Ternary phase diagram studies in Ti–Zr–Ni alloys

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Abstract

Equilibrium phase formation is reported for ternary Ti–Zr–Ni alloys near the i-phase-forming composition, for temperature slices between 500 and 700°C. Selected microstructural results in as-cast and annealed samples are discussed. Dominant equilibrium phases identified are the C^{14}-like Laves phase, a Ti_2Ni-like phase, $\alpha(Ti/Zr)$, the b.c.c. 1/1 W-phase and the i-phase. The i-phase forms over a small compositional range from a high-temperature equilibrium phase mixture of the Laves and $\alpha(Ti/Zr)$ solid solution phases. Lower annealing treatments have not been found to transform the i-phase, suggesting that in this alloy, the quasicrystal phase might be the ground state phase. Additions of small amounts of Pb and Pd, 1–2 at.%, are demonstrated to substantially effect the equilibrium phase formation for the i-phase and the W-phase. The addition of 1 at.% of Pb significantly orders the i-phase structure. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The disorder and metastability of many Ti/Zr-based icosahedral quasicrystals (i-phase) have made them less interesting for precision structural studies. Recently, a stable i-phase $Ti_{41.5}Zr_{41.5}Ni_{17}$ was prepared by low-temperature annealing (7 days at 570°C) [1]. No transformations from the i-phase were observed with lower temperature annealing treatments. The 1/1 approximant phase (W-phase) for this quasicrystal, a Bergman-cluster-based b.c.c. phase, was discovered following annealing treatments at a slightly higher temperature (600–610°C) [2]. These reports and the ability of the Ti–Zr–Ni i-phase to store large amounts of hydrogen (up to two hydrogen atoms per metal atom) [3] have led to an increased interest in the formation of icosahedrally coordinated phases in this alloy. Despite their stability, structural studies of the i-phase and the 1/1 phase have been hampered by an inability to produce samples with long coherence lengths, even with very long annealing times. This reflects the sluggish kinetics and small driving free energies for the formation of these phases from the high-temperature, tetrahedrally coordinated Laves phase.

Processing design to obtain a more favorable microstructure with better ordered phases requires a knowledge of the equilibrium phase diagram. Unfortunately, this is poorly known near the i-phase forming composition. This is not surprising, given the extreme reactivity of Ti/Zr alloys and the complex phases and microstructures found. Here, initial results of annealing studies in Ti–Zr–Ni alloys are presented. Shifts in phase stability and increased sample order by substitutions of small amounts of Pd and Pb are also explored.

2. Experimental methods

Alloy ingots of the desired composition were made by arc-melting mixtures of 99.9% pure elements on a water-cooled Cu hearth in a high-purity Ar gas atmosphere. Each ingot was melted, flipped, and remelted. This cycle was repeated three times to attempt to ensure sample homogeneity. X-ray and electron microscopy evidence, however, indicate poor mixing in some samples, making precise phase boundary determinations difficult. Pieces of these ingots were placed in graphite crucibles and sealed in fused silica tubes under a dynamic vacuum of 10^{-2}–10^{-1} Pa. The graphite crucible prevented possible Si contamination from the fused silica tube, which was known to promote crystal approximant and glass formation [5]. A Ti–Zr getter, located at some distance from the sample, was sealed in the same silica tube. Prior to sample annealing, the Ti–Zr getter was first heated to ≈ 1000°C for 10 min, keeping the alloy ingot and the graphite crucible near room temperature. This resulted in a dramatic decrease in the residual oxygen in the

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silica tube. The tube containing the sample and the getter was then annealed for varying times and temperatures, after which it was cooled to room temperature in air.

X-ray diffraction studies were made using a Rigaku powder diffractometer with Cu Kα radiation to ensure sample quality and to determine the phases present. Microstructural and phase information were obtained from powdered portions by transmission electron microscopy (JEOL 2000FX). Polished sections of the samples were examined by optical microscopy and scanning electron microscopy, using a Hitachi S4500 scanning electron microscope (SEM). Both the electron microscopes were equipped with a Noran energy dispersive X-ray spectrometer, allowing local compositional information to be obtained. Samples for optical microscopy studies were first etched for 1–5 s in a solution of one part HF (49 mol%), one part HNO$_3$ (70 mol%), and two parts glycerin.

3. Phase formation and equilibrium studies

As-cast samples contained primarily a hexagonal C^{14}-like Laves phase (hereafter referred to as C^{14}) and α(Ti/Zr) (Fig. 3a). The C^{14} phase is an hexagonal polytetrahedral Frank–Kasper phase (P6$_3$/mmc). It forms over a wide composition range, making it the dominant phase in the as-cast samples studied. The lattice constants for the C^{14} phase have a small composition dependence around the values $a = 0.523$ nm, $c = 0.855$ nm. α(Ti/Zr) is a solid solution phase of Ti and Zr, that has only a small solubility for Ni. It has an h.c.p. structure (P6$_3$/mmc), with lattice parameters that vary from $a = 0.326$ nm and $c = 0.515$ nm for pure Zr to $a = 0.295$ nm and 0.468 nm for pure Ti. The X-ray diffraction patterns from α(Ti/Zr) are typically broad, primarily reflecting a range of grain compositions due to the complete miscibility of Ti and Zr in α(Ti/Zr) and β(Ti/Zr) (the b.c.c. high-temperature solid solution phase). A few as-cast and annealed samples prepared with high Ni concentrations ([Ni]>25 at.%) contain a (Ti/Zr)$_2$Ni phase that is of the Ti$_2$Ni-type (Fd$\bar{3}$m) with a lattice parameter near $a = 1.21$ nm. The oxygen concentration of some of the starting materials ($\approx$ 1200 ppm) explains the formation of Ti$_2$Ni, which is known to be stabilized by oxygen. As-cast ingots of Ti$_{25}$Zr$_{25}$Ni$_{50}$ show extremely broad X-ray peaks, indicative of a metallic glass, or a fine-grained nanostructured material. Differential scanning calorimetry studies show that the transformation from β(Ti/Zr) to α(Ti/Zr) occurs quickly, explaining why no β(Ti/Zr) is found in the as-cast samples.

As expected from studies of as-cast materials, samples annealed at 700°C for 10 days contain primarily the C^{14} and α(Ti/Zr) phases (700°C anneal in Fig. 3c). High-temperature X-ray studies on Ti$_{60}$Zr$_{15}$Ni$_{25}$ alloy showed an α(Ti/Zr) to β(Ti/Zr) transformation between 650 and 700°C [6]. Likely, therefore, β(Ti/Zr) formed during the 700°C anneal and transformed to α(Ti/Zr) on cooling to room temperature. For lower temperature anneals, however, the formation of α or

β is less certain; future SEM and transmission electron microscopy (TEM) studies will address this. Anneals at 600°C for 7–10 days produced the 1/1 crystal approximant phase, in a phase field between 0.32–0.4 [Zr] and 0.44–0.52 [Ti], and 0.13–0.17 [Ni] (Fig. 3d). This b.c.c. phase ($a = 1.43$ nm) was originally reported to form at an optimum composition of Ti$_{44}$Zr$_{40}$Ni$_{16}$ [4]. In this study, however, a better ordered version of the 1/1 approximant (with sharper X-ray diffraction peaks) was found at Ti$_{50}$Zr$_{35}$Ni$_{15}$. The composition range for i-phase formation is smaller, centered near 17 at.% Ni, 40 at.% Ti and 43 at.% Zr. This agrees with the composition of the i-phase, Ti$_{41.5}$Zr$_{41.5}$Ni$_{17}$, reported in previous studies [1]. The i-phase appears to be formed by a peritectoid reaction from the C^{14} phase and α(Ti/Zr). Broad multiple-phase fields between the i-phase, 1/1 phase, C^{14} and α(Ti/Zr) are found.

To ensure sufficient time to allow phase equilibration, the annealing time at 500°C was 22 days (Fig. 3b). Due to these long times, the phase fields are less completely mapped out than at the higher temperatures. These data suggest, however, that the α(Ti/Zr), 1/1, and the i-phase fields contract. Annealing studies at low temperatures on samples of composition near Ti$_{41.5}$Zr$_{41.5}$Ni$_{17}$ indicate no transformation of the i-phase, suggesting that it could be the ground state.

X-ray diffraction patterns of as-cast alloys made near the 1/1-phase composition contain peaks corresponding to the C^{14} phase and α(Ti/Zr). SEM backscattered images of the microstructures of these alloys show dendrites of a low [Ni] phase (presumably α(Ti/Zr)) imbedded in the higher [Ni] C^{14} phase (Fig. 1b). This microstructure indicates that the primary crystallizing phase was β(Ti/Zr), which transformed to α(Ti/Zr) upon cooling. It is generally assumed that the similarity in local structure between the polytetrahedral C^{14} phase and the liquid gives a lower barrier to nucleation. The phase field of the C^{14} must, therefore, lie at a lower temperature. SEM backscattering images of as-cast alloys made near the i-phase composition (Fig. 1a) show a eutectic phase mixture of C^{14} and α(Ti/Zr), supporting this conclusion and indicating a eutectic in the equilibrium ternary phase diagram. This difference in as-cast microstructure also indicates why it is so difficult to produce more nearly phase-pure samples
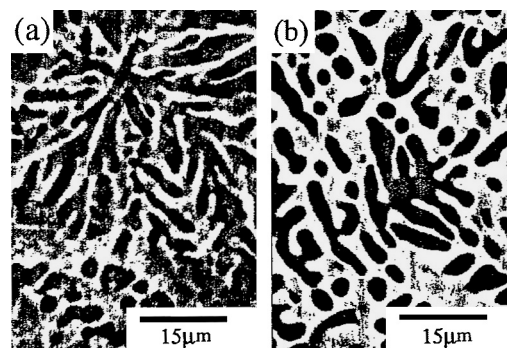

Fig. 1. SEM from as-cast (a) Ti$_{41.5}$Zr$_{41.5}$Ni$_{17}$ and (b) Ti$_{50}$Zr$_{35}$Ni$_{15}$, showing eutectic and dendritic morphologies, respectively.

of the 1/1 compared with the i-phase. The formation of the 1/1 phase requires long range diffusion for the decomposition of the C^{14} and α(Ti/Zr) grains.

4. Pd and Pb substitution

The data presented in the last section clearly show that the equilibrium $Ti_{41.5}Zr_{41.5}Ni_{17}$ i-phase forms by a solid-state transformation; the phase field does not extend to the liquidus. While this raises interesting questions about the origin of i-phase stability, it frustrates efforts to produce samples with large coherence lengths. Small amounts of Pb, having low solubility in the Ti–Zr–Ni alloys, were therefore added to the alloys to produce an alloy containing a liquid phase at 570–600°C. Additions were made to both the best 1/1 and i-phase forming compositions,
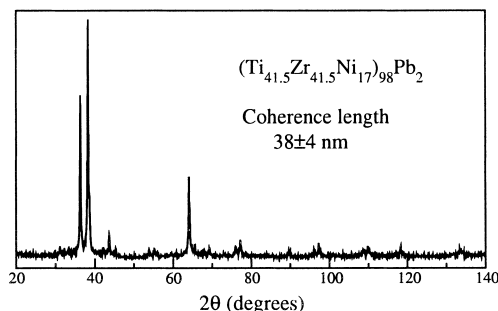

Fig. 2. $Ti_{41.5}Zr_{41.5}Ni_{17}$ with 1 at.% Pb, annealed at 570°C for 7 days. The width of (1 1 0 0 0 0) is partly due to a Ti_2Ni-like phase stabilized by residual oxygen.

giving samples of composition $(Ti_{50}Zr_{35}Ni_{15})_{1-x}Pb_x$ and $(Ti_{41.5}Zr_{41.5}Ni_{17})_{1-x}Pb_x$ with $x = 1, 2$. Small amounts of transition metals of different size were also added to the alloys to improve sample quality. Pd, e.g., was substituted for
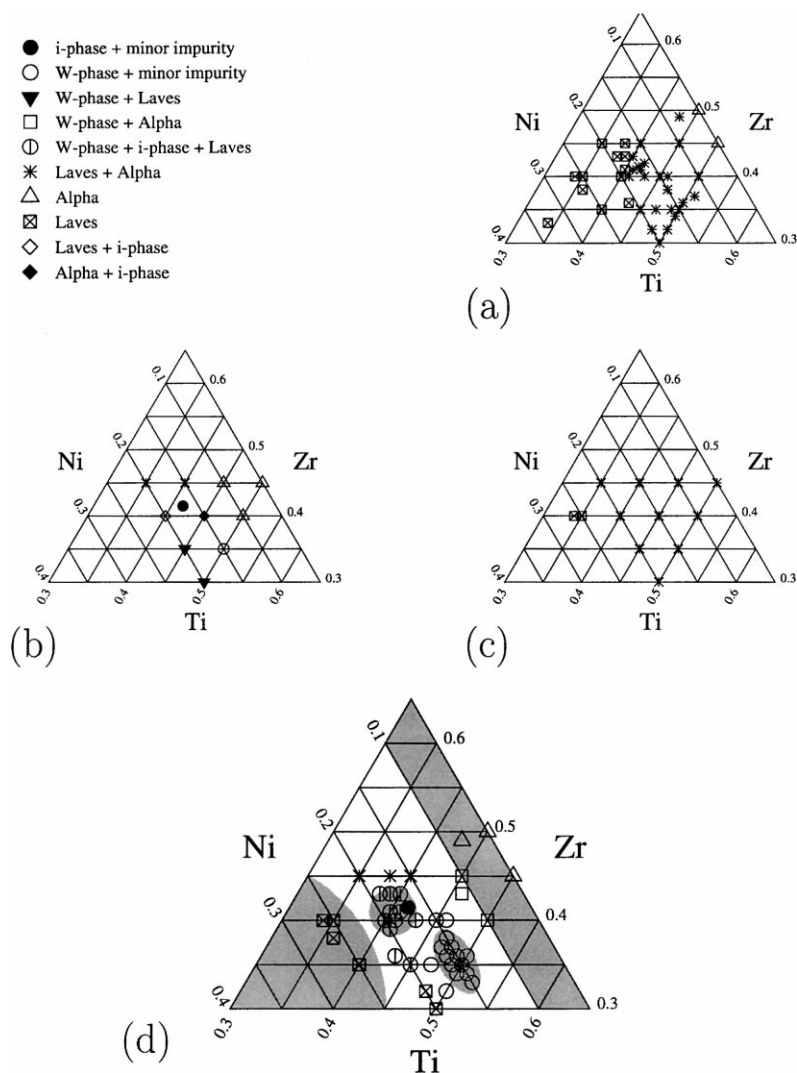

Fig. 3. Ternary phase diagrams for (a) as-cast, (b) 500°C, and (c) 700°C temperatures. The approximate phase fields are shown as shaded regions in (d) the 600°C plot. The low Ni side contains α(Ti/Zr), the large region at maximum Ni is C^{14} Laves, and the W-phase (1/1) and i-phase are centered at $Ti_{50}Zr_{35}Ni_{15}$ and $Ti_{41.5}Zr_{41.5}Ni_{17}$, respectively.

Ni in the 1/1 and i-phase compositions, $Ti_{50}Zr_{35}Ni_{15-x}Pd_x$ and $Ti_{41.5}Zr_{41.5}Ni_{17-x}Pd_x$, $x = 1, 2$. Ribbons of the icosahedral quasicrystal were produced from the alloy ingots by rapid quenching from a graphite crucible onto a rotating Cu wheel following a procedure described elsewhere [5]. With the addition of 1 at.% Pb, quenching, and annealing at 570°C, single i-phase forms with a coherence length of $(38 \pm 4\,nm)$, with the exception of a small amount of Ti_2Ni structure from residual oxygen in the raw material, see Fig. 2. Typical coherence lengths in as-quenched, annealed i-phase sample at this composition are $\approx 23\,nm$.

Interestingly, in almost all cases 1–2 at.% Pb promoted i-phase formation, sometimes eliminating the formation of the 1/1 phase, even at the best 1/1 composition. In contrast, small additions of Pd strongly promoted the formation of the 1/1 approximant, even at the i-phase forming composition. More than 2 at.% Pd and Pb, however, reduced or eliminated the icosahedral-based phases, favoring the formation of the C^{14} phase.

5. Conclusions

Initial determinations of the Ti–Zr–Ni equilibrium phase diagram for selected temperatures and at compositions near those of the i-phase and 1/1 phase were presented. These confirm that the Ti–Zr–Ni quasicrystal and 1/1 phase are thermodynamically stable, forming near 600°C over a narrow composition range by a solid-state reaction from the C^{14} and $\alpha(Ti/Zr)$ phase (Fig. 3). No evidence for the co-existence of the i-phase and a liquid phase has been found. As mentioned the precise phase boundaries are uncertain due to questionable mixing in some arc-melted samples; this will be refined using samples prepared by containerless RF-levitation methods. Small additions of Pb (1–2 at.%) stabilize the i-phase, producing samples with longer coherence lengths. The role of these additional elements is under investigation.

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