SYNOPSIS

Nickel based superalloys are high temperature materials which find application as blade and disc components of jet engines due to their ability to retain their mechanical properties at temperatures close to 0.8 of their melting point. The modern day nickel based superalloys are multicomponent alloys, containing up to 12 alloying elements which are added in balanced proportions to achieve high temperature strength and microstructural stability, Re and Ru have been the recent additions made to superalloy compositions in the last two decades. But the roles of Re and Ru in terms of partitioning among the phases γ and γ' and its effects on mechanical properties are still not clear. Hence an effort was made to study their effects under constrains of constant volume fractions of γ' and misfit between γ and γ', to isolate effects that result purely due to composition. Three model alloy systems (two ternary and one quaternary) of the type Ni-Al-xRe, Ni-Al-yRu and Ni-Al-xRe-yRu, x=2.5/4 and y=2.5/6 with minor additions of 1.4 Hf and 0.07 C for reasons of castability were synthesized by investment casting. This thesis deals with the solidification related aspects of these alloys.

Chapter 1 deals with a brief overview of Ni based superalloys in terms of their physical metallurgy, processing, microstructure and the effects of Re and Ru studied in literature. These are summarized and the objective of thesis laid out. The experimental details of the techniques employed for studying the cast structure such as optical microscopy, scanning electron microscopy, electron probe microanalysis and differential scanning calorimetry are discussed in Chapter 2

In Chapter 3, the experimental results concerning microstructure, chemistries (local and global), differential scanning calorimetry and supporting Thermo-Calc based simulations are presented. The composition of the directionally solidified alloys were estimated using quantitative EPMA spot analysis after homogenizing them to the best possible extent. The cooling rates experienced by the bottom, middle and tip sections (25mm, 150mm and 295mm respectively from chill plate) of the model alloys during casting was estimated using ProCAST^{TM} simulations. The simulations show the cooling rates to vary from 12.5 K/min to 6 K/min, corresponding to the range of thermal gradients 3000 K/m to 1500 K/m from bottom to tip sections. These estimations were performed assuming a constant withdrawal velocity of 24 cm/hr.

The morphological evolution of cast structure from bottom to tip section of the alloys was studied at a coarse scale with the aid of optical microscopy. A tendency towards increased branching of dendrites to form well developed tertiary arms is observed on moving from bottom to tip sections. Quantitative measurement of primary and secondary arm spacings (PDAS and SDAS) indicate that PDAS values increase from bottom to middle section and then saturates, whereas the SDAS values show an increase from bottom to tip sections. Also, the PDAS and SDAS values of MA-3 were observed to be larger than that of MA-2 and 1 for a given section. Another observable feature at this coarse scale is the evolution of inter-dendritic area fractions, which was observed to decrease from bottom to tip sections. The inter-dendritic areas were also observed to be less interconnected on moving from bottom to tip sections. Also the area fraction of inter-dendritic areas were found to be lesser in MA-3 compared to MA-1 and 2.

Scanning electron microscopy (SEM) operated in the BSE mode reveals finer scale details observed within the dendrites and in the inter-dendritic areas. The γ’ nodules

formed within the dendrites through solid state reaction were found to increase in size on moving away from the dendrite core towards the tip of the dendrites. The inter-dendritic areas were observed to form a fan like structure consisting of γ/γ' lamellae showing a variation of γ' size from fine to coarse depending on its location within the inter-dendritic region. The inter-dendritic regions also consisted of bright phases such as carbides, which were blocky in case of MA-1and in case of MA-2 and 3 it was found to be script like. The other bright phase observed was one consisting of alternate bright and dark contrast when viewed at higher magnifications. This phase was absent in the bottom section of the model alloys.

An estimate of composition of features observed in the cast structure was made using electron microprobe analyses, operated in spot analysis mode and X-Ray mapping mode to generate quantitative and qualitative data. Re, Ni and Ru partition to dendrite core, whereas Al and Hf partition to the liquid or inter-dendritic regions. The bright eutectic phase to be rich in Ni and Hf and also in Ru in case of MA-3. Compositional data from single and multiple dendrites collected in the form of a grid of spot analyses points were used to build iso-composition contour maps of elements. These maps provide complementary visual evidence of elemental partitioning, and they also reveal the anomalous distribution pattern of Re, Ni, Al and Hf. It is observed that Re and Ni are found to be enriched at the secondary dendrite arm to the same extent as at the core of dendrites, similarly Al and Hf are found to be depleted in these locations. Thermo-Calc based simulations were used to estimate the local melting temperatures from the EPMA composition contours, the contours of melting points complement the compositional data. The data were analyzed to obtain the variation of composition with fraction solidified.

The thermo-physical properties of the model alloys were determined through differential scanning calorimetric (DSC) studies. The estimated thermo-physical properties such as liquidus, incipient melting temperature, dendrite melting temperature and temperature for complete solidification of last liquid show an increase in value with Re addition the carbide formation temperature was observed to be the same for MA-1, 2 and higher than that of MA-3. The DSC method was also made use of to generate specific heat (Cp) vs temperature curves, through which the fraction solidified as a function of temperature during cooling was determined. These tests were performed at a heating/cooling rate of 12.5 K/min to simulate the solidification conditions of bottom sections. The Cp vs T curves indicate a decrease in amount of last liquid to solidify from MA-1 to 3.

In Chapter 4 the observations made in Chapter 3 are correlated with the help of Thermo-Calc based simulations. The efforts to predict critical transformation temperatures such as liquidus, incipient melting and final solidification temperature using Thermo-Calc resulted in an overestimation of these values by the software. However, the trends were predicted correctly. A comparison of the critical transformation temperatures with values reported in the literature concerning systematic studies on multicomponent Re/Ru alloys indicate the role of base composition on these effects. The estimated thermo-physical properties indicate the difficulty in homogenization of MA-1 due to its narrow homogenization window compared to MA-2 and 3. The EPMA results indicate that Re segregates strongly in comparison to the other elements.

Analysis of microstructural parameters such as PDAS and SDAS indicate the role of off-axial nature of heat flows to contribute to the development of secondary and tertiary arms far away from the bottom sections, where these effects are found to be prominent. These effect are thought to cause the saturation of PDAS from middle to tip sections. However, the SDAS is observed to depend only on local time for solidification which is found to increase linearly with decrease in cooling rate from bottom to tip sections. Also, among the model alloys the decrease in PDAS from MA-3 to 1 correlated well with the decrease in solidification range.

The thesis throws brings out some observed anomalies such as the saturation of PDAS from middle to tip section, the relation between well developed secondary and tertiary arms with reduction in eutectic volume fraction and the localized increase in Re, Ni and depletion of Al and Hf at the secondary arms. These observations provide scope for further investigation.