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Wanderka, N.; Macht, M. P.; Siedel, M.; Mechler, S.; Ståhl, Kenny; Jiang, Jianzhong

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

Hahn-Meitner-Institut Berlin, Glienicker Str. 100, D-14109 Berlin, Germany

K. Ståhl
Department of Chemistry, Building 207, Technical University of Denmark, DK-2800 Lyngby, Denmark

J. Z. Jiang$^a$
Department of Physics, Building 307, Technical University of Denmark, DK-2800 Lyngby, Denmark

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The formation of the quasicrystalline phase is observed as a first step of crystallization during isothermal annealing of the Zr$_{56.7}$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 of metallic bulk glasses. However, most of the reported work about quasicrystal formation is focused on thin ribbons. In this letter, we report the formation of quasicrystals in the Zr$_{46.7}$Ti$_{8.3}$Cu$_{7.5}$Ni$_{10}$Be$_{27.5}$ bulk glass, studied by x-ray powder diffraction and transmission 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 Elmers-Pyris1 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$_\alpha$ radiation in the $\theta$–2$\theta$ configuration by use of a Bruker AXS D8 diffractometer equipped with a graphite monochromator and a scintillation counter for $\lambda = 0.5$–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, 1.522 25(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°–80° in 2theta steps of 0.005°, 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 electchemically 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 $\Delta T = T_g - T_x = 122$ K between the glass transition at $T_g = 603$ K, and the onset of crystallization at $T_x = 725$ 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$_{46.7}$Ti$_{8.3}$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 \((q_1, q_2, q_3) = (\pm 1, 0, \pm 1)\). Six independent vectors are expressed by: \(q_1 = (1,0,0); q_2 = (1, -1, \delta); q_3 = (0,1,\delta); q_4 = (0,1,-\delta); q_5 = (\delta,0,1)\); and \(q_6 = (-\delta,0,1)\), where \(\delta\) is the golden mean, 1.618. As an example, the (110000) peak is found at \(\theta = 50\phi_1 + q_2 = (2,0,0)\) and \(Q_0 = 2\pi/\alpha\), where \(\alpha\) is the quasilattice constant. The quasilattice constant is found to be \(a = 4.779(1)\) Å. The peak (2theta=36°, \(q = 2.5\) 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 Zr\(_{46.8}\)Ti\(_{8.2}\)Cu\(_{7.5}\)Ni\(_{10}\)Be\(_{27.5}\) bulk glass annealed at 643 K for 17 h in vacuum.

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 \(2\theta \approx 39° (d \approx 2.3\) Å\) and \(41.5°\) together with quasicrystals and residual amorphous phase are observed in the pattern recorded for the sample annealed for 12 h. After 18 h, Be\(_2\)Zr,Zr\(_2\)Cu and some as yet unidentified phases (most likely, Ti\(_2\)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 \(\rightarrow\)quasicrystal \(\rightarrow\)amorphous + quasicrystal + Be\(_2\)Zr\(_2\)Cu + unidentified phases → Be\(_2\)Zr + Zr\(_2\)Cu + unidentified phases.
The atomic diffusion in the bulk metallic glass is fast at the example, in the Pd100 of metallic glasses strongly depends on the composition. For reported that the formation of quasicrystals by crystallization decomposition of quasicrystalline phase into intermetallic quasicrystalline phase at high temperatures may be due to the temperature XRD measurements performed at ESRF, compounds instead of quasicrystals. Preliminary high-
times and at low temperatures for long times. The crystalli-
tallized samples annealed at high temperatures for short 
the intermetallic compounds are almost identical in the crys-

ticrystals more difficult at high temperatures.

It has been shown that oxygen promotes the formation of quasicrystals.16 The ZrTiCuNiBe glasses are assumed to solve oxygen easily, which can degrade the glass forming ability and the stability of the glass.12 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 Zr46.7Ti8.3Cu7.5Ni10Be27.5 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 + Be2Zr + Zr2Cu + unidentified phases→Be2Zr + Zr2Cu + unidentified phases.

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