Materials and Design 69 (2015) 70–80

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Microstructure stability and mechanical properties of a new low cost hot-corrosion resistant Ni–Fe–Cr based superalloy during long-term thermal exposure

Wen Sun [a,b], Xuezhi Qin [b,*], Jianting Guo [b], Langhong Lou [b], Lanzhang Zhou [b]

[a] University of Science and Technology of China, Hefei 230022, China
[b] Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

ARTICLE INFO

Article history:
Received 9 October 2014
Accepted 18 December 2014
Available online 27 December 2014

Keywords:
Nickel superalloy
Thermal exposure
Microstructure stability
Mechanical properties
Cr addition

ABSTRACT

A new low cost hot-corrosion resistant Ni–Fe–Cr based superalloy is designed and fabricated. The microstructure evolution, mechanical properties and effect of minor Cr variation on the microstructure stability during long-term thermal exposure have been investigated in details. Microstructure observations reveal that the new Ni–Fe–Cr based superalloy is constituted of γ matrix, γ' precipitate, primary MC carbide and grain boundary (GB) $M_{23}C_6$ carbide after standard heat treatment. During long-term thermal exposure at 850 °C, the γ' precipitate coarsens greatly within 3000 h, which significantly degrades the room temperature hardness and stress-rupture life at 800 °C/294 MPa. The primary MC degenerates gradually by reactions of $MC + \gamma \rightarrow M_{23}C_6 + \gamma'$, $MC + \gamma \rightarrow M_{23}C_6 + M_6C + \gamma'$ and $MC + \gamma \rightarrow M_{23}C_6 + M_6C + \eta$, respectively. The growth of carbide and γ' along GB changes it from thin discontinuous chain structure to coarse continuous chain structure, which might lead to the intergranular fracture during stress-rupture. In addition, small amount of grain interior (GI) $M_{23}C_6$ carbide precipitates in the matrix, which has negligible influence on the stress-rupture property. Moreover, minor increase of Cr content (from 20% to 21%) extends the precipitating temperature range of σ phase and enhances its precipitating peak temperature, which results in a large amount of σ phase precipitates in the Ni–Fe–Cr based superalloy during long-term thermal exposure at 850 °C. The formation of σ phase increases the room temperature hardness but degrades the stress-rupture life and elongation of the Ni–Fe–Cr based superalloy greatly.

1. Introduction

Ni-base superalloys have been widely used to manufacture modern industrial gas turbine thermal components which experience high temperatures and stresses during service [1]. Furthermore, compared to aircraft engines, gas turbines for industrial applications have to be exposed to corrosive environment for prolonged periods of time and have more stringent requirements for the hot-end Ni-base superalloys components [2], such as good high temperature strength and excellent hot-corrosion resistance. In order to satisfy the requirement of gas turbines components and decrease the cost, Fe element is added to substitute for Ni element and large addition of Cr element is added to the Ni-base superalloy to keep its excellent hot-corrosion and oxidation resistance properties during service.

During the service of gas turbine, the long-term exposure degrades the microstructure of Ni-base superalloys through the γ' coarsening and coalescence, formation of continuous secondary $M_{23}C_6$ chains along the grain boundary, primary MC degeneration and formation of topologically close-packed (TCP) phases [3–7], which would degrade the mechanical properties, such as hardness, tensile strength and creep resistance [8,9]. Among them, the γ' coarsening and coalescence is the most principal factor that deteriorates the mechanical properties [10]. In addition, the primary MC degeneration and formation of continuous secondary $M_{23}C_6$ chains along the grain boundaries might facilitate the initiation and propagation of cracks during service [11], which is detrimental to the creep properties and service life. Also, the precipitation of TCP phases, such as σ, is another important factor to degrade the mechanical properties during service. These undesirable effects are caused by (1) accumulation of cracking due to the hard and brittle nature of TCP phases [12,13]; (2) softening of the matrix due to the depletion of strengthening elements, which form TCP phases [14,15] and (3) disturbance on the locally regular γ–γ'

* Corresponding author. Tel.: +86 24 83978469; fax: +86 24 83978045.
E-mail address: xzqin@imr.ac.cn (X.Z. Qin).

http://dx.doi.org/10.1016/j.matdes.2014.12.030
0261-3069/© 2014 Elsevier Ltd. All rights reserved.

rafted microstructure at high temperature by the TCP phases [16]. Accordingly, the microstructure stability is a very important consideration, which must be carefully examined and assured.

σ phase, one of the most common TCP phases, is usually precipitated during long-term thermal exposure in Ni-based superalloy [17]. It has been reported that the formation of σ phase is significantly affected by the chemical composition of alloys, especially Cr element [18,19]. Cr is beneficial to hot-corrosion and oxidation resistance property of cast Ni-base superalloy. It is also an effective solid solution strengthening element. However, high levels of Cr addition could promote the propensity for the formation of detrimental σ phase. When the Cr addition increases from 5.76 to 6.83, and 7.74 at.% in RR 2075, RR2072 and RR2074, the TCP volume fraction increases and high proportion of Cr concentrate in the TCP phases particular in σ phase [13], which indicates that the precipitation of TCP phase is sensitive to the Cr addition. Thus, moderate concentration of Cr in alloy is important to promise the excellent hot-corrosive and oxidation resistance, but also avoid the precipitation of TCP phases. In order to promise the microstructure stability of superalloy, many phase computation (PHACOMP) methods have been applied to predict the precipitation of σ phase during composition design, such as the electron vacancy N_v and d-electron concept M_d. It is well known that the critical N_v value for the σ formation is 2.45–2.50 [20]. When the N_v value is higher than the critical value, the alloy is prone to form σ phase or another TCP phase, but if the N_v is lower than 2.45–2.50, the alloy can avoid the σ phase precipitation.

In this paper, a new hot-corrosion resistant Ni–Fe–Cr superalloy, strengthened by the ordered γ′ phase formed by Al, Ti and Nb, and solid solution strengthened elements Cr, W and Mo, is designed and fabricated. The excellent hot-corrosion and oxidation resistance is ensured by the large addition of Cr and high Ti/Al ratio. In light of the microstructure stability directly related to the mechanical properties, it is important to investigate the microstructure stability and mechanical properties of the new hot-corrosion resistant Ni–Fe–Cr superalloy during long-term thermal exposure and this is the main aim of the present paper. In addition, the influence of minor increase Cr addition (from 20% to 21%) on the microstructure stability is also discussed in order to obtain reasonable Cr concentration.

2. Experimental details

Table 1 lists the alloy compositions studied in this paper. The chemical compositions of alloy 1 and 2 are almost similar except the Cr element. The Cr addition in the two alloys is 20% and 21%, respectively. The specimen materials of two alloys were melted in an industrial scale vacuum induction furnace and then cast into the rods of 15 mm in diameter and 220 mm in length.

The as-cast rods used for long term thermal exposure were subjected to a standard heat treatment (SHT), 1110 °C/4.5 h/AC + 800 °C/10.5 h/AC. After the SHT, the rods were exposed at 850 °C for 500, 1000, 3000, 6000 and up to 10,000 h, respectively. Finally, stress-rupture tests (gauge length 50 mm, gauge diameter 5 mm) were performed on the thermally exposure specimens at 800 °C/294 MPa. And room temperature microhardness was also measured on this series samples.

Table 1
Nominal alloy compositions and their N_v number (wt.%).

Alloys	C	Cr	Al	Ti	Nb	W	Mo	Fe	Ni	N_v
1	0.1	20	1.8	3.4	0.10	2.4	1.7	15	Bal.	2.44
2	0.08	21	1.8	3.4	0.10	2.4	1.7	15	Bal.	2.52

Thermodynamic calculations were performed to predict the phase stability in the alloys compositions using the Thermo-Calc program and Ni database established by Thermal-Tech. No modification was made to the database, and the only input to the calculations was the alloy composition.

Subsequently, the optical microscope (OM) and JEOL6340 Field Emission Gun Scanning Electron Microscope (FEGSEM) were used to examine the microstructures of specimens, which were prepared via mechanical polishing and etching, following by ultrasonic cleaning. Chemical etching was employed for the general microstructural observation using a solution containing 20 g $CuSO_4$, 50 ml HCl and 100 ml H_2O, which dissolves γ′. While deep etching method in an electrolyte containing 10% HCl and 90% methyl alcohol, which stripped away γ matrix, was employed for three-dimension observation of γ′ phase. The size and volume fraction of precipitates were measured using image analysis software by at least 20 different images.

TEM observation was performed on the TECNAI G2 F20 and F30 transmission electron microscopy (TEM). The photographs were recorded under bright-field (BF), dark-field (DF), and selected area diffraction pattern (SAED) for phase identification. The composition analysis was performed using an energy dispersive X-ray spectroscopy (EDS) attached to the TEM and JEOL 6340 FEG-SEM. Z-contrast imaging was also obtained in the TECNAI G2 F30 transmission electron microscopy equipped with a high-angle annular dark field (HAADF) detector.

3. Results and discussion

3.1. Microstructure after standard heat treatment

Microstructure observations on the Ni–Fe–Cr superalloy with standard heat treatment are shown in Fig. 1a and b. It can be seen clearly that minor Cr variation almost has no effect on the microstructure and both alloys show identical microstructure, which is consisted of γ matrix, γ′ phase, primary MC and GB carbides. The γ′ phase, with size about 30 nm and sphere morphology, distributes uniformly and densely in the matrix (Fig. 1c). The observation on the grain boundary shows that it is fine and decorated with γ′ precipitates, primary MC and fine $M_{23}C_6$ particles, as presented in Fig. 1d. Further TEM observation displays that the fine $M_{23}C_6$ distribute dispersedly along the grain boundary (Fig. 1e). The inset selected area electron diffraction (SAED) pattern of the $M_{23}C_6$ confirms its lattice parameters as $a \sim 10.51$ Å and exhibits the orientation relationship with the γ matrix of $(111)_{M23C6}//(111)_{\gamma}$ and $[110]_{M23C6}//[110]_{\gamma}$. The primary MC carbides, with the volume fraction about 1.2%, distribute in the interdendritic regions and on the grain boundary, and are confirmed as TiC type carbide by the combination of SAED and EDS analysis results, as shown in Fig. 1f. The EDS analysis shows that the M is mainly behalf on Ti, W and Mo, as well as low content of Nb, Ni and Cr elements.

3.2. Microstructure stability during long-term thermal exposure

During long-term thermal exposure, the constitutional phases of the Ni–Fe–Cr base superalloy experience severely degradation, including γ′ coarsening, primary MC decomposition, formation of continuous secondary $M_{23}C_6$ chains on the grain boundaries and precipitation of grain interior $M_{23}C_6$ carbide, which could generate great influence on the mechanical properties. Moreover, in contrast to alloy 1 with 20% Cr addition, the minor increase of Cr content (21%) in alloy 2 promotes the precipitation of large amount of TCP-σ phase.