Distribution of Platinum Group Metals in Ni-Base Single-Crystal Superalloys

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Abstract

The effects of platinum group metals (PGMs) addition on microscopic characteristics of Ni-Al-PGM ternary and Ni-base single crystal superalloys were investigated. Several Ni-19at%Al-Xat% PGM (PGM: Ru, Rh, Pd, Ir and Pt) ternary alloys were prepared by arc-melting in order to understand the distribution of PGMs in γ and γ' two phases. It is found from differential thermal analysis (DTA) that among PGMs, Ir and Ru increase the melting points whereas Pt and Pd decrease the melting points. These alloys were successfully solution treated at 1300°C for 4h. After ageing treatment, all Ni-19Al-1PGM alloys form γ and γ ' two-phase structure, while 9at% addition of Ir, Ru, Rh and Pd leads to the precipitation of PGM-enriched phase which is different from both y and y' phases, except for a Ni-19Al-9Pt alloy which maintains γ and γ' two-phase structure. SEM-EDX analysis revealed that Ir and Ru have a preference to partition to the y phase while Pt, Pd and Rh have a preference for the γ ' phase. Microscopic distribution of Ir and Ru in multi-component Ni-base single crystal superalloys were also investigated. Atomprobe field ion microscopy (APFIM) revealed that partitioning behaviour of Ir in multi-component Ni-base single crystal superalloys depends on alloy composition. For Re-free alloy TMS-79, Ir atoms have a small preference to be located in the γ phase, while for Recontaining TMS-80, Ir tends to partition to the γ' precipitates. On the other hand, Ru is found to prefer the γ phase in Re-containing TMS-91. These results suggest that among alloying elements, 'competition of partitioning' takes place in multi-component alloys. The order of alloying elements having stronger preference to the γ phase can be summarized as Re > Cr > (Mo, Ru, Co) > W > Ir.

Introduction

Ni-base single crystal superalloys, which have remarkable mechanical properties at elevated temperatures, have been designed for use as turbine blades in aeroengines. In order to develop higher efficiency engines, considerable efforts are still devoted to enhance the temperature capabilities of superalloys. In addition to Ni and Al, superalloys usually contain several alloying elements, such as Cr, Co, Mo, W, Ta. Among these alloying additions, much attention has recently been paid to Re since the development of CMSX-4⁽¹⁾ because of its contribution to improve both the creep and corrosion properties. However, the solubility limit of Re in Ni is rather low due to the difference in crystallographic structure between Re (hcp) and Ni (fcc). Also, since Re has a low diffusibility, Re

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atoms tend to be segregated in matrices. The addition of Re thus assists the formation of a topologically closepacked (TCP) phase, resulting in deteriorating the creep properties. On the other hand, the addition of platinum group metals (PGMs) in Ni-base superallovs is of particular interest. Since PGMs usually have high melting points and high hot corrosion resistance, addition of PGM is expected to enhance high temperature mechanical properties and hot corrosion resistance. Moreover, except for Ru and Os which have hcp structure, PGMs and Ni have the same fcc crystal structure and they form a complete solid solution system. Therefore we expect that a fairly high amount of PGMs can be alloyed in contrast to Re. However, there are few reports investigating the effect of PGM addition in Ni-base alloys⁽²⁻⁶⁾. The aim of this study is to investigate the distribution of PGMs, such as Ru, Rh, Pd, Ir and Pt, in Ni-base γ and γ' two phase alloys. This paper deals with two kinds of alloy systems. As a fundamental investigation, Ni-Al-PGM ternary alloys having γ and γ' two phases were examined. The microscopic distribution of Ir and Ru in multicomponent Ni-base single crystal superalloys were investigated as a next step, with discussing the change in partitioning behaviour of alloying elements as a function of alloy composition.

Table I Chemical composition of alloys (in at%)

Alloy	Ni	Al	Ir	Ru	Rh	Pd	Pt
1Ir	Bal.	18.1	0.95	-	-	-	-
3Ir	Bal.	18.5	2.81	-		-	-
5Ir	Bal.	18.0	4.72	-	-	-	-
9Ir	Bal.	18.1	8.60	-	-	-	
1Ru	Bal.	18.2	-	0.90	1	-	-
5Ru	Bal.	18.3	-	4.88	1	-	-
9Ru	Bal.	18.4	-	8.81	-	-	-
1Rh	Bal.	18.3	-	-	0.94	-	-
5Rh	Bal.	18.7	-	-	4.73	-	-
9Rh	Bal.	19.1	-	-	8.11	-	-
1Pd	Bal.	18.2	-	-	-	0.92	-
5Pd	Bal.	18.5	-	-	-	4.69	-
1Pt	Bal.	18.2	-	-	-	-	0.91
5Pt	Bal.	18.5	-	-	-	-	4.50
9Pt	Bal.	18.4	-	-	-	-	8.22

Ni-Al-PGM ternary alloys

Experimental procedure

In order to obtain alloys having γ and γ' two phases, several Ni-19at%Al-Xat%PGM alloys were arc-melted under Ar in a vacuum chamber. Chemical composition of the as arc-melted alloys was determined by fluorescent X-ray spectroscopy, and the result is listed in Table I. Hereafter, the alloy name is denoted as 1Ir, 5Pt etc. The SEM-EDX analysis for the as arc-melted alloys confirmed that in all the alloys, Ni, Al and PGM are uniformly mixed without segregation. DTA was then conducted to obtain melting points of the alloys. DTA runs were all performed at a heating / cooling rate of 10K / min starting from room temperature to 1550°C. The alloys were then heat-treated at 1300°C for 4h followed by water quenching and then aged at 1100°C for with 100h water quenching to investigate microstructural evolution. The heat-treated specimens were examined by optical microscopy (OM) and SEM-EDX analysis.

Results and Discussions

The melting temperatures of the as-cast ternary alloys were measured using DTA. Figure 1 summarizes the relationship between PGM content and liquidus points. It is found that liquidus temperatures of Ir-containing alloys linearly increase with increasing Ir content. The increment rate is roughly estimated to 4.7K / 1at%Ir.



Figure 1: The relationship between liquidus points and PGM content.



Figure 2: the (a) Ni-Ir, (b)Ni-Ru and (c)Ni-Pd binary phase diagrams⁽⁷⁾.



Figure 3: Typical SEM images of (a)11r, (b)1Rh, (c)1Pd and (e)1Pt alloys aged at 1100°C for 100h.

While Ru addition also increases melting points, Pt and Pd addition is found to decrease melting temperatures. These results can be explained from the Ni-PGM binary phase diagrams. Figure 2 shows the (a)Ni-Ir, (b)Ni-Ru and (c)Ni-Pd binary phase diagrams⁽⁷⁾. The phase diagram of the Ni-Rh system is similar to the Ni-Ir system and the Ni-Pt being similar to the Ni-Pd system, respectively. Ir, Rh, Pt and Pd all have identical crystal structure to Ni and they all have complete solid solubility with Ni at high temperatures. However, while Ni-Ir and Ni-Rh have a continuous series of (Ni, Ir) and (Ni, Rh) solid solution system and the melting points steadily increase with increasing Ir and Rh content, Ni-Pt and Ni-Pd systems exhibit a minimum in the liquidus. The decrease of melting points in Ni-Al-Pt and Ni-Al-Pd systems can be caused by this eutectic-like reaction of Ni-Pt and Ni-Pd. In designing Ni-base alloys, elemenets which increase melting temperature are favourable because at a given temperature, an alloy having a higher melting point generally has better mechanical properties. From this point of view, it is suggested that Ir, Ru and Rh are promising elements to increase the creep properties.

The alloys were heat treated at 1300°C for 4h followed by water quenching. OM and SEM analysis revealed that except for 5Rh, 9Rh, 9Ir and 9Ru, all the alloys showed almost uniform microstructure, indicating that the alloys can be fully solution-treated at 1300°C. Following the solution treatment, ageing treatment at 1100°C for 100 h was conducted. Figure 3 shows the typical SEM images of aged (a)1Ir, (b)1Rh, (c)1Pd and (d)1Pt alloys. All the alloys have γ and γ' two-phase structure, confirming that for all PGMs, 1at% of alloying addition is within the solubility limit in the γ and γ ' two-phase region. On the other hand, 9at% of PGM addition except for Pt exceeds the solubility limit for the γ and γ ' twophase region and leads to precipitate other phase as shown in Figure 4. It should be noted that 9Pd alloy has not yet been investigated. EDX analysis indicated that the third phase shown in this figure can be identified as

Figure 4: SEM images of (a)9Ir, (b)9Ru, (c)9Rh and (d)9Pt alloys after aged at 1100°C for 100h.

the β phase having B2 structure, or its higher order phase, with composition being approximately (Ni,PGM)50Al50.

According to Al-PGM phase diagrams⁽⁷⁾, only Pt and Al form the Pt₃Al phase with L1₂ structure. It is thus likely that Ni₃Al may equilibrate with Pt₃Al to form (Ni,Pt)₃Al. In this case, unlimited amount of Pt could be substituted for Ni in the γ and γ ' two-phase region. Other PGMs such as Ir, Ru, Rh do not form L1₂ structure, they only have B2 structure with Al in Al rich region. If this β phase seems to be chemically stable, increasing PGM content would change the microstructure from y and y' two-phase to $\beta + \gamma$ or $\beta + \gamma$ $\gamma + \gamma'$ etc. To confirm this hypothesis, however, further investigation will be required.

In order to determine the partitioning behaviour of alloying elements, EDX analysis was conducted for alloys having y and y' two phases. Whether an alloying element 'i' partitions to the γ phase or γ ' phase can be clearly shown by using a partitioning parameter k_i which is defined as

 $k_i = c_{i\gamma} / c_{i\gamma}$ where $c_{i\gamma}$ and $c_{i\gamma}$ are the concentrations of an alloying element 'i' in the y and y' phases, respectively. Thus, for example, when $k_i > 1$, the element 'i' has a tendency to be located in the y phase and vice versa. In Figure 5, partitioning parameters of PGMs are summarized as a function of k_i . Ru and Ir have a preference to partition into the y phase while Pt, Rh and Pd have a preference to partition into the y' phase. Elements to have larger atomic radii and to enrich in the y phase are of particular interest because they preferentially increase the lattice parameter of y phase and thus leads the lattice misfit $(a_r - a_r)/a_r$ towards negative direction⁽⁸⁾. It is also expected that alloys having a preference for γ phase play a role as a solid solution strengthner of the y phase. Since PGMs all have larger atomic radii than Ni, (When normalising the atomic radus of Ni as 1, the atomic radii of Rh, Ru, Ir, Pt and Pd are 1.079, 1.063, 1.089, 1.113 and 1.104, respectively⁽⁹⁾.) it is predicted that Ru and Ir lead the lattice misfits to negative direction while Pt, Rh

Figure 5: Partitioning behaviour of PGM in Ni-19Al-PGM ternary alloy systems.

and Pd leading to positive.

From these experimental results, it is expected that Ir and Ru, which increase the melting temperatures and partition to the y phase in ternary alloy systems, will play a favourable role in enhancing creep properties of Ni-base superalloys. The effects of Ir or Ru addition to multi-component Ni-base alloys are therefore discussed in the following section.

Multi-component Ni-base single-crystal superalloys

Experimental procedure

The compositions of alloys investigated here are listed in Table II. Among these alloys, composition of TMS-63 and TMS-75 were determined by using 'alloy design program' (ADP)^(10,11), which is the regression analysis based computer program developed by the authors, for designing Ni-base superalloys. The mechanical properties and microstructures of TMS-63^(10,11) and

Alloy	Ni	Al	Cr	Co	Mo	Ta	W	Re	Ru	Ir	
TMS-63	Bal.	12.8	7.8	-	4.6	2.8	-	-	-	-	
TMS-79	Bal.	12.6	7.7	-	4.6	2.7	-	-	-	1.8	
TMS-75	Bal.	13.7	3.6	12.6	1.3	2.1	2.0	1.7	-	-	
TMS-80	Bal.	13.6	3.5	12.4	1.3	2.0	2.0	1.7	-	1.0	
TMS-91	Bal.	13.3	3.5	12.3	1.2	2.0	2.0	1.6	0.9	-	

Table II Nominal composition of alloys (in at%)

TMS-75⁽¹²⁾ have already been reported in previous papers. The Re-free TMS-79^(2,3) was obtained by the 1.8at% of Ir addition to the base material TMS-63, and Re-containing TMS-80 and TMS-91 were obtained by the 0.8at% of Ir addition, and the 0.9at% of Ru and 1.5at% of Ni addition to the base material TMS-75, respectively. The alloys were solution treated at 1300°C for 1h followed by 1320°C for 5h and gas fan cooled. After then, TMS-91 was aged at 1150°C for 4h followed by gas fan cooled, and the other two alloys were aged at 1100°C for 5h and water quenched to form coherent cuboidal γ ' precipitates. The materials were then examined using SEM, TEM and atom-probe field ion microscopy (APFIM).

Results and Discussions

Figure 6 shows the typical SEM images of (a)TMS-75, (b)TMS-80⁽⁴⁾ and (c)TMS-91, respectively. SEM observation revealed that the as-aged alloys all have a coherent γ and γ ' two-phase structure with γ ' precipitates being ~0.5µm in size. Although the size of the γ ' precipitates is somewhat different among the alloys, the shape of the γ ' precipitates is almost identical, suggesting that Ir or Ru addition does not drastically change the microstructure of the alloys. It should also be noted that there are no detrimental phases such as TCP phases observed in all the alloys.

Since the average size of γ ' precipitates of the alloys is less than 1µm after heat treatment, it is very difficult to identify γ and γ ' phase compositions using SEM-EDX analysis. TEM and APFIM analyses were therefore conducted to understand the microscopic distribution of alloving elements. Figure 7(a) shows the dark-field transmission electron micrograph of heat-treated TMS-91. In this figure, primary precipitates with 100~400nm in size, together with the small secondary γ ' precipitates being ~10nm in size are clearly observed. It should be noted that the secondary y' precipitates are not observed in the narrow y channels, but they are observed in the central region of wide y channels. Since the APFIM analysis is chemical identification of atoms successively field evaporated from the surface, if the analysing region is such like Figure 7(b), chemistry change between a primary y' precipitate and a y matrix in the narrow channel can be obtained. Also, if the APFIM specimen is prepared like Figure 7(c), chemistry change between secondary cooling y' precipitates and a y phase in the wide channel can be obtained. Microscopic partitioning behaviour of alloying elements can be determined in this manner. In order to visualise the partitioning behaviour

Figure 6: Typical SEM images of (a) TMS-75, (b) TMS-80⁽⁴⁾ and (c)TMS-91.

of alloying elements, so-called 'ladder diagram' is used, where the cumulative number of each solute atom is plotted against the total number of detected atoms. Hence, the horizontal axis includes depth information and the gradient of each curve corresponds to the local concentration of each element, respectively. Figure 8 is the typical ladder diagram of TMS-91 showing the

Figure 7: (a)Dark field TEM image of TMS-91 and schematic diagrams of APFIM specimen for analysing (b)narrow γ channel and γ' , and (c)wide γ channel and cooling γ' .

chemistry change in a wide γ channel. The specimen used in this analysis corresponds to Figure 7(c). This figure indicates that Ru, together with Cr, Co, Mo, W and Re, have a preference to partition into the γ phase whereas Ta having a preference for the secondary γ' precipitates. In Ru-containing TMS-91, partitioning behaviour of alloying elements between (a) primary cuboidal γ' phase and wide γ channel with secondary γ' precipitates, (b) primary γ' phase and wide γ channel without secondary γ' phase, (c) primary γ' phase and narrow γ channel, and (d) secondary cooling γ' precipitates and wide γ channel, are determined in this manner and they are summarised in Figure 9. This figure indicates that (1) Ru always partitions to the γ phase with k_{Ru} ~1.6 to 2.5. (2) partitioning of case (d) is less

Figure 9: Partitioning behaviour of alloying elements in TMS-91 as a function of k_r .

prominent than the other cases. (3) partitioning parameters of alloying elements for case (b) are almost identical to those for case (c), suggesting that alloying elements in the γ phase almost uniformly distribute either in a narrow channel or a wide channel, provided that secondary cooling γ ' phase is omitted. From these results, the diffusion of alloying elements during cooling process can be explained as follows. Under equilibrium condition, γ ' volume fraction increases as temperature decreases. Therefore, when the alloy is cooled, supersaturated solute atoms in the γ phase at γ and γ ' interface tend to dissolve into the growing γ ' precipitates. On the other hand, in the middle of wide γ channel, there remains the supersaturated γ region where nucleation of secondary y' precipitates occurs. Once secondary y' phase is precipitated, solute atoms in the wide γ channel would either dissolve into the primary γ ' precipitates or secondary cooling y' precipitates. In this way, concentration of alloying elements in the y phase becomes uniform. It is thus suggested that case (a) should be used to describe the partitioning behaviour of alloving elements at the aged temperature. It should also be noted that even though chemical identification of extracted y' phase is regarded as the most accurate way of determining y' phase composition, it does not always describe the composition of y' phase at a certain temperature if the extracted y' includes both primary and secondary precipitates.

The partitioning behaviour of Ir in Ni-base single crystal superalloys has also been investigated. Figures 10 and 11 are the ladder diagrams of TMS-79⁽²⁾ and 80⁽⁴⁾ showing composition change at γ / γ ' interfaces, respectively. As for partitioning, all the alloving elements except for Ir behaves similarly to TMS-91. that is, Cr, Co, Mo, W and Re have a preference to partition into the y phase whereas Ta having a preference for the y' phase. Note that while having a slight preference for the γ phase in the Re-free alloy TMS-79, Ir tends to partitione to the y' phase in the Recontaining alloy TMS-80. Experimental results for Ni-Al-Ir ternary alloys confirmed that Ir inherently has a preference to partition to the γ phase rather than the γ ' phase. However, since the partitioning tendency of Re to the γ phase is much stronger than that of Ir, Ir atoms are rejected from the γ phase due to the presence of Re. These results suggest that among alloying elements, 'competition of partitioning' takes place in Ni-base superalloys.

Partitioning behaviour of alloying elements in TMS-75, Ru-containing TMS-91 and Ir-containing TMS-80 are summarized by the partitioning parameter k_i , as shown in Figure 12. In TMS-91, Ru prefers to partition to the γ phase with $k_{Ru} \sim 2.0$. When compared with TMS-75, k_w decreases from 1.6 to 1.3 while k_{Re} keeps constant by the addition of Ru. O'Hara et al reported in their patent document that the addition of Ru to their alloys causes the partition of Al and Ti to γ phase, while Re, W and Cr in concentration in the γ ' phase⁽⁶⁾. Although our study almost supports O'Hara's report, there are some discrepancies. For instance, partitioning behaviour of Re should be re-considered. In TMS-80, on the other hand, Ir addition does not affect the partitioning behaviour of

Figure 10: The ladder diagram of TMS-79 showing composition change at γ / γ' interfaces⁽²⁾.

Figure 11: The ladder diagram of TMS-80 showing composition change at the γ / γ^2 interface⁽⁴⁾.

other alloying elements. From these results, it is suggested that there is an order of alloying elements having stronger preference to partition to the γ phase, which can be determined from the partitioning parameters as Re > Cr > (Mo, Ru, Co) > W > Ir. Further investigation is now being conducted to investigate the distribution of other PGMs in multicomponent Ni-base superalloys and their mechanical properties.

Figure 12: Partitioning behaviour of alloying elements in TMS-75, 80 and 91.

Conclusions

The distribution of PGMs in Ni-base γ and γ' two phase alloys was investigated and the following results have been obtained

1. For Ni-Al-PGM ternary alloys:

(1) addition of Ir and Ru increases, whereas addition of Pt and Pd decreases the melting temperatures.

(2) The third phase enriched in Al and PGM is precipitated in 5Rh, 9Rh, 9Ru and 9Ir alloys. This phase may be attributed to β phase with composition being approximately 50at% of (Ni+PGM) and 50% of Al.

(3) For alloys having γ and γ' two phase structure, Ru and Ir have preference to partition to the γ phase while Pt, Pd, and Rh prefer the γ' phase.

2. For Ru- and Ir-containing multi-component Ni-base single crystal superalloys:,

(1) Ru has a preference to partition into the γ phase while partitioning behaviour of Ir is composition dependent, in the Re-free alloy TMS-79, Ir behaves similarly to ternary alloys, whereas in Re-containing TMS-80, Ir has a preference to partition to the γ ' phase. (2) The order of alloying elements having stronger preference to the γ phase can be determined from the partitioning parameters as Re > Cr > (Mo, Ru, Co) > W > Ir.

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