

## Phase Diagram and Electrostatic Levitation Undercooling Studies of Polytetrahedral Phases in Ti-Fe-Si-O and Ti-Zr-Ni Alloys

T.K. Croat, J.P. Davis, A.K. Gangopadhyay, K.F. Kelton, G.W. Lee, J. Simmons, Dept. of Physics, Washington University, St. Louis, MO; Robert W. Hyers, Michael B. Robinson, Jan Rogers, Larry Savage, NASA/George C. Marshall Flight Center, Huntsville, AL; Thomas J. Rathz, University of Alabama, Huntsville, AL.

### ABSTRACT

New information on the phase diagrams of Ti-Fe-Si-O and Ti-Zr-Ni alloys near the quasicrystal and rational approximant compositions is presented.  $\alpha(\text{TiFeSiO})$ , the 1/1 rational approximant, is shown to form in a peritectic mode from the liquid, indicating the possibility to produce single-crystal samples. Very long duration annealing studies demonstrate unambiguously that the  $\text{TiZrNi}$  i-phase and 1/1 approximant form at low temperatures by a solid-state transformation; their phase fields do not extend to the liquidus temperatures. The first undercooling measurements of electrostatically-levitated droplets of the Ti-Zr-Ni alloys are presented. These nucleation studies provide new information on the structural relations between polytetrahedral phases and the undercooled liquid, and on the phase transformation processes. The reduced undercooling for the polytetrahedral phases in these alloys is less than for crystal phases of a similar composition, demonstrating a low interfacial energy between the polytetrahedral phase and the liquid.

### INTRODUCTION

Ti/Zr-based quasicrystals are important for fundamental and practical reasons. They are replete with polytetrahedral phases, including icosahedral quasicrystals, high-order Fibonacci rational approximants, and Laves phases. The required oxygen concentration in Ti-(Cr,Mn,Fe)-Si alloys is high, between 6 and 20 at. %, to form the icosahedral quasicrystal (i-phase) and rational approximant [1]. This is true of no other quasicrystal. While the Ti-(Cr,Mn,Fe)-Si-O i-phases are metastable, the  $\text{TiZrNi}$  i-phase is stable and can be formed by a solid-state transformation at low temperatures rather than directly from the liquid, as is true for all other stable quasicrystals. This raises the possibility that  $i(\text{TiZrNi})$  is a case where the quasicrystal phase is the ground state. The Ti/Zr-based quasicrystals and approximants may have important technological uses, particularly in coating and hydrogen storage applications. An improved understanding of the phase diagrams for these alloys is required to address the fundamental issues mentioned, to prepare better ordered samples for structural studies, and to develop improved processing routes for technological samples. We report results from *solid-state* annealing and electrostatic levitation (ESL) experiments that provide information on primary phase fields of the competing phases, the liquidus and solidus temperatures, and the kinetics of phase solidification. The ESL experiments are particularly important, allowing accurate measurements of the high temperature features for these reactive alloys, without container contamination. The amount of undercooling observed as a function of composition, coupled with the knowledge of the phases formed by primary solidification, can be related to the nucleation rate at each composition, allowing an exploration of the structural relationship between the undercooled liquid and the polytetrahedral phases.

## EXPERIMENT

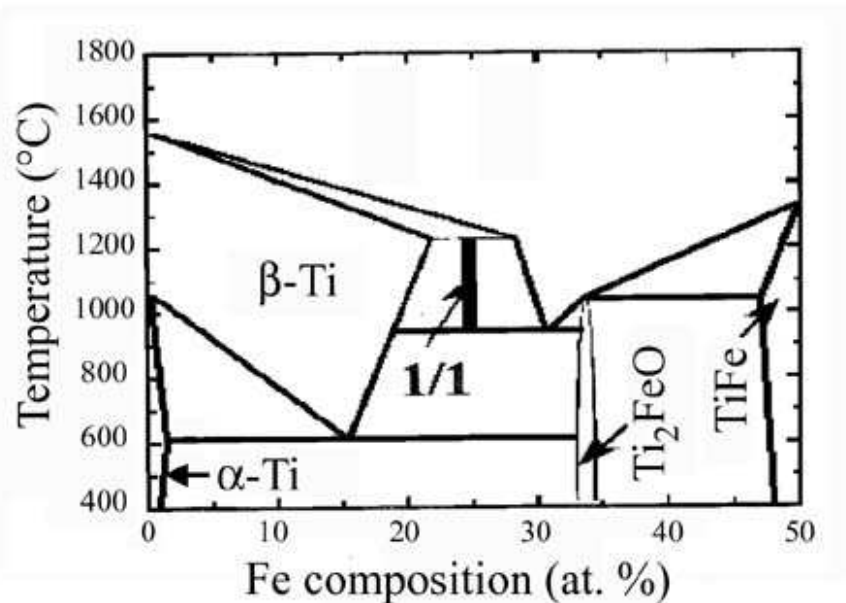
Elemental components (Ti 99.97%, Zr 99.9%, Ni 99.995%, Fe 99.98%, Si 99.999% and SiO<sub>2</sub> 99.99%) were mixed in the correct proportions and arc-melted repeatedly under Ar-gas atmosphere to produce homogeneous ingots. The degree of mixing of alloys was improved by first melting the more miscible elements several times (Ti/Zr and Ti/Si/O); the final element was then incorporated and the alloy was melted and flipped 4-5 times. For annealing, sample ingots were placed in a graphite cup and sealed under vacuum in a fused silica crucible, with a Ti getter also included in the crucible. After sealing, the getter was rf-heated to 900°C to scavenge any remaining oxygen in the tube; the sample remained at room temperature during this treatment. This technique has increased the repeatability of results for the oxygen-sensitive Ti-Zr-Ni alloys. For the electrostatic levitation experiments, small spheres (2.3-2.5 mm) were prepared by arc-melting broken pieces from a larger master ingot. The samples were levitated in vacuum ( $\approx 10^{-8}$  torr) between two electrostatic plates and laser heated. Details on the electrostatic levitation apparatus, including charging methods, can be found elsewhere [2]. Microstructure and phase information were obtained from powder x-ray diffraction (XRD) using CuK $\alpha$  radiation, scanning electron microscopy (SEM), using a Hitachi S-4500 SEM equipped with a backscattered electron detector, and transmission electron microscopy (TEM) using a JEOL 2000-FX TEM.

## RESULTS AND DISCUSSION

### Phase Diagram Studies of Ti-Fe-Si-O

Previous studies of as-cast samples have shown that the 1/1 approximant, a large unit cell bcc phase with a lattice constant of 1.31 nm, is the dominant phase over the range Ti<sub>x</sub>Fe<sub>94-x</sub>Si<sub>4</sub>(SiO<sub>2</sub>)<sub>2</sub> {66 < x < 71} [3]. Further, electromagnetic levitation (EML) studies have shown that the 1/1 approximant is the primary solidification phase over the composition range 67 at. % < Ti < 69 at. %. The stability of this phase requires large oxygen concentrations, in the range of 2-8 at. %. However, at higher oxygen concentrations the solid solution  $\alpha$ -TiO phase is stabilized and forms directly from the melt as dendrites.

Isothermal annealing experiments up to 1200°C, followed by water quenching, demonstrate the stability of the 1/1 phase at higher temperatures. It was not possible to anneal up to the liquidus temperature, however, due to the difficulty in maintaining an inert annealing atmosphere above the softening temperature of the fused silica tube. While other data (e.g. EML and ESL) suggest that the 1/1 phase field may extend to the liquidus temperatures, the annealing studies could not be extended to confirm this. A reversible transformation from the 1/1 approximant to the bcc Ti<sub>2</sub>Fe phase was observed at a lower temperature, suggesting that the 1/1 phase may be entropically stabilized. The transformation temperature depended on the oxygen content and decreased from about 1100°C for the 8 at.% oxygen samples to below 1000°C for the 4 at.% oxygen samples. Based on these studies, a sketch of the vertical section of the phase diagram, for fixed concentrations of 6 at.% Si and 4 at. % O, is presented in figure 1. The liquidus data were measured from the EML experiments. This diagram suggests that peritectic formation of the  $\alpha$ -1/1 approximant may occur from the liquid at 1200°C near the composition Ti<sub>67</sub>Fe<sub>27</sub>Si<sub>4</sub>(SiO<sub>2</sub>)<sub>2</sub>. However, it is unclear whether the TiFe bcc phase is stable in this range; if so, this would inhibit the growth of large 1/1 approximant crystals. Measurements of the undercoolability in Ti<sub>x</sub>Fe<sub>94-x</sub>Si<sub>4</sub>(SiO<sub>2</sub>)<sub>2</sub> (66 < x < 71) using the EML technique were reported earlier [3]. Primary solidification of the 1/1 approximant phase is observed at a reduced undercooling of  $\Delta T/T_{\text{melt}} \approx 0.11$ . This is lower than the undercooling observed for the solid



**Figure 1.** Portion of the Ti-Fe-Si-O phase diagram for fixed 6 at. % Si and 4 at. % O.

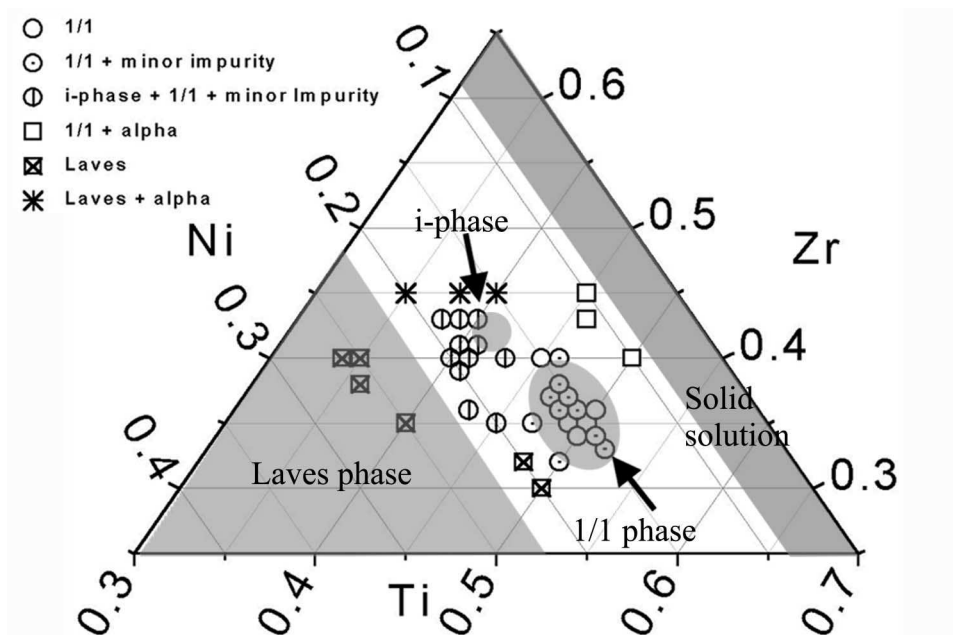
solution phase that forms at nearby compositions ( $\Delta T/T_{\text{melt}} \approx 0.18$ ). These results suggest a structural similarity between the 1/1 approximant and the undercooled liquid.

To investigate the effect of a more quiescent melt environment on undercooling, we have recently performed solidification experiments on Ti-Fe-Si-O alloys near the 1/1 approximant phase forming compositions, using the ESL technique. Although the results were essentially similar, some important differences have been observed in the ESL studies. The single recalescence event seen in EML studies, marking the solidification of the 1/1 approximant from the undercooled liquid, was also observed in the ESL experiments at a similar temperature when the samples were superheated below 1500 - 1550°C (depending on the oxygen content). However, when superheated to higher temperatures, an additional recalescence event appeared at a temperature above that of the formation of the 1/1 approximant phase. It is not clear whether this difference was due to higher superheating used in ESL, or if it had some relation to the quiescent nature of the melt in the ESL as opposed to vigorous stirring in the EML experiments. Presently, work is in progress to understand this difference and identify the high temperature event.

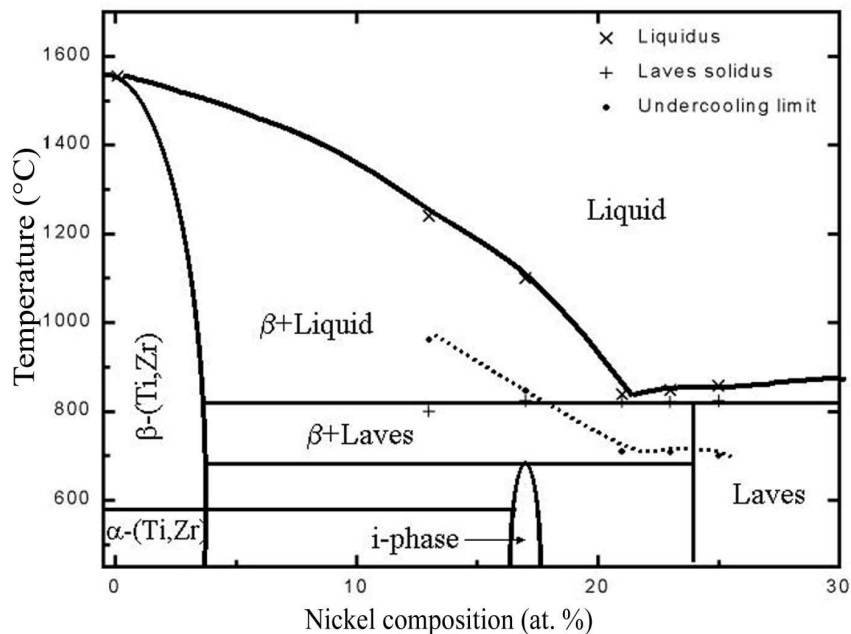
### Phase Diagram Studies of Ti-Zr-Ni

A number of icosahedrally related structures form in Ti-Zr-Ni alloys, including the *i*-phase (with quasi-lattice constant  $a_q = 0.51\text{nm}$ ) and a related 1/1 rational approximant phase (bcc-type with lattice constant  $a = 1.43\text{nm}$ ). DSC studies of as-quenched *i*-phase ribbons show an endothermic transition below 650°C upon heating, suggesting that the *i*-phase is stable [4]. This is confirmed by the formation of the *i*-phase by annealing below 600°C in as-cast ingots that initially contained only the  $\text{MgZn}_2$ -type Laves (C14) phase and the  $\beta(\text{Ti,Zr})$  solid solution phase [5]. Lower temperature anneals for extended periods of time (30 days) show no transformation from the quasicrystal, raising the possibility that is the ground-state structure. The upper temperature of the *i*-phase field is also important. Were the phase field to extend to the liquidus, it would be possible to grow ordered single crystals of the *i*-phase and allow studies of *i*-phase

nucleation. Nucleation studies might still be possible if the upper stability temperature for the i-phase were sufficiently close to the liquidus to undercool past competing crystal phases. To answer these key questions, phase formation in Ti-Zr-Ni alloys was examined extensively at various compositions in the range  $\{30 < \text{Ti} < 50, 30 < \text{Zr} < 45, \text{ and } 10 < \text{Ni} < 30 \text{ at.}\%\}$ . As-cast ingots were annealed isothermally at 500, 600 and 700°C. The results of these annealing studies at 600°C are summarized in the ternary section shown in figure 2. At 600°C, both the i-phase, centered around  $\text{Ti}_{41.5}\text{Zr}_{41.5}\text{Ni}_{17}$ , and the 1/1 approximant, centered around  $\text{Ti}_{49}\text{Zr}_{35}\text{Ni}_{16}$ , were stable. The widths of both phase regions was about 10 at.% in Ti or Zr, with limited variation in Ni. In most cases, the samples obtained were not completely phase pure; the i-phase samples contained minor fractions of the 1/1 phase and the 1/1 phase samples often contained another minor impurity phase. Preliminary data from 22 day anneals at 500°C show that, while the i-phase formed over the same composition range as at higher temperatures, the volume fraction decreased. This either signals a decrease in the width of the 1/1 phase field, or results from the small driving free energy for transformation and the decreasing diffusion coefficient with decreasing temperature, preventing the transformation from reaching completion. The icosahedral and 1/1 phases were not stable at higher temperatures (above 700°C), indicating that these phases cannot be formed directly from the liquid. The dominant phases near those compositions at higher temperatures were the solid solution phases ( $\alpha$ -(Ti,Zr) and  $\beta$ -(Ti,Zr)) and MgZn<sub>2</sub>-type (C14) Laves phase. Samples with lower Ni concentrations (<13 at. %) contained significant amounts of the solid solution phase ( $\alpha$ -TiO at low temperature) along with the Laves phase. Above 20-21 at. % Ni, the icosahedrally-related phases did not form, but were replaced by a Laves phase that formed over a wide composition range ( $\text{Ti}_{30-50}\text{Zr}_{20-45}\text{Ni}_{15-33}$ ). ESL experiments were conducted to determine the liquidus temperatures, to better study phase formation from the liquid, and to determine whether it was possible to undercool the liquid into the icosahedral and 1/1 phase forming regions. A subset of the ESL data vs. Ni concentration, showing the vertical section for equal Ti and Zr concentrations, is presented in



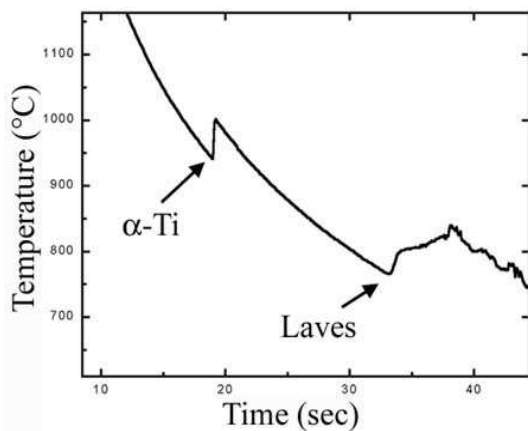
**Figure 2** Isothermal section of Ti-Zr-Ni phase diagram at 600°C



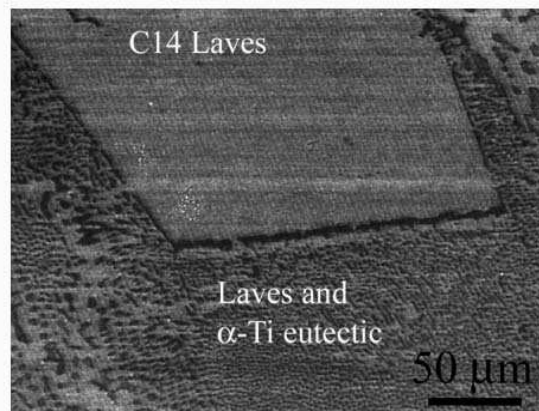
**Figure 3.** Vertical section of Ti-Zr-Ni phase diagram as a function of Ni composition (with at. %Ti = at % Zr).

figure 3; the measured liquidus and solidus lines and the maximum undercoolings achieved (dashed line) are shown. Clearly, undercooling into the *i*-phase region from the liquid is not possible under these conditions. The polytetrahedral MgZn<sub>2</sub>-type (C14) phase always nucleated at a temperature higher than the stability range of the *i*-phase or the 1/1 approximant phase; the lowest temperature for nucleation of the C14 phase was approximately 650°C. This trend persisted even as the Ti/Zr ratio was shifted toward that of the 1/1 approximant phase. For lower Ni concentrations, the solid solution phase nucleated prior to cooling into the stability range of the icosahedral or 1/1 approximant phase regions. The relative undercooling of the solid solution phase ( $\Delta T/T_{\text{melt}}=0.18$ ) exceeded that of the Laves phase ( $\Delta T/T_{\text{melt}}=0.11$ ). This is expected since the polytetrahedral Laves phase presumably has a structure closer to that of the undercooled liquid, and consequently a smaller interfacial free energy barrier to its formation. As also expected, the thermal profiles indicate a substantially slower solidification velocity of the more complex Laves structure compared to that of the simpler bcc solid solution phase  $\beta$ -Ti (see figure 4).

A microstructural analysis of the ESL-solidified samples containing low nickel (<17 at. %) indicated primary nucleation and growth of  $\beta$ (Ti,Zr), followed by solidification of the remaining liquid to the C14 Laves phase. Further increases in the Ni concentration (from 17 to 20 at. % Ni) led to a more dendritic morphology for the primary solidifying  $\beta$ (Ti,Zr), due to the partitioning of excess Ni from the growing interface. Beyond 20 at. % Ni with nearly equal Ti and Zr concentrations, the C14 phase became the primary crystallizing phase, with large plate-like grains that comprised  $\approx 80\%$  of the sample. This was followed by the solidification of the remaining liquid to a eutectic mixture of the solid solution phase and the C14 phase (see figure 5). Other eutectic microstructures were observed when the alloy composition was shifted away from an equal concentration of Ti and Zr. These were likely due to simultaneous solidification of the Laves phase and either of the Zr<sub>2</sub>Ni or the Ti<sub>2</sub>Ni phases.



**Figure 4.** ESL temperature profile from optical pyrometry on  $\text{Ti}_{37}\text{Zr}_{50}\text{Ni}_{13}$ , showing  $\alpha$ -TiO solid solution and Laves solidification events.



**Figure 5.** SEM microstructure of  $\text{Ti}_{45}\text{Zr}_{30}\text{Ni}_{25}$  sample, showing phase mixture of large C14 Laves grains and fine rod-like eutectic of Laves and solid solution.

## CONCLUSIONS

The temperature and compositional stability of the icosahedral and 1/1 approximant phases have been determined for both Ti-Fe-Si-O and Ti-Zr-Ni alloys. In Ti-Fe-Si-O alloys, the 1/1 approximant is found to be a high temperature equilibrium phase that likely extends up to the liquidus, but transforms to  $\text{Ti}_2\text{Fe}$  at lower temperatures. In Ti-Zr-Ni, both the i-phase and the 1/1 approximant are the equilibrium phases below approximately  $600^\circ\text{C}$ , but are not stable to the liquidus temperatures. This information is useful both for practical applications and as a foundation for further studies of undercoolability as a function of composition.

The results from the first electrostatic levitation undercooling experiments for Ti-based quasicrystal-forming alloys were presented. In the Ti-Fe-Si-O alloys, the undercooling of the 1/1 approximant phase was found to be smaller than for the simple crystalline phases (e.g. solid solution), indicating that this polytetrahedral phase had a greater structural similarity to the undercooled liquid. Some differences in the observed undercooling behavior between the EML and ESL studies, however, still need to be resolved. In the Ti-Zr-Ni alloys, the undercoolings were insufficient to reach the stability range of the icosahedrally-related phases; instead solidification occurred to the Laves and solid solution phases. Similar to the Ti-Fe-Si-O system, lower relative undercoolings were found for the polytetrahedral C14 Laves phase, compared to the solid solution phases.

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