Synthesis of the NiZr₂ intermetallic compound nanophase materials

K. Lu¹, X.D. Liu*¹, F.H. Yuan

National Laboratory for RSA, Institute of Metal Research, Academia Sinica, Shenyang 110015, China

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Abstract

The NiZr₂ intermetallic compound nanocrystalline materials were synthesized by completely crystallizing an amorphous NiZr₂ alloy under proper annealing conditions. The microstructure of the NiZr₂ nanophase was characterized by means of transmission electron microscopy (TEM), high resolution electron microscopy (HREM), and X-ray diffraction (XRD), respectively. It was found that the NiZr₂ nanophase sample consists of ultrafine lamellae with thicknesses of a few nanometers and there are well-defined twin boundaries between the neighboring lamellae. The dependence of the annealing temperature on the mean grain size was determined. The formation process of the NiZr₂ nanophase during a polymorphic crystallization of the amorphous phase was monitored by a differential scanning calorimeter (DSC) and its kinetics was analyzed.

1. Introduction

A complete crystallization of amorphous alloys may lead to the formation of nanocrystalline (NC) materials under proper heat treatment conditions [1]. Compared with other synthesis methods for nanocrystalline materials (e.g., the consolidation of ultrafine particles [2] and ball milling [3]), the crystallization method has some unique advantages including: (i) it is very simple in preparation procedures; (ii) it can produce porosity-free NC samples [4]; (iii) the transformation from the amorphous to the NC state provides a unique opportunity for studying the interface formation and thermodynamic properties of interfaces in the NC samples [5,6]. Therefore, this method has been successfully applied in various kinds of alloy systems in obtaining nanometer-sized polycrystalline structures, such as in Ni–P [1], Fe–Si–B [7], Co–Zr [8], Fe–Co–Zr [9], etc.

In previous studies, nanostructured systems crystallized from amorphous alloys are frequently composed of two or more crystalline phases (they are actually nanocomposites), because most amorphous alloys have their compositions close to the eutectic compositions with which the glass forming ability is large. However, for an intensive quantitative investigation on the formation process of nanostructures, it is significant to have a transformation from an amorphous phase into a single NC phase. This is possible only when the amorphous sample has a composition of an intermetallic compound or a pure element. An attempt has been made to a pure selenium system by Zhang et al. [10], and they succeeded in obtaining pure NC tetragonal Se through the crystallization.

* Corresponding author.
¹ Also with International Center for Materials Physics, Institute of Metal Research, Academia Sinica, Shenyang 110015, China.
In this paper, we report an investigation on the synthesis of a single NiZr$_2$ intermetallic compound nanophase by means of the crystallization of an amorphous Ni–Zr alloy. The microstructure characterization and the nanocrystallization kinetics will be studied. Some other results on mechanical properties and defects of this NiZr$_2$ nanophase sample will be reported elsewhere [11].

2. Experiments

The initial Ni–Zr ingots were prepared by induction melting of the mixtures of nickel and zirconium elements (with a purity of 99.99%) having a composition of Ni$_{33.3}$Zr$_{66.7}$ (at%). An amorphous Ni–Zr ribbon was obtained by using a single roller melt-spinning machine. The as-quenched ribbon of about 35 µm thick, 2.0 mm wide and a few meters long was bright and uniform. The amorphism of the alloy ribbon was proven by X-ray diffraction (as shown in Fig. 1) and thermal analysis experiments.

Isothermal annealing treatment to the as-quenched amorphous Ni–Zr alloy was carried out in a differential scanning calorimeter (DSC-7, PerkinElmer) under an Ar atmosphere, in order to crystallize it into nanophase materials. The procedure of the isothermal annealing is heating the as-quenched sample at a heating rate of 320 K/min up to an annealing temperature, holding at the temperature for a certain period of time (after the amorphous sample was completely crystallized) before cooling rapidly (at a rate of about 160 K/min) down to room temperature. The DSC-7 was also used to monitor the transformation process from the amorphous to the NC state. The temperature (with an accuracy of ± 0.2 K) was calibrated using standard pure In and Zn samples. Aluminum pans (for both the sample and the reference) were utilized.

X-ray diffraction (XRD) experiments were performed in a Rigaku X-ray diffractometer (D/max, 12 kW) using Cu Kα radiation. Microstructure observations were carried out on a transmission electron microscope (TEM, Philips EM420 with an accelerating voltage of 120 kV) and a high resolution electron microscope (HREM, JEOL-200cx with 200 kV).

3. Results and discussion

3.1. Formation and characterization of the NiZr$_2$ nanophase

Fig. 1 shows the XRD spectrum of the as-quenched Ni–Zr amorphous alloy. It is seen that the pattern consists of two broad peaks owing to the structure characteristics of the amorphous Ni–Zr alloy. A very small amount of quenched-in crystalline nuclei was indicated by the slight diffraction peaks, as seen in Fig. 1.

When the as-quenched amorphous Ni–Zr ribbon was annealed at 683 K for about 26 min, the sample was crystallized completely into nanometer-sized polycrystalline materials. Fig. 2 is the XRD pattern for the as-crystallized Ni–Zr sample. From the XRD spectrum, we found that only one phase of a Ni$_2$Zr$_2$ intermetallic compound (body-centered tetragonal Al$_2$Cu type structure, BCT) was formed as crystallization products. The lattice parameters of the NiZr$_2$ phase formed during the crystallization were found to be exactly the same as those for the equilibrium NiZr$_2$ phase. The XRD lines are evidently broadened, such as the (4 1 1), (3 3 2) and (4 1 3) lines, which revealed the fact that the grain size of the NiZr$_2$ intermetallic compound is very small. However, broadenings of various XRD lines are different, indicating the grain sizes vary with the crystallographic directions chosen for the grain size determination. The average grain sizes estimated from (4 1 1) and (3 3 2) lines according to the Scherrer equation are 9.9 and 15.1 nm, respectively.

![Fig. 1. X-ray diffraction pattern for the as-quenched amorphous Ni–Zr alloy ribbon.](image-url)
Fig. 2. X-ray diffraction pattern for the as-crystallized NiZr₂ NC sample after annealing the as-quenched amorphous sample at 683 K for 20 min.

A small amount of oxidation at the sample surface was found, as indicated in the XRD spectrum.

Fig. 3 shows the TEM observation results of the as-crystallized NiZr₂ nanophase sample. From the TEM results, it was found that the amorphous sample was completely crystallized and no residual amorphous regions were detected. The crystallization product consists of irregular-shaped crystalline “regions” with random orientations, each “region” being approximately 150 nm across, and contains ultrafine lamellae (Fig. 3(a)). Selected area electron diffraction patterns (Fig. 3(b)) within the crystalline “regions” indicated there are microtwins.

HREM observations revealed that, as shown in Fig. 4, the crystalline region consists of ultrafine lamellae, which are a few nanometers (1–4 nm) thick and about 100 nm long. The interfaces between neighboring lamellae are planar coherent twin boundaries with index (1 1 0). A specified orientation relationship exists between the nanocrystalline NiZr₂, [00 1] // [1 1 1₂], (1 1 1) // (1 1 0₂), which agrees with the observations by Beeli et al. [16]. The dimension in the [1 1 0] direction (i.e., the thickness of the lamella) is only a few atomic layers. These observations indicate that the nanocrystals are anisotropic, which can also be found in the XRD experiments.

The formation mechanism of the nanometer-sized NiZr₂ phase during an isothermal crystallization of the amorphous Ni–Zr alloy is not clear now. As the amorphous NiZr₂ phase has a short-range order that closely resembles that of the crystalline NiZr₂ [17], it may be assumed that in small domains of the amorphous phase a preferred orientation of bonds existed, which is parallel to that in the crystalline domains [16]. This explanation is somewhat similar to the concept of the new crystallization mechanism of amorphous alloys that it
includes not only the atomic diffusion but also the ordered cluster (which are existing in the amorphous state) deposition process [18]. Formation of the nanocomposite of Ni/Ni$_3$P from the amorphous Ni–P alloy has been well understood following this cluster deposition model [1, 19]. However, further investigations on the nanocrystallization of NiZr$_2$ should be extended in order to clarify the nature of the transformation.

The influence of the annealing temperature on the resultant mean grain size in the as-crystallized NiZr$_2$ sample was determined, as plotted in Fig. 5. In all the measured samples, the grain sizes obtained from (3 3 2) XRD lines are always larger than those from (4 1 1) lines, but similar variation tendencies with $T_a$ were obtained. It is seen that the mean grain size is almost independent of the annealing temperature in the range of 650–800 K, and shows an increasing tendency with the annealing temperature above 800 K. A significant increase in grain size with $T_a$ was observed when $T_a$ exceeds 973 K, which is about 0.7$T_m$ ($T_m$ is the melting point of the NiZr$_2$ intermetallic compound). This means the NiZr$_2$ nanophase exhibits rather intrinsic grain size stability.

Such a stable ultrafine microstructure might be understood by taking the low-energy coherent twin boundaries in these nanophase samples into account. The grain size stability of a polycrystalline material is strongly dependent on the morphologies and energy of the grain boundaries. The straight and low-energy coherent twin boundaries (as seen in the HREM images), which have no strain energy and very small chemical energy, might be an origin of the stable nanostructures.

![Fig. 4. A HREM image of the NiZr$_2$ nanophases.](image)

![Fig. 5. Variation of the mean grain sizes (determined from two XRD lines and their average value) with the annealing temperature.](image)
3.2. The nanocrystallization kinetics

The crystallization temperature of this as-quenched amorphous Ni–Zr sample was measured by means of DSC. We noticed that the crystallization begins at about 669.2 K when heated at a constant heating rate of 10 K/min. The crystallization temperature shifts to higher temperatures with an increased heating rate.

Fig. 6 is a typical isothermal DSC curve for the as-quenched amorphous Ni–Zr alloy at 673 K. A single exothermal peak was detected in the DSC curve corresponding to an isothermal crystallization process. The XRD pattern of the annealed sample at 673 K for 50 min (immediately after the exothermal peak) shows evidently a single nanophase of NiZr₂ intermetallic, as indicated in Fig. 2.

By integrating the exothermal peak for the amorphous-to-NC transformation, the crystallization volume fraction as a function of time can be obtained, as shown in Fig. 7(a), which shows an “S” type curve. The isothermal crystallization kinetics of amorphous alloys is always described by means of the Johnson–Mehl–Avrami equation [12]:

\[ x = 1 - \exp[-K(t - \tau)^n], \]

where \( x \) is the transformed volume fraction, \( \tau \) a time lag, \( K \) a kinetic parameter dependent on temperature, and \( n \) is called the Avrami exponent which reflects the transformation mechanism [12].

Plotting \( \ln(\ln(1/x)) \) versus \( \ln(t - \tau) \) (or called a JMA plot), one may get the value of \( n \). Fig. 7(b) shows a JMA plot using the data from Fig. 7(a). It is evident that the slope of the plot is about 2.9, which is close to the value of 3.0 that corresponds to a growth process of pre-existing crystalline nuclei in 3 dimensions [13]. This result is understandable as there are some quenched-in crystalline nuclei existing in the as-quenched amorphous ribbon, which can act as pre-existing nuclei and grow directly (without any nucleation process) during the crystallization process.

Annealing at different temperatures leads to the similar crystallization behavior. With a decreasing annealing temperature, the exothermal peak becomes flatter and shifts to longer times. Table 1 lists some characteristic times for the crystallization at
Table 1
Three characteristic times in the isothermal DSC measurements of the as-quenched amorphous Ni-Zr sample at different annealing temperatures (T_a). t_2%, is the time when x = 2%, t_50%, is for x = 50%, and t_98%, for x = 98%.

<table>
<thead>
<tr>
<th>T_a (K)</th>
<th>643</th>
<th>648</th>
<th>653</th>
<th>658</th>
</tr>
</thead>
<tbody>
<tr>
<td>t_2% (min)</td>
<td>13.20</td>
<td>11.92</td>
<td>5.01</td>
<td>3.48</td>
</tr>
<tr>
<td>t_50% (min)</td>
<td>24.00</td>
<td>19.72</td>
<td>10.26</td>
<td>7.04</td>
</tr>
<tr>
<td>t_98% (min)</td>
<td>36.50</td>
<td>28.40</td>
<td>18.51</td>
<td>13.32</td>
</tr>
</tbody>
</table>

Fig. 8. Arrhenius plots for calculation of the activation energies using three characteristic temperatures.

Using these data, we may calculate the activation energy for the amorphous-to-NC transformation according to the Arrhenius relation:

\[ t = t_0 \exp \left( \frac{E}{RT} \right), \]

where \( t \) is a characteristic time, such as \( t_2\%), \( t_{50}\%), \( t_{98}\%), \( t_0 \) a time constant, \( R \) the gas constant, and \( E \) the activation energy for the transformation. Fig. 8 shows the Arrhenius plots of \( \ln(t) \) versus \( 1/T \) for three different times. The values of activation energy can be obtained from these straight lines, being 345.4, 307.5, and 245.0 kJ/mol for \( t_{2\%}, t_{50\%}, \) and \( t_{98\%}, \) respectively. This means the activation energies at different stages of the crystallization process are different. At the very beginning of the crystallization, \( E \) is large and is comparable to the value obtained by Walter et al. [14]. On increasing the crystallized volume fraction, the activation energy decreases, which means the energetic barrier for the nanocrystallization is higher at the beginning of the transformation. Nevertheless, the Avrami exponent \( n(x) \) indicated there is only a single growth process of pre-existing crystalline nuclei within the whole transformation range. The variation of the activation energy implies that the nature of the transformation mechanism is changing at different stages of the nanocrystallization of the amorphous Ni-Zr alloy. A similar variation tendency has been observed in the crystallization of an amorphous Ni-P alloy [15]. The explanation to this phenomenon needs further intensive investigations.

4. Conclusions

Nanocrystalline materials with a single phase of NiZr_2 intermetallic compound have been synthesized by completely crystallizing the amorphous Ni-Zr alloy. Ultrafine lamellae of the NiZr_2 phase with thicknesses of a few nanometers, as well as a large amount of coherent twin boundaries between the neighboring lamellae, are formed during the isothermal crystallization. An intrinsic grain size stability in the NiZr_2 nanophase samples was found, which might be attributed to the low energetic configuration of the coherent twin boundaries. For the nanocrystallization process, an Avrami exponent of 2.9 was detected indicating that only a three-dimensional growth process of pre-existing crystalline nuclei dominates the transformation. The activation energy changes at different stages of the nanocrystallization process. The micromechanism for the crystallization of the intermetallic nanophase from the amorphous state requires further investigations.

Acknowledgements

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References