The microprocesses of the quasicrystalline transformation in $Zr_{65}Ni_{10}Cu_{7.5}Al_{7.5}Ag_{10}$ bulk metallic glass

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The microprocesses of the amorphous-to-quasicrystalline transformation in $Zr_{65}Ni_{10}Cu_{7.5}Al_{7.5}Ag_{10}$ bulk metallic glass were studied in detail by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). It was found that the amorphous-to-quasicrystalline transformation in the present system undergoes a series of interprocesses and follows the sequence of the phase transformation of amorphous →FCC Zr_2Ni→Tetragonal Zr_2Ni→Tetragonal Zr_2Ni with a domain structure →Quasicrystals. HRTEM indicated that a domain structure with a high density of stacking faults was formed in the sample at the stage just prior to the formation of quasicrystals. This special structure seems to possess the structural symmetries similar to those of icosahedral quasicrystals. Nanobeam energy dispersive x-ray spectrum revealed that atomic diffusion was involved in all interprocesses of the phase transformations. This suggests that the amorphous-to-quasicrystalline transformation in the present bulk metallic glass is a nonpolymorphous reaction. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1801677]

It has recently been reported that an icosahedral quasicrystalline phase could precipitate from amorphous phase upon annealing in a number of Zr-based bulk metallic glass forming systems.[1,2] The amorphous-to-quasicrystalline transformation in these systems usually occurred at the initial stage of crystallization and the quasicrystal formation is very sensitive to the oxygen content and the cooling rate in the sample preparation.[3–6] However, the ability of quasicrystals to form from Zr-based amorphous alloys could be considerably enhanced by adding noble metals and refractory metals.[7–10] Concerning the mechanism for the transformation, it is generally believed that the amorphous-to-quasicrystalline transformation in the Zr-based system follows the traditional nucleation/growth mechanism. There are also conflicting views on the role of atomic diffusion in the transformation. Some have considered the transformation to be polymorphous, i.e., long-range atomic diffusion is not involved;[9] while others have argued that it is nonpolymorphous, i.e., atomic diffusion is involved.[11] In this work, transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were employed to study the detailed process of the quasicrystalline transformation in $Zr_{65}Ni_{10}Cu_{7.5}Al_{7.5}Ag_{10}$ bulk metallic glass. It will be shown that the amorphous-to-quasicrystalline transformation in the system does not follow a traditional nucleation/growth mechanism. Instead, the transformation undergoes a set of interprocesses of phase transformation prior to the final formation of quasicrystals, and atomic diffusion is actually involved in the whole process of the transformation.

A rod sample of the $Zr_{65}Ni_{10}Cu_{7.5}Al_{7.5}Ag_{10}$ bulk metallic glass with a diameter of 2 mm was prepared by suck-casting from a master alloy ingot prepared by arc melting pure metal elements on a Ti-gettered Ar atmosphere. Oxygen content of the as-cast sample was measured to be about 1200 ppm by using a Leco-136 analyzer. Thermal analysis was performed with a differential scanning calorimetry (DSC-7) at a heating rate of 5 °C/min under a flow of argon. Figure 1 shows the DSC trace of the as-cast sample, which exhibits a distinct glass transition at 358 °C, followed by two exothermic reactions with onset temperatures of 396 and 469 °C, respectively. XRD demonstrated that the first reaction corresponds to the amorphous-to-quasicrystalline transformation, while the second one results from the formation of a supersaturated Zr_2Cu from the postformed quasicrystals.[12] In order to understand the microprocess of the quasicrystalline formation from the amorphous phase, the samples were heat-treated, excatly following the DSC trace, to different temperatures from point *A* to *E*, as shown in Fig. 1, and then examined by TEM and HRTEM. It is worth mentioning that the first peak has a broad tail, which always exists there regardless of what

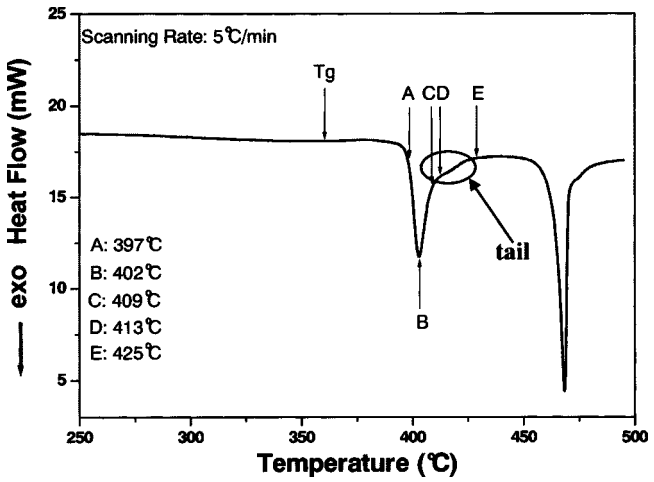

FIG. 1. The DSC curve of $Zr_{65}Ni_{10}Cu_{7.5}Al_{7.5}Ag_{10}$ bulk metallic glass at a scanning rate of 5 °C/min.

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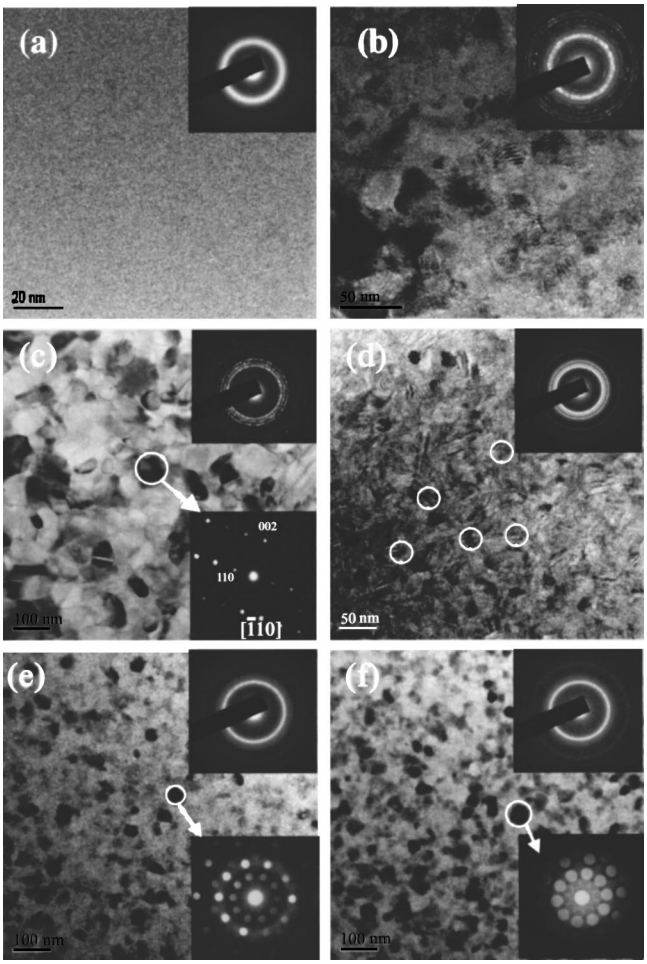

FIG. 2. The structural evolution of $Zr_{65}Ni_{10}Cu_{7.5}Al_{7.5}Ag_{10}$ BMG in the process of annealing. (a) TEM BF image and SAD pattern of the as-cast sample; (b) BF image and SAD pattern of the sample annealed to 397 °C; (c) BF image and SAD pattern of the sample annealed to 402 °C. The insert at the bottom right-hand corner refers to the NBD pattern of an individual crystal. (d) BF image and SAD pattern of the sample annealed to 409 °C, the circles indicate the crystals formed have a stacking-like structure. (e) BF image and SAD pattern of the sample annealed to 413 °C, the insert at the bottom right-hand corner refers to the NBD patterns of one individual crystal; (f) BF image and SAD pattern of the sample annealed to 425 °C, the insert at the bottom right-hand corner refers to the NBD patterns of one individual crystal.

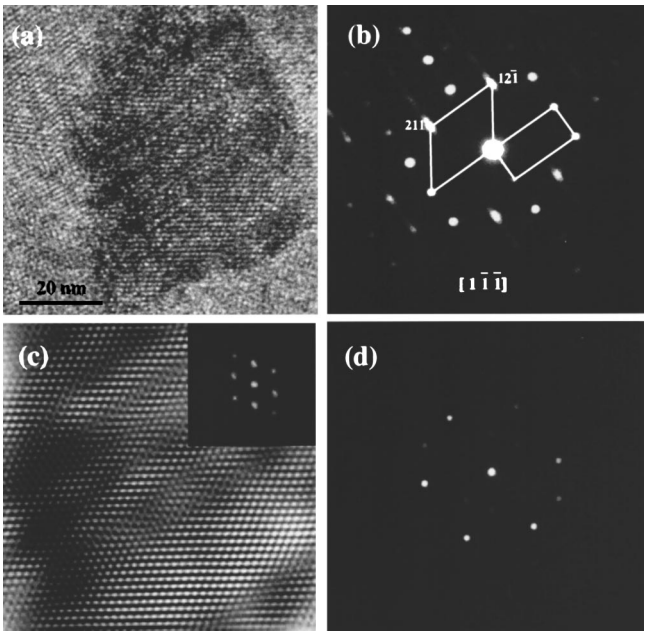

FIG. 3. (a) HRTEM image of one crystal in the sample annealed to 409 °C, which exhibits a domain structure apart from the fundamental lattice fringes; (b) NBD pattern of the crystal; (c) IFT image from the diffraction pattern with the parallelogram frame; (d) the NBD pattern of a quasicrystal with twofold axis parallel to the incident beam.

scanning rate was used. Therefore, much attention was paid to the tail in the study. TEM was carried out with a JEM 2010 microscope coupled with nanobeam diffraction (NBD) and Nanobeam EDX with a beam size of 10 nm.

Figure 2 shows the structural evolution of $Zr_{65}Ni_{10}Cu_{7.5}Al_{7.5}Ag_{10}$ bulk metallic glass with the progress of annealing. The as-cast sample is basically amorphous, as indicated by the less-contrasting morphology in the bright field (BF) image and a broad diffused diffraction ring in the selected-area diffraction (SAD) pattern [Fig. 2(a)]. When the sample was heated to point *A* (397 °C), which is slightly above the onset temperature of the first peak, the BF image and the SAD pattern demonstrated that the sample had almost crystallized [Fig. 2(b)], although a trace amount of amorphous phase still existed at the boundary regions between crystals. The SAD pattern indicates that the major phase at this stage is fcc Zr_2Ni, with the coexistence of a minor phase of tetragonal Zr_2Ni and some unknown phases. The composition of a number of particles in the sample was measured by a nanobeam EDX, and it was found that the crystals examined involved all of the five elements, but the compositions among the particles varied widely. However, the overall composition is still close to the nominal composition of the as-cast sample. This demonstrates that atomic diffusion was indeed involved in the phase transformation. Figure 2(c) shows a BF image and a SAD pattern of the sample heated to point *B* with a temperature of 402 °C. The crystals at this stage were well developed as compared with the previous sample. The indexing of the SAD pattern reveals that the sample consisted of a major phase of tetragonal Zr_2Ni, a minor phase of tetragonal Zr_2Ag and, possibly, of fcc Zr_2Ni. Therefore, it is concluded that a phase transformation from fcc Zr_2Ni to tetragonal Zr_2Ni occurred during the annealing process. The nanobearn diffraction pattern shown as the insert at the bottom-right-hand corner in Fig. 2(c), which corresponds to the diffraction of tetragonal Zr_2Ni, confirms the transformation. Further increasing the temperature to 409 °C, which is at the point just before the inflexion of the tail, led to the formation of the stacking-like structure, as indicated by the circles shown in Fig. 2(d). The SAD pattern indicates that the sample contains almost the single phase of tetragonal Zr_2Ni. In order to clarify the detailed structure of the crystals, some particles were further examined by HRTEM and nanobeam diffraction (NBD). Figure 3(a) shows the HR image of one crystal as an example. It can be seen that, apart from the fundamental lattice fringes, the particle also displays a domain structure. Figure 3(b) is the NBD pattern of the crystal, which actually involves two patterns as sorted by the parallelogram and the rectangle frames, respectively. To clarify which pattern results from the fundamental lattice, we have carried out Fourier transfer and inverse Fourier transfer (IFT) treatments on each pattern based on the HR image. Figure 3(c) shows an IFT image from the parallelogram pattern, which apparently displays very similar lattice fringes as the fundamental structure of the crystal. On

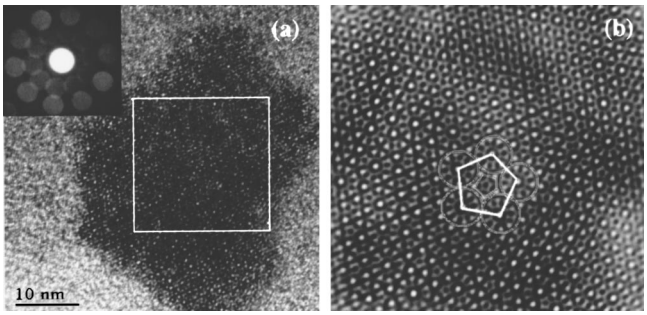

FIG. 4. (a) The high-resolution image of one particle in the sample after being heated to 425°C, the end point of the transformation; the sharp and clear boundary of the crystal is displayed, the insert is the NBD of the particle, which exhibits a fivefold symmetry; (b) the IFT image from the highlighted region in (a).

the other hand, a number of stacking faults can also be observed in the particle. These defects should be the cause of the distortion of some of the diffraction spots shown in Fig. 3(b). The indexing indicates that the pattern with a parallelogram frame corresponds to tetragonal Zr_2Ni with a zone axis of $[\bar{1}11]$. However, the other pattern with the rectangle frame has not yet been indexed. It is possibly from a new structure coexisting in the crystal or is caused by the interaction of the defects with the fundamental lattice. To confirm the morphology and the structure at the stage, another sample was heated to the same stage (i.e., just before the tail) with a faster scanning rate (40°C/min). TEM investigations gave again the same results. The formation of quasicrystals was realized when the sample was heated up to point *D* with a temperature of 413°C, as indicated by the SAD and NBD patterns shown in Fig. 2(e). Continuous heating to point *E* (425°C), the end point of the transformation, left the quasicrystal structure unchanged, but the size of the quasicrystal increased slightly [Fig. 2(f)]. Figure 4(a) shows an HR image of one crystal with its fivefold zone axis parallel to the incident beam, which demonstrates that the quasicrystals that have formed have a clear and sharp grain boundary. Its IFT image [Fig. 4(b)] indicates clearly that the quasicrystal is highly ordered, with very good fivefold symmetry.

On the basis of the above-mentioned TEM/HRTEM results, it is realized that, in the present $Zr_{65}Ni_{10}Cu_{7.5}Al_{7.5}Ag_{10}$ BMG, the amorphous-to-quasicrystalline transformation undergoes a series of interprocesses with the preferential formation of fcc Zr_2Ni, then with tetragonal Zr_2Ni with a domain structure and, finally, with the icosahedral quasicrystalline phase. The formation of metastable fcc Zr_2Ni prior to the formation of tetragonal Zr_2Ni with stacking defects was previously reported in $Zr_{66.7}Ni_{33.3}$ system, and it is suggested that fcc phase being structurally closer to amorphous should be the reason for its preferential formation.[13] This is probably also the case in the study. Different from the binary Zr–Ni system, tetragonal Zr_2Ni was further transformed into quasicrystals in the present multicomponent system, demonstrating that tetragonal Zr_2Ni is still not thermodynamically favorable with respect to the quasicrystalline phase. Generally, oxygen content is crucial for quasicrystals to form in Zr-based BMGs without containing noble metals. It has been reported that an icosahedral phase can be precipitated from the amorphous phase only if the oxygen content is higher than 1800 ppm.[10] However, this is not the case for systems containing noble metals, where quasicrystals can be formed even though the oxygen content is as low as 800 ppm. The formation of quasicrystals in these systems is more sensitive to the content of noble metals.[14] As for the function of Ag in the present system, measurements of composition and analyses of structure revealed that Ag was mainly dissolved into the Zr_2Ni basic structures (both fcc and tetragonal), and caused the extension of lattice parameters of the basic structures.[15] The supersaturated solid solution of Ag should also be the cause of the formation of a high density of stacking faults in the Zr_2Ni basic structures, as displayed in Fig. 3(a). It is thus proposed that the dissolution of Ag may play an important role in the formation of quasicrystals in the present system, although the real mechanism is still unclear. It is noticed that the structure at point *C* (409°C) is quite critical, as it almost completely transferred into quasicrystals with a slight increase in temperature. A further analysis of the diffraction pattern of the sample at point *C* (409°C) reveals that the diffraction pattern seemingly involves the basic diffraction unit of a quasicrystal with twofold symmetry. For comparison, a NBD pattern of a quasicrystal whose twofold axis parallels the electron beam is given in Fig. 3(d). The similarity of both patterns [comparing Fig. 3(b) with Fig. 3(d)] indicates that the sample at point *C* possibly involves the quasicrystal-like structure.

In conclusion, we report a pathway of the amorphous-to-quasicrystalline transformation in $Zr_{65}Ni_{10}Cu_{7.5}Al_{7.5}Ag_{10}$ BMG during continuous annealing. The transformation undergoes a series of interprocesses from amorphous →FCC Zr_2Ni (major phase) →Tetragonal Zr_2Ni (major phase) →Tetragonal Zr_2Ni with a domain structure →Quasicrystals. Atomic diffusion was indeed involved in the phase transformations in all of the above-mentioned processes. A domain structure caused mainly by staking faults was formed before the final formation of quasicrystals. This domain structure possibly involves the icosahedral quasicrystal-like structure. The dissolution of Ag in the tetragonal Zr_2Ni may play a critical role in the formation of quasicrystals.

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