Quasicrystals in the Ti-Zr-Ni system

S. A. Sibirtsev, V. N. Chebotnikov, V. V. Molokanov, and Yu. K. Kovneristyĭ
A. A. Baĭkov Institute of Metallurgy, Academy of Sciences of the USSR

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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 $Zr_{80}Ni_{20}$.

For a more detailed study we selected the alloy $Ti_{53.5}Zr_{26.5}Ni_{20}$, which falls in the low-temperature region of compositions on the equilibrium state diagram. According to the x-ray analysis, the structure of the alloy in its initial cast state consists of the Laves phase ZrTiNi and a solid solution based on the low-temperature polymorphic hcp modifications of Ti and Zr. In the rapidly quenched tape, the plastic regions, up to 15 μm thick, were amorphous. In the thickness interval 20–80 μm ($v_{\rm cool} = 10^7 - 6\times 10^5$ K/s) the tapes had, at the sensitivity of our method, a single-phase icosahedral structure. At tape thicknesses above 100 μm, we detected, in addition to the icosahedral phase, the presence of the ZrTiNi phase, whose concentration increased with increasing thicknees.

Figure 1 is a line diagram of the diffraction pattern of the rapidly quenched alloy $Ti_{53.5}Zr_{26.5}Ni_{20}$, which has an icosahedral structure. The experimental values of the ratio d_{100000}/d_i agree well with the calculated values. The diffraction pattern of the icosahedral phase corresponds best, at a qualitative level to the diffraction patterns of the Mg–Al–Zn (Ref. 4) and Ga–Mg–Zn (Ref. 5) icosahedral phases. Along with the latter phases, it differs from that for the Al–Mn icosahedral phase[3] in terms of the intensities of the two most intense lines, (100000) and (110000), and in the essential absence of the small-angle (110001) and ($11\bar{1}0\bar{1}0$) lines.

The resistivity of the icosahedral phase is $\rho_{300} = 185\ \mu\Omega\cdot$cm. This value is close to the values of ρ which we found previously for amorphous alloys which crystallize in accordance with a polymorphic type with a precipitation of the Laves ZrTiNi phase. The microhardness of the icosahedral phase is $HV = 7300$ MPa, close to the value found for a cast alloy of this composition.

It was established by differential thermal analysis that the icosahedral phase retains its stability up to 968 K (at a heating rate of 30 K/min). The recrystallization was inferred from an endothermic effect which is equal in intensity to the heat of the polymorphic transition. The activation energy calculated for the phase transition by the Kissinger method is $E_a = 5.5$ eV/atom. The crystallization and recrystallization stages during the heating of rapidly quenched alloys are usually accompanied by exothermic effects. This type of transition of the icosahedral phase is evidence of its thermodynamic stability with respect to the high-temperature structural state.

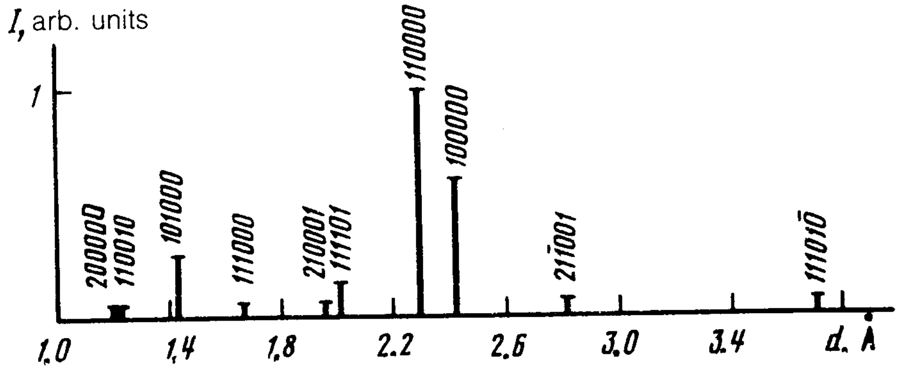

FIG. 1. Line diagram of a diffraction pattern of a rapidly quenched $Ti_{53.5}Zr_{26.5}Ni_{20}$ alloy, having the icosahedral structure. The indices of the reflecting planes, the distances between planes, and the relative intensities of the lines are shown.

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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The spin topological index of ^{3}He

A. V. Balatskiĭ
Institute of Theoretical Physics, Academy of Sciences of the USSR

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A domain wall in ^{3}He-B is used to show that the quasiparticle spectrum depends on the spin. A modified topological index, which implies that there is a "coupling" of energy with the spin, is shown to exist.

The topological properties of the quasiparticle spectrum of the superfluid phases of ^{3}He have recently attracted increased interest.[1–4] The complexity of the order parameter of a superfluid ^{3}He gives rise to many mechanisms for various topological perturbations (domain walls, vortices, etc.) which in turn manifest themselves in the topology of the quasiparticle spectrum.

