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


Department of Physics, Washington University, St. Louis, MO 63130, USA

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, whiles samples containing more than 21 at.% Hf 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-xHfxNi 17 Ti45Zr(38-x)HfxNi17 Liquids and Solids

1 Washington University in St. Louis, 2 Ames Lab USDOE, 3 University of Massachusetts Amherst, 4 NASA Marshall Space Flight Center, 5 Iowa State University, 6 Argonne National Laboratory

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 T2Ni-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 Bamiline Electro-Static Levitation (BESL) technique [1].

Structural simulation results

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

Quantifying structure

● Honeycutt-Anderson (HA) index [8] and Bond Orientational Order parameter [9] (BOO) analyses used to quantify order in the RMC structures
● HA index describes bonded neighbors of a root pair, i.e.

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

References and acknowledgments


Electron configurations:

Zr: [Ar]4s24p65s25p66s2 6p6
Hf: [Xe]4f145d106s26p6

Other studies

● High resolution scattering data collected to 14.5 inverse Å
● S(q) and g(r) generated by PDFgetX2 software [5]
● 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 measured using a photographic technique with droped edge-fitting [5]
● Normalized density, coefficient of thermal expansion peaked at boundary composition

Heat of mixing for a regular solution

$\Delta H_{mix} = \Delta H_{Li} + \Delta H_{Ni}$

Estimates of the enthalpy of mixing favor mixing of Ni-Hf below the phase boundary; Ni-Zr above
● Atomic volumes (cm$^3$/mol)

Ti: 10.6  Zr: 14.1  Hf: 13.6  Ni: 6.6

In cooling liquics below the phase boundary, Hf will tend to mix with Ni and Ti in the inner shell, above the boundary Zr is more likely

Structural simulation results

Hf21 1200°C
Hf18 1050°C
Hf18 1000°C
Hf18 avg number density

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