MICROSTRUCTURES AND PROPERTIES OF DZ40M Co-BASED SUPERALLOY AFTER LONG-TERM AGEING AT 850 ℃①

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ABSTRACT DZ40M is a newly developed directionally solidified Co-based superalloy. Its microstructural characteristics and mechanical properties at room and elevated temperatures after ageing for 100~ 1 000 h at 850 ℃ were studied. The results showed that 100 h ageing at 850 ℃ results in a substantial increase of tensile strength at room temperature and stress-rupture life at elevated temperatures, serious decrease of ductility at room temperature and improvement for stress-rupture ductility. With increasing ageing time, stress-rupture life tends to decrease and the other properties keep at essential constant. During ageing, primary carbides M_7C_3 and MC decompose sluggishly, fine $M_{23}C_6$ precipitates copiously around them and M_6C forms on the surface of some M_7C_3. The increased strength of the aged alloy is attributed to a strong interaction between $M_{23}C_6$ and dislocations.

Key words directional solidification Co-based superalloy long-term ageing mechanical property

1 INTRODUCTION

DZ40M is a newly developed directionally solidified cobalt-based superalloy based on conventional X40. Compared with X40, it has a higher strength and ductility and its service temperature can be raised 45 ℃[1, 2]. Because of their excellent hot corrosion resistance, high rupture stress as well as high incipient melting temperature, cobalt-based superalloys are widely used to manufacture combuster liners and guide vanes of gas turbine engines, which generally serve in lower stress but higher temperature condition. It is of significance to understand the microstructural evolution and the change of mechanical properties during high temperature long-term exposure. The present work studied the microstructures and mechanical properties of DZ40M after long-term ageing at 850 ℃, aiming at knowing the phase stability and the operation of DZ40M.

2 EXPERIMENTAL

The master alloy was prepared in a 25 kg vacuum induction furnace, whose nominal composition is as follows (%): C0. 45, B0. 05, Al0. 8, Zr0. 15, Ni11, Cr25, W7. 5, Mo0. 2, Ta0. 25 Ti0. 15, Co balance. The directional solidification of the alloy was performed in a conventional vacuum unidirectional solidification furnace with a mould withdrawal device. Cylindrical rods of the alloy, 16 mm in diameter and 140 mm in length, were produced at a withdrawal rate of 7 mm/ min and a thermal gradient of about 50~ 60 K/ cm at the solid/ liquid interface.

Cast rods were aged for 100, 500 and 1 000 h at 850 ℃, respectively. Then, they were machined into standard specimens for mechanical

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property test. Tensile property at room temperature and stress-rupture property at 980 ℃, 83 MPa were measured. The microstructures were observed under optical microscopy, scanning electron microscopy and transmission electron microscopy.

3 RESULTS

3.1 Mechanical properties

Fig. 1 shows room temperature tensile properties of alloy aged for various times at 850 ℃. After 100 h of ageing, ultimate tensile strength σ_b and yield strength $\sigma_{0.2}$ rose appreciably, whereas elongation δ and area reduction ϕ dropped markably. But, when ageing time was prolonged to 500 and 1 000 h respectively, there was no substantial change in strength and ductility, indicating that ageing time has less effect on room temperature mechanical properties. For DZ40M aged at 850 ℃, its stress-rupture property at 980 ℃, 83 MPa is shown in Fig. 2. After 100 h of ageing, stress-rupture life increased obviously. Furthermore, with increasing ageing time, it tended to decrease, and after 1 000 h of ageing, it approached that of as-cast alloy. At the same time, the aged alloy still had an excellent stress-rupture ductility like as-cast alloy. Those results indicated that the long-term ageing at 850 ℃ did not impair high temperature stress-rupture property, on the contrary, improved it.

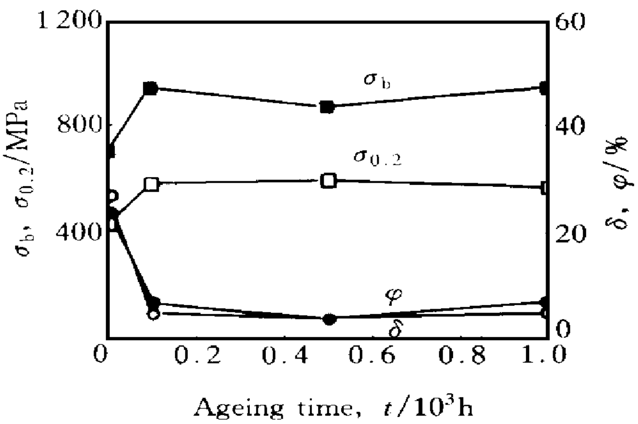

Fig. 1 Effect of DZ40M aged at 850 ℃ for different time on tensile properties

3.2 Microstructures

3.2.1 In as-cast alloy

The microstructure of as-cast DZ40M was composed of cobalt-base solid solution and the primary carbides M_7C_3 and MC. The solid solution matrix was columnar grains with ⟨001⟩ direction parallel to the growth axis (Fig. 3(a)). The primary carbides were located at grain boundaries and interdendritic regions. The chromium-rich M_7C_3 was in the form of rod and eutectic, while the MC rich in Ta, Ti, Zr, W was present as a discrete, blocky dispersion and a Chinese script morphology (Fig. 3(b)).

3.2.2 In aged alloy

After the alloy was aged at 850 ℃, the primary carbides thinned out considerably, which indicated that their solutioning and a profusion of fine secondary precipitates were produced. The precipitates were unevenly distributed, agglomerating around the primary carbides (Fig. 4). With increasing ageing time, the precipitates grew gradually, but the microstructures aged for various times were similar.

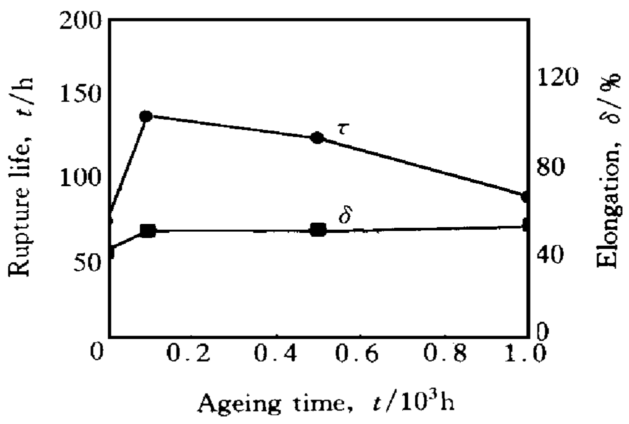

Fig. 2 Effect of DZ40M aged at 850 ℃ for different time on its stress-rupture properties at 980 ℃, 83 MPa

Transmission electron micrograph (Fig. 5(a)) revealed that the precipitates assumed spherical and rod-like shape. The electron diffractions analysis demonstrated that these precipitates possessed the same crystal structure and their characteristic reflections were present at every one-third position of the fcc matrix reflection (Fig. 5(b)). This indicated that the precipitates had a fcc structure with a lattice constant that was nearly three times of the matrix, and they also assumed a cube-cube orientation relationship with the matrix:

$\{100\}_{precipitate} // \{100\}_{matrix}$

$\langle 001 \rangle_{precipitate} // \langle 001 \rangle_{matrix}$

These are characteristic features of the chromium-rich $M_{23}C_6$ carbide[3]. Energy dispersive analysis of X-rays demonstrated that the precipitates were rich in chromium, and also contained Co, W, Ni etc. Consequently, a great amount of the secondary precipitates in DZ40M aged at 850 ℃ were the chromium-rich $M_{23}C_6$.

A tungsten-rich phase was found by SEM and EDAX (Fig. 6). Electron diffraction analysis showed that the tungsten-rich phase was M_6C (Fig. 7). Extensive microstructural observations showed that the M_6C precipitated only on the surface of those M_7C_3 which were adjacent to the tungsten-rich MC. During ageing, the tungsten-rich MC decomposed and released tungsten

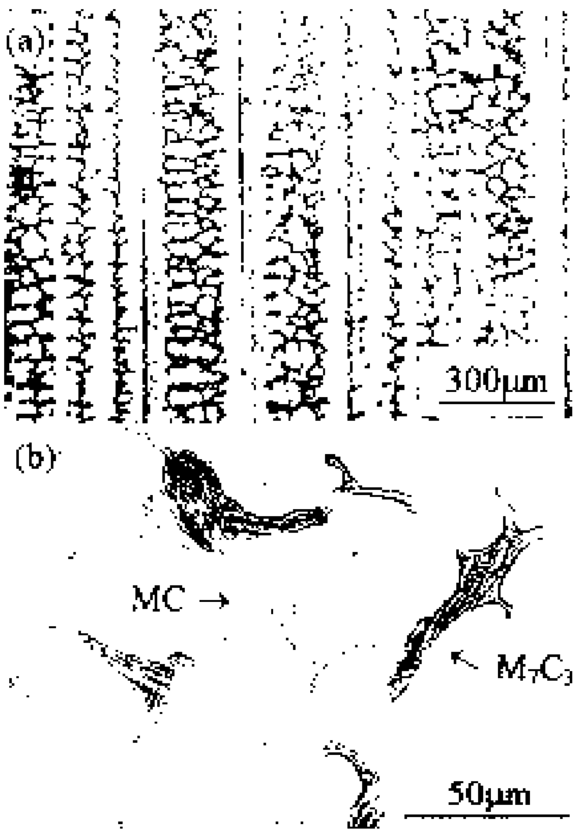

Fig. 3 Microstructures of as-cast DZ40M alloy
(a) —Longitudinal section; (b) —Transverse section

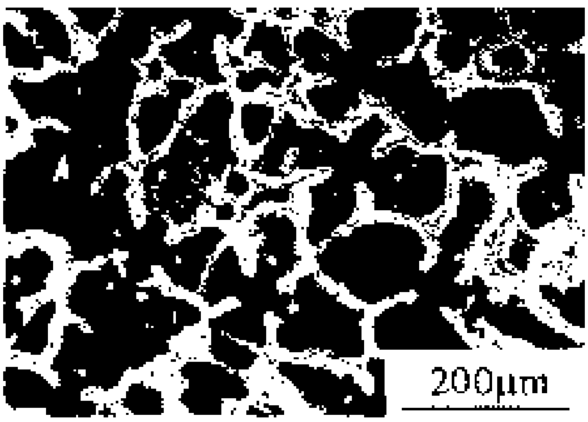

Fig. 4 SEM micrograph of DZ40M alloy aged for 100h at 850 ℃

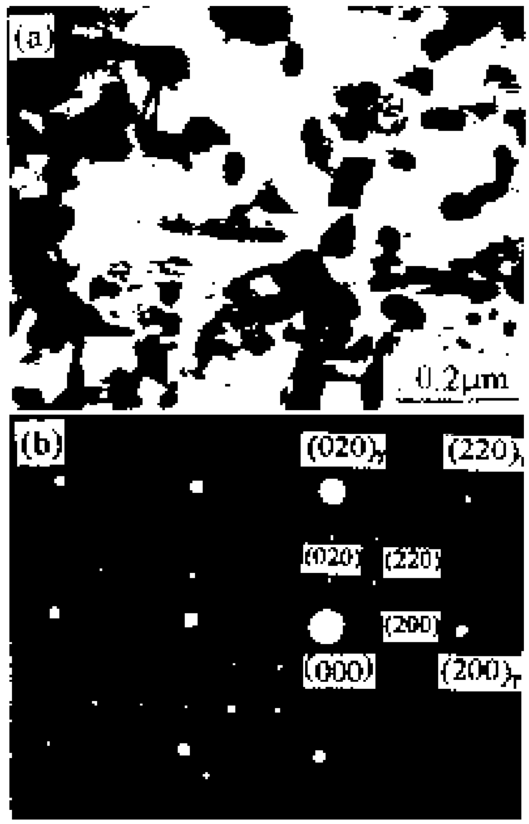

Fig. 5 TEM micrographs showing morphology of precipitates in matrix
(a) —Bright field; (b) —Their diffraction pattern

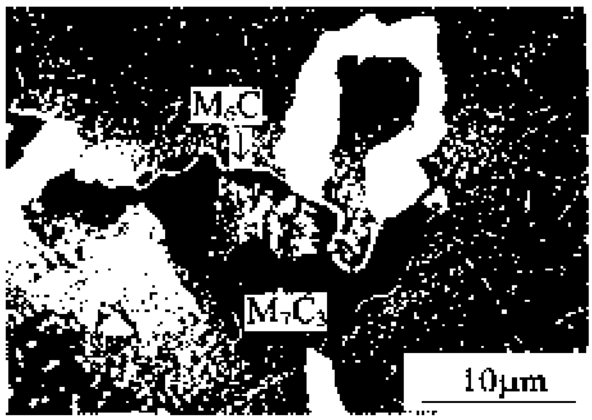

Fig. 6 Precipitation of a tungsten-rich phase on surface of M_7C_3

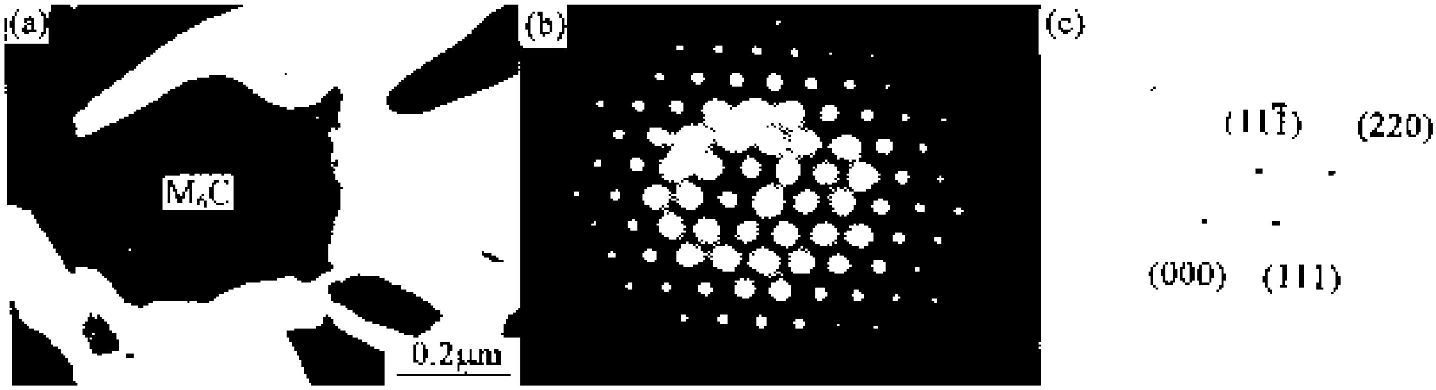

Fig. 7 TEM micrographs
(a) —Morphology of M_6C; (b) —Diffraction pattern; (c) —Key diagram

atoms. The tungsten atoms diffused to the surface of the M_7C_3, forming the M_6C precipitates.

4 DISCUSSION

After long-term ageing at 850 ℃, DZ40M alloy still had excellent mechanical properties at room and elevated temperatures. The room temperature tensile strength increased substantially and high temperature stress-rupture life and ductility increased too. Although the ductility at room temperature reduced seriously, the elongation was still about 5%, while that of as-cast equiaxed X40 alloy is 8%[4]. After DZ40M alloy aged at 850 ℃, the change of its mechanical properties is closely related with its microstructural evolution.

During high temperature ageing of DZ40M, the primary carbides M_7C_3 and MC dissolved sluggishly, the fine $M_{23}C_6$ precipitated profusly in matrix and M_6C formed on the surface of some M_7C_3, forming a more thermodynamically stable structure. Increased strength resulted from a strong interaction between fine $M_{23}C_6$ and dislocations. In stress-rupture tests at high temperatures, dislocations transformed to a subgrained structure. $M_{23}C_6$ pinned up subgrained boundaries, inhibiting their movement and stabilizing subgrains (Fig. 8). As well known, in superalloys secondary phases at grain boundaries lock grain boundaries and hinder their migration, improving their high temperature mechanical properties. However, the primary carbides M_7C_3 and MC at grain boundaries in DZ40M were in a thermodynamically unstable state, which dissolved at high temperatures. Fortunately, M_6C, a thermodynamically stable phase, formed on the surface of M_7C_3 and limited its decomposition. As strengthening phases, M_6C and M_7C_3, locked grain boundaries together, which enhanced high temperature strength of grain boundaries. The microstructure of DZ40M aged at elevated temperatures was relatively stable. After 100 h ageing at 850 ℃, $M_{23}C_6$ and M_6C precipitated in matrix and on the surface of some M_7C_3, respectively. When ageing time was prolonged to 500 and 1000 h, the microstructure did not change substantially and no detrimental phase appeared.

The present work shows that the precipitation of $M_{23}C_6$ occurred mainly around the primary carbides, forming a segregation zone. It is

Fig. 8 TEM micrograph showing a substructure of DZ40M aged for 100 h at 850 ℃ after 980 ℃, 83 MPa stress-rupture test

thought that $M_{23}C_6$ formed from a direct reaction between Cr and C atoms in the matrix. In the matrix the content of chromium was high, up to about 25%, while that of carbon was rather low, most of which was in the primary carbides. Therefore, the precipitation reaction of $M_{23}C_6$ was controlled by the content of carbon. During ageing, the primary carbides, M_7C_3 and MC, dissolved and released carbon atoms, establishing a carbon-rich zone around them. Consequently, the precipitation of $M_{23}C_6$ took place there, forming a peculiar microstructure, concentrating the segregation of $M_{23}C_6$ on the primary carbides. The dissolution of the primary carbides provided the formation of $M_{23}C_6$ with indispensable carbon atoms. The primary carbides was a carbon reservoir.

The tungsten-rich M_6C was uncommon in cast cobalt-base superalloys, which was usually found in wrought cobalt-based superalloys such as HS188[5]. Usually, M_6C appears only if the content of tungsten and/or molybdenum was as high as 15%[6]. The tungsten-rich M_6C was absent in conventional X40, for its content of tungsten was only about 7%. The present DZ40M alloy was a modification of X40 with Ta, Ti, Zr, Mo and Al. Its content of tungsten was the same as that of X40, the content of molybdenum was only 0.2%, and their sum was much less than the critical value to form $M_{23}C_6$. The addition of strong carbide forming elements, Ta, Ti, Zr, resulted in the formation of MC type carbide. EDAX showed that there were four kinds of MC in DZ40M, i.e. tantalum-rich, titanium-rich, zirconium-rich and tungsten-rich carbides[7]. It is the tungsten-rich MC that caused the precipitation of M_6C. During high temperature ageing, thermodynamically unstable carbides (M_7C_3 and MC) decomposed, resulting in a segregation zone of corresponding carbide forming elements. In the segregation zone of tungsten, the content of tungsten may reach the critical value to form M_6C, which favored the precipitation of M_6C thermodynamically. The preferential precipitation of M_6C on the surface of M_7C_3 may be explained by interfacial thermodynamic consideration. The surface of M_7C_3 could act as a nucleating site of M_6C, promoting its precipitation. Hamar-Thibault reported that {100} of M_7C_3 was a good nucleating base of M_6C[8]. In sum, during high temperature ageing of DZ40M the precipitation of M_6C is attributed to the peculiar microstructure resulted from minor alloying.

5 CONCLUSIONS

(1) After DZ40M aged for 100h at 850 ℃, its room temperature tensile strength and high temperature stress-rupture life increases drastically, its room temperature ductility decreases seriously and stress-rupture ductility increases slightly. With increasing ageing time, its stress-rupture life tends to drop, while the others retains essentially constant.

(2) During high temperature ageing, the primary carbides M_7C_3 and MC decomposes sluggishly, the chromium-rich $M_{23}C_6$ precipitates profusly in the matrix and the tungsten-rich M_6C forms on the surface of some M_7C_3.

(3) Inhomogeneous precipitation of $M_{23}C_6$ and M_6C should be attributed to the uneven distribution of alloying elements in the alloy.

(4) After DZ40M aged for long-term at high temperatures, its change of mechanical properties is closely related to microstructural evolution and there is a strong interaction between fine $M_{23}C_6$ and dislocations.

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