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Microstructural stability and mechanical properties of a boron modified Ni–Fe based superalloy for steam boiler applications

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ABSTRACT

Ni–Fe based superalloys are being considered as boiler materials in 700 °C advanced ultra-supercritical (A-USC) coal fired power plants due to their excellent oxidation and hot corrosion resistance, outstanding workability and low cost. In this paper, the microstructural stability and mechanical properties of a boron (B) modified Ni–Fe based superalloy designed for 700 °C A-USC during thermal exposure at 650–750 °C for up to 5000 h were investigated. The results show that adding boron has no apparent influence on the major precipitates, including spherical γ' and blocky MC. However, the amount of $M_{23}C_6$ decreases markedly after standard heat treatment. During long-term thermal exposure, the addition of boron has no influence on γ' coarsening, η phase precipitation and primary MC degeneration, but decreases the growth rate of $M_{23}C_6$ along grain boundary. The stress rupture life and ductility are obviously improved after the addition of B. Meanwhile, the yield strength of B-doped alloy almost keeps the same level as that without boron addition. The fracture surface characterization exhibits that the dimples increase significantly after adding boron. During long-term thermal exposure, the elongation of the alloy with B addition increases slightly, but, for the alloy without B addition, the elongation obviously increases. The improvement of the stress rupture life and ductility can be attributed to the increase of grain boundary strength and the optimization of $M_{23}C_6$ carbide distribution at grain boundary.

1. Introduction

In the twenty-first century, the world faces the critical challenge of providing abundant and cheap electricity to meet the economic development while, at the same time, preserving the environment. In order to save energy and reduce CO_2 emissions from fossil power plants, it is imperative to convert energy in a more efficient and cleaner way. The most straightforward way of increasing thermal efficiency is to raise the temperature and pressure in steam boiler [1]. Therefore, it is hoped that the next generation of advanced ultra-supercritical (A-USC) coal fired power plants could operate at service temperatures between 700 and 720 °C and steam pressures up to 35 MPa [2]. However, the requirements of 700 °C A-USC, especially the creep strength (100 MPa for 10^5 h), are greatly beyond the temperature capacity of the currently used ferritic or austenitic steels for 600 °C A-USC power plants [3]. Superalloys, such as CCA617, Nimonic 263 and IN740, with better high-temperature creep strength are considered as the most appropriate candidates in the hottest boiler and turbine sections [4–6]. But, these alloys are prohibitively expensive due to a high content of Co and/or Mo, W and the workability is poor [7]. In China, alloy GH984 (Ni–Fe based superalloy) is now being considered as a promising candidate alloy as boiler material in 700 °C A-USC due to its excellent oxidation and hot corrosion resistance, outstanding workability and low cost [8]. However, at present the creep strength of alloy GH984 is slightly lower than the requirement of 700 °C A-USC. Therefore, to improve the creep strength of GH984 alloy, great attempts have been made [9,10].

It is now recognized that the addition of small amount of boron (B) can markedly improve the creep life and crack propagation resistance of some superalloys. However, its use is controversial and the mechanism still remains unclear [11–17]. Nowadays the general results can be explained by supposing that adding boron increases the grain boundary strength. Superalloys contain many alloying elements and have a metastable microstructure after standard heat treatment [18,19]. The microstructures of superalloys are degraded by γ' coarsening, primary MC degeneration, precipitation and evolution of secondary carbides, η and TCP phase formation, and so forth during service or thermal exposure [20]. These features exert significant influence on the mechanical properties of superalloys [21,22]. However, the influence of B addition on microstructural stability is unclear during long-term thermal exposure. Few works referring to the influence of B on

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microstructural stability and mechanical properties are available and there exist controversy. As an alloy primarily strengthened by γ' phase, the long-term stability of γ' phase is very important for high temperature application. Some results show that adding B can stabilize γ' phase [11]. But Wasson et al. find that γ' coarsening rate increases after the addition of B [16]. The morphology, size, distribution and amount of the precipitated carbides have a great effect on the mechanical properties. The fine particle-like carbide is beneficial to the mechanical properties. During long-term thermal exposure, it is recently found that the addition of B can suppress the agglomeration of $M_{23}C_6$ carbide due to the segregation of B at $\gamma/M_{23}C_6$ interface [11,17]. However, during long-term thermal exposure, the influence of adding B on size and amount of $M_{23}C_6$ and the degeneration of primary MC carbide is still unclear. For Ni–Fe based alloy with high Ti/Al ratio, the precipitation of η phase deteriorates mechanical properties, but, limited information is available concerning the influence of B addition on η phase precipitation behavior. Additionally, there is no report about the influence of adding B on the stability of tensile properties during long-term thermal exposure. Superalloys are multicomponent and multiphase alloys. Better understanding of the influence of adding B on the microstructural evolution and its influence on tensile properties during long-term thermal exposure is significantly important for clarifying the influence mechanism of B addition and enhancing the high-temperature capability of Ni–Fe based superalloys.

Although it is recognizing the beneficial effect of B on the mechanical properties, the influence mechanism is unclear. it is expected that the overall properties of the GH984 alloy can be improved by adding B and the influence mechanism can be further clarified. Additionally, up to now, there have been few studies about the influence of B on microstructure evolution and its influence on tensile properties during long-term thermal exposure. Therefore, in this paper, the influence of B on microstructural stability and mechanical properties of GH984 alloy was investigated.

2. Experimental procedures

Alloy GH984, containing 20% Cr and 2.2% Mo for solid solution strengthening, about 3% (Nb+Al+Ti) for precipitation hardening, 0.04% C for grain boundary strengthening and without B addition, is used. Moreover, more than 30% Fe was added to reduce cost. Table 1 lists the nominal composition of the alloys investigated in the present study. To minimize compositional variations among the heats, the master alloy without B addition was first prepared by a 500 kg industrial vacuum induction furnace, then remelted in a 25 kg vacuum induction furnace. The alloy with 0.006% B addition was prepared by adding Ni–B alloy before pouring. The experimental alloys G1 and G2 are without and with B addition respectively. The ingots of G1 and G2 alloys were homogenized at 1150 °C for 2 h and hot-forged and rolled into bars of 16 mm in diameter at 1150 °C. The as-processed bars were subjected to standard heat treatment: 1100 °C/1 h air cooling + 750 °C/8 h air cooling, followed by a long-term thermal exposure at 650, 700 and 750 °C for 5000 h, respectively.

The tensile tests at 700 °C were carried out on a Shimadzu AG-250KNE machine following the standard heat treatment and long-term thermal exposure. The stress rupture properties at 700 °C/400 MPa and 750 °C/350 MPa were measured on a CSS-3905 machine after standard heat treatment.

Microstructure was characterized by the JEOL 6340 Field Emission Gun Scanning Electron Microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) microanalysis and a TECNAI G2 F20 transmission electron microscope (TEM). SEM

Table 1
Nominal composition of the experimental alloys (wt%).

Alloy	C	B	Cr	Mo	Nb+Al+Ti	Fe	Ni
G1	0.04	–	20	2.2	2.8	34	Bal.
G2	0.04	0.006	20	2.2	2.8	34	

samples were grounded to 2000-grit, mechanically polished, and then etched by two different solutions. A solution of 200 g KCl, 50 g citric acid, 200 ml HCl and 1000 ml H_2O was used for general microstructure observation. Deep etching method with a solution of 10% H_2CrO_4 (CrO_3+H_2O), which can strip away γ matrix and etchgrain boundary clearly, was employed for three-dimension observation of the lath-like η phase (Ni_3Ti-base) and ultra-fine γ' phase. TEM samples were mechanically thinned down to about 100 μm in thickness, and electropolished with a 10% perchloric acid methanol solution, using a double-jet electropolisher.

3. Results and discussion

3.1. Microstructure characteristic after standard heat treatment

Fig. 1 illustrates the microstructural characterization of alloys without (G1) and with (G2) B addition after standard heat treatment. It is evident that adding B has no obvious influence on the microstructure characterization. Both two alloys present an equiaxed microstructure. Typical grain size is between 20 and 110 μm, and the average grain size is about 60 μm. Moreover, the intragranular area contains numerous annealing twins, which is beneficial to the strength. The primary precipitates are γ', MC and $M_{23}C_6$ (Fig. 1c–e). The ultrafine coherent γ' particles, which contribute to the main strengthening effect, are spherical with the size about 20 nm and homogeneously distribute within grain interior (Fig. 1e). The blocky MC carbide precipitates both at the intragranular area and at grain boundary and is Nb and Ti enriched by EDS. The $M_{23}C_6$ carbide appears only at grain boundary and is Cr enriched [23]. However, from Fig. 1c and d, it can be seen that the amount of $M_{23}C_6$ obviously decreases. Some results show that B mainly segregates at the grain boundary [11,17]. The segregation of B at the grain boundary may reduce the nucleation and growth rate of $M_{23}C_6$ by decreasing grain boundary diffusion rate and defects. Therefore, the amount of $M_{23}C_6$ decreases after the addition of B.

3.2. Coarsening behavior of γ' phase

The coarsening behavior of γ' phase was investigated by SEM after long-term thermal exposure. Fig. 2 shows the changes of γ' characteristic that occur during thermal exposure at 700 and 750 °C for different times. With increasing thermal exposure temperature and time, the γ' phase has an obvious growth, particularly with increasing thermal exposure temperature. But, the morphology of γ' phase is still spherical due to the low γ–γ' lattice misfit even if the size increases markedly after thermal exposure at 700 °C for 5000 h. In addition, no coalescing behavior has been observed during long-term thermal exposure. The addition of B has no evident influence on the stability of γ' morphology during long-term thermal exposure at 700 and 750 °C. The stable shape of γ' phase is beneficial to the mechanical properties during high-temperature long-term service. This long-term thermal stability is one of the major considerations for high-temperature applications of superalloys.

The average radius of γ' phase (defined as d) obtained after various thermal exposure time (defined as t) at three temperatures