

Thermal stability of primary carbides and carbonitrides in two cast Ni-base superalloys

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Received 4 July 2007; accepted 25 November 2007

Available online 28 November 2007

Abstract

Thermal stability of primary MC carbide and M(CN) carbonitride in K452 and K446 alloys is investigated. In K452 alloy, primary MC is very unstable relative to M(CN) for the former contains a higher content of the weakeners (W and Mo) than the latter. The ratios of element contents (at.%) (W+Mo)/Cr, (W+Mo)/(Ti+Nb) and Nb/Ti are three important parameters, which together determine the thermal stability of primary MC. Also, primary MC degeneration plays an important role in the microstructural instability of K452 and K446 alloys.

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Keywords: Ni-base superalloy; Thermal exposure; Microstructure; Carbide; Carbonitride

1. Introduction

In nitrogen-doped Ni-base superalloys, MC carbide and M(CN) carbonitride are two ordinary primary phases [1].

During thermal exposure and service, primary MC is generally unstable and degenerates by various forms of decomposition reactions. For example, two classical reactions, $MC + \gamma \rightarrow M_{23}C_6 + \gamma'$ and $MC + \gamma \rightarrow M_6C + \gamma'$, are often operative in many traditional alloys [2]. And, recently some novel manners, e.g. $MC + \gamma \rightarrow M_{23}C_6 + \eta$ [3] and $MC + \gamma \rightarrow M_{23}C_6 + \alpha - (W, Mo) + \eta$ [4], are reported in some superior superalloys with much higher operating temperatures and longer service lifetimes.

However, limited information is available concerning how M(CN) behaves during thermal exposure and service, though it was characterized to be more stable than MC during the remelting of alloys [5].

The microstructural degradation of superalloys was widely studied, including γ' coarsening, precipitation of secondary carbides, topologically close-packed (TCP) phase formation, and primary MC degeneration [6–10]. However, the interconnections among these features have been paid little attention.

In this paper, not only the thermal stability of primary MC and M(CN) in both K452 and K446 alloys is compared, but also the relationship between the stability of primary MC and the precipitation of secondary carbides or TCP phases is estimated.

2. Experimental

The compositions of K452 and K446 alloys are given in Table 1.

The heat treatment regime of K452 alloy has been reported in Ref. [4]. In contrast, K446 alloy was homogenized for 4.5 h at 1110 °C and subsequently an annealing treatment was carried out for 10.5 h at 750 °C. Then, specimens were exposed at 800, 850 and 900 °C for 1000, 3000 and up to 10,000 h, respectively.

The microstructures were examined by scanning electron microscopy (SEM) with an energy dispersive X-ray spectroscopy (EDS). And, transmission electron microscopy (TEM) was utilized for phase identification.

3. Results

3.1. Thermal instability of primary MC and M(CN) in K452 alloy

During thermal exposure, the primary MC and M(CN) suffer different degrees of deterioration, as illustrated in Fig. 1.

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Table 1
EDS composition of the investigated alloys and the phases involved in the primary MC degeneration process (at.%)

		Ti	W	Nb	Mo	Cr	Fe	Ni	Al	Co	C
Alloy	K452	4.1	1.1	0.2	0.4	22.7	/	Bal.	5.2	10.7	0.5
	K446	3	1.6	0.7	2.1	18	15.8	Bal.	3.9	/	0.5
MC in K452		71.5	9.7	11.6	0.9	2.5	/	4.7	/	/	
M(CN) in K452		92.8	2	1.6	/	1.8	/	1.8	/	/	
Decomposition products	M ₂₃ C ₆	2.4	3.4	/	1.4	70.6	/	17.7	1.5	3	
	α-(W, Mo)	8	47	1.3	5.3	4	/	29.7	1.1	3.6	/
MC in K446		51.6	7.7	30.2	6.4	1.5	0.9	1.7	/		
Decomposition products	M ₂₃ C ₆	1.5	3	/	5.1	65.3	7.5	17.6	/		
	M ₆ C	5.2	16.5	4.4	32.7	29.4	8.1	3.8	/		

The primary MC degenerates severely via three reactions, viz. MC + γ → M₂₃C₆ + γ' (Reaction I), MC + γ → M₂₃C₆ + η (Reaction II) and MC + γ → M₂₃C₆ + α-(W, Mo) + η (Reaction III) and the products involve γ', M₂₃C₆, η and α-(W, Mo) (Fig. 1(a)–(c)) [4,10]. Also, at the grain boundaries the degeneration is much faster than within the grains [11].

However, the M(CN) is so stable that it degenerates only to a tiny extent (Fig. 1(a')–(c')), and the reaction concerned is determined be M(CN) + γ → M₂₃C₆ + γ' + N. There are no nitrides found around the degenerated carbonitride, suggesting that N cannot combine with other alloy elements due to its inactivity. Whether at the grain boundary or within the grain, the M(CN) does not almost decompose (Figs. 1(a')–(c') and 2(b)).

In Fig. 2, the stability of primary MC and M(CN) at the grain boundaries is vividly contrasted: when the primary MC has decomposed completely, the M(CN) is still intact.

3.2. Thermal stability of primary MC in K446 alloy

In K446 alloy, primary MC, both at the grain boundaries and within the grains, slightly degenerates as shown in Fig. 3. The reaction concerned is principally MC + γ → M₆C + γ', which operates throughout the whole exposure; whereas, occasionally MC + γ → M₂₃C₆ + γ' occurs at the late stage of exposure.

The carbide product of primary MC degeneration in K446 alloy is mainly M₆C, rather than M₂₃C₆ as in K452 alloy. The reasons are probably: i) K446 alloy has a higher (W+Mo)/Cr ratio (0.53) than K452 alloy (0.2) with the same level of C content; ii) the primary MC in K446 alloy has a higher (W+Mo)/Cr ratio (9.4) than that in K452 alloy (4.2) (Table 1). Since W and Mo are the most important M₆C forming elements while Cr is the most important M₂₃C₆ forming element, M₆C forms more easily than M₂₃C₆ in K446 alloy during

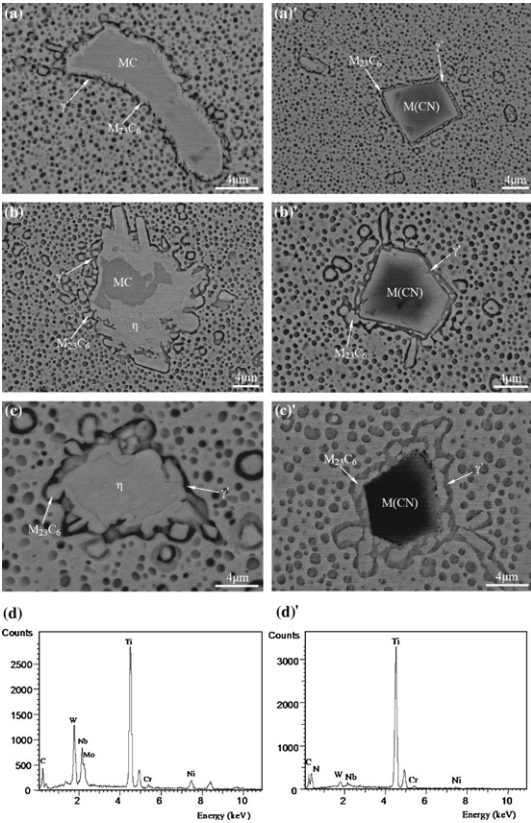


Fig. 1. SEM back-scattered electron micrographs and EDS patterns of MC and M(CN) in K452 alloy exposed at 900 °C for different times: (a) and (a') 1000 h; (b) and (b') 5000 h; (c) and (c') 10,000 h; (d) pattern of MC; (d') pattern of M(CN).

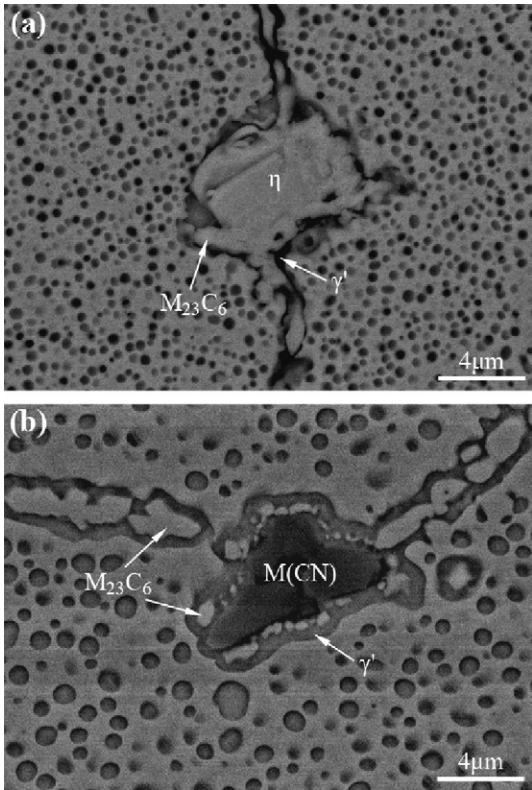


Fig. 2. Degeneration of primary MC and M(CN) at the grain boundaries: (a) 900 °C/1000 h; (b) 900 °C/5000 h.

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