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Original Research

Coupling effects of tungsten and molybdenum on microstructure and stress-rupture properties of a nickel-base cast superalloy☆

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ABSTRACT

In order to comprehensively understand the forming mechanism of abnormal phases solidified in a nickel-base cast superalloy with additives of tungsten and molybdenum, the coupling effects of W and Mo on the microstructure and stress-rupture properties were investigated in this paper. The results indicated that the precipitation of primary α-(W, Mo) phase depended tremendously on the amount of W and Mo addition. When the total amount of W and Mo was greater than 5.79 at%, α-(W, Mo) phase became easily precipitated in the alloy. With increasing of Mo/W ratio, the dendrite-like α-(W, Mo) phases were apt to convert into small bars or blocky-like phases at the vicinities of γ′/γ eutectic. The morphological changes of α-(W, Mo) phase can be interpreted as the non-equilibrium solidification of W and Mo in the alloy. Since the large sized α-(W, Mo) phase has detrimental effects on stress-rupture properties in as-cast conditions, secondary cracks may mainly initiate at and then propagate along the interfaces of brittle phases and soft matrix. During exposing at 1100 ℃ for 1000 h, the α-(W, Mo) phases transformed gradually into bigger and harder M_6C carbide, which results in decreasing of stress-rupture properties of the alloy. Finally, the alloy with an addition of 14W-1Mo(wt%) maintained the longest stress lives at high temperatures and therefore it revealed the best microstructure stability after 1100 ℃/1000 h thermal exposure.

1. Introduction

A novel nickel-base cast superalloy was developed for using in isothermal forging dies deriving from its high temperature thermal capability and high corrosion resistance as well as relatively low product cost [1]. Unlike other superalloys for blade, multiple properties was emphasized for dies [2,3]. Beside the necessary of enough high temperature strength, the superalloy developing for dies must possess excellent stress-rupture properties in order to raise its operating temperatures. High refractory elements were usually added up to 20 wt% to meet the high temperature resistant requirements, where 14–17 wt% tungsten was usually used as the main strengthening element to stabilize γ′ and to increase the pre-melting temperatures. However, excessive additions may cause the alloys to yield topologically close-packed(TCP) phases, such as μ, σ or Laves phases [4–6]. The alloy would be unstable and apt to form α-W phase in the as-cast state because of excess amount of W. The abnormal phases can decrease the stress-rupture strength and do harm to maintaining good microstructural stability. In order to reduce the precipitation of α-W phase, many attentions have been paid in recent years. For instance, inhibiting the precipitation of primary α-W phase was performed through controlling the amount of γ′/γ eutectic by balancing the (Al + Ta) content [7] and raising the cooling rate [8]. In order to increase the stress-rupture strength and maintain good microstructural stability as well as excellent high temperature strength, molybdenum with lower stacking fault energy than tungsten is often used to partially replace W, in which it makes improving the creep rupture life [9]. Mo is usually used in single crystal to substitute Re or Ru to achieve better creep properties at moderate temperature in low cost superalloys [10,11]. However Liu [12] had found that addition of Mo led to microstructural instability and altered the precipitation behavior of TCP phases during exposure to 1100 ℃. The increasing content of Mo is prone to form much more TCP phases, and on the other hand Mo has stronger effect on formation of μ phase than W [13]. So tungsten cannot be completely replaced by Mo. However, up to date, not many works have been done about the coupling effect of W and Mo on the cast superalloy with high W content.

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Table 1
Chemical composition of the alloys.

Alloy no.		C	Co	Cr	W	Mo	Al	Ti	Ta	Nb	B	Zr	Ni
1	wt%	0.1	10.05	2.92	16.95	0	5.50	1.23	2.58	2.00	0.013	0.026	Bal.
	at%	0.52	10.71	3.52	5.79	0	12.80	1.61	0.90	1.35	0.08	0.02	Bal.
2	wt%	0.095	10.03	3.00	14.18	1.02	5.60	1.16	2.48	1.96	0.015	0.026	Bal.
	at%	0.49	10.50	3.56	4.76	0.66	12.80	1.49	0.85	1.30	0.09	0.02	Bal.
3	wt%	0.10	9.85	2.84	13.92	1.94	5.44	1.20	2.56	1.94	0.01	0.03	Bal.
	at%	0.52	10.35	3.38	4.69	1.25	12.49	1.55	0.88	1.29	0.07	0.02	Bal.
4	wt%	0.1	10.06	2.90	14.2	3.94	5.60	1.16	2.56	1.98	0.015	0.032	Bal.
	at%	0.52	10.66	3.48	4.82	2.57	12.96	1.51	0.88	1.33	0.09	0.02	Bal.
5	wt%	0.11	9.96	2.88	10.01	3.96	5.58	1.13	2.54	1.95	0.012	0.032	Bal.
	at%	0.56	10.24	3.36	3.30	2.50	12.54	1.43	0.85	1.27	0.07	0.02	Bal.

Above all, in this paper, the partial W was replaced by Mo in a nickel-base cast superalloy with high W content, and the coupling effect of Mo and W was investigated on formation of abnormal phase, including α-W phase, etc. and the microstructural stability as well as stress-rupture properties. This study aimed to elucidate the formation mechanism of the abnormal phases in high W containing nickel-base cast superalloy as molybdenum, another important strengthening element, was used.

2. Material and experimental procedure

Five alloys with different contents of Mo and W which were named as Alloy1 to Alloy5 respectively were prepared by vacuum induction melting(VIM). The chemical compositions of these alloys are listed in Table 1, in which the starting composition had a nominal composition of Ni-3Cr-10Co-10-17W-5.5Al-1Ti-2.5Ta-2Nb-0.01B-0.02Zr-0.1C(wt. %). From Alloy1 to Alloy4, the Mo content varied from 0 wt% to 4.0 wt %. To maintain high temperature strength, the W content of Alloy1 increased up to 17 wt%. Compared with Alloy4, Alloy5 has a relatively low W content in 10 wt%, meanwhile Mo had a constant content in 4.0 wt%. The master ingots of Alloy1 to Alloy5 were then re-melted at 1470 °C and poured into investment molds with back-filling sand preheated to 900 °C. Thereafter, the polycrystalline ingots were cut into bar-shape specimens for thermal exposure and stress rupture tests as well as microstructural inspections. The reason for inapplicability of heat treatment for the alloy was that large size components were usually obtained from this alloy and thermal stress can also be introduced during heat treatment simultaneously, especially, solution heat treatment temperature as high as 1250 °C. In addition, thermal stress had more serious influence than heat treatment on the lives of large size components. So, the properties of as cast state were taken into consideration.

The thermal exposure test was carried out for the specimens exposed at 1100 °C for 1000 h, then followed by air cooling. In order to simulate practical work circumstance, the stress-rupture test was performed for the specimens with 25 mm gauge length and 5 mm gauge diameter in air at 1100 °C/70 MPa. The stress-rupture test result of an individual specimen in this study was averaged at least from two specimens conducted in the same conditions in accordance with Chinese Standard GB/T 2039-2012.

The metallographic specimens were etched in a solution of 12 vol% phosphoric acid, 40 vol% nitric acid and 48 vol% sulfuric acid for microstructure observation. And the etchant of 25 vol% nitric acid, 50 vol % hydrofluoric acid and 25 vol% glycerin was used to investigate the cracks close to the fracture surface along longitudinal sections of the alloys.

The morphology of γ′ and carbide was examined by scanning electron microscopy(SEM). FM-700 Microhardness tester was used to measure the microhardness of α-(W, Mo) and M_6C carbides. The volume fractions of MC(mainly M_6C) and α-(W, Mo) phases were measured using Image-pro Plus software through at least 5 different OM or SEM images. Transmission electron microscopy(TEM) typed JEM-2010 was used for phase identification, where thin foils were prepared on MTP-1 twin-jet electro-polisher with a solution of 5% perchloric acid and 95% ethanol at − 35 °C using direct current of 50 mA. JXA-8100 electron probe microanalysis(EPMA) was used to detect the constituent of different phases from Alloy1 to Alloy5. The segregation ratio (SR) of element was defined as $SR_i = C^i_{interdendrite}/C^i_{dendrite}$, where $C^i_{interdendrite}$ and $C^i_{dendrite}$ denoted the average concentration of element *i* inside the interdendrite and dendrite core of samples, respectively. More than five regions in the interdendrite and dendrite core were measured for every sample when SR was calculated. The samples after being exposed at 1100 °C for 1000 h, they were also measured the constituents of γ matrix and γ′ phase respectively. At least five datasets were collected for each sample as calculating the γ/γ′ partitioning ratio(*k*). The partitioning ratio *k* of each alloying element was calculated by $k_i = C_{i\gamma}/C_{i\gamma'}$, where $C_{i\gamma}$ and $C_{i\gamma'}$ are the compositions of alloying element *i* in γ and γ′ phases, respectively.

3. Results and discussion

3.1. As-cast microstructures

As shown in Fig. 1, the microstructures in all alloys consisted of script-like MC carbides, γ′/γ eutectic and there occasionally precipitated M_3B_2 borides, and γ′ phase throughout the γ matrix. The α phase colonies were observed in Alloy1, Alloy3 and Alloy4, respectively. The length of α phase can attain about several hundred micrometers. Moreover, script-like phases were found in the interdendritic region of Alloy4. Through electron probe microanalysis(EPMA), it was found that the net-shape phases were M_6C phase, as shown in Fig. 1(f). The composition of α-W, MC and M_6C phases were shown respectively in Table 2. It should be noted that the amount of γ′ was about 70–75% with volume fraction in alloys and the morphology remains almost constant with the variation of W and Mo in this experiment, as presented in Fig. 1(g) and (h).

Table 2 showed that increasing content of Mo in Alloy1 to Alloy4 promoted the formation of α-(W, Mo) phase, which was also displayed on the metallographic samples as shown in Fig. 2. It can be seen from Table 3 that the precipitation of primary α-(W,Mo) phase was dependent not only on the content of (W + Mo), but also on the Mo/(W + Mo) ratio of the alloys. When the content of (W + Mo) greater than 5.79 at%, the alloy was unstable and prone to precipitate primary α-(W,Mo) phase. With increasing of Mo/(W + Mo) ratio, dendritic α-(W,Mo) phases changed into smaller bar or blocky-shape phases precipitated at the vicinities of γ′/γ eutectic. However, when the content of W decreased from 4.69 to 3.3 at%, the Mo/(W + Mo) ratio attained 0.76 and there was no α-(W,Mo) phase appeared. As it was reported there are two kinds of α phases in different alloys [8]. Dendritic α-(W,Mo) phase in Alloy1 (Fig. 2(a)) and smaller bar or blocky-shape α-(W,Mo) phases precipitated in γ′/γ eutectic in Alloy4(Fig. 2(b)). The formation process of α phase can be schematically interpreted in Fig. 3. In Alloy1 (Fig. 3(a)), because element W is a negative