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Formation of quasicrystals in Zr$_{46.8}$Ti$_{8.2}$Cu$_{7.5}$Ni$_{10}$Be$_{27.5}$ bulk glass

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The formation of the quasicrystalline phase is observed as a first step of crystallization during isothermal annealing of the Zr$_{46.7}$Ti$_{8.3}$Cu$_{7.5}$Ni$_{10}$Be$_{27.5}$ bulk glass. The structure of the quasicrystals and the sequence of phase formation have been investigated by x-ray powder diffraction and transmission electron microscopy. The structure of the quasicrystals is determined to be primitive icosahedral with a quasilattice constant of 4.779 Å. The quasicrystals decompose into several intermetallic compounds after prolonged annealing at lower temperatures or in a short time period (less than 5 min) at high temperatures above 683 K. © 2000 American Institute of Physics.

Since the discovery of the icosahedral phase (i phase) in rapidly quenched binary or ternary Al-based alloy systems, there have been extensive studies on quasicrystals. Some studies showed that crystallization of amorphous alloys may evolve quasicrystalline phases, as in the case of Pb$_{60}$U$_{20}$Si$_{20}$ glasses. There have been extensive studies on quasicrystals. Some rapidly quenched binary or ternary Al-based alloy systems, such as ZrCuAl, ZrCuNiAl, ZrCuAlPd, ZrTiCuNiAl, and ZrAlNiCu beugles, have potential technical applications due to their favorable physical and mechanical properties and excellent processing capabilities. Several investigations of the crystallization behavior of these glasses have been undertaken during the last few years. In this letter, we report the formation of quasicrystals as a first stage in the crystallization process of the Zr$_{46.7}$Ti$_{8.3}$Cu$_{7.5}$Ni$_{10}$Be$_{27.5}$ (V4) bulk glass, studied by x-ray powder diffraction (XRD) and transmission electron microscopy (TEM).

Ingots of the V4 bulk glass were produced by alloying the pure components by induction melting in a levitation mold, to obtain 60 mm long rods with diameters of 5 mm. The average cooling rate was estimated to be $>20$ K/s. Samples from both ends of the rods were mechanically polished and analyzed by optical microscopy and scanning electron microscopy to ascertain the absence of undesirable primary crystals, which cannot be detected by XRD below a volume fraction of about 3%. The thermal behavior of the glass between 473 and 873 K was studied by a Perkin Elmer-DPyris1 differential scanning calorimetry (DSC) at a heating rate of 4 K/min under a flow of purified argon.

The long time heat treatments were performed at 643 and 653 K for times between 2 and 156 h in a tube furnace under vacuum of 10$^{-4}$ Pa. The annealing temperatures were controlled to be better than ±1.5 K. The XRD spectra were measured with CuK$_{a}$ radiation in the $θ$–$2θ$ configuration by use of a Bruker AXS D8 diffractometer equipped with a graphite monochromator and a scintillation counter for $λ=0.3$ Å. High-temperature x-ray powder diffraction measurements were performed using synchrotron radiation at beamline I711 at the MAX II synchrotron in Lund, Sweden, utilizing a Huber G670 imaging plate Guinier camera. The wavelength, 1.5225(1) Å, was determined using a Si standard. In order to exclude oxygen from the sample, the alloy was mounted on the top of a quartz capillary, which was pumped down to 10$^{-4}$ Pa and then sealed. The diffraction patterns were collected in the range 30$^0$–80$^0$ in 2theta steps of 0.005$^0$, and accumulated for 5 min. The temperature stability of the sample was ±1 K. TEM specimens were prepared from thin slice cut from the rod and thinned electrochemically by jet polishing at 263 K with 30 V, using a solution of CH$_3$COOH and HClO$_4$ in the ratio of 9:1. Subsequently, the specimens were ion beam thinned in a Gatan 600 ion mill. The microstructure of selected samples and high-resolution TEM linked with nanobeam electron diffraction was characterized by a Philips CM 30 microscope operated at 300 kV.

By the DSC scan in Fig. 1 the thermal behavior of the V4 bulk glass is indicated. This glass shows a wide supercooled liquid region of $ΔT=T_x=T_s=122$ K between the glass transition at $T_x=603$ K, and the onset of crystallization at $T_s=725$ K. The crystallization behavior is characterized by only one main heat release peak in a narrow temperature range. Figure 2 shows the x-ray powder diffraction pattern of Zr$_{46.8}$Ti$_{8.2}$Cu$_{7.5}$Ni$_{10}$Be$_{27.5}$.
the V4 bulk glass annealed at 643 K for 12 h in vacuum. A primitive icosahedral structure was found to be the most promising indexing scheme. The icosahedral Miller indices are generated by cyclic permutations of \((q_1, q_2, q_3) = (1, \pm \delta, 0)\). Six independent vectors are expressed by: 
\[
q_1 = (1, \delta, 0) ; 
q_2 = (1, -\delta, 0) ; 
q_3 = (0, 1, \delta) ; 
q_4 = (0, 1, -\delta) ; 
q_5 = (\delta, 0, 1) ; \text{ and } q_6 = (-\delta, 0, 1), 
\]
where \(\delta\) is the golden mean, 1.618. As an example, the 
\((110000)\) peak is found at \(q = Q_0(q_1 + q_2) = (2, 0, 0)\) and \(Q_0 = 2\pi/a\), where \(a\) is the quasilattice constant. The quasilattice constant is found to be \(a = 4.779(1) \text{ Å}\). The peak \((2\theta = 36^\circ, q = 2.5 \text{ Å}^{-1})\) is a choice for the basic \(100000\) reciprocal lattice vector. The nanobeam electron diffraction patterns obtained from the sample annealed at 643 K for 17 h can also be indexed according to the icosahedral Miller indices mentioned earlier. It is found that quasicrystalline particles formed in the annealed sample have a size distribution from about 20–60 nm and a nonspherical morphology. They are homogeneously dispersed in the amorphous matrix. Figure 3 exemplifies a TEM image with a five-fold zone axis of an icosahedral phase embedded in an amorphous matrix and the corresponding nanobeam electron diffraction pattern for the V4 bulk glass annealed at 643 K for 17 h.

Figure 4 depicts the crystallization behavior of the V4 bulk glass at 643 K for various annealing times. After 5 h annealing no indication of crystallization is visible, i.e., the diffraction pattern is identical to the as-casted sample. After 6 h, tiny quasicrystals are observed while they increase in intensity with the annealing time. Two new peaks at \(2\theta \approx 39^\circ\) \((d \approx 2.3 \text{ Å})\) and \(41.5^\circ\) together with quasicrystals and residual amorphous phase are observed in the pattern recorded for the sample annealed for 12 h. After 18 h, \(\text{Be}_2\text{Zr}_2\text{Zr}_2\text{Cu}\) and some as yet unidentified phases (most likely, \(\text{T}_2\text{Ni-like and NiZr}_2\)-like phases) appear. Simultaneously a strong decrease of the volume fraction of the glass with annealing time is observed by DSC measurements. With further annealing, the amount of the quasicrystalline phase decreases while the peak intensities of the intermetallic compounds increase. This result indicates the quasicrystals formed in the early stage of crystallization are metastable phase, which decompose into intermetallic compounds. The crystallization processes of the V4 bulk glass at low temperatures as a function of annealing time is suggested to be: amorphous \(\rightarrow\) amorphous + quasicrystal \(\rightarrow\) amorphous + quasicrystal + \(\text{Be}_2\text{Zr} + \text{Zr}_2\text{Cu} + \text{unidentified phases}\) \(\rightarrow\) \(\text{Be}_2\text{Zr} + \text{Zr}_2\text{Cu} + \text{unidentified phases}\).
It has been shown that oxygen promotes the formation of quasicrystals. The ZrTiCuNiBe glasses are assumed to solve oxygen easily, which can degrade the glass forming ability and the stability of the glass. The ZrTiCuNiBe glass of our production was found to contain between 0.1 and 0.3 at. % of oxygen. At the present state it cannot be excluded that this oxygen promotes the formation of quasicrystals also in the V4 glass.

In conclusion, as a first step of crystallization during isothermal annealing of the Zr_{46.7}Ti_{5.3}Cu_{24}Ni_{10}Be_{27.5} bulk glass the formation of a quasicrystalline phase is observed. This process has been investigated by XRD and TEM. The structure of the quasicrystals was determined to be primitive icosahedral with a quasilattice constant of 4.779 Å. The quasicrystals are only formed at annealing temperatures between 643 and 663 K after a rather long incubation period. They decompose into several intermetallic compounds after prolonged annealing at lower temperatures or in a short time period less than 5 min at high temperatures above 683 K. The crystallization sequence of the V4 bulk glass at the lower temperatures is amorphous→amorphous + quasicrystal→amorphous + quasicrystal + Be_{2}Zr+Zr_{2}Cu+unidentified phases→Be_{2}Zr+Zr_{2}Cu+unidentified phases.

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