PHASE TRANSFORMATIONS IN HAFNIUM-BEARING CAST NICKEL-BASE SUPERALLOYS

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Ni_5Hf phase in Hafnium-bearing cast nickel-base superalloy was identified. It was found that following reactions occurred in these alloys during themal exposure:

$$Ni_5Hf+\gamma(C) \longrightarrow MC_{(2)}+\gamma$$
$$\gamma'(Hf)+\gamma(C) \longrightarrow MC_{(2)}+\gamma$$

The effects of these reactions on the microstructure stability of the alloys were discussed.

INTRODUCTION

At the end of 60's, a lot of scientific research works on microstructure for Hafnium-bearing alloys has been carried out. Among them, Kotval[1], Dahl[2] and Collins[3] had described the change of the amount of eutectic $(\gamma+\gamma')$, the composition and morphology of MC carbide in Hafnium-bearing alloys. Up to date, Some problems on Ni_5Hf phase and its transformation in thermal exposure have not been revealed. The precipitation character of secondary $MC_{(2)}$ carbide, the relation between its character and the stability of their microstructure have not been reported. The object of this investigation is to study the phase transformation of three Hafnium-bearing cast alloys, and to pay special attention to transformation of Ni_5Hf phase and precipitation of secondary $MC_{(2)}$.

MATERIALS AND PROCEDURES

Chemical compositions of the superalloys studied are listed in Table 1.

Table 1. Chemical Composition of Studied Alloys

Alloys	Analyzed Composition wt%.											
	Cr	Ni	Co	W	Mo	Al	Ti	Nb	Ta	Hf	C	B
A	10.0	base	9.59	4.78	3.57	5.42	2.28	—	—	1.59	0.09	0.017
B	5.62	〃	11.70	9.49	2.21	6.08	1.35	3.14	—	1.74	0.11	0.037
C	9.64	〃	9.84	10.13	0.57	5.85	1.71	—	2.43	1.68	0.13	0.02

In order to study the effects of temperature and time on phase transformation, specimens were exposed for 1000 hours at 850, 900, 950, 1000 and 1050℃, respectively. In order to study phase transformation at high temperature, the specimens were soaked at a range of 1100—1240℃, at 20℃ intervals.

The cast-and exposed-specimens were studied by metallography, electron diffraction, X-ray and chemical phase analysis. Mono-phase revelation method is used. For Ni_5Hf phase, 10ml nitric acid, 20ml hydrofluoric acid, 30ml glycerin solution is used to etch electrolytly. Current density is less than $0.025A/cm^2$, 3~5 seconds. For secondary carbide $MC_{(2)}$, Samples are tinted at 380—400℃/30min. In this condition the secondary $MC_{(2)}$ appeared as dark-blue, the secondary M_6C and $M_{23}C_6$ not be revealed either. Carbide extraction is carried out with 50ml hydrochloric acid, 100ml glycerin, 1050ml methyl alcohol solution at −5℃, current density $0.01A\ cm^2$.

EXPERIMENTAL RESULTS

Cast Microstructure

At as-cast condition, hafnium-bearing nickel-base alloys consist of γ, γ', eutectic $(\gamma+\gamma')$, MC, M_3B_2, M_2SC and Ni_5Hf. The formation process of these phase and their revealing distinguishing technique refer to[4]. In this paper two phases related closely to Hafnium (that is $MC_{(2)}$, and Ni_5Hf) were examined in detail.

Primary $MC_{(2)}$ Carbide. Hf rich primary $MC_{(2)}$ was also formed in Hf-bearing alloys, beside Nb-, Ta-, Ti-rich primary $MC_{(1)}$. Generally both carbides are isolated, but sometimes conjugated, i.e. $MC_{(1)}$ exists at the centre and Hf-rich $MC_{(2)}$ at its edge (Fig.1) . Both carbides in three alloys were systematically studied by electron microprobe, quantitative metallography and phase analysis methods. The results were listed in Table 2.

Table 2 Composition and Amount of Both MC in Various Alloys

Alloys	Kinds of MC	Formula of MC [a]	MC Amount in Alloys vol% [b]	Hf Content in MC wt% [c]
A	$MC_{(1)}$	$(Ti_{.75}W_{.13}Mo_{.10}Hf_{.02})C$	0.42	0.23
	$MC_{(2)}$	$(Hf_{.44}Ti_{.36}Mo_{.15}W_{.05})C$	0.44	
B	$MC_{(1)}$	$(Nb_{.52}Ti_{.21}W_{.11}Mo_{.09}Hf_{.07})C$	1.00	0.11
	$MC_{(2)}$	$(Nb_{.46}Hf_{.41}Ti_{.09}W_{.02}Mo_{.02})C$	0.09	
C	$MC_{(1)}$	$(Ti_{.47}Ta_{.28}W_{.17}Hf_{.08})C$	0.92	0.13
	$MC_{(2)}$	$(Hf_{.52}Ta_{.10}Ti_{.18}W_{.11})C$	0.26	

a. electron microprobe results b. quantitative metallography
c. chemical phase analysis results

Table 2 shows that even though the content of C and Hf in three alloys is similar, but the tendency of $MC_{(2)}$ formation is different. It is interesting to notice that in the same alloy the change of carbon content in a very wide range has little effects on amount of $MC_{(2)}$, but it has a significant effect on amount of $MC_{(1)}$. For example, the amount of $MC_{(2)}$ increased from 0.44% to 0.47 vol% and that of $MC_{(1)}$ increased from 0.42% to 0.63 vol%, as content of carbon in Alloy A increased from 0.09% to 0.15 wt%, respectively.

Ni_5Hf Phases. Ni_5Hf generally occurs in nickel-base alloys containing Hf more than 0.4 wt%. This phase is usually found around eutectic($\gamma+\gamma'$)and appears as small blocks or in cellular form(Fig.2). Results by electron microprobe indicated that Ni_5Hf has a composition of $(Ni_{.80}Co_{.20})_5(Hf_{.60}Cr_{.29}W_{.06}Ti_{.05})$ in Alloy B. Ni_5Hf phase was identified by X-ray diffraction and electron diffraction at extraction replica. Table 3 shows diffraction results of alloyed Ni_5Hf.

In the same alloy the volume percent of Ni_5Hf increases with

Table 3 X-ray Diffraction Results of Alloying Ni_5Hf Phase

Observed Value		ASTM17 −27		hkl	Obseved Value		ASTM17 −27		hkl
d	I/I_0	d	I/I_0		d	I/I_0	d	I/I_0	
		3.82	30	111	1.26	40	1.283	60	533 511
		3.31	30	200			1.18	60	440
2.35	30	2.35	60	220			1.128	20	531
2.025	100	2.007	100	311			1.113	20	600 442
1.97	40	1.920	50	222	1.069	60	1.055	40	620
		1.528	30	331	1.024	50	1.018	50	533
		1.489	30	420			1.007	40	622
1.36	20	1.361	50	422			0.935	20	711 551

the amount of Hf. For different alloys even though content of Hf is the same, but the volume percent of Ni_5Hf is different. The volume of Ni_5Hf is slightly influenced by the variation of carbon concentration. The main factors influenced on volume of Ni_5Hf are the alloying element, amount of MC former and the degree of alloying.

Effects of Thermal Exposure on Microstructure

During above thermal exposure, the following reactions occurred in these alloys:

$$Ni_5Hf+\gamma(C) \longrightarrow MC_{(2)}+\gamma \quad (1)$$

$$\gamma'(Hf)+\gamma(C) \longrightarrow MC_{(2)}+\gamma \quad (2)$$

In metallic radical of secondary $MC_{(2)}$ precipited from above reactions, the Hf is predominent. A marjor source of Hf is either from Ni_5Hf or from eutectic γ', whereas that of Carbon is the Carbon which liberated by $MC_{(1)}$ decomposition or solutioned in γ matrix.

Transformation of Ni_5Hf during Thermal Exposure. Ni_5Hf is instable above 900℃ temperature and easily changed into Hf-rich $MC_{(2)}$.

Time-Temperature Transformation curve of Ni_5Hf phase in Alloy B obtained by experiment (Fig. 3) showed that the effect of temperature on transformation of Ni_5Hf is more significant than that of the time. The time for complete transformation is about 400 hours

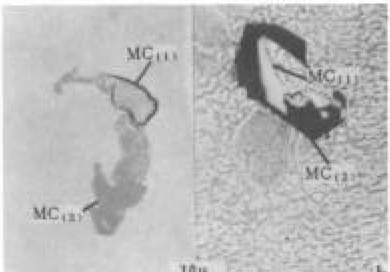

Fig. 1. Primary $MC_{(1)}$ and $MC_{(2)}$ in as-Cast Alloy A and B.
a) Alloy A as-Polished;
b) Alloy C 450℃/30min Heat Tinting.

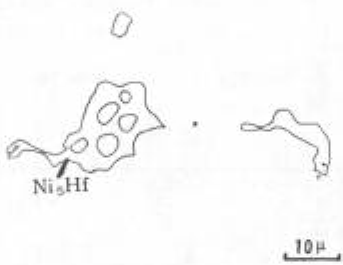

Fig. 2. Ni_5Hf Phase in Alloy B.

at 1050°C and it is only two hours at 1180°C. The incipient melting of Ni_5Hf occurs above 1190°C and this phase precipitated again during subsequent air cooling.

With continuous reaction the amount of Ni_5Hf constantly decreases and the volume percent of $MC_{(2)}$ constantly increases. It can be seen that $MC_{(2)}$ nucleates around Ni_5Hf and grows at the expense of Ni_5Hf (Fig.4) . The soaked samples at various temperature and time were analysed by quantitative metallography, as shown in Fig.5.

Formation of Secondary $MC_{(2)}$ Carbide. The secondary $MC_{(2)}$ forms according to reactions(1) and(2). Different reactions occur in different alloys. The reaction(1) is dominent in Alloy B and the reaction(2) is dominent in Alloy A and C. The $MC_{(2)}$ formed by reaction(1) often concentrated in clusters in Ni_5Hf area (Fig.4)and the $MC_{(2)}$ formed by reaction(2) distributed more dispersively in eutectic γ' (Fig.6) . It is different from secondary M_6C and $M_{23}C_6$ that this secondary $MC_{(2)}$ is enclosed by γ. This phenomenon itself is an evidence of the reaction(1) and(2).

X-ray diffraction results showed that diffraction lines of $MC_{(2)}$ after 1050°C/100 hours was clearer than that of cast condition. The lattice parameters of $MC_{(1)}$ and $MC_{(2)}$ measured are about 4.40 and 4.50 Å, respectively.

The secondary $MC_{(2)}$ precipitated from reactions(1) and(2) was analysed by electron microprobe. The composition of secondary $MC_{(2)}$ for Alloy A, B and C may be expressed by following formula: $(Hf_{.91}Ti_{.09})C$, $(Hf_{.59}Nb_{.37}Ti_{.04})C$ and $(Hf_{.81}Ta_{.11}Ti_{.05}W_{.03})$ C, respectively.

It can be seen that the major former of secondary $MC_{(2)}$ is Hf, Nb and Ta, the Ti enters slightly secondary $MC_{(2)}$. In view of composition the substantial different between secondary $MC_{(2)}$ and primary $MC_{(2)}$ is that the former contains more Hf. For Nb-, Ta-free alloys, secondary $MC_{(2)}$ is substantially HfC.

For long-time exposed samples at various temperature, the phase analysis was performed and results summarized in Fig. 7. This figure also shows that $MC_{(1)}$ progressively decomposed and secondary $MC_{(2)}$ progressively precipitated with the increase of temperature.

If alloys were different, the tendency to precipitate secondary $MC_{(2)}$ would be different. The volume percent of precipitated $MC_{(2)}$ in Alloy A, B and C after 1050°C 200hr exposure is 0.09, 0.28 and 0.05 vol. %, respectively. It may be seen that Alloy B with highest

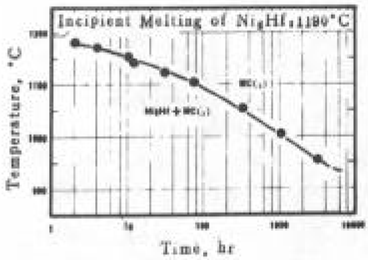

Fig. 3. Time-Temperature-Transformation (TTT) Curve of Ni_5Hf Phase in Alloy B.

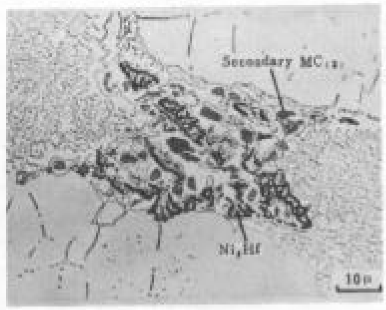

Fig. 4. Ni_5Hf Partially Changed into $MC_{(2)}$ after 950℃/2000hr Exposure in Alloy B.

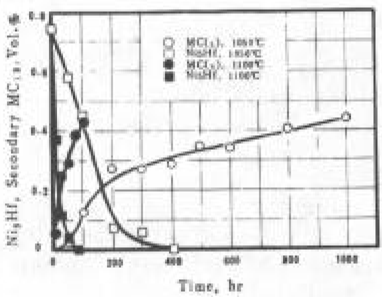

Fig. 5. The Relation between the Volume Percent of Ni_5Hf, $MC_{(2)}$ and the Time at Various Temperature in Alloy B.

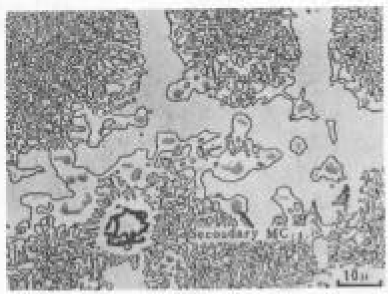

Fig. 6. Dispersive Secondary $MC_{(2)}$ Pricipitated in Eutectic γ' in Alloy C after 1050℃/1000hr Exposure.

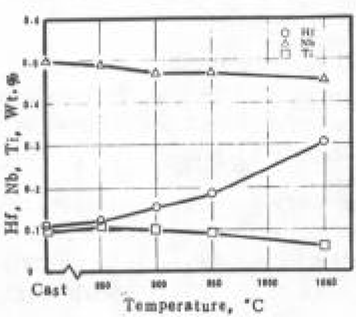

Fig. 7. The Change of Content of Hf, Nb and Ti in MC after 1000hr Exposure at Various Temperature for Alloy B.

content of Ni_5Hf will precipitate secondary $MC_{(2)}$ most easily.

In Hf-bearing alloys, because of existing the primary and secondary $MC_{(2)}$ carbide, the formation of M_6C and $M_{23}C_6$ Carbide is strongly restricted, so that the total amount of minor phase only change slightly. In Alloy A with and without Hf, even though both are exposured at 900℃/1000hr, total amount of minor phase increased by 1.22 time in Hf-free alloy and only increased by 63% in Hf-bearing alloy.

DISCUSSION OF RESULTS

In Sims's work(5), there is a preferred order for MC-former, determined to be Ta, Nb, Ti and V. In view of our results the preferred order is Hf, Nb, Ta and Ti. The reasons are as follows: 1. not only Hf entered into $MC_{(1)}$, but alone form Hf-rich $MC_{(2)}$ in all as-cast Hf-bearing alloy; 2. $MC_{(1)}$ is predominately Ti-rich in the alloys wich contained Ti alone (Alloy A) and its marjor composition is Nb in the alloy contained simultaneously Nb and Ti; 3. Hf in secondary $MC_{(2)}$ is the richest one, Nb is the second, Ta is the third, Ti entered slightly into secondary $MC_{(2)}$. In addition, Hf-free Alloy B precipitates secondary NbC at high temperature exposure and Hf-free Alloy C does not precipitate secondary TaC.

It can be seen from the above that Nb has stronger affinity with Carbon and is inferior to Hf. It was proved by systematic research works of Restall and Toulson(6) that Nb forms MC more easily than Ta

In a word, primary and secondary Hf-rich $MC_{(2)}$ is very stable at high-temperature, this part of Carbon which was got by $MC_{(2)}$ does not take part in the reactions of M_6C and $M_{23}C_6$ precipitation. However, the secondary $MC_{(2)}$ can be formed by the Carbon wich is liberated by decomposition of $MC_{(1)}$ at high-temperature exposure and the residual Carbon in the matrix. These two reactions restrict the formation of secondary M_6C and $M_{23}C_6$, however for majortty of Hf-bearing alloys the concentration of Cr, Mo, and W is much higher than that of Hf, degree of the segregation of various elements are different, so that completely repressing precipitation of M_6C and $M_{23}C_6$ is rather difficult.

CONCLUSIONS

1. An intermetallic phase Ni_5Hf occurs in Hf-bearing cast nickel-base superalloys with high degree of alloying.

2. During long time thermal exposure above 900℃, the following reactions may occur in Hf-bearing cast nickel-base superalloys:

$$Ni_5Hf+\gamma\ (C) \longrightarrow MC_{(2)}+\gamma$$

$$\gamma'\ (Hf)\ +\gamma\ (C) \longrightarrow MC_{(2)}+\gamma$$

Because of the above two reactions, the formation of M_6C and $M_{23}C_6$ is restricted.

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