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Influence of high-temperature air pre-exposure on mechanical strength of a directionally solidified cobalt-base superalloy

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The present work investigated the influence of air pre-exposure at 850°C for 1000 h on the mechanical properties and microstructures of the directionally solidified cobalt-base alloy DZ40M. The results show that the air pre-exposure did not embrittle the alloy, but resulted in a marked strengthening. Microstructural observations and energy dispersive X-ray spectroscopy (EDS) indicates that the air pre-exposure caused a substantial external and internal oxidation, which is assumed to protect the alloy from being oxidized further and make a significant contribution to alloy strengthening, respectively. The immunity of the alloy to air embrittlement is attributed to elimination of transverse grain boundaries by directional solidification. *© 2001 Kluwer Academic Publishers*

1. Introduction

It has long been recognized that air exposure at high temperature can significantly influence mechanical properties of superalloys. Research work in this field has been concentrated on nickel-base superalloys. In fact, many nickel-base superalloys undergo air embrittlement [1]. This embrittlement is most severe in an intermediate temperature near 800°C. It is manifested in a loss in ductility in both tensile and creep testing and is associated with intergranular failure. However, cobalt-base superalloys seem to be less susceptible to air embrittlement. For instance, the cobalt-base superalloy MAR-M509 suffered no loss in stress-rupture life after high-temperature air pre-exposure compared with the same exposure in vacuum. On the other hand, a loss of tensile ductility was also observed for alloy MAR-M509 [2]. Regarding cobalt-base superalloys, the effect of air pre-exposure at high temperature is less understood, because their application is not so wide as nickel-base superalloys.

DZ40M alloy is a modified directionally solidified X-40 superalloy, which was recently developed at the Institute of Metal Research, Academia Sinica. The directional solidification not only eliminates transverse grain boundaries, but also produces a structure of columnar-grained matrix with the [001] direction parallel to specimen axis, resulting in a substantial improvement on ductility [3]. The modification of the alloy with beneficial elements (tantalum, titanium, zirconium) resulting in the formation of primary MC type carbides, very effective strengthening phases, can increase the stress-rupture strength. It is intended that this material will be used in industrial and aircraft turbines for vanes and combuster sections. Hence, the resistance against environmental attack at high temperature is a requirement for the alloy.

Aim of the present study is to investigate the influence of high-temperature air pre-exposure on the mechanical properties and microstructures of the DZ40M alloy so as to provide a base for appropriate applications of the alloy.

2. Experimental procedure

The DZ40M alloy was prepared in a conventional vacuum furnace with mold withdrawal device. The nominal chemical composition of the alloy is shown in Table I. Cylindrical rods of the alloy, 16 mm in diameter and 140 mm long, were produced at a withdrawal speed of 7 mm/min and a thermal gradient of about 50–60 K/cm at the solid/liquid interface.

Two kinds of high-temperature treatments were made, i.e. with and without air environment. Some as-cast bars were firstly machined to specimens with a gauge length of 50 mm and a diameter of 8 mm. Then, they were exposed in air at 850°C for 1000 h. This was designated as air pre-exposure. In order to eliminate

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TABLE I Nominal composition of the alloy

	Cr	Ni	W	Mo	Ta	Ti	Zr	Al	B	C	Co
wt%	25	11	7.5	0.2	0.25	0.15	0.15	0.8	0.05	0.45	bal

environmental influence, before machined to specimens for mechanical property testing, some other as-cast bars were firstly suffered from the same thermal exposure. It is believed that the latter specimens only endured a thermal aging alone, free of air environment effect. It was refereed as to thermal aging.

Tensile testing at room temperature and stress-rupture testing at high temperature were conducted on the specimens suffered from two kinds of the heat treatments, i.e. the air pre-exposure and the thermal aging. For the purpose of comparison, mechanical properties of the as-cast alloy were also measured. The stress-rupture testing was performed in air at 980°C and 83 MPa.

Scanning electron microscope (SEM) in combination with energy dispersive X- ray spectroscopy (EDS) was employed to characterize microstructural evolution of the alloy during the high-temperature treatments and the stress-rupture tests. The metallographical samples in longitudinal section were prepared and etched in a solution consisting of 40 pct HCl, 10 pct H_2O_2 and 50 pct H_2O.

3. Results

The room-temperature tensile test data obtained for the alloy after two kinds of high-temperature treatments are given in Table II, which also includes those of the as-cast alloy. It can be seen that both the thermal aging and air pre-exposure resulted in a substantial increase in alloy strength. But, at the same time, the excellent ductility of the as-cast alloy, which results from the columnar-grained matrix with ⟨001⟩ preferential orientation, was deteriorated severely. Furthermore, it is worthy to note that the air-exposed specimen has higher yield strength than that aged thermally. This indicates that the air pre-exposure exerted a greater strengthening effect upon the alloy than the thermal aging.

The stress-rupture properties of the high-temperature treated alloys are given in Table III and compared with those of the as-cast alloy. The high-temperature treatments exhibited an important influence on the stress-rupture properties. Compared with the as-cast alloy, both thermal aging and air pre-exposure increased stress-rupture lives and ductilities at 980°C and 83 MPa. Particularly, the air pre-exposure demonstrated a surprising improvement on stress-rupture life, which prolonged the stress-rupture life of the as-cast alloy by fourfold. In addition, it can be found that the high temperature treatments did not cause a dramatic loss in rupture ductility, as previously observed in the room-temperature tensile test, but an obvious improvement. Furthermore, it is surprising to notice that the air-exposed specimens possess higher rupture ductility than that aged thermally.

TABLE II Tensile properties of the DZ40M alloy at room temperature

State	0.2% Yield strength, MPa	Ultimate tensile strength, MPa	Elongation, %
As-cast	437	704	24.0
Thermally-aged	568	942	5.2
Air-exposed	600	841	4.0

TABLE III Stress-rupture properties of the DZ40M alloy

	980°C/83 MPa	
State	Stress-rupture life, h	Elongation, %
As-cast	71.4	41.0
Thermally-aged	88.3	52.0
Air-exposed	352.2	59.6

The as-cast alloy consists of an austenite matrix and primary carbides, i.e. chromium-rich M_7C_3 and MC that contains tantalum, titanium, zirconium, and tungsten. The matrix is composed of well-developed columnar grains with ⟨001⟩ preferential orientation. The primary carbides are located at grain boundaries and in interdendritic regions [4].

The high-temperature treatments, both the thermal aging and air exposure, resulted in a substantially microstructural evolution of the alloy. Fig. 1 is a typical microstructure of the thermally-aged alloy. It can be seen that a great number of fine secondary precipitates were produced throughout the matrix. But, it appears that they are unevenly distributed and there is a denser distribution around the primary carbides. A previous work confirmed that these precipitates were secondary chromium-rich $M_{23}C_6$ carbide [4, 5]. Microstructural difference between the thermally-aged and air-exposed alloys reflects in the surface and sub-surface of specimens. Fig. 2 shows the microstructure of the air-exposed alloy in the region adjacent to the surface. It is observed that a severe oxidation occurred adjacent to the surface of the specimens, causing the formation of a few cavities within oxidized layer. Comparing Fig. 1 with Fig. 2, it yields the conclusion that there are denser fine precipitates in sub-surface adjacent to the oxidized layer than in the interior. Therefore, it is reasonable to deduce that the precipitates in the sub-surface area must be products of internal oxidation. This indicates

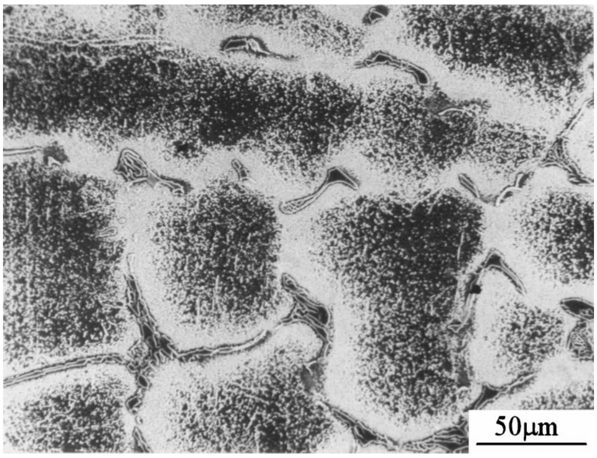

Figure 1 Microstructure of the air-exposed alloy within the matrix in longitudinal section.

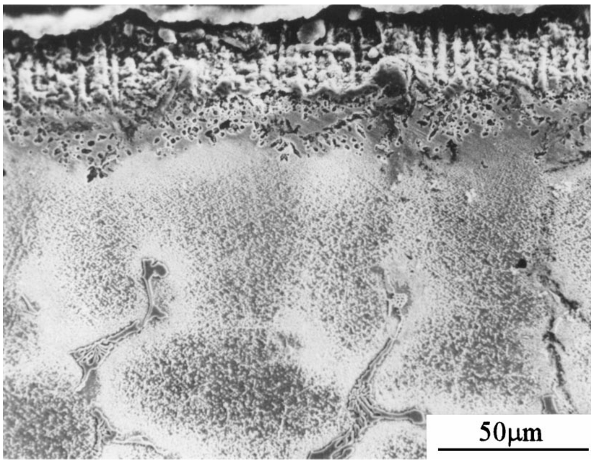

Figure 2 Microstructure of the air-exposed alloy in the region adjacent to the surface.

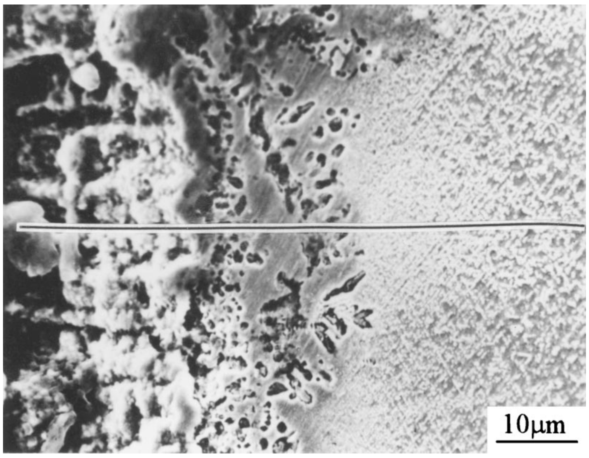

Figure 3 Microstructure of the air-exposed alloy in the region adjacent to the surface. The line indicates the location of the composition profile measured (Fig. 4).

that an obvious internal oxidation must have happened during the high-temperature air pre-exposure. Due to their small size, the internal oxides could not be identified by EDS. They are probably Al_2O_3 precipitates. EDS was conducted on the surface and sub-surface of the air-exposed specimens along the line indicated in Fig. 3. The result demonstrates that the oxidation products are Cr_2O_3 and $CoCr_2O_4$ from the surface to the sub-surface, respectively, as shown in Fig. 4. This is a typical constitution of oxidation products of cobalt-base superalloys containing more than 25%Cr [6]. Furthermore, it can be found that in the sub-surface area below $CoCr_2O$, there is also Cr_2O_3, which resulted from oxidation of chromium-rich M_7C_3 carbide. In cobalt-base superalloys, carbides tend to be oxidized preferentially, causing their degeneration [7].

During the stress-rupture test at 980°C and 83 MPa in air, both the thermally-aged and air-exposed specimens suffered a marked oxidation. Fig. 5 shows an aggressive oxidizing attack on the thermally-aged specimen. It can be seen that the continuity of the surface of the specimen was severely broken down. A few cracks were formed on the surface of the specimen and propagated toward the interior perpendicular to the stress axis. Fig. 6 shows further oxidation of the air-exposed specimen during the stress-rupture test. A relatively

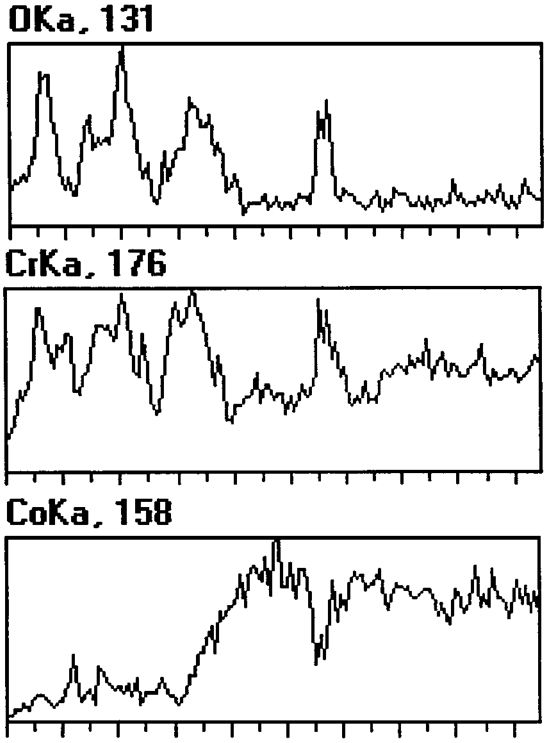

Figure 4 EDS linescan of the air-exposed alloy in the region adjacent to the surface (Fig. 3).

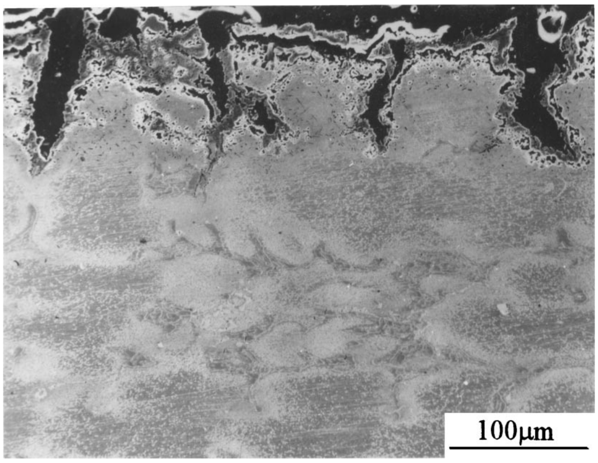

Figure 5 Microstructure of the thermally-aged alloy adjacent to the surface after stress-ruptured at 980°C and 83 MPa.

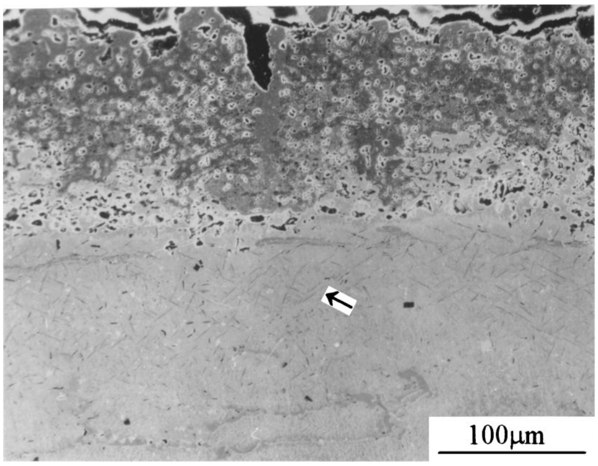

Figure 6 Microstructure of the air-exposed alloy adjacent to the surface after stress-ruptured at 980°C and 83 MPa.

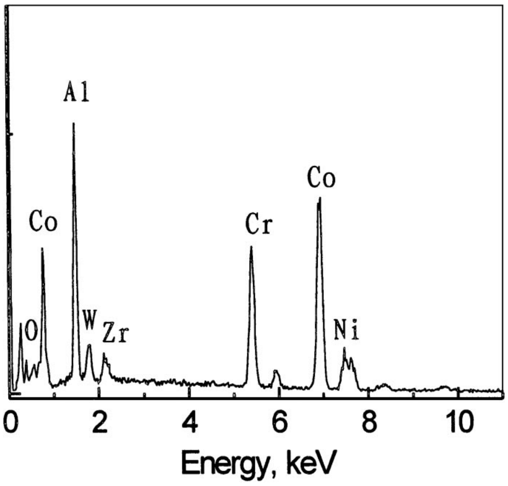

Figure 7 EDS of the rod-like phase in Fig. 6 as indicated by an arrow.

thick continuous oxidized layer was formed on the surface of the specimen, which is obviously different from that of the thermally-aged specimen. Some cracks are occasionally observed on the surface, but they are much less aggressive than those in the thermally-aged specimen. It is worthy to note that there are a lot of rod-like precipitates in the zone just below the oxidized layer. Evidently, they are internal oxidation products, which substantially grew during the stress-rupture test. EDS analysis indicates that the internal oxides are Al_2O_3 precipitates, as shown in Fig. 7.

4. Discussion

During high-temperature aging or service of cobalt-base superalloys, their most obviously microstuctural change is a heavy precipitation of secondary $M_{23}C_6$ carbide, which makes a great contribution to alloy strengthening. The secondary $M_{23}C_6$ carbide precipitation is associated with the degeneration of primary carbides [4, 8, 9]. That is why the thermal aging of the specimens was selected for the comparison in this work.

The present work shows that the microstructural evolution throughout the thermally-aged alloy and in the interior of the air-exposed alloy is similar. The effect of high-temperature air pre-exposure on the alloy consists mainly in the severe oxidation in the region adjacent to the surface of the alloy. At high temperature, Cr atoms diffuse to surface and react with O in air, forming Cr_2O_3. Due to the diffusion of Cr atoms, a gradient of Cr content from the surface to the sub-surface layer was formed. Therefore, a spinel $CoCr_2O_4$ was produced in the sub-surface layer where Cr content was insufficient to form Cr_2O_3. It has been established that the formation of continuous Cr_2O_3 on the surface can impede the penetration of oxygen, preventing the alloy from being oxidized further. This is one of Cr alloying roles in superalloys. Like Cr, Al also has a high affinity to O. It reacts with O diffused to the sub-surface layer, forming an internal oxide Al_2O_3. Due to the limitation of resolution of EDS, it failed to determine the constitution of individual fine precipitate. But, considering the denser distribution of the fine particles just beyond the oxidizing layer, it is reasonable to deduce that there must exist a few of fine internally oxidized products, which mixed with the $M_{23}C_6$ precipitates. Indeed, it is confirmed by the fact that the internally oxidized products are Al_2O_3 in the air-exposed specimens after stress-ruptured at 980°C, in which internal oxides assume a little coarse rod-like morphology.

As shown in Table II, the high-temperature treatments, both the thermal aging and air exposure, greatly increased the room-temperature tensile strength. As well-known, carbide hardening is the most important strengthening mechanism in cobalt-base superalloys. The high-temperature treatments induced a great number of $M_{23}C_6$ particles to precipitate in the matrix, which were absent in the as-cast alloy. Those fine $M_{23}C_6$ particles could interact with dislocations, strengthening the matrix effectively. Worthy to note, the air pre-exposure exhibited a greater hardening effect than the thermal aging. During the air pre-exposure, severe oxidization occurred, leading to formation of oxides and cavities. They decrease the load-bearing section of the alloy impairing the alloy strength. Evidently, the hardening produced by the air pre-exposure must be connected with the internal oxidization. As discussed previously, the fine internal oxides Al_2O_3 were formed during the air exposure. They exerted a substantial strengthening impact, which not only compensated the reduction of the load bearing capability, but also enhanced the alloy strength further.

Both the high-temperature treatments deteriorated the excellent tensile ductility of the alloy heavily, which resulted from columnar grain matrix with $\langle 001 \rangle$ preferential orientation. Obviously, the loss of the ductility caused by the high-temperature treatments should be attributed to the precipitation strengthening. A little distinction between that of the thermal aging and air exposure may result from their different strengthening effects. Indeed, the air exposure lead to a more marked strengthening. Consequently, the high-temperature air pre-exposure did not cause embrittlement of the alloy at room temperature.

The high-temperature treatments exhibited a strong influence on the stress-rupture properties at high temperature too. They improved the stress-rupture properties, both lives and ductilities, at 980°C and 83 MPa. In particular, the air pre-exposure revealed a more markedly strengthening effect, prolonging the rupture life up to fourfold and triple with the respect to those of the as-cast alloy and the thermally-aged alloy, respectively. It may be related to a more severe environmental oxidization during the stress-rupture test at 980°C. Comparing Figs 5 and 6, it yields the conclusion that the uniform oxide layer on the surface of the specimen developed by the air pre-exposure at 850°C must have played a protecting role from oxygen penetration, which was thickened greatly during the later stress-rupture test. The thermally-aged alloy was attacked severely by high-temperature air environment combined with applied stress. In spite of protecting the alloy from oxygen penetration, the oxide layer itself contains a few cavities that decreased the load-bearing capability of the specimens. The internal oxidation strengthening made a great contribution to the improvement of the stress-rupture properties of the air-exposed alloy. It is the extraordinarily long stress-ruptured life of the air-exposed alloy that made the internal oxides substantially grow into a little coarse rod-like morphology, and thus, could be identified by EDS as Al_2O_3. Consequently, the excellent stress-rupture properties of the air-exposed alloy should result from two kinds of environmental effects, i.e. the strengthening from the internal oxidation and the surface protection of the oxide layer.

The high-temperature treatments did not deteriorate the stress-rupture ductility, but improved it, which is different from their effect on the room-temperature tensile ductility. Particularly, the air-exposed alloy has higher ductility than those of both as-cast and thermally-aged ones. This indicates that the alloy did not suffer any environmental embrittlement at high temperature. Such improvement on the ductility must be related to its more effective strengthening, which extended the stress-rupture life dramatically.

The present work shows that the air pre-exposure at 850°C for 1000 h did not embrittle the DZ40M alloy, but increased its room-temperature tensile strength and improved the stress-rupture properties. The alloy is immune to the environmental embrittlement. Indeed, cobalt-base superalloys usually exhibit less embrittlement than nickel-base superalloys. In the latter, the penetration of oxygen along grain boundaries has been shown to be responsible [1] and a mechanism involving grain boundary pinning has been proposed [10]. The DZ40M alloy is a directionally solidified alloy. The directional solidification not only eliminates transverse grain boundaries, but also develops a coarse grain structure. This minimizes the role of grain boundaries to a great extent, which may be a potential path of the penetration of oxygen. Consequently, the DZ40M alloy suffers no susceptibility to the air embrittlement.

5. Conclusions

1. The directionally solidified cobalt-base alloy DZ40M is immune from air embrittlement following air pre-exposure at 850°C for 1000 h.

2. The air pre-exposure improved the room-temperature tensile strength and stress-rupture properties at high temperatures dramatically.

3. During the air pre-exposure, a substantial external and internal oxidation occurred, which protected the alloy from being oxidized further and contributed to strengthening greatly, respectively.

4. The effect of the air pre-exposure on the mechanical properties of the alloy is related also to elimination of transverse grain boundaries by directional solidification.

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