A stable Ti-based quasicrystal

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The thermal stability of the icosahedral phase (i phase) in $Ti_{45}Zr_{38}Ni_{17}$ alloys is demonstrated. As-cast alloys containing initially only the C14 hexagonal Laves and α-solid-solution phases transformed primarily to the icosahedral phase upon annealing in vacuum for 64 h at 570 °C. This confirms previous evidence for i-phase stability and firmly establishes this quasicrystal as the first nonaluminum stable icosahedral phase. Diffraction data show that this stable i phase is primitive; energy dispersive x-ray spectroscopy measurements place its composition near $Ti_{41.5}Zr_{41.5}Ni_{17}$. These and other results suggest that the structure of this i phase is similar to that of i(AlLiCu). © *1997 American Institute of Physics.* [S0003-6951(97)03824-2]

The second largest class of quasicrystals, following the aluminum-based ones, are found in rapidly quenched titanium alloys. That these have been less well studied may be due partially to the reactivity of titanium alloys, making sample preparation difficult. Further, their frequently strong disorder and metastability are undesirable for precision structural studies. An unprecedented number of icosahedrally co-ordinated phases, however, and promising technological possibilities, such as novel hydrogen storage and hydride battery materials, make Ti quasicrystals and their related crystalline and amorphous phases of fundamental interest.

All Ti-based quasicrystals reported to date could be produced only by rapid quenching from the melt, suggesting that they are metastable.[1] Some Ti–Zr–Ni quasicrystals, however, showed hints of stability. Differential scanning calorimetry (DSC) studies of rapidly quenched ($Ti_{45}Zr_{38}Ni_{17}$) alloys, for example, showed several endothermic transitions, including one from the i phase to the hexagonal C14 ($MgZn_2$-type) Laves phase near 660 °C.[2,3] Further, when annealed to 600 °C, the hydrogenated $Ti_{45}Zr_{38}Ni_{17}$ icosahedral phase (initially containing approximately 1.7 hydrogen atoms for each metal atom) crystallized to a phase mixture of hexagonal C14 and fcc C15 Laves phases. Surprisingly, the i phase reappeared on continued heating to 661 °C, only slightly below the i-phase transformation temperature measured by DSC.[4] A failure to obtain the i phase again by slowly cooling from the melt, or by cooling transformed samples to lower temperatures was suggested to be a kinetic effect, arising from the difficulty in renucleating the i phase at low temperatures. Due to the small enthalpy difference between the i phase and the C14 phase (approximately 700 J/g at.), a sufficiently large driving force for i-phase nucleation requires that the temperature be so lowered below the transition temperature that diffusion is suppressed. The problem is exacerbated by competition with a fcc Ti_2Ni-type phase, which is strongly stabilized by residual oxygen levels in the evacuated sample containers used for annealing or in the DSC sample chamber. Finally, though the amount of hydrogen in the samples showing reappearance of the i phase is believed to be small (<2 at. %), the strains introduced in the lattice on hydrogen cycling could influence the kinetics and favor the reappearance of the i phase. Residual levels could even shift the phase equilibrium.

Here, the *stability* of the i phase is firmly established. We demonstrate the formation of the i phase by annealing as-cast alloy ingots of composition $Ti_{45}Zr_{38}Ni_{17}$ that initially contained only the C14 Laves and α-Ti/Zr solid solution phases. The formation of the Ti_2Ni phase was avoided by placing a gettering material close to the sample in an evacuated sealed tube, further establishing that this phase is stabilized by oxygen in these alloys. This first unequivocal demonstration of a stable nonaluminum icosahedral phase now makes possible serious structural studies in this long-neglected class of quasicrystals.

Alloys of the desired composition ($Ti_{45}Zr_{38}Ni_{17}$) were prepared by arc-melting mixtures of the pure elements on a water-cooled copper hearth in a high-purity argon gas atmosphere. Pieces of these alloys were placed in graphite crucible and sealed under dynamic vacuum (10^{-5}–10^{-6} Torr) in a fused silica tube. The graphite crucible prevented possible Si contamination from the fused silica, which was known to promote crystal approximant and glass formation.[5] A piece of Ti–Zr alloy was sealed in the same silica tube, located at some distance from the sample, to act as an oxygen getter. Prior to sample annealing, the Ti–Zr getter was first heated to 900 °C by rf induction and held for 10 to 20 min, resulting in a dramatic decrease in the residual oxygen in the silica tube. The tube, containing the sample and getter, was then annealed at 570 °C for 64 h, after which it was cooled to room temperature in air. Microstructural and phase information were obtained from powdered samples of annealed $Ti_{45}Zr_{38}Ni_{17}$ by x-ray diffraction and transmission electron microscopy (TEM). Microscopy investigations were made using a JEOL 2000FX TEM equipped with a Noran energy dispersive x-ray spectrometer. X-ray diffraction patterns were obtained with a Siemens x-ray diffractometer, using Cu $K\alpha$ radiation.

The initial and final phases are identified in Fig. 1. Figure 1(a) shows a typical x-ray diffraction pattern of as-cast $Ti_{45}Zr_{38}Ni_{17}$ alloys. As indicated, these contain primarily the hexagonal C14 Laves phase and the hcp low-temperature solid-solution phase, α-Ti/Zr. Figure 1(b) shows the x-ray

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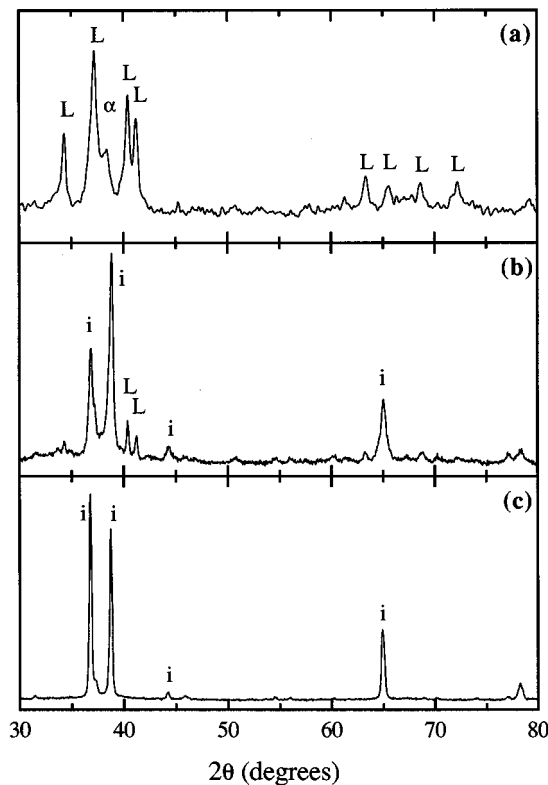[b]Present address: Naval Research Laboratory, Washington, D.C. 20375.

FIG. 1. X-ray powder diffraction patterns of (a) as-cast sample of $Ti_{45}Zr_{38}Ni_{17}$ containing only the C14 hexagonal Laves and α-solid-solution phases; (b) annealed at 570 °C for 64 h, now containing primarily the i phase; and (c) rapidly quenched ribbons, containing primarily the i phase.
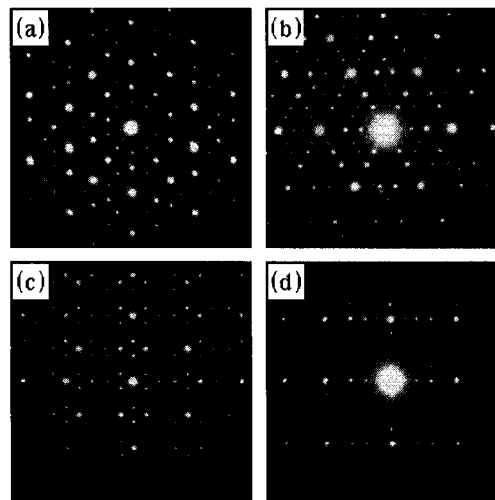

FIG. 2. SAD patterns from grains of the i phase along the prominent zone axis: (a) $[\bar{1}\tau 0]$; (b) $[-\tau^2 10]$; (c) [010]; and (d)$[\bar{\tau}10]$.

diffraction pattern after these samples were annealed at 570 °C for 64 h. The i phase is now the most abundant phase, with some (presumably untransformed) C14 Laves phase remaining. For comparison, an x-ray diffraction pattern obtained from a rapidly quenched $Ti_{45}Zr_{38}Ni_{17}$ alloy, consisting almost entirely of the i phase, is shown in Fig. 1(c). Based on peak locations of the annealed samples, the quasilattice constant a_q is 0.516 nm, within 0.001 nm of that found for the rapidly quenched samples. Within the precision possibly due to overlap between the peaks of the i phase and minor crystalline phases, the coherence lengths, computed from x-ray peak widths, are similar for the annealed and rapidly quenched samples.

The selected area diffraction patterns (SAD) obtained by TEM were typical of those obtained in other primitive icosa-hedral phase alloys. Figure 2 shows representative patterns along the fivefold $[\bar{1}\tau 0]$, threefold $[-\tau^2 10]$, twofold [010], and $[\bar{\tau}10]$(indexed following Chattopadhyay et al.[6]). The pattern symmetries and the angles between them agree with those required by the icosahedral point group. No evidence of the strong localized diffuse scattering, common in the electron diffraction patterns from rapidly quenched Ti–$3d$ transition metal–Si–O (Ti–TM–Si–O) (Ref. 7) and Ti–Zr–Fe (Ref. 8) quasicrystals, is observed; diffuse scattering is also not observed for the rapidly quenched i(TiZrNi).

Energy dispersive x-ray spectroscopy measurements place the i-phase composition at $Ti_{41.5\pm 1}Zr_{41.5\pm 1}Ni_{17}$. An-nealed samples prepared at this composition, however, give only marginally greater concentrations of the icosahedral

phase. This again reflects the slow kinetics, due to a low diffusion rate and a small driving free energy for the trans-formation from the C14–α(Ti/Zr) phase mixture, since for both ingots, the composition was spatially inhomogeneous. Increasing the annealing time to one week leads to only small increases of the amount of i phase. Much longer an-nealing studies are underway to clarify this point further.

Ti–TM–Si–O quasicrystals are often disordered, with strong diffuse scattering diffraction artifacts, short coherence lengths of order 5–10 nm, and quasilattice constants, a_q, between 0.46 and 0.48 nm. They appear to be structurally based on Mackay icosahedra, which are stabilized by inter-stitial oxygen.[9,10] In contrast, Ti–Zr–Ni quasicrystals are more ordered, showing no diffuse scattering, having longer coherence lengths of 50–100 nm, and larger quasilattice con-stants, $a_q \approx 0.51$–0.52 nm. A new classification method based on the correlation between the atomic separation, esti-mated from density measurements, and the quasilattice con-stant, supports this argument of two classes of titanium-based quasicrystals, suggesting that the Al–TM–Si–O, the Ti–TM–Si–O, and the Ti–Zr–Ni quasicrystals are structur-ally different.[11] Indirect evidence indicates that the local or-der in the Ti–Zr–Ni quasicrystals is more similar to that of clusters found in the Bergman phase (AlMgZn). The unam-biguous demonstration of the stability of this i phase pro-vided here, and a diffraction pattern for a primitive, rather than a centered, icosahedral phase support this, linking the structure of i(TiZrNi) with that of the stable i(AlLiCu).

In summary, we have demonstrated the thermal stability of the icosahedral phase in $Ti_{45}Zr_{38}Ni_{17}$ alloys. Since the i-phase composition is closer to $Ti_{41.5}Zr_{41.5}Ni_{17}$, refinements in alloy composition and annealing duration should result in single-phase samples, allowing structural refinement by x-ray diffraction studies.

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