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# Effects of platinum group metals addition on the precipitation of topologically close-packed phase in Ni-base single crystal superalloys

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ABSTRACT

Precipitation of topologically close-packed (TCP) phase in Ni-base single crystal superalloys with additions of platinum group metals (PGMs) was investigated by in situ transmission electron microscopy (TEM). Pt, Ir and Ru additions are all helpful to suppress the precipitation of TCP phase, among which Ru has the largest efficiency while Pt has the least one. Comparing with the TCP precipitation in non-PGMs alloys, addition of Ru mainly retards the nucleation rate of TCP phase, but Pt and Ir mainly reduces the growth rate of TCP precipitates. Elemental partitioning investigation reveals that Pt and Ir prefer partitioning to the surrounding γ matrix rather than in the precipitated μ phase, and Ru distributes homogenously in both γ matrix and μ phase. Cr distribution in precipitated μ phase is higher in Pt/Ir-containing alloys than in Ru-containing alloy, which is supposed to be related to the different metallic bonding energy of Cr–Pt, Cr–Ir and Cr–Ru.



## 1. Introduction

Ni-base single crystal superalloys have been widely used for the key part of aero-gas turbine blades. In order to achieve an excellent creep resistance during long-time high temperature exposure, high contents of refractory elements are added to single crystal superalloys [1,2]. However, when the concentration of refractory elements exceeds the solid solution concentration limit of gamma matrix, excess amounts of W, Mo and Re promote the occurrence of TCP phase heavily [3,4]. It is widely accepted that the precipitation of TCP phases degrade the high temperature mechanical performance extremely by decreasing both solid solution strengthening behavior and creep resistance [5,6].

Recently, Ru has been revealed as a crucial addition for single crystal superalloy because of its positive suppressing effect on TCP precipitation [7–9]. Besides, other PGMs such as Ir and Pt also draw many attentions on their abilities of stabilizing microstructure for superalloys. Favorable data has shown that the additions of Ir and Pt help to increase the oxidation and hot corrosion resistance of the superalloys [10,11]. Yokokawa et al. [12] investigated the distribution of PGMs in superalloys previously. It was found that Ru segregates weakly to γ matrix, Pt segregates weakly to γ′, while Ir distributes homogenously. Moreover, PGMs addition also affects the segregation of non-PGMs elements. Carroll et al. [13] reported that Ru and Cr alter Re segregation together by changing system thermodynamics, but Reed et al. [14] held the opposite viewpoint. Sluytman et al. [15] found that element Ir affects the partition behavior of both PGMs and non-PGMs elements in spite of its equal partition between γ and γ′ phases.

Although some literatures have reported the effects of PGMs addition on the phase stability of Ni-base single crystal superalloys, their investigations are still in the preliminary stage now. Most of them focused on the γ and γ′ phases, but few of them concentrated on the detrimental TCP phases. The suppression mechanism of PGMs elements and their partition behavior during TCP phase precipitation were seldom studied. In this work, the precipitation behaviors of TCP phase in PGMs-containing superalloys were investigated by in situ TEM, which gives the direct evidence for suppression effects of PGMs additions on TCP precipitation. Combining the elemental mapping of TCP precipitates, the distributions and partitions of PGMs as well as other TCP component elements were revealed. These results are of great significance to discuss the effects of PGMs addition on the precipitation of TCP phase quantitatively.

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### 1.1. Experimental procedure

Chemical compositions of experimental alloys are listed in Table 1. Three percent in weight percentage of Pt, Ir and Ru were added in original alloy, which were named as alloy 3Pt, 3Ir and 3Ru respectively. Single crystal bars were casted along [001] direction, and the whole heat treatment procedures were listed in Table 2. Long-term aging was conducted to shorten the inducing time of TCP precipitation as well as to eliminate elemental segregation between dendritic and interdendritic areas. To prepare TEM samples, experimental alloy bars were cut perpendicular to [001] direction into pieces with 800 um thick firstly. Then these pieces were mechanically ground into 20 um thick. Subsequently, 3 mm diameter discs were punched out and thinned by argon guns into electron transparent films.

In situ heating experiment was conducted in a JEM-2100 transmission electron microscope with a single tilt heating holder at an elevated temperatures of 950 and 1050 °C, respectively. Although an amount of TCP phases had already precipitated in alloys before heating, in situ observations were conducted in primary γ matrix far from any pre-existed TCP phase. Elemental EDS analysis was also conducted on the selected primary γ matrix before in situ experiments to ensure a similar composition for different samples of PGMs addition. Therefore, the impacts of chemical composition of γ matrix on TCP precipitation can be appropriately ignored. After cooling down to room temperature from in-situ heating, the precipitated TCP phase was further characterized using a double-tilt holder. Scanning transmission electron microscopy (STEM) and high angle annular dark field (HAADF) observations were conducted in a Tecnai F20 transmission electron microscope with an EDS spectrometer. An image processing software was used to analyze the precipitated TCP area fraction and length over representative areas for each sample.

## 2. Results and discussions

### 2.1. In-situ precipitation of TCP phase in different PGMs-containing alloys

Alloy samples were heated up to 950 °C and kept for different minutes to observe the in situ precipitation behaviors of TCP phase as shown in Fig. 1. Without any addition of PGMs element, TCP phases nucleated and grew up quickly from γ matrix in the original alloy sample (Fig. 1(a)–(d)). By addition of Pt (Fig. 1(e)–(h)) and Ir (Fig. 1(i)–(l)), the size of precipitated TCP phase reduced much showing an effect of suppression. For example, the average sizes of TCP precipitates are decreased from over 200 nm in original alloy (Fig. 1(d)) to less 50 nm in alloy 3Ir (Fig. 1(l)). TCP precipitation is severely restrained by Ru addition as shown in Fig. 1(m)–(p), where few nucleus and precipitate was observed in primary γ matrix even after 45 min exposure (Fig. 1(p)). In order to study the suppression effects of PMGs addition further, in situ heating experiments at a higher temperature of 1050 °C were also conducted on different alloy samples. As shown in Fig. 2, TCP precipitation was accelerated, and a larger quantity of TCP phases formed in the original and Pt/Ir-containing alloys after 45 min heating (see Fig. 2(d), (h) and (l)). It is found that additions of element Pt and Ir have fewer suppression effects on TCP precipitation at 1050 °C, but element Ru still keeps an outstanding microstructure stabilizing ability (see Fig. 2(p)).

To compare the suppression effects quantitatively, the area fractions and lengths of TCP phases in different alloys were calculated by statistical analysis. Considering the approximately equal thickness of the observed area, the measured TCP area fraction can be considered as the actual TCP volume fraction namely. Based on the observed in situ TCP precipitation images including those in Figs. 1 and 2, the combined area fractions of precipitated TCP phases were measured and presented in Fig. 3 as a function of exposure time. At both 950 °C (Fig. 3(a)) and 1050 °C (Fig. 3(b)), the TCP area fraction curves show the same trend from highest to lowest as: original alloy, alloy 3Pt, alloy 3Ir and alloy 3Ru. Therefore, it is demonstrated that additions of Pt, Ir and Ru all lead to the decrease of TCP precipitation. Element Ru has the most efficient effect and element Pt has the least effect. For example in Fig. 3(a), TCP area fraction after 45 min for original alloy, alloy 3Pt, alloy 3Ir and alloy 3Ru is about 21%, 12%, 2% and 1% respectively. Thus, it can be calculated that TCP suppression rate with Pt, Ir and Ru addition is approximately 2 (21/12), 10 (21/2) and 21 times. When temperature goes up to 1050 °C in Fig. 3(b), TCP area fractions after 45 min exposure are more than that of 950 °C in PGMs-containing alloys, especially for alloy 3Ir of about 14% which is far beyond the original data of 2%. This should be related to the accelerated atomic diffusion rate at a higher temperature especially for Ir element. However, the TCP area fraction of the original alloy only increased little from 21% of 950 °C to about 22% of 1050 °C, which indicates that almost all the refractory elements in original alloy are depleted to devote into TCP precipitation at both 950 and 1050 °C.

After 45 min exposure at high temperature, the length of about 100 TCP phases in different alloys was measured and statistically plotted in Fig. 4. At 950 °C of Fig. 4(a), the peak of TCP size distribution is in the range of 50–99 nm for alloy 3Ir, 100–149 nm for alloys 3Pt and 3Ru, and 200–249 nm for original alloy. When the temperature was increased to 1050 °C (Fig. 4(b)), the size peak moves to 150–199 nm for alloys 3Ir and 3Pt, 200–249 nm for alloy 3Ru, and 250–299 nm for original alloy. Of course, the TCP length at 1050 °C is larger than that of 950 °C due to the accelerated diffusion rate of atoms during precipitation. There is even no TCP phase smaller than 100 nm at 1050 °C.

The TCP area fraction is controlled by TCP quantity, individual TCP area/size and γ matrix area. Although γ matrix area might vary a little bit for four alloys, it only affects the total TCP area fraction slightly. The quantity of TCP precipitates in alloys 3Pt and 3Ir is similar to that in the original alloy as shown in Figs. 1 and 2. However, with the addition of element Pt and Ir, TCP length is obviously smaller than that in original alloy. Even at 1050 °C the majority of TCP length with Pt or Ir addition is still under 200 nm, while in original alloy it is far over 200 nm (see Fig. 4). Therefore, it is believed that the addition of Pt and Ir elements can slow down the growth rate of TCP phases, hence suppress the TCP precipitation in Fig. 3. On the other hand, the average TCP length/size in alloy 3Ru is larger than those in alloys 3Pt and 3Ir but smaller than those in the original alloy. For example, most of TCP lengths are larger than 200 nm at 1050 °C in alloy 3Ru, while those in alloys 3Pt and 3Ir are less than 200 nm. However, alloy 3Ru has the smallest TCP area fraction among four alloys, implying the strongest suppression effect. Its final TCP area fraction after 45 min exposure at 1050 °C is only about 4%, far below 22% of original alloy (See Fig. 3(b)). Combining its large TCP size but small area fraction, it can be concluded that addition of element Ru can inhibit the nucleation of TCP phase efficiently.

In advanced single crystal superalloy, formation of TCP phase is a solid-phase transformation process. The volume free energy

**Table 1**
Nominal chemical compositions of experimental alloys (wt.%).

| Alloy | Co | Cr + Mo + W | Re | Pt/Ir/Ru | Al | Ta | Ni |
|---|---|---|---|---|---|---|---|
| Original | 12.0 | 12.0 | 5.0 | – | 6.0 | 8.0 | bal |
| 3Pt | 12.0 | 12.0 | 5.0 | 3.0Pt | 6.0 | 8.0 | bal |
| 3Ir | 12.0 | 12.0 | 5.0 | 3.0Ir | 6.0 | 8.0 | bal |
| 3Ru | 12.0 | 12.0 | 5.0 | 3.0Ru | 6.0 | 8.0 | bal |