Analysis of Boron on microstructure and composition of IC10 superalloy

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Abstract. The microstructure and composition of IC10 superalloy containing B (0 wt%, 1.1 wt%) were studied in this paper. DSC and microstructure analysis were used to compare the formation process of the microstructure and composition of the IC10 alloy with or without boron content. Precipitation temperatures and sequence of initial phases of IC10 alloys with or without B content were researched. The results shows that the exothermal peaks of formation for γ, MC carbide, (γ+γ') eutectic and secondary γ' phase reveal on DSC cooling curves. The alloys with 1.1% B have amephase component and the formation sequence of six phasesis γ, MC, (γ+γ') eutectic, secondary γ', M3B2 and Ni5Hf in turn. The boron content enhances the volume fraction of M3B2 and (γ+γ') eutectic, decreases the temperature of liquids and solidus and also delays the formation of MC and (γ+γ') eutectic obviously.

1. Introduction

Composite and intermetallics, including those based on Ni3Al, are increasingly used in modern gas turbine construction[1]. In the Ni-Al system, there are phases of the γ' and β-phases[2]. Phase γ' is an ordered intermetallic with a face-centered lattice, in which Cr, Mo, W are bound to dissolve with decreasing solubility in this row. Metals such as Ti, Ta and Nb dissolve in the γ-phase and strengthen it[3]. Hardening occurs due to the formation of a hardened structure during crystallization, which is stable up to 1250 °C. Due to alloying, the intermetallic Ni3Al acquires high mechanical properties and stability in oxidizing environment and combustion products of fuel[4].

Early studies have shown that the addition of 0.01%B can improve the high temperature strength and plasticity of Ni-based superalloy and reduce the notch sensitivity[5]. Early studies have shown that B has the most obvious effect on the durability of GH135 alloy. The content of B is about 0.006% (mass fraction), and the durability time reaches the peak, which is 3 times more than that of the original alloy, and the durability plasticity is better than the original alloy[6].

In this work, the effect of B element on the solidification characteristics of high temperature gold in directionally solidified IC10 was studied, the precipitation sequence of primary phase and the range of precipitation temperature were determined, and the effect of B in the high-B-containing of IC10 superalloy was compared and analyzed.
2. Experimental

2.1. Experimental materials
The IC10 alloy used in the test material is a directionally solidified columnar superalloy based on intermetallic compound Ni3Al. With good oxidation resistance, corrosion resistance and stable microstructure at high temperature, it can withstand service temperature of 1100 °C. The high temperature durability, good cold and thermal fatigue resistance of IC10, makes it widely used in the manufacture of aero-engine gas turbine guide vane[7]. The nominal chemical composition of IC10 alloy with or without B content can be shown in Table 1.

Table 1. Chemical composition of IC10 alloys with or without B content (%)

|   | W   | Al | Cr | Co  | Hf | Ta | C   | B   | Ni |
|---|-----|----|----|-----|----|----|-----|-----|----|
| 1 | 4.8~5.2 | 5.6~6.2 | 6.5~7.5 | 11.5~12.5 | 1.3~1.7 | 6.5~7.5 | ≤0.012 | ≤0.02 | rest |
| 2 | 4.8~5.2 | 5.6~6.2 | 6.5~7.5 | 11.5~12.5 | 1.3~1.7 | 6.5~7.5 | ≤0.012 | 1.1   | rest |

2.2. Experimental methods
The experimental materials were taken from IC10 directional solidification rods without boron content. Differential thermal analysis experiment: the small disk samples of 3mm×2mm were cut off on the test rod, heated in STA409 thermal analyzer to melt at 1400 °C, and then the DSC curve of cooling was obtained by decreasing the cooling rate of 10 °C/min to 1100 °C, and the formation temperature of each phase was measured. It provides the basis for the selection of temperature in Isothermal solidification experiment. The microstructure of IC10 alloys with or without B content were analyzed by optical microscope, scanning electron microscope and electron probe, and the phase type, composition, content of IC10 alloy with or without boron content were determined.

3. Results and discussion

3.1. The thermogram of IC10 without B content
From the known triple and quadruple phase diagrams, the phase γ’ borders on one of the following two-phase regions: γ+σ, γ+μ, γ+R, γ+P, where σ, μ, R and P are TCP phases[8]. These phases bind a significant number of basic alloying refractory elements and impoverish them with the γ phase. The region of precipitation of TCP phases is in the temperature range 1000~1150 °C. The thermogram of the IC10 alloy analog is shown in Fig.1.

Figure 1. Thermogram of the melted alloy IC10 after complete heat treatment: 1 - heating, 2 - cooling

When analyzing the differential thermal curves for an analogue of the IC10 alloy in the initial state without thermal treatment, it is established that when the temperature of the phase transformations is heated, they are:

- γ’- solvus, i.e. temperature of complete dissolution of a dispersed γ’-phase in a γ-solid solution $T_{γ'} = 1250$ °C(according to the data[9], this temperature fluctuates in the interval 1209-1359 °C, depending on the ratio of the alloying elements);
- solidus temperature $T_s = 1340$ °C;
- fusion interval of carbide eutectic $T_{γ'} + MC = 1320 - 1345$ °C(1295 - 1345 °C);
- fusion completion temperature $T_c = 1385 (1369 - 1441$ °C)[9].

Upon cooling, crystallization of γ-dendrites with simultaneous formation of MC monocarbides in the interendritic regions in the eutectic reaction occurs in the interval $T_{γ'} + MC = 1355 - 1350$ °C[9-10];
It is known [9-10] that in the case of high-temperature nickel alloys with multicomponent alloying, the presence of many phases of which the number increases substantially with the introduction of boron is characteristic[11]. First of all, we note the strengthening γ’-phase of the Ni3Al, Ni3(Al, Ti) and other intermetallide η-phase Ni3Ti phases, the γ”- phase Ni3Nb, the MC carbons, M23C6, M6C, M7C3(NbC, HfC, Cr23C6(Cr, W, Mo)23C6, Nb3Co3C, Ta3Co3C, hexagonal carbide Cr7C3), tetragonal borides M3B2(Ta3B2, Nb3B2, (Mo, Ti, Cr, Ni)3B2), topologically close-packed (TCP) Laves phases Co2Ta, Co2Ti, and in the presence of iron Fe2Nb, Fe2Ti, Fe2Mo, μ - phases of Co2W6, Co7(Mo, W)6, σ - phases of CrCo, CrNiMo, and in the presence of iron FeCr, FeCrMo, CrFeMoNi. The isolation of these phases occurs in different temperature ranges and conditions and is accompanied by many thermal effects both during heating and cooling.

The thermogram of the IC10 alloy with 1.1% B can be seen in Fig.2. Boron significantly reduces the thermal stability of the γ’ phase and the alloy as a whole. In addition, eutectic γ+Ni3B with a rather narrow crystallization interval is formed in the alloys. The temperatures of the start of fusion and the start of crystallization of this eutectic, regardless of the amount of boron introduced into the alloy, practically coincide within the error of the method (the eutectic temperature in the Ni-B TNi‒Ni3B = 1093°C[12]). Regardless of the amount of boron introduced into the alloy, the temperature of the nonequilibrium solidus (or local melting of the eutectic phase Τγ’+γ).

A comparison of the chemical composition, structure and thermograms shows that the alloy IC10 and its analog differ very little and both are close to the boundary concentrations of the alloying elements. This narrows the possibility of varying their composition in the development of solder, in spite of the fact that alloying with boron leads to a significant change in the phases and temperatures of the phase transformations.

![Figure 2. Thermogram of the melted alloy IC10 with 1.1% B: 1- heating, 2- cooling](image)

3.2. The microstructure of IC10 alloy without Boron content

The chemical composition of the IC10 analogue is shown in Table 1. It contains on the average (wt%): 0.085 C, 7.2 Cr, 11.63 Co, 4.67 W, 1.49 Mo, 5.61 Al, 7.44 Ta, 1.6 Hf, 2.0 Ti, the rest is Ni. The analogue differs from IC10 in that the analog contains 2.0% Ti. The microstructure of the analog after complete heat treatment, like the chemical composition. The structure of the analogue is shown in Fig.2, and the chemical composition in Fig.3.

![Figure 3. Microstructure of the alloy IC10 along (a) and across the axis (b) of the "finger" sample](image)

The thermal treatment of the analogue was carried out according to the mode recommended for the IC10 alloy. As can be seen from Fig.4, the structure of the alloy is homogeneous. The chemical composition throughout the sample area is close. The results of chemical analysis obtained by X-ray spectroscopy on REMMA-102-02 were additionally checked on the Spectrolab spectrometer, which
showed the following composition (wt %): 0.085 C; 6.35 Al; 6.38 Cr; 11.63 Co; 1.6 Mo; 4.7 W; 7.44 Ta; 1.41 Hf; 0.02 Nb; 0.005 Ti; 0.003 B.

To calculate the properties of the heat-resistant alloy IC10, the program PHASOMP was used. The composition of the $\gamma$ and $\gamma'$ phases was calculated, the inclination to sigmatization by the number of electron vacancies, critical temperatures. According to calculations, the $\gamma$ phase includes (at %): 48.93 Ni; 21.10 Co; 20.92 Cr; 1.68 Mo; 1.69 W; 4.98 Al; 0.36 Ti; 0.34 Ta; in the $\gamma'$-phase: 65.74 Ni; 16.29 Al; 8.52 Co; 1.53 W; 2.80 Ta; 2.28 Ti; 0.51 Mo. The volume content of the $\gamma'$ phase in the alloy is 71.3% at. and carbides and borides of 1.38% at.

| No  | Cr  | Co  | Mo  | W   | Al  | Ta  | Hf  | Ni  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Point1 | 7.73 | 11.95 | 0.91 | 1.54 | 12.55 | 2.64 | 0.51 | base |
| Point2 | 7.65 | 11.83 | 0.89 | 1.52 | 12.42 | 2.61 | 0.50 | base |

Figure 4. Microstructure (a) and chemical composition (b) of IC10 analogue after complete heat treatment

The number of electronic vacancies in the $\gamma'$-phase is 2.341, in the $\gamma$-phase it is 2.240. At such values of the number of electronic vacancies, alloys are considered resistant against sigmatization. Metallographic studies of the analogue of the IC10 alloy showed that in the initial heat-treated state it has a homogeneous dispersed ($\gamma + \gamma'$) structure with a high volume fraction of the hardening $\gamma'$ phase (68–70% by volume). The structure and chemical composition of the IC10 alloys and its analogue are identical (see Fig.5, Table 2, etc.). In the cross section, a dendritic structure is clearly observed on metallographic sections. On the outer contour of the dendritic cell are located large colonies of eutectic ($\gamma + \gamma'$) - phases.

3.3. The microstructure of IC10 alloy with 1.1% Boron content

A general view of the microstructure of an analog of the IC10 alloy alloyed with 1.1% B and the chemical composition of the metal when scanning over the sample area without heat treatment is shown in Fig.4. It is seen from Fig.4 that the structure of the melted metal is homogeneous, which is confirmed by the distribution of elements over the area (Fig.5, b). At large magnifications, phases of different shapes, colors and chemical composition are visible. This structure of the metal is shown in Fig.5. Over a larger area, the alloy has a content of elements close to the composition obtained by scanning the area shown in Fig.5 (see Point 1 in Fig.5). At points 2 and 3, the low Al content is general, but in Point 2 the concentration of Ni is about 24%, Ta and W are 24 and 22%, respectively, and Point 3 Ni = 55; Ta = 11; W = 2.75%, despite the similarity of the structure. Point 4, not shown on the microstructure, is in a black phase with blurred boundaries and a smooth transition from one phase to another.
Primary carbides of the MC type are formed during crystallization in the form of large (15–40 μm), arbitrarily arranged particles of cubic or skeletal morphology. There is a preferential order of formation of these carbides, associated with a decrease in their resistance: TiC, TaC, and NbC. Molybdenum and tungsten can partially replace metals in these carbides, forming phases like (Ti, Mo, W) C, (Ti, Nb, Mo, W) C.

![Microstructure and chemical composition](image)

| No  | Cr  | Co  | Mo  | W   | Al  | Ti  | Nb  | Zr  | Ta  | Hf  | Ni  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Point1 | 3.38 | 7.8 | 0.03 | 1.62 | 12.32 | 1.56 | – | 0.31 | 3.37 | – | base |
| Point2 | 16.51 | 7.24 | 6.68 | 10.73 | 3.53 | 2.21 | – | 4.08 | 11.81 | 0.94 | 23.65 |
| Point3 | 8.09 | 14.92 | 0.36 | 0.99 | 3.02 | 3.01 | 0.56 | 0.25 | 4.12 | 2.38 | base |
| Point4 | 0.48 | 0.73 | 0.05 | 0.15 | 1.11 | 0.19 | – | 0.05 | 0.11 | 0.06 | base |
| Point5 | 17.19 | 11.15 | 1.52 | 1.16 | 5.43 | 2.24 | – | 0.5 | – | 0.92 | base |
| Point6 | 7.88 | 11.1 | 7.14 | 13.98 | 2.55 | 1.38 | – | 2.09 | 19.74 | – | 34.15 |

Figure 5. Microstructure (a) and chemical composition (b) of the analogue of the IC10 alloy containing 1.1% B.
In alloyed alloys, the morphology and composition of the carbide phases change substantially. In high-temperature nickel alloys with equiaxed dendritic structure, carbide phases of various types can exist: on the basis of titanium, niobium, tantalum, and hafnium monocarbides (MC-carbides); based on chromium carbides type $M_23C_6$; complex carbides ($M_6C$) based on refractory metals W, Mo and nickel[13].

MC carbides formed from the melt during crystallization of the alloy can undergo transformations into other types of carbides in accordance with the following solid-phase reactions: $MC$+$\gamma$→$M_23C_6$+$\gamma'$; $MC$+$\gamma$→$M_6C$+$\gamma'$. $M_23C_6$ carbides are stable to temperatures of 750-950 °C; at higher temperatures, double carbides of the $M_6C$ type are stable, which are formed in high-temperature alloys with a high content of refractory metals and are characterized by a wide range of compositions within $M_xC-M_xC$. Typical compositions of double carbides are (Ni, Co)$_2$Mo$_2$C, (NiCo)$_3$W$_4$C and Ni13 (W, Mo)$_3$C[14-15]. They are distributed mainly along the periphery of the branches of the dendrites and grain boundaries, reaching a size of 200-300 μm$^2$ (Fig.5, a), but are sometimes observed along twinning lines and on packing defects.

Carbide phases of $M_23C_6$ type are formed along grain boundaries surrounded by a plastic $\gamma'$-phase (Fig.5, c), which prevents embrittlement of alloys and increases the resistance to grain-boundary sliding.

The boride phases of $M3B$ (where $M$ is Mo, W, Ti, Cr, Ni, Co) in the form of grain-boundary precipitates can grow from the boundary into the interior of the grain[16] (Fig.5). Located in the junction of lattices of different orientations, they increase the resistance to creep deformation.

The combined volume fraction of the carbide and boride phases increases from 20% by volume for the alloy with 1.1% B to 30%. The chemical composition of the phases is given in Table 2.

| %B   | Ni   | Cr  | Al   | Co  | Mo  | Ta  | Ti   | W   | Hf  | Zr  | Nb  |
|------|------|-----|------|-----|-----|-----|------|-----|-----|-----|-----|
| %1.1 | 58.08| 5.60| 4.55 | 9.12| 1.34| 10.35| 1.69 | 6.36| 1.94| 0.97| -   |
|      |      |     |      |     |     |      |      |     |     |     |     |
| Along the horizontal | | | | | | | | | | | |
| %1.1 | 63.40| 2.92| 6.86 | 7.62| 0.80| 8.64 | 1.36 | 6.94| 0.44| 0.94| 0.07 |
|      |      |     |      |     |     |      |      |     |     |     |     |
| $\gamma'$-phase | | | | | | | | | | | |
| %1.1 | 66.96| 2.89| 5.47 | 7.56| 0.49| 10.04| 1.23 | 4.89| -   | 0.46| -   |
|      |      |     |      |     |     |      |      |     |     |     |     |
| $\gamma'$+\gamma'-phase | | | | | | | | | | | |
| %1.1 | 24.17| 11.39| 1.64 | 4.90| 8.95| 20.27| 1.12 | 23.96| 0.63| 2.80| -   |
|      |      |     |      |     |     |      |      |     |     |     |     |
| $M_6C_\gamma$ | | | | | | | | | | | |
| %1.1 | 55.96| 8.34| 2.94 | 9.53| 0.86| 9.82 | 2.12 | 6.13 | 3.91| 0.22| 0.17 |
|      |      |     |      |     |     |      |      |     |     |     |     |
| $M_3B$ | | | | | | | | | | | |

4. Conclusion

The microstructure and composition of IC10 superalloy containing B (0 wt%, 1.1 wt%) were investigated. The following conclusions can be drawn from this study:

(1) There are six phases in the as-cast microstructure of IC10 alloy, which are divided into gamma, MC carbides, ($\gamma'$+\gamma) eutectic, secondary $\gamma'$, $M_3B_2$ and Ni5Hf according to the order of formation.

(2) When the boron content of IC10 alloy increased from 0% to 1.1%, the content of $M_3B_2$ borides and ($\gamma'$+\gamma) eutectic increased significantly; the temperature of liquid phase line and solid phase line decreased, and the formation of MC carbide and ($\gamma'$+\gamma) eutectic was delayed at the same time.
(3) The eutectic of $\gamma$, MC, ($\gamma+\gamma'$) can be shown on the differential scanning Calorimetric (DSC) curve, and the precipitation peak of secondary $\gamma'$ can be displayed. The alloy IC10 with or without B and its analog differ very little and both are close to the boundary concentrations of the alloying elements.

Acknowledgments
The authors gratefully acknowledge the financial support by the GDAS’ Project of Science and Technology Development (No. 2018GDASCX0113), Key Program for International Cooperation of Science and Technology (No. 2015DFR50310). The authors thanks Professor Viktor. Biktop for experimental assistance and useful discussions.

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