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論 文 内 容 要 旨

Ni based superalloys are being considered for effective high temperature material among various heat resistant alloys due to their excellent microstructure stability at elevated temperature. Since Ni based superalloys have been developed, many works are being introduced to improve the high temperature performances with advancing the fabrication methods and microstructural stabilities. From the modification of fabrication method, grain structure in as cast condition can be controlled by mainly equiaxed grain structure (conventional casting), longitudinal columnar grain structure and single crystal structure (directional solidification). Because inter granular fracture is easily progressive during in service under creep stress, grain boundary morphologies in macro scale play a crucial role to develop at elevated temperature. On the other hand, microstructure stabilities can be modified by change of misfit strain between γ matrix and γ' precipitate as well as volume fraction of γ' precipitate which contribute to dislocation movement during high temperature deformation. Thus, high temperature performance of Ni based superalloys could be optimized.

Inconel 713C (IN-713C) alloy is one of conventional casting Ni based superalloy which is early developed one among casting alloys. This alloy is being applied for the materials of turbine wheel and waste gate valve in automotive turbocharger parts. Recently, however, according to strengthened emission gas regulation, application of turbocharger is being extremely extended from diesel engine (used at around 1123K) to gasoline engine (used at around 1273K). In addition, even if competitive Ni based superalloy such as Mar-M247 alloy which has higher strength of 20% than IN-713C alloy has been considered, application could not be progressive because of high cost of refractory element addition. Therefore, alternative investigation to develop the high temperature properties of IN-713C alloy should be considered by low cost effect and it can be achieved with micro alloying element addition.

As one of candidate for micro alloying element in Ni based superalloy, numerous researches for rare earth element additions have been introduced with mainly Cerium (Ce), Lanthanum (La) and Yttrium (Y). High temperature mechanical properties, oxidation resistance and microstructure characteristics could be advanced with extremely small amounts of addition as ppm order. Although addition contents are extremely small in alloy system, because of thermodynamically stable precipitation formation along grain boundary, they could modify the overall high temperature mechanical properties in Ni based superalloy. However, detailed mechanisms for their addition effects on microstructure evolution are still not solved. Furthermore, previous studies for IN-713C alloy using with rare earth element addition have not been concerned yet. Therefore, objective of this research is to find out the relationship between high temperature mechanical properties and microstructure as well as their metallurgical behavior by micro alloying rare earth element addition. As target element, Yttrium addition has been investigated which is regarded as more conventional element in heat resistant alloy than other rare earth elements.

The entire research sequence is followed by effect of Yttrium addition on high temperature mechanical property and microstructure in as cast IN-713C alloy in chapter 2, and secondly study for solidification behavior and relationship between segregation during solidification and microstructure evolution in chapter 3, and effect of heat treatment on microstructure evolution in chapter 4, and finally controlling the solidification structure of precisely fabricated IN-713C alloy by electron beam melting process.

In as cast IN-713C alloy, small amount of Yttrium addition as 0.05 and 0.09 mass% effectively modified the solidification structure. Equiaxed grains in center of ingot showed higher fraction in Yttrium added alloy than conventional IN-713C alloy. At the same time, length and fraction of columnar grain decreased more and more. However, Yttrium addition does not affect the grain refinement effect in as-cast IN-713C alloy. In addition, high temperature ultimate tensile strength and elongation could be enhanced by 0.05%Y added IN-713C alloy, while 0.09%Y added alloy IN-713C alloy showed decreased elongation which means 0.09%Y addition in IN-713C alloy is detrimental. Furthermore, 0.05%Y added IN-713C alloy showed low error range for high temperature rupture life compared with conventional and 0.09%Y added IN-713C alloy. Therefore, optimum composition of Yttrium addition in as cast IN-713C alloy was shown with 0.05 mass%. Consequently, changed solidification structure with large fraction of equiaxed grain could be main factor to enhance the reproducibility of high temperature mechanical properties in IN-713C alloy. In order to solve the reason for solidification structure evolution by Yttrium addition, solidification behavior has been extensively discussed in chapter 3.

Theoretically, solidification behavior which affects to solidification structure during dendritic growth, is governed by solute rejection at solid liquid interface depending on distribution behavior of alloying element and cooling rate as well. In order to clarify the Yttrium addition effect on solidification behavior, specimens were prepared with differently cooled IN-713C alloys during casting process. By nine number of specimens, tendencies of Yttrium addition effects have been researched. In all the examined cooling condition, Yttrium promoted the equiaxed dendritic grains in center of ingot. Dominant factors affecting the formation or equiaxed grain have been investigated with various experiments. As results, dendrite fragmentation occurred by elemental segregation during solidification was predicted to act as nucleation site for equiaxed grain, and its process might be accelerated by Yttrium addition. Furthermore, the relationships between Yttrium addition and factors affecting dendrite fragmentation have been investigated with extensive microstructure observation. Finally, solidification behavior and microstructure evolution mechanism were clarified in chapter 3. was studied as well. Moreover, in chapter 5, tendency to form the equiaxed grains has been investigated with electron beam melting technique which can precisely control the solidification behavior during manufacturing process. Yttrium added alloy showed equiaxed grains compared with other commercial Ni based superalloys in similar process parameters.

However, interdendritic segregation in as cast microstructure is always regarded as detrimental effect for high temperature mechanical property in Ni based superalloys due to chemical inhomogeneity. The key to reduce the dendritic segregation can be achieved by post heat treatment process.

In chapter 4, effect of homogenization treatment (solution treatment) and aging treatment on microstructure evolution has been introduced. Under standard solution treatment for IN-713C alloy, morphological changes of primary γ' phase have been observed by Yttrium addition. Fraction of undissolved primary γ' phase became abundant by Yttrium addition, which means Yttrium might change the solvus temperature of γ' precipitation. Furthermore, Yttrium changed the elemental partitioning behavior for γ matrix and γ' phase during heat treatment. After long time aging treatment, coarsening behavior of γ' phase has changed. Yttrium addition effectively retarded the coarsening rate of γ' phase after aging for 200h. It is well stated for Ni based superalloy that coarsening of γ' phase is governed by Ostwald ripening. Ostwald ripening of γ' phase is considered with elastic misfit strain effect between γ matrix and γ' phase as well as diffusivity of γ' phase. In this study, calculated misfit strain showed weak difference by Yttrium addition. Moreover, elemental partitioning behavior obviously changed that partition coefficient for Al and Ti in γ' phase was stronger in Yttrium added IN-713C alloy which means, because Al and Ti in γ' phase have low diffusivity at high temperature, those elements might play a role to retard the diffusivity of γ' phase, thereby lower coarsening rate of γ' phase in Yttrium added IN-713C alloy. Consequently, small amount of Yttrium addition effectively changed the dissolution and coarsening behavior of γ' phase during heat treatment.

In this dissertation, effect of Yttrium addition on microstructure evolution in as cast and heat treated IN-713C alloy has been introduced. Based on entire research results, Yttrium addition influence is beneficial for high temperature mechanical properties as well as microstructure stability during in long time service when its addition contents are extremely low.

論文審査結果の要旨

インコネル 713C (IN-713C) 合金は、鋳造用耐熱合金として開発された Ni 基超合金の 1 つである。当該合金は、自動車用ターボチャージャー部品などとして適用されているが、最近の排出ガス規制強化により、より高温領域での使用が求められるようになっている。本論文は、 インコネル 713C 合金の耐熱性を含む力学的特性改善を目的として、希土類元素（Y）のマイクロアロイング効果について、力学的特性と微細組織との関係について調査を行い、耐熱性改善の指針について記述するもので、以下の 6 つの章からなる。

第 1 章は序論であり、研究の背景と目的について述べている。

第 2 章では、希土類元素として Y を選択し、Y をマイクロアロイングした IN-713C 合金の高温強度特性の評価を行っている。その結果、Y 添加は IN-713C 合金の鋳造組織の等軸化に効果を発揮し、高温領域における延性と高温クリープ特性を改善することを見出している。これは、Y のマイクロアロイング（0.05mass%）効果により、均一な鋳造組織が得られたことに起因するとしている。

第 3 章では、IN-713C 合金の鋳造組織形成に及ぼす冷却速度の影響について、Y 添加効果とともに詳細に調べている。その結果、冷却速度の増加はγ'相の微細析出を促し、γ/γ'共晶コロニー組織形成の要因となるデンドライト/デンドライト間の偏析を助長する。Y のマイクロアロイングにより等軸デンドライト組織が形成しやすく成り、またγ/γ'共晶コロニー組織よりもむしろγ/γ'偏晶組織を形成させることを示している。

第 4 章では、Y をマイクロアロイングによって改良した IN-713C 合金の熱処理による微細組織の変化について調べている。その結果、鋳造時に導入されるγ/γ'共晶コロニー組織は均一化熱処理により除去されるが、Y 添加はその熱処理効果を高める。さらに、IN-713C 合金のγ'相は熱処理により一方向へ粗大粒成長するが、Y のマイクロアロイングにより粒成長が抑制されることを見出し、耐クリープ性の改善に寄与することを指摘している。

第 5 章では、電子ビーム積層造形（EBM）によって製造された Y のマイクロアロイングにより改良された IN-713C 合金の組織を調べ、急速凝固された際に生じるご微細組織変化について詳細に調査を行っている。結果として、EBM によって作製された合金試料にはデンドライト/デンドライト境界に生じる Y 偏析は消失し、強度低下の原因となる、γ/γ'共晶コロニー組織が除去される。また、粒界に沿って形成される炭化物も 1μm 以下程度の微細な析出物となることを明らかにし、耐熱 Ni 基超合金の製造プロセスとして EBM プロセスの高い可能性を示している。

第 6 章では、以上の成果を総括し、今後の研究の指針を提案している。

本研究は IN-713C 合金の凝固挙動に対する Y のマイクロアロイング効果について詳細に調べ、耐熱性向上についての指針を示している。また、EBM プロセスの有する超急冷効果を利用することで Y 添加された IN-713C 合金の耐熱特性の改善に関して高い可能性を示し、今後の Ni 基耐熱合金の技術開発の指針を示しており、材料システム工学の発展に寄与するところが少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。