Role of Hf on phase formation in Ti$_{45}$Zr$_{38-x}$HfxNi$_{17}$ liquids and solids


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Hafnium and zirconium are very similar, with almost identical sizes and chemical bonding characteristics. However, they behave differently when alloyed with Ti and Ni. A sharp phase formation boundary near 18-21 at.% Hf is observed in rapidly-quenched and as-cast Ti$_{45}$Zr$_{38-x}$HfxNi$_{17}$ alloys. Rapidly-quenched samples that contain less than 18 at.% Hf form the icosahedral quasicrystal phase, while samples containing more than 21 at.% form the 3/2 rational approximant phase. In cast alloys, a C14 structure is observed for alloys with Hf lower than the boundary concentration, while a large-cell (11.93 Å) FCC Ti$_2$Ni-type structure is found in alloys with Hf concentrations above the boundary.

To better understand the role of Hf on phase formation, the structural evolution with supercooling and the solidification behavior of liquid Ti$_{45}$Zr$_{38-x}$HfxNi$_{17}$ alloys (x=0, 12, 18, 21, 38) were studied using the Beamline Electrostatic Levitation (BESL) technique using 125keV x-rays on the 6ID-D beamline at the Advanced Photon Source, Argonne National Laboratory. For all liquids primary crystallization was to a BCC solid solution phase; interestingly, an increase in Hf concentration leads to a decrease in the BCC lattice parameter in spite of the chemical similarity between Zr and Hf. A Reitveld analysis confirmed that as in the cast alloys, the secondary phase that formed was the C14 below the phase formation boundary and a Ti$_2$Ni-type structure at higher Hf concentrations. Both the liquidus temperature and the reduced undercooling change sharply on traversing the phase formation boundary concentration, suggesting a change in the liquid structure. Structural information from a Honeycutt-Anderson index analysis of reverse Monte Carlo fits to the $S(q)$ liquid data will be presented to address this issue.
**Role of Hf on Phase formation in Ti45Zr38-xHfxNi 17 Ti45Zr(38-x)HfxNi17 Liquids and Solids**


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### Introduction

- Initial studies revealed a sharp boundary in phase formation around 21 at% Hf (x=21) in the Ti45Zr38-xHfxNi17 system. In quenched alloys the i-phase forms below the boundary, while a 3/2 rational approximant to the quasicrystal forms above. In cast alloys, the C14 Laves phase forms below and a T2N1-type (cF96) forms above. Further study of the liquid structure and evolution and the influence of Hf on phase formation and physical properties were studied using the Bamlime Electro Static Levitation (BESL) technique [1].

#### Experimental methods

- High resolution scattering data collected to 14.5 inverse Å
- Si(002) and Ni(001) generated by PDFguiX2 software [2]
- Evolution of g(r) at constant reduced temperature indicates local expansion (1st neighbor) and expansion then contraction upon traversing phase formation boundary at 2nd neighbor distances.
- What effects are causing the structural changes at near and extended length scales?

#### Liquid density measurement

- Liquid density measured using a photographic technique with droplet edge-fitting [3]
- Normalized density coefficient of thermal expansion peaking at boundary composition
- Heat of mixing for a regular solution

#### Structural simulation results

- Reverse Monte Carlo (RMC) simulation
- Rejection sampling algorithm using quality of fit (q) as energy function in Metropolis Monte Carlo (MMC)
- RMC reveals random arrangement of Zr and Hf generates best agreement to experimental data.

#### Experimental results

- Hf21 1000°C
- Hf21 1050°C
- Hf21 1100°C
- Hf18 950°C
- Hf18 1000°C
- Hf0 1000°C
- Hf0 1050°C
- Hf0 1100°C
- Hf0 1200°C

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### References and acknowledgments