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STUDIES OF NUCLEATION, GROWTH, SPECIFIC HEAT, AND VISCOSITY OF UNDERCOOLED MELTS OF QUASICRYSTALS AND POLYTETRAHEDRAL-PHASE-FORMING ALLOYS

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ABSTRACT

Undercooling experiments and thermal physical property measurements of metallic alloys on the International Space Station (ISS) are planned. This recently-funded research focuses on fundamental issues of the formation and structure of highly-ordered non-crystallographic phases (quasicrystals) and related crystal phases (crystal approximants), and the connections between the atomic structures of these phases and those of liquids and glasses. It extends studies made previously by us of the composition dependence of crystal nucleation processes in silicate and metallic glasses, to the case of nucleation from the liquid phase. Motivating results from rf-levitation and drop-tube measurements of the undercooling of Ti/Zr-based liquids that form quasicrystals and crystal approximants are discussed. Preliminary measurements by electrostatic levitation (ESL) are presented.

I. Introduction

Many metallic liquids can be significantly undercooled below their equilibrium melting temperature without crystallization. This is often taken as evidence for a large amount of polytetrahedral order (generally assumed to be icosahedral) that is incompatible with the translation periodicity of crystal phases. This constitutes a nucleation barrier, which is manifest as a large interfacial energy. Nucleation of a phase of the same composition as the parent phase has been studied extensively, both experimentally and theoretically (e.g. [1,2]). Interestingly, only limited studies exist for phase transformations involving a composition difference between the initial and final phase. This common case for most practical phase transformations warrants systematic study.

Quasicrystals are a new type of condensed matter; they contain extended polyhedral order that is believed to be similar to the short-range order in the undercooled liquid [3]. This is supported by diffraction experiments and by studies of the nucleation of quasicrystals from undercooled liquids and glasses [4]. The amount of undercooling appears to be less than for simpler crystal phases of similar composition, indicating a smaller interfacial energy, presumably reflecting a similar order in the quasicrystal and the interfacial liquid [5]. Similar results are found for complex crystal

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phases (crystal approximants), which are believed to have a local order that is similar to that of the quasicrystal. It appears reasonable, then, to expect a strong composition dependence of the undercooling for liquid alloys that crystallize directly to quasicrystals or crystal approximants.

Ti/Zr-based quasicrystals are particularly interesting [3]. The Ti-TM-Si-O quasicrystals require prodigious amounts of oxygen, between 10 and 20 at.%, to form the quasicrystals and crystal approximants. This is true of no other quasicrystal. Experimental and theoretical studies suggest that the oxygen bonds with the Ti atoms, forming a network of stable clusters that may exist even in the undercooled liquid. The mechanism of phase transformation from the liquid to the quasicrystal or the approximant is unclear. In these alloys, the crystal approximant is stable, but the quasicrystal is metastable. The quasicrystal is the stable phase in Ti-Zr-Ni alloys. Further, those quasicrystals may have technological applications as hydrogen storage materials. Several fundamental questions for quasicrystals remain unanswered. Key among these are: (i) what are the local atomic structures of quasicrystal and related complex crystal phases and what is their relation to undercooled liquids; (ii) what are the nucleation and growth mechanisms for such complex periodic and non-periodic phases?

Extensive measurements of the undercooling and growth velocity as a function of composition in these alloys will lead to improved understanding on these points. Containerless conditions are critical for the success of the proposed experiments. The samples of interest are highly reactive and have high liquidus temperatures; the transformations are often dominated by heterogeneous nucleation on container walls or gas impurities. As will be discussed, limited ground-based studies have been made by drop-tube and electromagnetic (rf) and electrostatic levitation techniques. These can be extended and necessary thermophysical properties can be measured by levitation studies in microgravity. Such studies are planned using the rf-levitation facility, Advanced TEMPUS, on the International Space Station (ISS).

II. Ti-(Cr,Mn,Fe)-Si-O Alloys

The α -1/1 phase is a bcc phase, $a_0 = 13.1 \text{ \AA}$, constructed from two double-shell Mackay icosahedra, one located at the cube corner and the other at the cube center. Because the local structure of α -1/1 phase is presumed to be similar to that of the quasicrystal [6], the nucleation properties of these two phases should be comparable. Undercooling studies were therefore made on rf-levitated droplets of Ti-(Cr,Mn,Fe)-Si-O alloys with compositions near that of α -1/1 [7,8]. The samples were inductively heated above their liquidus temperatures, and subsequently cooled at tens of degrees per second using a helium gas jet. Heating and cooling cycles were applied multiple times to ensure repeatability. The maximum undercooling on solidification (ΔT) was measured using a one-color pyrometer. Microstructure and phase information of the solidified droplets were obtained by powder x-ray diffraction (XRD) using $\text{CuK}\alpha$ 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. Phase composition was determined in SEM and TEM by energy dispersive x-ray spectroscopy (EDS).

The α -1/1 phase is the dominant phase in as-cast Ti-Cr-Si-O and Ti-Mn-Si-O alloys of the compositions studied. SEM microstructural investigations of containerlessly solidified drops, however, showed that the primary crystallizing phases are the hexagonal α -Ti and the bcc β -Ti solid solution phases. The 1/1 approximant, $\alpha(\text{TiFeSiO})$, is the primary crystallizing phase in undercooled Ti-Fe-Si-O alloys of the appropriate composition, making that a more suitable system for the nucleation studies

discussed. Based on x-ray diffraction and SEM studies of annealed samples of as-cast alloys, the α -1/1 has a narrow stoichiometry near $\text{Ti}_{72}\text{Fe}_{24}(\text{SiO}_2)_4$. From preliminary solidification data and consideration of the binary phase diagrams, a simplified sketch of the vertical section of the phase diagram near the 1/1 composition can be made as a function of Ti/Fe, for constant Si and O (Figure 1a). The primary crystallizing phase is a strong function of the oxygen concentration of the alloy; increasing it only slightly moves from the $\beta(\text{TiFe})$ primary field to the $\alpha(\text{TiFe})$ primary field and leads to the formation of Ti_2Fe at lower temperatures.

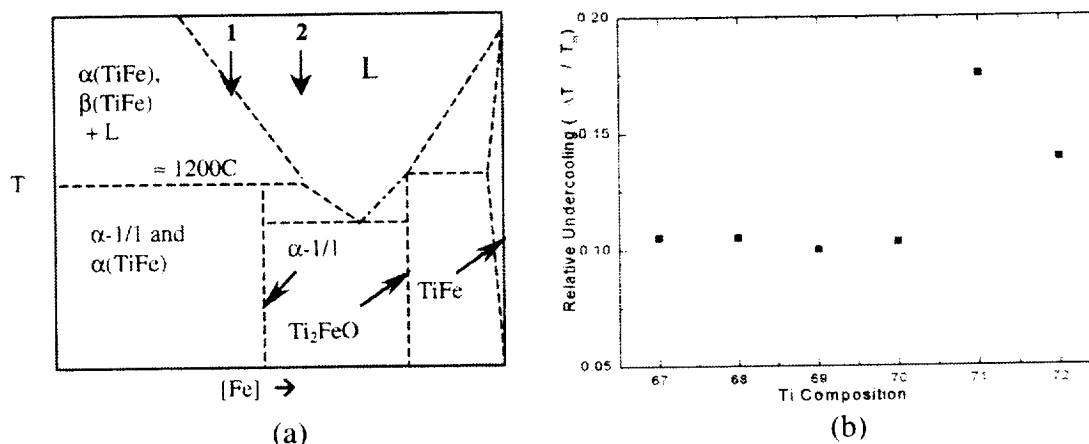


Figure 1(a). Simplified preliminary schematic of the vertical section of the phase diagram for TiFeSiO alloys (constant Si and O) near the α -1/1 crystal approximant composition as a function of increasing Fe/Ti. Strictly, the Ti_2Fe phase appears at slightly higher oxygen concentrations than for this cut. (b) Relative undercooling as a function of [Ti] for constant Si and O. Figure 1b. shows the maximum reduced undercooling ($\Delta T_r = \Delta T/T_l$) for alloys as a function of Ti and Fe in $\text{Ti}_{94-x}\text{Fe}_x\text{Si}_4(\text{SiO}_2)_2$ alloys, $22 \leq x \leq 27$ (near the α -1/1 stoichiometry). ΔT_r falls sharply as the Ti composition is decreased below 71 at. % and remains constant over a significant range, corresponding to the region of primary solidification of $\alpha(\text{TiFeSiO})$.

Figure 2a shows a backscattered SEM image of solidified $\text{Ti}_{71}\text{Fe}_{23}\text{Si}_4(\text{SiO}_2)_2$, close to the ideal 1/1 composition (Figure 1a). The dendrites of the β solid solution phase (bcc, $a_0 = 3.0 \text{ \AA}$) are the primary crystallizing phase; $\alpha(\text{TiFeSiO})$ forms at lower temperatures. The microstructure for $\text{Ti}_{68}\text{Fe}_{26}\text{Si}_4(\text{SiO}_2)_2$, near the peritectic liquid composition (Figure 1a), is shown in Figure 2b. Here, the α -1/1 nucleates from the liquid, followed by the later formation of TiFe (CsCl-type, $a_0 = 3.0 \text{ \AA}$). The lower relative undercooling of alloys that solidify first to the α -1/1 presumably reflects a higher nucleation rate due to the strong similarity in local atomic structures between the crystal approximant and the liquid.

III. TiZrNi

As cast-samples of TiZrNi prepared near $\text{Ti}_{41.5}\text{Zr}_{41.5}\text{Ni}_{17}$ contain primarily the C14 Laves phase (an hexagonal, polytetrahedral, Frank-Kasper phase that forms over a wide composition range) and the $\alpha(\text{Ti/Zr})$ solid solution phase. When annealed at 570°C these samples form the stable icosahedral quasicrystal phase (i-phase)[6]. Higher temperatures lead to a 1/1-crystal approximant that is different from the one in the Ti-TM-Si-O alloys, the W-phase. Higher-order crystal approximants that are very similar to the quasicrystal have also been reported in these alloys [3]. Because this alloy system is replete with polytetrahedral phases, the nucleation behavior of these from the liquid is of great interest.

The phase diagram near the i-phase forming region is under investigation; it has been best studied at 600°C , near the formation temperature for the i-phase and W-phase. Anneals of as-cast samples for

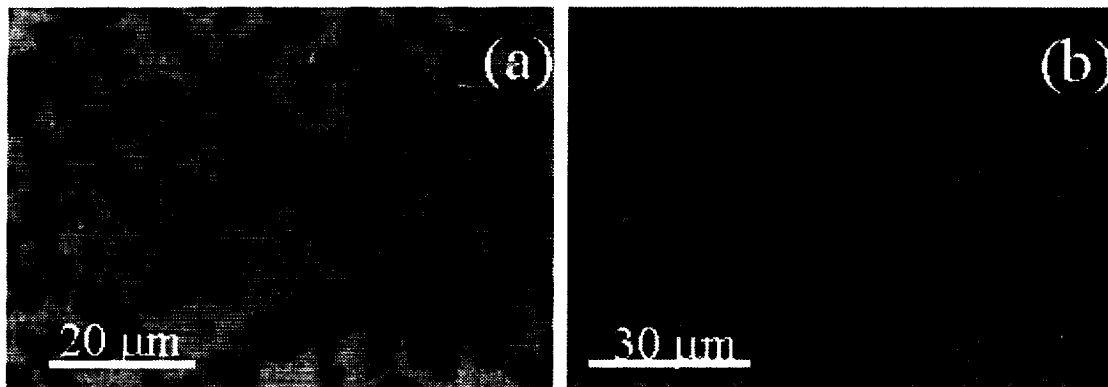


Figure 2. (a) Microstructure of undercooled $\text{Ti}_{71}\text{Fe}_{23}\text{Si}_4(\text{SiO}_2)_2$ (arrow 1 in Figure 1.a). The dendritic character of the dark phase, $\beta(\text{TiFe})$ solid solution, indicates that it crystallized first (possibly as $\alpha(\text{TiFe})$). The gray α -1/1 phase formed from the liquid at a lower temperature. (b) Microstructure of undercooled $\text{Ti}_{68}\text{Fe}_{26}\text{Si}_4(\text{SiO}_2)_2$ (arrow 2 in Figure 1.a). The convex shapes of the grains of the gray, α -1/1, phase indicate that they formed directly from the liquid. These are surrounded by the TiFe (light) phase, which grew from the remaining liquid at a lower temperature.

7-10 days produced the W-phase in a phase field between 0.32 and 0.4[Zr], 0.44-0.52 [Ti], and 0.13-0.17 [Ni]. While this bcc phase was originally reported to form at an optimum composition of $\text{Ti}_{44}\text{Zr}_{40}\text{Ni}_{16}$, more recent studies gave a better-ordered version at $\text{Ti}_{50}\text{Zr}_{35}\text{Ni}_{15}$ [9]. The composition range for i-phase formation is smaller, centered near 17 at.% Ni, 40 at.% Ti, and 43 at.% Zr, in reasonable agreement with the i-phase composition reported in previous studies. Initial studies suggest that the i-phase forms by a peritectoid reaction from the C14 phase and $\alpha(\text{Ti/Zr})$.

Unfortunately, the high density and low liquidus temperatures of the TiZrNi prohibit terrestrial rf-levitation studies near the quasicrystal or crystal approximant forming compositions in these alloys. For electrostatic levitation (ESL), charged droplets are held between two charged plates and melted by laser heating, decoupling the power required for levitation and allowing the study of TiZrNi alloys. X-ray diffraction patterns of as-cast alloys made near the 1/1-phase composition contain peaks corresponding to the C14 phase and $\alpha(\text{Ti/Zr})$. SEM backscattered images of the microstructures of these alloys show dendrites of a low [Ni] phase (presumably $\alpha(\text{Ti/Zr})$) imbedded in the higher [Ni] C14 phase (Figure 3.b). That the polytetrahedral C14 phase is not the primary phase (although the nucleation barrier should be less than for the solid solution phase) indicates that the phase field of the C14 must lie at a lower temperature. These conclusions are supported by initial undercooling studies in the ESL (Figure 3). The microstructure of undercooled alloys that were superheated to 1150°C showed equiaxed grains of the solid solution phase, with the C14 phase forming between the grains. The size and morphology of the solid solution phase indicated incomplete melting; the temperature was only above the solidus temperature for the C14 phase. By contrast, samples that had been superheated to 1350°C showed a finer grain structure, which is consistent with the primary crystallization of the solid solution phase from the liquid.

IV. Conclusions

Ground-based investigations have identified two alloy systems, Ti-Fe-Si-O and Ti-Zr-Ni, of interest for studies of the formation of ordered condensed phases with strong tetrahedral order. The 1/1 icosahedral crystal approximant, $\alpha(\text{TiFeSiO})$, $\text{Ti}_{72}\text{Fe}_{24}(\text{SiO}_2)_4$, forms by a peritectic transformation at approxi-

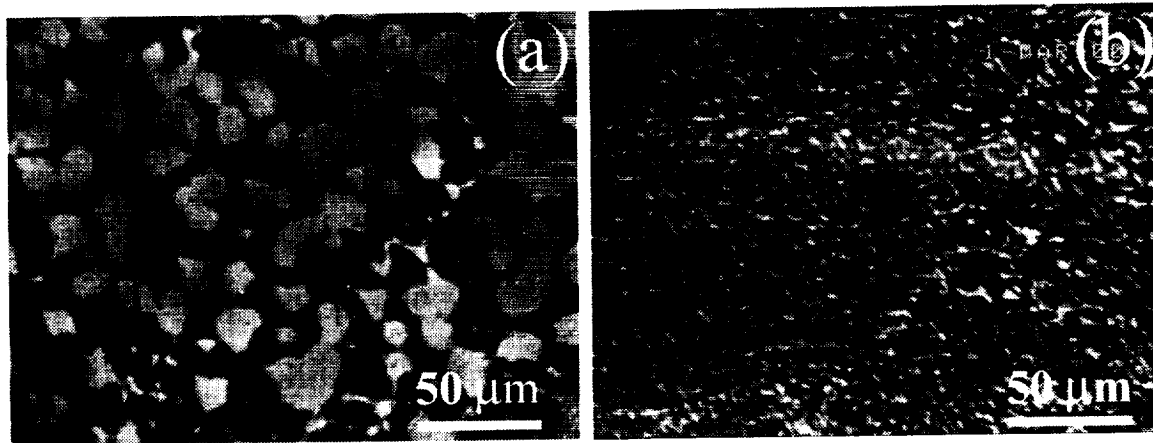


Figure 3. (a) Undercooled $\text{Ti}_{41.5}\text{Zr}_{41.5}\text{Ni}_{41.5}$ sample that had been superheated to 1150°C , showing large grains of the $\alpha(\text{Ti/Zr})$ solid solution phase (light), indicating incomplete melting of sample; (b) undercooled sample after superheating to 1350°C , showing finer grain structures, indicating solidification of complete sample.

mately 1200°C . The TiZrNi crystal approximant, W-phase, forms by a peritectoid transformation from the C14 Laves phase and the $\alpha(\text{Ti/Zr})$ solid solution phase. Undercooling studies of the C14 phase, also a polytetrahedral phase, are of interest in that alloy system. Undercooling studies in Ti-Fe-Si-O alloys show a broad minimum in the relative undercooling for alloy compositions near $\text{Ti}_{67-70}\text{Fe}_{27-24}\text{Si}_4(\text{SiO}_2)_2$, close to the peritectic liquid composition. This presumably reflects the ease of nucleation of the crystal approximant, due to a similar local atomic structure of that phase and the undercooled liquid.

To ensure that these results reflect homogeneous nucleation, to minimize convective effects so that diffusion effects on nucleation [10] and growth might be observed, and to obtain measurements of the thermophysical properties of the undercooled liquid, studies on the ISS using Advanced TEMPUS are planned. These future results will be coupled with continuing ground-based results of the undercooling. The local structures of the polytetrahedral phases will be contrasted with those of the liquids using x-ray scattering measurements of the undercooled liquids, made in collaboration with S. Krishnan.

V. Acknowledgements

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