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Decomposition of primary MC carbide and its effects on the fracture behaviors of a cast Ni-base superalloy

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Abstract

Primary MC degeneration in long-term thermally exposed cast Ni-base superalloy K452 was investigated in detail. It is shown that the primary MC degeneration is a diffusion-controlled process where various transformation products are sequentially present within the reaction region during exposure. The primary MC degeneration produces a DM or SM microstructure on the MC/γ interface at the initiation of exposure, which hinders the diffusion of alloying elements via its ordered γ' layers and leads to the presence of the η and α-(W, Mo) phases, respectively during the intermediate and late exposure. In addition, the primary MC deterioration is examined to be detrimental to the long-term thermally exposed alloy due to its contribution to the cracking incidence especially when the MC is present at the grain boundaries.

Keywords: Ni-base superalloy; Thermal exposure; Carbides; MC decomposition; Fracture property

1. Introduction

Ni-base superalloys are employed under high temperatures and stresses and undergo various microstructural changes during service, including γ' coarsening, formation of continuous grain boundary carbide network, TCP phase formation and MC carbide degeneration. Most of these features are detrimental to mechanical properties such as tensile strength and creep resistance [1–4]. However, MC degeneration has been debated. Some researchers thought that it played an important role in strengthening the alloys [5,6], whereas others insisted that it was deleterious [7,8].

Concerning the MC degeneration, two important reactions, $MC + \gamma \rightarrow M_{23}C_6 + \gamma'$ and $MC + \gamma \rightarrow M_6C + \gamma'$, were reported in many traditional superalloys and extensively accepted by modern superalloy metallurgists [5–7,9]. However, in the recent years, as superior superalloys have been introduced into industrial applications with much higher operating temperatures and longer service lifetimes, MC degeneration in these alloys tends to present some brand-new forms. For instance, Ref. [8] reported that when IN-738 and GTD-111 served at 1100 °C or so beyond 20,000 h, primary MC carbide decomposed in the form of $MC + \gamma \rightarrow M_{23}C_6 + \eta$.

Hence, in an attempt to better understand the MC degeneration and further upgrade the properties of modern superalloys, more extensive study in the field must be done. In this article, not only the primary MC degeneration is characterized in detail, but also its contributions to the rupture properties of a new gas turbine vane material K452 are carefully evaluated.

2. Experimental

The nominal composition of K452 alloy is given in Table 1. Specimens were subjected to homogenization for 4 h at 1170 °C followed by furnace cooling to 900 °C and then air cooling to room temperature; subsequently, two annealing treatments (4 h at 1050 °C + 16 h at 850 °C) were carried out. After the heat treatment, specimens were exposed at temperatures of 800, 850 and 900 °C for times of 1000, 3000, 5000 and up to 10,000 h, respectively. Finally, tensile- and stress-rupture tests (gauge length 50 mm, gauge diameter 5 mm) were performed at 900 °C and 900 °C/201 MPa, respectively.

The microstructures were examined using scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscope (EDS). Chemical etching with a solu-

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Table 1
Composition of K452 alloy

	Cr	Co	Al	Ti	Nb	Mo	W	C	Ni
wt.%	20.9	11.15	2.5	3.5	0.25	0.6	3.5	0.11	Balance
at.%	22.7	10.7	5.2	4.1	0.2	0.4	1.1	0.5	Balance

tion containing 20 g $CuSO_4$, 50 ml HCl and 100 ml H_2O, which dissolves only γ′-phase, was employed for the general microstructural observation. Deep etching with an electrolyte of 200 g KCl + 50 g citric acid + 200 ml HCl + 1000 ml H_2O, which removes both γ matrix and γ′-phase, was employed for the three-dimensional observation of carbides. Transmission electron microscopy (TEM) was utilized for phase identification. Foils for TEM were prepared on a twin-jet electropolisher with a solution of 10% perchloric acid and 90% ethanol at −25 °C.

3. Results and discussion

3.1. Process and mechanism of primary MC carbide decomposition

The microstructures of heat-treated K452 alloy contain γ matrix, γ′ precipitate, γ–γ′ eutectic, grain boundary $M_{23}C_6$ precipitate and intact coarse primary MC carbide. Most of the MC carbides have an irregular blocky morphology and are located both at the grain boundaries and in the interdendritic regions. Occasionally, regular-shaped Ti(CN) cores are present in the center of primary MC carbides (Fig. 1a). In contrast, the thermally exposed microstructures are distinctly different from the heat-treated ones. Apart from the $M_{23}C_6$ precipitation within the grain interiors, primary MC carbides, which are instable owing to the high W and Mo content of nearly 30 wt.% (Table 2) [9], decompose markedly and a well-defined reaction region is always formed on their peripheries (Fig. 1b). Since the Ti(CN) carbonitride, which dissolves W and Mo elements less than 7 wt.% in total, is so stable relative to the MC carbide, it decomposes only to a tiny extent and accordingly its degeneration is not anatomized in the present paper.

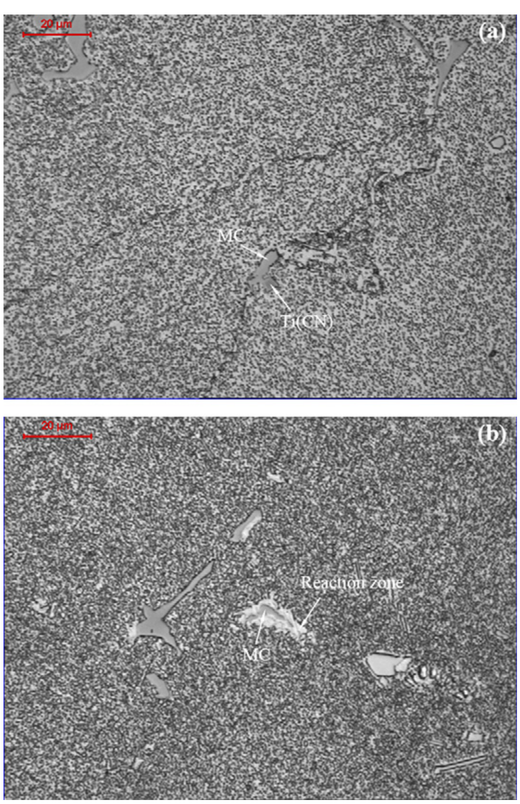

Fig. 1. Optical micrographs of the microstructures of the heat-treated (a) and exposed-at-800 °C/10,000 h (b) K452 alloy specimens.

Table 2
Chemical composition of phases involved in the primary MC degeneration process (wt.%)

	Co	Cr	Al	Ti	W	Nb	Mo	Ni
γ	11.6	21.5	2.2	3.5	4.2	–	1.0	56.0
γ′	4.7	3.9	5.1	8.6	4.3	–	–	73.4
η	5.6	4.9	2.1	13.0	4.5	3.4	–	66.5
MC	–	3.5	–	47.2	26.2	15.8	3.4	3.9
α-(W, Mo)	1.8	1.8	0.3	3.2	72.9	1.0	4.3	14.8
$M_{23}C_6$	3.1	64.4	0.7	2.0	9.2	–	2.3	18.3

The typical process of primary MC degeneration in the present alloy is illustrated in Fig. 2. During long-term thermal exposure, the primary MC severely deteriorates and various decomposition products are sequentially present on the periphery of the original MC core with increased exposure temperature or time.

A thin γ′ layer decorated with small and discrete Cr-rich $M_{23}C_6$ particles occurs on the MC/γ interface at the initiation of thermal exposure (Fig. 2a). These $M_{23}C_6$ particles grow larger and larger, tend to link one another and form, together with their surrounding γ′, a γ′–$M_{23}C_6$ dual microstructure (DM) (Fig. 2b) or a γ′–$M_{23}C_6$–γ′ sandwich microstructure (SM) with prolonged exposure (Fig. 2c). As the primary MC decomposes, it acts as a source of C and Ti while the γ matrix is the source of Ni, Al and Cr. Since C diffuses a lot more rapidly than any other elements, it combines with Cr to form $M_{23}C_6$ on the MC/γ interface; and then, the local enrichment of γ′ forming elements (Ni, Al and Ti), which is caused by the precipitation of the $M_{23}C_6$ carbide, leads to the formation and growth of γ′ precipitate around the $M_{23}C_6$ carbide. This is how and why the DM or SM is formed on the periphery of primary MC at the early stage of thermal exposure.

A deep etching technique was used in order to reveal the DM and SM more clearly as presented in Fig. 3, from which one can see that the $M_{23}C_6$ carbide in the DM or SM changes in shape from small discrete particles to large block-shaped ones and finally to a honeycomb-shaped wall with prolonged exposure and that the advent of a large gap between the wall and the remaining MC illuminates that the MC carbide has been suffering a significant extent of deterioration.

With the accumulation of γ′ and $M_{23}C_6$ on the perimeter of primary MC, the exchange of elements between the primary MC and the γ matrix becomes difficult. Specifically the diffusion of Al and Ti is severely blocked by the γ′-phase in the DM and SM (Al and Ti diffuse in the ordered γ′ much more slowly than in the disordered γ [10–12]). As a result, a high Ti/Al ratio,