, the Avrami exponent is n = \frac{2}{3} [7].

To confirm the JMA analysis of the MTA measurement data of the amorphous-to-NC transformation process, a metallographic observation of the samples was performed. Fig. 3 shows the cross-section morphologies of three samples annealed for different periods of time. It is evident from the observation that the transformation starts at the sample surfaces, and in the middle stage, bulk crystallization dominates with nucleation and growth of the spherical crystals. When the annealing time is 3900 s, the whole sample is crystallized, i.e., the amorphous sample is completely transformed into nanocrystalline phases. These observations are in a good agreement with the JMA analysis results. For the last reaction, as the sample is totally nanocrystalline, a segregation or precipitation of solute atoms to dislocations or grain boundaries may occur because in the nm-sized Ni solid solution phase the P atoms are supersaturated. The supersaturation has been deduced from the temperature variation [13]. The increasing susceptibility of the nanocrystalline sample with the isothermal annealing may be attributed to the dissolving of the supersaturated P atoms.

From the JMA plot, one can easily determine the starting and the finishing time for the bulk crystallization process, t₀ and tₚ, respectively, as indicated in Fig. 2, which are agree with the morphological observations.

FIG. 4. JMA plots for the measurement data at four annealing temperatures: a: 598 K, b: 587 K, c: 579 K, and d: 564 K.

FIG. 5. Arrhenius plots for calculation of activation energies by using three sets of specific times: tₛ = starting time for the surface crystallization, tₚ = starting time for the bulk crystallization, tₚ = finishing time for the bulk crystallization.
Figure 4 shows the JMA plots for the transformation processes at four annealing temperatures, which show a similar behavior to that in Fig. 2. The values of Avrami exponents at different stages are measured and listed in Table 2, from which we can see that the Avrami exponents at different stages seem to be independent of the annealing temperature.

The starting and the finishing times for the bulk process at various temperatures are obtained, as listed in Table 1. Using these specific times, one can calculate the activation energies for the transformation process.

### TABLE 1.
Specific times for the isothermal transformation from the amorphous to the NC phases measured in the MTA experiments.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_a$ (K)</td>
<td>start. time</td>
<td>start. time</td>
<td>fin. time</td>
</tr>
<tr>
<td>$t_s^a$ (s)</td>
<td>$t_f^a$ (s)</td>
<td>$t_f^b$ (s)</td>
<td>$t_f^b$ (s)</td>
</tr>
<tr>
<td>598</td>
<td>200</td>
<td>400</td>
<td>820</td>
</tr>
<tr>
<td>587</td>
<td>400</td>
<td>970</td>
<td>1910</td>
</tr>
<tr>
<td>579</td>
<td>600</td>
<td>2000</td>
<td>3900</td>
</tr>
<tr>
<td>564</td>
<td>1600</td>
<td>7600</td>
<td>15000</td>
</tr>
</tbody>
</table>

### TABLE 2.
Avrami exponents of the three stages at different annealing temperatures.

<table>
<thead>
<tr>
<th>$T_a$ (K)</th>
<th>$n_1$ (±0.2)</th>
<th>$n_2$ (±0.2)</th>
<th>$n_3$ (±0.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>598</td>
<td>1.5</td>
<td>3.5</td>
<td>0.5</td>
</tr>
<tr>
<td>587</td>
<td>1.3</td>
<td>3.6</td>
<td>0.7</td>
</tr>
<tr>
<td>579</td>
<td>1.3</td>
<td>3.5</td>
<td>0.7</td>
</tr>
<tr>
<td>564</td>
<td>1.4</td>
<td>3.6</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Usually, the Arrhenius relation is used to determine the activation energy for the isothermal crystallization processes of amorphous alloys [14], which relates the transformation time and temperature in

$$t(T) = t_0 \exp\left(-\frac{E}{RT}\right)$$

where $t_0$ is a time constant, $R$ the gas constant, and $E$ is an activation enthalpy for the process. By plotting $\ln(t)$ vs. $T^{-1}$, one can derive the value of $E$ from the slope of the plotted straight line.

Figure 5 shows the Arrhenius plots for the amorphous-to-NC transformation by using three sets of specific times, $t_s^a$, $t_f^b$, and $t_f^b$, respectively. The subscripts are s=start and f=finish, and the superscripts are s=surface and b=bulk. It can be seen that straight lines are obtained for each set of data. The activation energies are about $173.3 \pm 5.0$ kJ mol$^{-1}$ from the $t_s^a$ data, and $241.4 \pm 5.0$ and $240.0 \pm 5.0$ kJ mol$^{-1}$ from $t_f^b$ and $t_f^b$, respectively. It is clear that for the bulk crystallization process, two values of the activation energy obtained by using $t_f^b$ and $t_f^b$ are very close, indicating both sets of the specific time are actually belong to the same reaction. The activation energy for the bulk process is evidently larger than that of the surface transformation. This provides a strong evidence that the surface crystallization is easier to be started than the bulk crystallization, which should be taken into account in designing applications for the amorphous alloy ribbons.

Comparing the present JMA analysis of the transformation process measured by using a magnetothermal analysis and that by using a DSC reported previously [9], we found that the former method provides more information than the latter one. In the DSC measurement [9], only a small part of the surface crystallization was detected and it is difficult to determine the starting time of the bulk process from the JMA plots of the DSC data. The great difference between the results measured by using the two methods may be originated from the difference between the enthalpy change and the actual transformed volume fraction, which is discussed elsewhere [15]. Furthermore, the last stage of the transformation, i.e., the segregation of solute atoms to grain boundaries, was not detected by the DSC measurements, probably because the enthalpy of this process is too weak to be measured by the microcalorimeter.

### Conclusions
The transformation kinetics from the amorphous to the nanocrystalline state was studied on a Ni–P alloy using magnetothermal analysis. The JMA analysis of the data reveal that there are three stages in the transformation: (i) a surface crystallization with $n = 1.3$; (ii) a bulk transformation process of nucleation and growth of three-dimensional crystallites with $n = 3.5$; and (iii) a segregation of solute atoms to the grain boundaries with $n = 0.7$.

The activation energies for the transformation process were obtained by use of the Arrhenius relation and the
activation energy for the surface crystallization was found to be smaller than that of the bulk process.

By comparison of the results from the MTA and DSC experiments, it seems the MTA method is more sensitive in detecting the formation of nanometer-sized crystallites.

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References

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