Role of Hf on phase formation in Ti$_{45}$Zr$_{38-x}$Hf$_x$Ni$_{17}$ 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$_{38-x}$Hf$_x$Ni$_{17}$ 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$_{38-x}$Hf$_x$Ni$_{17}$ 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-xHfxNi17 Liquts 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 Ti2Ni-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 Bamelie Electro-Static Levitation (BESL) technique [1].

Experimental methods

- Measurements were done using a DIPXe2 diffractometer to obtain the pair distribution function from X-ray powder diffraction data. [3] The X-ray data was used to study the structural differences between liquid and solid.

Quantifying structure

- Remarkable supercooling below the phase boundary (c ≤ 18), roughly constant above
- Local icosahedral order more prominent in mixed Zr-Hf than in end points
- Effect of Hf above the phase formation boundary is to suppress the tendency to increase local icosahedral order with cooling; system is effectively jammed

Conclusions

- Remarkable undercooling has been observed, and can be attributed to increasing mismatch of undercooled liquid and BCC solid solution, due to increasing bond strength of Hf.
- Local cluster size is expanding with increasing Hf due to strain effects, while extended cluster size changes dramatically upon traversing phase boundary
- Below the boundary icosahedral order increases, allowing i-phase formation in quenching; above the boundary the local order is jammed allowing formation of the 3/2 RA
- Chemical effects, heats of mixing, cluster dynamics

Chemical effects, heats of mixing, cluster dynamics

References and acknowledgments

[6] Reverse Monte Carlo (RMC) simulation generates atomic configuration
[7] Rejection sampling algorithm using quality of fit (r2) square as analog to energy in Metropolis Monte Carlo (MMC)
[8] RMC reveals random arrangement of Zr and Hf generates best agreement to experimental data

Structural simulation results

- Reverse Monte Carlo (RMC) simulation generates atomic configuration
- Rejection sampling algorithm using quality of fit (r²) square as analog to energy in Metropolis Monte Carlo (MMC)
- RMC reveals random arrangement of Zr and Hf generates best agreement to experimental data

Electron configurations: Zr [Kr][5d¹⁰] Hf [Xe][6d⁴] [5f⁶⁰]
- Observed contraction of BCC lattice due to undercooling of 5d electrons in Hf
- Intermediate phases index to C14 (hexagonal) structure and cF96 (FCC) structure with residual beta
- C14 lattice parameters
  - a = 5.245 Å
  - c = 8.560 Å
  - packing frac. = 0.575
- cF96 lattice parameters
  - a = 11.92 Å
  - packing frac. = 0.565
- Crystal images adapted from [4]