Quasicrystals in the Ti-Zr-Ni system

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An icosahedral phase with the composition $Ti_{80-x}Zr_xNi_{20}$ ($x = 20$–60) has been observed over a wide concentration range in rapidly quenched alloys of the Ti-Zr-Ni system. The structure and physical properties of the $Ti_{53.5}Zr_{26.5}Ni_{20}$ quasicrystal have been studied.

A metastable phase having the symmetry of an icosahedron (an icosahedral phase) and having a long-range orientational order and a long-range translational order was first discovered in a rapidly quenched $Al_{86}Mn_{14}$ alloy.[1] By now, quasiperiodic phases have been identified in several alloys [including $(Ti_{1-x}V_x)_2Ni$, with $x = 0.0$–0.3; Ref. 2], most of which contain a Frank-Caspar phase in their equilibrium state. Analysis of equilibrium state diagrams has shown that many rapidly quenched icosahedral phases lie near the eutectics formed by an interaction of Frank-Caspar phases with a disordered bcc or fcc solid solution. On the basis of this premise we selected for study the $Ti_{80}Ni_{20}$-$Zr_{80}Ni_{20}$ cut through the Ti-Zr-Ni diagram, which passes through the eutectic regions formed by the interaction of the intermetallic compounds Ti_2Ni, the Laves ternary phase ZrTiNi (of the $MgZn_2$ type), and Zr_2Ni (of the $CuAl_2$ type) with a bcc solid solution of Ti,Zr.

The alloys $Ti_{80-x}Zr_xNi_{20}$ ($x = 0.0$, 20.0, 26.5, 33.0, 40.0, 47.0, 60.0, 80.0) were prepared from iodides of Ti and Zr (99.98%) and electrolytic Ni (99.99%) in an arc furnace in a helium atmosphere. Rapidly quenched tapes of the alloys with a thickness of 50 μm and a width of 1.5–2.0 mm were fabricated by spinning the melt in a helium atmosphere. During the fabrication of the rapidly quenched tape of the alloy $Ti_{53.5}Zr_{26.5}Ni_{20}$, we stopped the quenching disk during the pouring of the melt, so we were able to fabricate tapes ranging in thickness from 10 to 300 μm.

An x-ray diffraction phase analysis was carried out on powders in Cu$K\alpha$ radiation. The error in the measurement of the distance between planes was no greater than 0.01 Å. The diffraction lines were indexed in the system of icosahedral indices by the technique of Ref. 3. The microhardness HV was measured at a load of 0.98 N. The resistivity of the tapes was measured by a four-contact dc method, for which we used samples 200 mm long. Differential thermal analysis was carried out during continuous heating/cooling over the range 300–1173 K at rates of 7.5, 15, 30, and 60 K/min.

The rapidly quenched tapes of all compositions were brittle. An x-ray analysis showed that the icosahedral phase is present over a wide range of compositions, with Zr ranging from 20 to 60 at %. We observed no diffraction peaks corresponding to other phases at the tape cooling rate used in the present experiments, $v_{cool} = 10^6$ K/s. We did not detect the presence of the icosahedral phase in the tapes with the compositions $Ti_{80}Ni_{20}$ and $Zr_{80}Ni_{20}$.

The decay of the icosahedral phase occurs completely only after three heating-cooling cycles over the range 300–1000 K. Each successive heating leads to a decrease in the effect on the thermogram and to a lowering of the phase transition temperature by 20–50 K (depending on the heating rate), apparently because of a change in the composition of the icosahedral phase.

It was established by x-ray structural analysis that in an alloy heated to 973 K and cooled to 300 K the structure of the icosahedral phase is conserved completely. After three heating-cooling cycles (300–1000 K), there is no icosahedral phase in the alloy. Its structure consists of the ZrTiNi phase and an hcp Ti,Zr solid solution.

The relative thermal stability of the icosahedral phase is rather high, amounting to 0.87 of the melting point $T_m = 1113$ K. These results are evidence that high-temperature thermal effects can be used to produce stable, bulk, quasicrystalline samples.

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