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Nano-icosahedral quasicrystalline phase formation from a supercooled liquid state in Zr–Fe–Ni ternary metallic glass

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It was found that an icosahedral quasicrystalline phase was formed as a primary precipitation phase from the supercooled liquid region of the melt-spun $Zr_{70}Fe_{20}Ni_{10}$ ternary metallic glass. The precipitation of an icosahedral phase takes place at 673 K at the heating rate of $0.67\,K\,s^{-1}$. The precipitated icosahedral particle has a nearly spherical morphology and a fine grain size in the diameter range of 5–10 nm. The second crystallization reaction proceeds through a broad exothermic peak and results in the formation of Zr_2Ni and Zr_2Fe phases. The formation of nanoscale icosahedral phase by the addition of Fe as well as noble metals such as Pd, Au, and Pt indicates the possibility of existence of an icosahedral short-range order in the various Zr-based metallic glasses.
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Since the discoveries of the reproducible icosahedral phase formation in the Zr–Al–Ni–Cu–M (M=Ag, Pd, Au, and Pt) metallic glasses,[1,2] great attention has been paid to clarify the effect of the constitutional elements on the icosahedral phase formation. We have clarified that the M element leads to decreasing the grain growth rate of icosahedral phase.[3] Expecting an increase of nucleation rate by addition of M,[4] it is suggested that icosahedral short-range ordering in correlation with the stability of the glassy phase exists. Recently, the formation of an icosahedral phase has found even in the Zr–Ni–TM (TM=Pd, Au, and Pt) ternary systems.[5] The results also suggest the existence of icosahedral short-range ordering in the atomic configurations of the two major strong pairs of Zr–Ni and Zr–TM. This assumption implies the possibility of forming an icosahedral phase for the another additional element with similar chemical affinities. Here we report that a nanoscale icosahedral phase is formed in the $Zr_{70}Fe_{20}Ni_{10}$ ternary metallic glass, where the Fe element has a large negative mixing enthalpy with Zr and a small chemical affinity with Ni.[6]

The melt-spun ribbon sample with a cross section of $0.03\times 1\ mm^2$ was produced from a $Zr_{70}Fe_{20}Ni_{10}$ alloy ingot prepared by arc melting in an argon atmosphere. Thermal properties were measured by DSC at a heating rate of $0.67\,K\,s^{-1}$. The structure of annealed sample was examined by x-ray diffractometry with Cu $K\alpha$ radiation and transmission electron microscopy (TEM). The oxygen content of the ribbon sample prepared by this method is approximately 700 ppm mass %, where the influence of oxygen impurity on the transformation behavior has been clarified to be ignored.[7]

Figure 1 shows a differential scanning calorimetry (DSC) curve of the melt-spun $Zr_{70}Fe_{20}Ni_{10}$ metallic glass. The glass transition is observed clearly and its onset temperature, T_g is 646 K. The crystallization proceeds with a single sharp exothermic peak of which the onset temperature, T_x is determined to be 673 K. Moreover, a broad exothermic peak is observed at the temperature of approximately 900 K. Figure 2 shows the x-ray diffraction pattern of the sample annealed at 670 K for 120 s, which was subjected to the transformation corresponding to the first sharp exothermic peak. Almost all the peaks can be identified as an icosahedral phase. Bright-field TEM image (a), selected-area electron diffraction (b), and nanobeam electron diffraction patterns (c)–(e) of the $Zr_{70}Fe_{20}Ni_{10}$ alloy annealed at 670 K for 120 s are shown in Fig. 3. Very fine particles in the diameter range of 5–10 nm are seen over the whole area. They are distributed homogeneously and have a nearly spherical morphology. The selected-area electron diffraction pattern taken from a region of 1 μm in diameter can be identified as the icosahedral phase. The nanobeam electron diffraction patterns taken from the precipitated particles with a beam diameter of

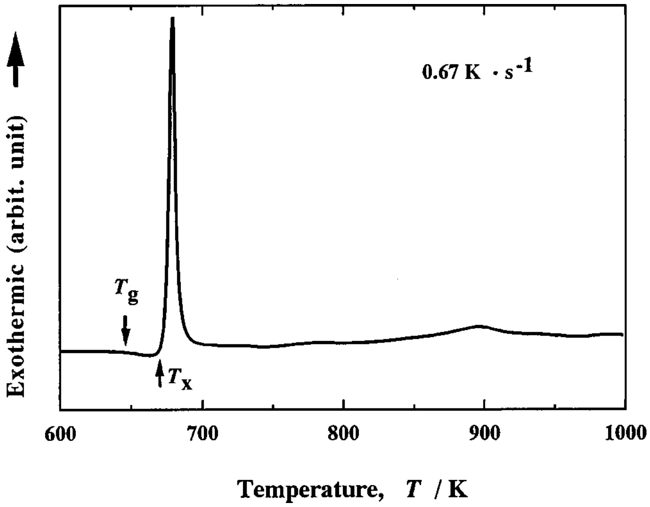

FIG. 1. DSC curve of the as-quenched $Zr_{70}Fe_{20}Ni_{10}$ metallic glass at the heating rate of $0.67\,K\,s^{-1}$.

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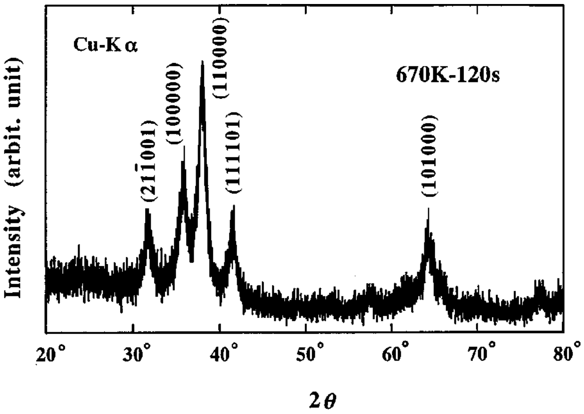
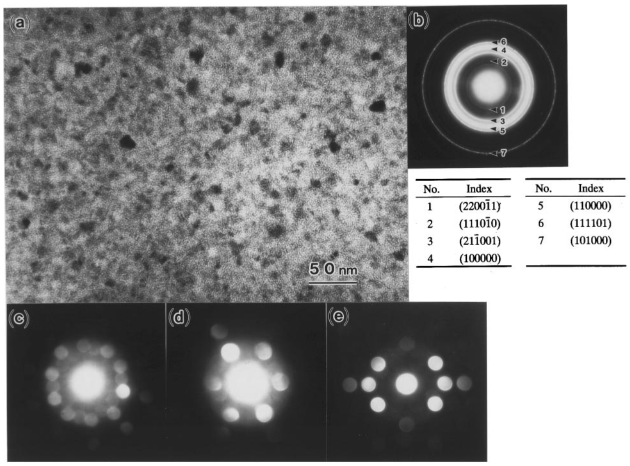


FIG. 2. X-ray diffraction pattern of the $Zr_{70}Fe_{20}Ni_{10}$ metallic glass annealed at 670 K for 120 s.

2.4 nm clearly reveal the five-, three-, and two-fold symmetries, indicating the formation of the icosahedral phase.

Figure 4 shows the x-ray diffraction pattern of the $Zr_{70}Fe_{20}Ni_{10}$ alloy annealed at 873 K for 60 s corresponding to the temperature just above the second exothermic peak in order to examine the thermal stability of the icosahedral phase. The diffraction peaks are identified as Zr_2Ni and Zr_2Fe and neither residual existence of icosahedral phase nor broad peak due to the amorphous phase is observed, implying that the second broad exothermic peak corresponds to the transition from the icosahedral phase to crystalline phases. Therefore, the icosahedral phase is a metastable phase as a primary precipitation.

The formation of the icosahedral phase has also been reported in the melt-spun Zr–Al–Cu (–O) and Zr–Al–Ni–Cu (–O) glassy alloys.[7–9] However, considering that no icosahedral phase is precipitated in the oxygen concentration range below 1700 ppm mass %, the correlation between the local structure in the glassy state and an icosahedral structure is not clarified due to the change in structure with a large amount of oxygen content. In the present study, the icosahedral phase was found in the Zr–Fe–Ni alloy, in addition to the Zr–Ni–TM alloy systems,[5] suggesting that the local structure in the Zr-transition metal-based metallic glasses contains an icosahedral short-range ordering.[10,11] We have clarified that the effect of addition of noble metals on the precipitation behavior is attributed to an increase in the nucleation rate and a decrease in the grain growth rate of the icosahedral phase in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{7.5}Ag_{10}$ and $Zr_{65}Al_{7.5}Ni_{10}Cu_{7.5}Pd_{10}$ metallic glasses.[12] It is, therefore implied that the precipitation of nano-icosahedral particles also results from the large nucleation rate and low growth rate in the present alloy.



No.	Index	No.	Index
1	(2200$\bar{1}$1)	5	(110000)
2	(1110$\bar{1}$0)	6	(111101)
3	(21$\bar{1}$001)	7	(101000)
4	(100000)		

FIG. 3. Bright-field TEM image (a), selected area electron diffraction pattern (b), and nanobeam electron diffraction patterns (c)–(e) of the $Zr_{70}Fe_{20}Ni_{10}$ metallic glass annealed at 670 K for 120 s. The beam diameter is approximately 1 μm for selected area diffraction (b) and is approximately 2.4 nm for nanobeam diffraction (c)–(e).

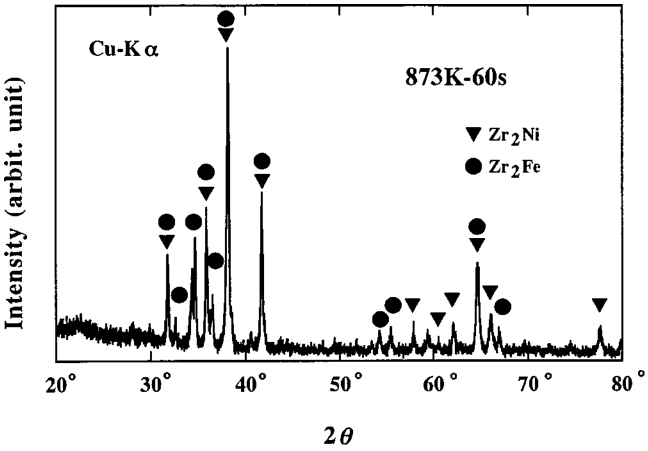


FIG. 4. X-ray diffraction pattern of the $Zr_{70}Fe_{20}Ni_{10}$ metallic glass annealed at 873 K for 60 s.

We have reported that the icosahedral phase is formed in the Zr–Ni–TM ternary glassy alloys,[5] of which the local structure in the as-quenched state depends on the chemical affinity of the constitutional elements. The heats of mixing of Ni and Pd with Zr, for example, have large negative values of −165 and −338 kJ mol^{-1}, respectively, while no chemical affinities between Ni and noble metals exist.[6] Therefore, the local structure consists of the two major chemical affinities of Zr–Ni and Zr–TM. A similar tendency is recognized in Zr–Fe–Ni alloy, where the mixing enthalpies of Fe with Zr and Ni are −85 and −6 kJ mol^{-1}, respectively. The mixture of two strong chemical affinities of Zr–Ni and Zr–Fe may be one of the factors to restrain long-range atomic orderings to form crystalline phases.

In conclusion, it was found that the $Zr_{70}Fe_{20}Ni_{10}$ ternary glass transforms to an icosahedral quasicrystalline phase. The icosahedral phase precipitates as a primary metastable phase and transforms to Zr_2Ni and Zr_2Fe at the higher annealing temperature. The icosahedral particles have a nearly spherical morphology and extremely fine grain size in a diameter range of 5–10 nm. The additional element which has a strong chemical affinity with Zr and no chemical affinities with Ni, plays a significant role on the increase of nucleation rate and the decrease of grain growth rate of the icosahedral phase. It is strongly suggested that the icosahedral short-range ordering exists in the glassy Zr–Fe–Ni alloy. It is therefore interpreted that the coexistence of two major strong pairs with Zr in the Zr-based metallic glass can restrain the long-range rearrangement of the constitutional atoms for crystallization and is one of the important factors for the precipitation of icosahedral particles through the formation of icosahedral shortrange ordering.

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