



Effect of silicon on microstructure and stress rupture properties of a corrosion resistant Ni-based superalloy during long term thermal exposure

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ABSTRACT

The influence of silicon on microstructure and stress rupture properties of GH3535 nickel-based superalloy during long term thermal exposure at 700 °C was investigated. After long term thermal exposure, the secondary carbides precipitated along grain boundaries. Si addition induced the formation of $M_{12}C$ carbides, while only M_6C carbides were observed in Si free alloy. The secondary $M_{12}C$ carbides exhibited particular orientation relationship with matrix for the alloy with Si, but the secondary M_6C carbides are incoherent with matrix for the Si free alloy. It is believed that the difference in the types of the secondary carbides was originated from Si. The stress rupture life decreased after 1000 h thermal exposure for the Si free alloy, but no noticeable changes could be detected for the alloy with Si. The interface between the secondary M_6C carbides and matrix became the main site for crack initiation after 1000 h thermal exposure for the Si free alloy. But no cracks was detected at the interface between the secondary $M_{12}C$ carbides and matrix even after 10,000 h thermal exposure, which may be related to the strong interfacial cohesive force between secondary carbides and matrix.

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1. Introduction

As one of the most promising next generation reactors, molten salt breeder reactor (MSBR) has attracted more and more attentions in recent years [1,2]. The most important structural material in MSBR was polycrystalline Ni–Mo–Cr superalloy, Hastelloy N, which was developed and used in MSBR at Oak Ridge National Laboratory (ORNL). The alloy was strengthened by solid-solution of Mo and Cr, and the dispersed primary and secondary carbides [3,4]. Though the reactor has operated successfully for 4 years in 1960s at ORNL, there still remain many problems [5,6].

Driven by the materials demand of MSBR, a Ni–Mo–Cr alloy (GH3535) with excellent corrosion resistance and good high temperature strength was developed. Silicon is added to enhance the corrosion resistance [7,8] and the oxidation resistance of the alloy [9].

Silicon was reported to have great effect on diffusion of carbon in the alloy, which will influence the formation and stability of carbides [10–14]. It was reported that Si can stabilize the carbides

during high temperature annealing [4,15–16], especially at temperatures above 1180 °C, which may improve the mechanical properties of the alloy [17]. But some works showed that Si is disadvantage to the mechanical properties of the alloy [18]. The high temperature brittle phase (possibly the NiMo intermetallic) was observed during high temperature exposure, such as welding and high temperature annealing, when approximately 0.6 wt% Si was added [4,19,20], and resulted in the reduction of rupture ductility [4].

As the alloy is expected to be used in molten fluoride salt for more than ten years [21], the long term microstructure and mechanical properties are extremely important. During long term thermal exposure the evolution of carbides are important for the stress rupture properties of the alloy [22,23]. Gehlbach et al. [6] found that the as-cast microstructure of Hastelloy N was characterized by stringers of massive primary M_6C (Ni_3Mo_3C) carbides which remained stable during solution heat treatment. During long term thermal exposure between 500 °C and 1000 °C, secondary M_6C (Ni_2Mo_4C) carbides precipitated at the grain boundaries [24]. While Leitanker et al. [25] found that the primary and secondary carbides were all $M_{12}C$ in Hastelloy N after long term thermal exposure at 815 °C for 10,000 h. Svistunova et al. [16] thought that the appearance and stability of $M_{12}C$ carbide was attributed to the addition of element Si in Ni–Mo alloy. Although

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these alloys all contain Si, there was still controversy on type of the primary and secondary carbides i.e., whether these are M_6C or $M_{12}C$ carbides was not conclusive, and the influence of these carbides on mechanical properties was not clear neither.

Moreover, the influence of Si on the grain size and mechanical properties during long term thermal exposure was also not clear. Therefore, the effect of Si on the grain size and the type, amount, distribution and stability of the carbides in GH3535 alloy, and their effects on stress rupture properties during long term thermal exposure at 700 °C have been systematically investigated in this paper. The microstructure evolution mechanisms and the factors influence the stress rupture properties have also been discussed.

2. Experimental

The nominal chemical composition (wt%) of the experimental alloy is given in Table 1. The master alloy was melted into 10 kg ingot via vacuum induction melting (VIM) furnace. The ingot was homogenized and subsequently forged into bars of 30 mm × 30 mm in cross section. Then these bars were rolled into round bars of 16 mm in diameter. Samples were cut from these round bars using an electric discharge machine (EDM).

All of the samples were subjected to solution heat treatment at 1177 °C for 1 h, followed by water quenching, and then exposed at 700 °C from 50 h to 10,000 h. Some were used for stress rupture tests, and the others were used for microstructure observation and composition analysis. The stress rupture tests were conducted at 650 °C /324 MPa.

Samples for optical microscopy (OM), and scanning electron microscopy (SEM, HITACHIS-3400N) observation were mechanically polished. Some samples were etched by a solution of 3 g $CuSO_4 + 10$ ml $H_2SO_4 + 40$ ml $HCl + 50$ ml H_2O , and others were deep etched by a solution of 50 ml $HCl + 50$ ml H_2O_2 . The volume fractions of carbides were measured using an image analysis method. Each measured value is the average of 50 readings obtained from 50 different fields for each sample. The electronic probe microanalysis (EPMA) and X-ray diffraction (XRD) were employed for compositional analysis and phase identification. Selected samples were mechanically dimpled and then ion milled for transmission electron microscopy (TEM) observation. A Tecnai G2F20 TEM with combination of energy dispersive spectrum (EDS) was used in the present experiment.

3. Results and discussion

3.1. Microstructure after heat treatment

Microstructure of the alloys after solution heat treatment (1177 °C for 1 h) is presented in Fig. 1.

The morphologies of OM and SEM located in the bottom left corner in Fig. 1(a) and (b) show that there were many twin boundaries in alloys with or without Si. The microstructure consists of γ matrix and primary carbides for both alloys. And the primary carbides which located at grain boundaries as well as in grain interiors were M_6C determined by the selected area electron diffraction (SAED) pattern as shown in Fig. 1(c) and (d). The average diameters of the blocky carbides and the grains are 1–2.8 μm and 40 μm , respectively, for the Si free alloy. The corresponding diameters are 1–3 μm and 35 μm , respectively in alloy with Si.

The XRD patterns of these two alloys are similar (Fig. 2), which indicated that both alloys consist of primary M_6C carbides and γ matrix phase.

The EPMA results of the primary carbides in the solution heat treated samples are shown in Table 2. It can be seen that these

Table 1

The nominal chemical composition of the experimental alloy (wt%).

	Si	C	Fe	Cr	Mo	Mn	Ti+Al+Ta	Ni
Si free alloy	0	0.04	4	7	16	0.5	<2	Bal.
Alloy with Si	0.45	0.04	4	7	16	0.5	<2	Bal.

carbides are rich in Mo, Ni, Cr, and C for the Si free alloy, and the carbides in the alloy with Si are rich in Mo, Ni, Cr, C and Si. The mole ratio of the metal atoms to carbon atoms is near 6:1 for both alloys, which further verify that the primary carbides in these two alloys are M_6C carbides.

3.2. Microstructure evolution during long term thermal exposure

3.2.1. Carbides

The deeply etched microstructure of the alloy after different thermal exposure time is presented in Fig. 3. It shows that in the solution treated samples no secondary phase precipitated at grain boundaries and twin boundaries except the primary blocky M_6C carbides for both alloys, as shown in Fig. 3(a) and (e). After 50 h thermal exposure, secondary carbides like incalculable granules formed and overspread the grain boundaries for both alloys, as shown in Fig. 3(b) and (f). After 100 h, carbides precipitated gradually along grain boundaries as shown in Fig. 3(c) and (g). Some carbide grows and contacts with each other gradually after 500 h exposure as shown in Fig. 3(d) and (h). The morphology of secondary carbides for both alloys shows no remarkable difference, but the secondary carbides for Si free alloy are larger than those of the alloy with Si after the same time of thermal exposure.

Microstructure evolution of the samples during long term thermal exposure at 700 °C is presented in Fig. 4. Besides the γ matrix and the primary carbides secondary carbides was shown along the grain boundaries in each alloys after more than 500 h thermal exposure. The microstructure has no noticeable difference for both alloys, but the secondary carbides for the Si free alloy are always larger than those of the alloy with Si as shown in Table 3.

The TEM morphology and corresponding SAED patterns of the secondary carbides at the grain boundaries in 700 °C, 1000 h aged alloys are shown in Fig. 5. It was found that the secondary carbides in alloys without and with Si are M_6C and $M_{12}C$, respectively.

The phase of both alloys aged at 700 °C for 1000 h, 3000 h, and 10,000 h was analyzed by XRD (Fig. 6). Compared with XRD patterns of the solution treated samples, only M_6C carbides was detected in Si free alloy after 1000 h to 10,000 h thermal exposure (Fig. 6(a)). On the contrary, $M_{12}C$ carbides were found in the alloy with Si addition as shown in Fig. 6(b).

The EPMA quantitative analysis of the primary and secondary carbides in both alloys after 1000 h thermal exposure was shown in Table 4. The chemical compositions of the primary carbides for both alloys are similar, and the mole ratio of the metal atoms to carbon atoms was approximately 6:1, which further confirmed that the primary carbides of both alloys was M_6C . Secondary carbides show no obvious composition difference for both alloys, the mole ratio of metal atoms to carbon atoms is nearly 6:1 and 12:1, respectively, for the alloy without Si and with Si. It indicates that Si only affects the formation of secondary carbides.

The EPMA results showed no obvious difference of the chemical compositions of the primary and secondary carbides in 1000 h and 10,000 h annealed alloys with Si (Tables 4 and 5). It indicates that the primary and the secondary carbides are still M_6C and $M_{12}C$, and these carbides were stable during long term thermal exposure at 700 °C.

The structures of the M_6C and $M_{12}C$ carbides with the same lattice and space group are almost the same. The same distribution

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