Synopsis

The thesis introduces a novel alloy system based on submicron distributions of intermetallic phases realised through eutectic solidification in the ternary system Ni-Al-Zr. Various compositions in this system comprising of intermetallic phases distributed in different eutectic structures show ultra-high strength at temperatures upto 700°C combined with reasonable tensile plasticity, exceptional oxidation resistance and high temperature structural stability.

Intermetallics have long been used in high temperature alloys systems such as in the classical Ni-base superalloys that derive their strength from nanoscale dispersions of the aluminide, Ni_3Al(γ') in a matrix of disordered fcc Ni (γ), alloyed with expensive, high density refractory elements such as Re and Ru. The high temperature applications of intermetallics derive from their strength retention to high temperatures, creep resistance enabled by low diffusion rates, and attractive oxidation resistance based on high concentration of elements such as Al that forms stable oxides.

Several decades of effort on the development of new generation of intermetallic alloys through the 80's and 90's have gone unrewarded, with the exception of TiAl based alloys that are now used in recent generation aircraft engines. The promise of intermetallics as high temperature candidate materials is limited by their poor ductility or toughness arising from several intrinsic properties such as low grain boundary cohesive strength (in the case of Ni_3Al) or an insufficient number of slip systems (as in NiAl) or extrinsic effects such as embrittlement by hydrogen (Fe_3Al) that derive fundamentally from the existence of directionality in bonding.

However, low ductility or toughness can often be alleviated by limiting the length scale for slip. We have therefore examined the possibility of combining intermetallics in the form of eutectic structures, potentially limiting slip lengths within each intermetallic constituent. Eutectic structures in binary systems limit the choice of intermetallic combinations so that finding such combinations with engineering potential is difficult. On the other hand combinations of three elements or more would enable a significantly larger set of permutations of eutectic intermetallics, provided the constituent binary phase diagrams contain either eutectic or peritectic reactions involving intermetallic phases, as well as intermediate intermetallic phases.

The ternary Ni-Al-Zr system met our criterion in several ways. The Ni-Al binary phase diagram shows a peritectic reaction from liquid and NiAl ($Pm\overline{3}m$, B2 with a lattice parameter of 0.288nm) to form Ni_3Al ($Pm\overline{3}m$, $L1_2$ with a lattice parameter of 0.356 nm), intermetallics that have been extensively investigated in earlier literature. The Ni-Zr system shows a peritectic reaction between liquid and the Ni_7Zr_2 (C12/m1 with a lattice parameters a=0.469nm, b=0.823nm, c=1.219nm) phase to form the intermetallic Ni_5Zr ($F\overline{4}3m$ with a lattice parameter of 0.670nm). Further the NiAl and Ni_7Zr_2 are both intermediate phases and should therefore form a mono-variant eutectic on the composition line joining these two phases in the ternary system. We note that Zr participates in many glass forming systems. In the Ni-Zr system, for example, glass forming ability has been associated with the structure of the liquid phase and associated low diffusivity. As a consequence, a fine scale eutectic structure may be expected. Zr has also been reported to strengthen and ductilise Ni_3Al and NiAl. Finally, both Al and Zr form stable oxides and might promote oxidation resistance.

After introducing the thesis in **Chapter 1**, the experimental details are outlined in the **Chapter 2**. The experimental results and subsequent discussions are presented in three subsequent chapters. **Chapter 3** reports the microstructural aspects of as cast alloys in this ternary system Previous literature and our analysis of phase equilibria in the Ni-Al-Zr system based on Thermo-Calc, suggested that solidification from the liquid to form the Ni_3Al + Ni_5Zr, Ni_3Al + Ni_7Zr_2 and NiAl+ Ni_7Zr_2 eutectics is possible. We obtained eutectic structures involving combinations of these intermetallic phases along a constant zirconium section at 11 at. %. The alloy A (Ni-77 at.%, Zr-11at.% and rest Al) contains eutectic structures containing the Ni_3Al and Ni_5Zr phases in two morphologies, a planar, lamellar structure and a more irregular form. The alloys B (Ni-74 at.%, Zr-11at.% and rest Al) and C (Ni-71 at.%, Zr-11at.% and rest Al) contain two different eutectic structures that combine the Ni_3Al and Ni_7Zr_2 phases, and the NiAl and Ni_7Zr_2 phases. These phases were identified by a combination of X-ray diffraction, transmission electron microscopy coupled with energy dispersive spectroscopy and electron probe microanalysis. The volume fraction of each eutectic constituent is different in the two compositions in that alloy B(Ni-74 at.%, Zr-11at.% and rest Al) contains significantly higher volume fractions of the eutectic containing the Ni_3Al and Ni_7Zr_2 phases than the alloy C (Ni-71 at.%, Zr-11at.% and rest Al).

In order to understand effect of individual phases we have melted several other alloys (alloy D to I) bounding these eutectic alloys (7-25 at.% Al, 5-15 at.% Zr and rest Ni) that form primary solidification phases of the intermetallic structures that constitute the eutectics.

Chapter 4 discusses the mechanical behaviour of the fully eutectic alloys alloys as well as alloys with a combination of primary phases along with a eutectic. Mechanical behaviour was assessed in vacuum arc melted and suction cast material. The compressive strength of eutectic and off-eutectic compositions has been evaluated as a function of temperature. Very high strength levels of around 2 GPa could be achieved accompanied by reasonable room temperature tensile plasticity in the range 3-4%. The introduction of the respective primary phases of NiAl, Ni_3Al, Ni_5Zr and Ni_7Zr_2 results in decrease of strength. We have explored the origins of strength and tensile plasticity in alloys through micro and pico indentation (hardness) measurements and an examination of slip lines and crack initiation on pre-polished surface of the tensile tested samples as well as by transmission electron microscopy.

Chapter 5 explores the oxidation resistance of these alloys in isothermal tests. The oxidation resistance of alloys compares well with recently developed cast single crystal alloys. Clearly, the oxide scale is extremely adherent and no spalling occurs. Electron microprobe analysis shows the presence of a fine scale, layered oxide structures and reaction zones within the substrate. The oxidation behaviour has been characterized using TGA, XRD and EPMA. We have attempted to understand the mechanism of oxidation through analysis of rate constants and activation energy coupled with microstructural observations.

Chapter 6 presents a summary of the current work and present the scope for further work.