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HOT CORROSION BEHAVIOR OF Ni-BASED SUPERALLOY WITH HIGH Cr CONTENTS – PART 1. EXPERIMENTAL STUDY

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ABSTRACT A systematic study of the effects of Ti, Ta and Nb on the hot corrosion behavior of alloy system Ni-16Cr-9Al-2W-1Mo-4Co-(0 ~4)Ti-(0 ~4)Ta-(0 ~4)Nb (at%) was conducted. The results showed that, in certain compositional regions, the hot corrosion resistance in 75% Na_2SO_4+25% NaCl molten salt of the experimental alloys was similar to that of IN738LC alloy. The hot corrosion property balances with other properties, which provides the basis for selecting alloy compositions to develop single crystal superalloys of high performance hot corrosion resistance.

KEY WORDS hot corrosion, superalloy, alloying effects

HIGHER temperature capability of the blade materials in gas turbines is one of the important requirements to attain higher turbine inlet temperatures for improving thermal efficiency and specific power. The wrought or conventional cast superalloys currently used could not satisfy the requirements, since the corrosion environment encountering in marine turbines and low-grade fuels used in industrial turbines cause severe hot corrosion problems. Thus the proper balance between hot corrosion resistance and mechanical property must be emphasized in alloy design and development. Up to now, only few results in this field have been reported[1].

The alloys studied in this project were selected from the hot corrosion resistant alloy system determined by the d-electrons alloy design theory[2, 3]. The alloy design method was developed based on the DV-X_α cluster calculation of the electronic structures of the alloying elements in a certain alloy matrix[4~6]. The electronic parameters *Md* and *Bo* (d-orbital energy level and bond order of alloying metals) are employed as the key factors controlling the phase stability and properties. The details of this alloy design concept can be found elsewhere[5~9]. For an alloy, the average values of *Md* and *Bo* are defined by taking the compositional average as,

$$\left.\begin{aligned}\overline{Mdt} &= \sum X_i(Md)_i \\ \overline{Bot} &= \sum X_i(Bo)_i\end{aligned}\right\} \qquad (1)$$

where X_i is the atomic fraction of component i in the alloy, $(Md)_i$ and $(Bo)_i$ are the Md and Bo values for component i, respectively.

Based on the widely used hot corrosion resistant superalloy IN738, the high Cr content hot corrosion resistant alloy system Ni-16Cr-9Al-4Co-2W-1Mo-(0 ~ 4)Ti-(0 ~ 4)Ta-(0 ~ 4)Nb (at%) was selected for the study by the d-electrons alloy design concept and considerations of the alloying features of the single crystal and hot corrosion resistant superalloys[2,3]. The results of the study of this alloy system show that, in certain compositional regions, the alloys have the desired balance of the properties including microstructure stability, solidification behavior, single crystal castability as well as hot corrosion resistance. These alloys are promising for further characterization. The result of effects of Ti, Ta and Nb on the hot corrosion resistance of this alloy system is reported here.

1 EXPERIMENTAL

Figure 1 shows the distribution of the experimental alloys in a Ti-Ta-Nb compositional triangle in which the alloys distributed homogeneously. Table 1 shows the compositions of the alloys selected for this study. The compositional triangle is similar to the common ternary phase diagram, in which each line parallel to one of the bottom lines represents a contour line of the element on the corresponding top. The cross-point of two contour lines will determine the composition of an alloy with another condition of the total content of Ti, Ta and Nb being 4at%. The contour lines of three important parameters $\overline{Mdt}$, $\overline{Bot}$ and ρ (density) for the alloy design process are given in the Ti-Ta-Nb compositional triangle , in which the $\overline{Mdt}$, $\overline{Bot}$ and ρ are changed in the ranges of 0.977 ~ 0.983, 0.705 ~ 0.728 and 8.3 ~ 8.9 (g/cm^3), respectively. The $\overline{Mdt}$ and $\overline{Bot}$ values are calculated following the equations[7]:

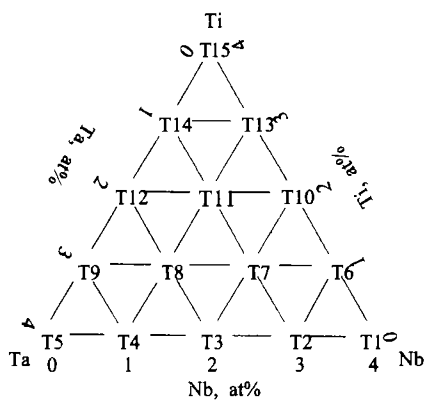

Fig.1 Distribution of the designed alloys (Ni-16Cr-9Al-4Co-2W-1Mo-Ti-Ta-Nb(at%)) in the Ti-Ta-Nb compositional triangle

$$\left.\begin{aligned}\overline{Mdt} &= 0.717\mathrm{Ni} + 1.142\,\mathrm{Cr} + 1.90\,\mathrm{Al} + 1.655\,\mathrm{W} + 1.55\,\mathrm{Mo} + 0.777\,\mathrm{Co} + 2.271\,\mathrm{Ti} + \\ &\quad 2.224\,\mathrm{Ta} + 2.117\,\mathrm{Nb} \\ \overline{Bot} &= 0.514\,\mathrm{Ni} + 1.278\,\mathrm{Cr} + 0.533\,\mathrm{Al} + 1.73\,\mathrm{W} + 1.611\,\mathrm{o} + 0.679\,\mathrm{Co} + 1.098\,\mathrm{Ti} + \\ &\quad 1.67\,\mathrm{Ta} + 1.594\,\mathrm{Nb}\end{aligned}\right\} \quad (2)$$

where the compositions are given in atomic percent. The $\overline{Mdt}$ values are changed within the limit of the phase stability boundary condition ($\overline{Mdt} \le 0.991$)[2] , which wi guarantee a stable microstructure.

High pure metals were used for the experimental alloys. Button size samples (about 10 g) were made by a tri-arc furnace in purified argon atmosphere. The electrodes were

Table 1 Compositions of the alloys studied (%)

Alloy	Ti	Ta	Nb	Al	Cr	W	Mo	Co	Ni
T1	0.00	0.00	6.30	4.11	14.09	6.23	1.63	3.99	63.65
T2	0.00	3.02	4.65	4.05	13.89	6.14	1.60	3.93	62.71
T3	0.00	5.95	3.06	3.99	13.69	6.05	1.58	3.88	61.81
T4	0.00	8.80	1.51	3.94	13.49	5.69	1.56	3.82	60.93
T5	0.00	11.57	0.00	3.88	13.30	5.88	1.53	3.77	60.07
T6	0.82	0.00	4.76	4.15	14.20	6.28	1.64	4.02	64.14
T7	0.81	3.04	3.13	4.08	13.99	6.19	1.61	3.96	63.19
T8	0.79	6.00	1.54	4.02	13.79	6.01	1.57	3.85	61.37
T9	0.78	8.86	0.00	3.97	13.59	6.01	1.57	3.85	61.37
T10	1.65	0.00	3.20	4.18	14.31	6.33	1.65	4.06	64.64
T11	1.62	3.07	1.57	4.16	14.10	6.23	1.63	3.99	63.67
T12	1.60	6.04	0.00	4.05	13.89	6.14	1.60	3.94	62.74
T13	2.49	0.00	1.61	4.21	14.42	6.38	1.66	4.09	65.14
T14	2.45	3.09	0.00	4.15	14.21	6.28	1.64	4.03	64.16
T15	3.35	0.00	0.00	4.24	14.54	6.43	1.68	4.12	65.65
IN738	3.40	1.70	0.90	3.40	16.00	2.60	1.70	8.50	61.80

water-cooled tungsten. Alloy melting was conducted in water-cooled copper crucible with a melting voltage of 80 V and a current of 40 A. The molten samples rotated within the crucible because of the electromagnetic action of the three electrodes and the surface tension of the melt, which was beneficial to compositional homogenization. Each button was turned over and remelted five times to achieve homogeneity and complete dissolution of refractory metals. Mass losses were always less than 1% after the five remelts.

According to the DTA results, the alloys were divided into three groups for heat treatment:
(1) 1 260 ℃ /4 h/AC+1 050 ℃ /16 h/A C +850 ℃ /48 h/A C (for T3, T4, T5, T7, T8, T9, T11, T12 and T14 alloys); (2) 1 230 ℃ /4 h/A C+1 050 ℃ /16 h/A C +850 ℃ /48 h/A C (for T2, T6, T10, T13 and T15 alloys); (3) 1 120 ℃ /2 h/A C+850 ℃ /24 h/A C. (for T1 and IN738LC alloys).

The specimens after heat treatment were employed for hot corrosion experiment with the crucible method. The test pieces were polished down to #1000 dry abrasive papers. The composition of mixed salts was 75 Na_2SO_4+25 NaCl (volumic fraction). The selection of such composition of molten salt was based on the consideration that such salt mixture usually showed strongly aggressive to the Cr_2O_3 type scale[10], while in the alloys studied, the contents of Cr were high and the Cr_2O_3 scale would be formed during hot corrosion tests, so that a possible severe test medium was selected. Figure 2 shows the hot corrosion experimental arrangements. The specimens were held in the molten salt at 900 ℃ for 24 h and then the mass loss (mg/cm^2) was determined after descaling. The corrosion products on the surfaces of the specimens were descaled in two steps:

(1) To be boiled in a solution of $KMnO_4$(5 g)+NaOH(8 g)+distilled water (77 g) for 30 min and be washed with ultrasonic; (2) To be boiled in a solution of $(NH_4)_2HC_6H_5O_7$)

(5 g)+distilled water (45 g) for 20 min and be washed with ultrasonic.

After fully dried, the mass of each specimen was measured and the mass loss was calculated. The constituents of the corrosion products in the surface scale were determined by X-ray diffraction. The microstructures of the alloys were studied by optical, SEM, EPMA and imaging analyzer. Before the observation, the specimens were polished and etched by a solution of $CuSO_4$(20 g)+HCl (100 ml)+H_2O(80ml) +H_2SO_4(5 ml).

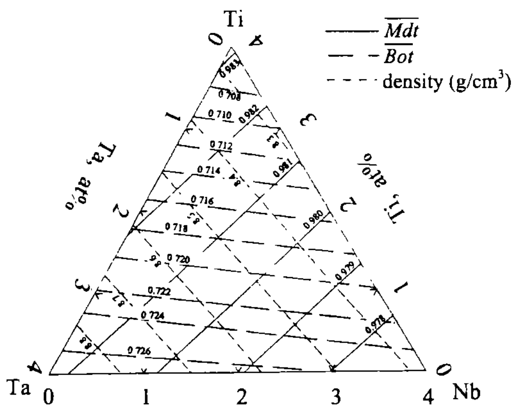

Fig.2 Contour lines of the parameters $\overline{Mdt}$, $\overline{Bot}$ and ρ considered in the alloy design in the Ti-Ta-Nb compositional triangle

2 RESULTS AND DISCUSSION

The results of hot corrosion experiments are summarized in a Ti-Ta-Nb compositional triangle (Fig. 3). In the Ti and Nb-rich corners, the alloys show better hot corrosion resistance than those in the Ta-rich corner, with alloy T6 showing the best hot corrosion resistance (mass loss =7.08 mg/cm^2) and alloy T9 showing the poorest behavior (fluxed during test). In general, Ta can improve the high temperature mechanical properties as well as the hot corrosion resistance of superalloys with low Cr contents[11~13]. While in the alloys with high Cr contents, the effect of Ta on hot corrosion resistance changed in this study. It deteriorated the hot corrosion resistance of the alloys, and caused the most severe hot corrosion attack around the Ta-rich corner (Fig. 3). As for the effect of Ti on hot corrosion resistance of the designed alloys, it was similar to those reported in the literature, i. e., it improved the hot corrosion resistance of the nickel-based superalloys[14, 15]. At present no unanimous conclusions have been drawn for the effect of Nb on hot corrosion resistance of superalloys[16]. Sims, et al[17] showed the unfavorable effect of Nb on hot corrosion resistance. While, alloy S-816 with up to 4% Nb showed a satisfied hot corrosion resistance at 870 ℃ [18]. Another example should be noticed is that in the well-known hot corrosion resistant superalloy IN738, about 1% Nb was added. So the effects of

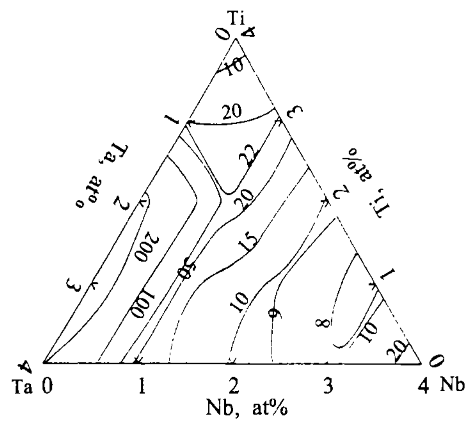

Fig. 3 Summary of the hot corrosion tests (crucible method, 900 ℃ /24 h in a molten salt 75% Na_2SO_4+25% NaCl). The numbers in the graph represent the mass loss (mg/cm^2)

alloying elements on hot corrosion resistance will change greatly according to the alloy system and the actual experimental conditions, even conversed results could be gotten. Analysis of the results should be done according to the actual situation. Cr is unanimously believed to be beneficial to improve the hot corrosion resistance of superalloys and it is the most effective and important alloying element for this purpose[19, 20]. Al is also generally beneficial to improve hot corrosion resistance of superalloys.

Table 2 gives the results of the major corrosion reaction phases identified by X-ray diffraction with powders taken from the surface layers. It is not difficult to identify the differences of hot corrosion products and microstructures of the scales in the typical alloys. The formation of the corrosion scale will be discussed in the following paper.

Figure 4 shows the dependence of hot corrosion resistance upon corrosion time of a typical experimental alloy T7 and the reference alloy IN738LC up to 300 h at 900 ℃. Similar behavior for the two alloys was obtained. It should be pointed out that in this study, polycrystalline specimens were used in the hot corrosion tests, which usually show lower corrosion resistance compared to the single crystal specimens. If single crystal specimens were used, the hot corrosion resistance would be at the same level as IN738LC, which was proved in a related investigation[21].

As summarized in Fig. 5, the promising compositional ranges are determined, in which most of the important factors considered in alloy development are included except the mechanical properties. The alloys in these promising ranges have the

Table 2 Phases identified by XRD

Phase	T6	T5	T15
Simple	NiO	NiO	NiO
oxide	Al_2O_3	Al_2O_3	Al_2O_3
	Cr_2O_3	Cr_2O_3	Cr_2O_3
	(Cr_2O_5)	(Cr_2O_5)	(Cr_2O_5)
			TiO_3
			(Ti_3O_5)
Complex	$NaAlO_2$	$NaAlO_2$	$NaAlO_2$
oxide	$(NaNiO_2)$	$(NaNiO_2)$	$(NaNiO_2)$
	Na_2CrO_4	Na_2CrO_4	Na_2CrO_4
		$CrWO_4$	
		$AlWO_4$	
Sulfide	NbS_2	Cr_3S_4	Cr_3S_4

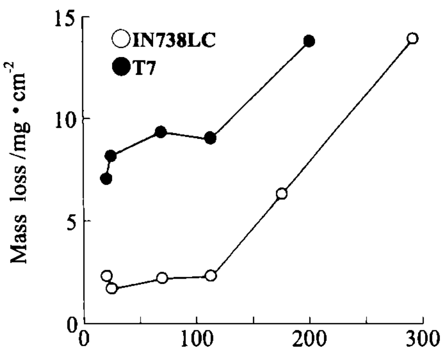

Fig.4 Dependence of hot corrosion resistance on corrosion time

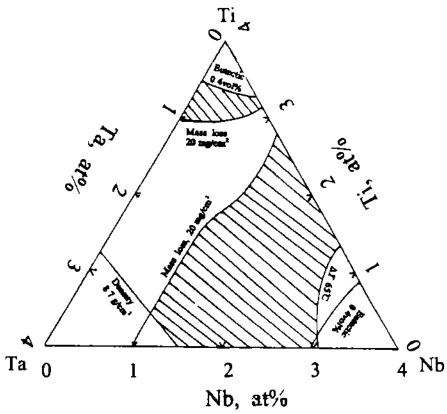

Fig. 5 Summaries of the properties of the experimental alloys, in which the shadowed regions show promising balanced comprehensive properties

excellent comprehensive properties including single crystal castability, microstructural stability, hot corrosion resistance and density. Promising compositions can be selected within the regions for further evaluation. The results have been published elsewhere[21].

3 CONCLUSIONS

From the results of characterization of the hot corrosion resistance of the alloy system Ni-16Cr-9Al-4Co-2W-1Mo-Ti-Ta-Nb(at%), following conclusions could be drawn: In Ti and Nb-rich corners, the alloys show satisfying hot corrosion resistance; while in Ta-rich corner, poor hot corrosion results have been gotten. In a certain compositional region, hot corrosion resistance of the experimental alloys is near the level of IN738LC alloy. The hot corrosion property balances with other the properties, which provides the basis for selecting alloy compositions to develop high performance hot corrosion resistant single crystal superalloys.

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高 Cr 含量镍基高温合金热腐蚀行为研究
——I. 实验研究

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摘要 系统研究了合金元素 Ti，Ta 和 Nb 对合金系统 Ni-16Cr-9Al-2W-1Mo-4Co-(0～4)Ti-(0～4)Ta-(0～4)Nb(at%)热腐蚀行为的影响。结果表明 在一定的成分范围内，实验合金在 75Na_2SO_4+25NaCl(体积分数) 溶盐中的热腐蚀抗力类似于 IN738LC 合金。在较高的热腐蚀抗力条件下，合金系列保持了较好的其它性能，这就为开发高性能抗热腐蚀单晶高温合金提供了成分选择的基础。

关键词 热腐蚀，高温合金，合金化影响