NEUTRON ACTIVATED MICRORADIOGRAPHY DETERMINATION OF BORON DISTRIBUTION IN A CAST NICKEL-BASE SUPERALLOY

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In this study boron distribution in a cast nickel-base superalloy was investigated by the technique of neutron activated microradiography. It was found that boron initially segregated to the grain boundaries: within the grains as the borocarbide phase $M_{23}(CB)_6$, and at carbide/matrix interfaces. When the specimens were exposed to various temperatures for different periods of time, boron changed location. As a result of boron segregation to the MC carbide particle boundaries, more $M_{23}(CB)_6$ particles were formed from the degeneration of MC. Resulting fracture effects and temperature ductility effects are discussed.

INTRODUCTION

A very small addition of boron to a superalloy can have a very appreciable effect on its high-temperature strengths and ductilities. Effectual role of boron is not only related to the amount, but also to the location and form of boron present. Therefore, understanding boron effects in superalloys depends on determining the location of boron as a function of the thermal history of the alloy. In this study boron distribution in a cast-base superalloy was investigated by the technique of neutron activated microradiography.

ALLOY INVESTIGATED

The chemical composition of the alloy investigated is as follows: 0.08% C; 18.5% Cr; 18.5% Co; 3% Ti; 3% Al; 4% Mo; 0.005% B (wt.%) Ni, the remainder.

All specimens were vacuum-induction melted and precision cast. Different treatments were applied to the alloy: the as-cast condition; primary solution-treatment 1150°C/4hr/AC (air cooling); primary plus secondary solution-treatment 1150°C/4hr/AC+1080°C/4hr/AC; normal heat treatment 1150°C/4hr +1080°C/4hr/AC+760°C/16hr/AC; and normal heat treatment plus long-time aging at temperatures 650°C; 816°C; 860°C for 1000, 3000, 5000, 8000 and 10,000 hrs. The structure of this alloy in the as-cast condition, as well as in the normally heat-treated condition and after long-time aging consists of γ, γ', Mc and $M_{23}C_6$ phases, no borides were found.

EXPERIMENTAL PROCEDURE

The technique used to sense boron is an automicroradiographic technique based on the reaction $^{10}B+^{1}n-^{7}Li+^{4}\alpha$ occurring during neutron activation of boron atoms. The products from the $^{10}B(n\alpha)^{7}Li$ reaction produce tracks in a cellulose acetobutyrate replica. The replica is then etched and examined under the optical microscope (1). The experimental procedure was established elsewhere (2).

Specimens for examination were generally of 3x3x1 mm. They were mounted in bakelite which has a low neutron-absorption cross section and can withstand a temperature of 150°C. The mounted specimens were polished but not etched. A small piece of cellulose acetobutyrate film was applied to the polished surface of the specimen with the minimum amount of acetone needed to give good contact. The specimens with film were heated at 140°C for 10-12 hrs. Then the specimens were put in a woody bucket and were irradiated in a reactor with a level of neutron dose $4x10^{14}n/cm^2$ sec. for 4-5 hrs. After irradiation the film was mechanically stripped off the polished surface and etched with an aqueous solution (100 ml H_2O + 50g NaON plus a little $KMnO_4$) at 50°C for 10-30 min. Films were washed, mounted and then dried. Chromium splashing was applied to increase the contrast. The films were examined under the optical microscope.

The replicas were registered with the figures of boron atoms fission tracks which directly describe the distribution of boron atoms in the microscopic structures of specimen. Track density is proportional to the amount of boron in situ. Consequently, the location of boron can be thus determined. In addition, the precipitated phases were electrolytically extracted and identified by X-ray diffraction and chemical analysis.

EXPERIMENTAL RESULTS

In the as-cast condition the boron atoms are segregated in the interdendritic areas and at the grain boundaries. There are no boron tracks in the primary carbide phase MC.

After a 1150°C/4hr/AC or 1150°C/4hr/AC + 1080°C/4hr/AC solution treatment this dendritic segregation and grain boundary segregation are apparently eliminated and boron is found uniformly distributed in the matrix(Fig.1). There is no evidence of intergranular segregation of boron in these specimens.

After normal heat-treatment (1150°C/4hr/AC + 1080°C/4hr/AC + 760°C/16hr/AC) in addition to uniform distribution of boron in the matrix, the enrichment of boron along the grain boundaries is again observed (Fig.2). The microstructure of the same specimen shows the formation of $M_{23}C_6$-type precipitates at the grain boundaries during subsequent ageing at 760°C/16hr. Boron tracks coincide with the location of $M_{23}C_6$ precipitates.

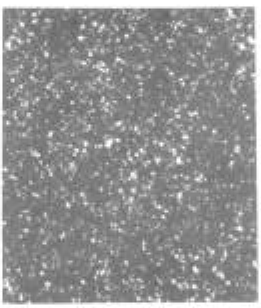

Fig.1
Autoradiograph
1150°C/4hr/AC
dark field x300

Fig.2
Autoradiograph
normal treatment
light field x300

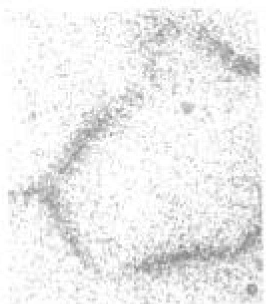

Fig.3
Autoradiograph
650°C 1000hr
light field x300

During the long-time ageing at vorious temperatues marked changes in the distribution of boron occur. After ageing at 650°C for 1000 and 3000 hrs boron is segregated in the grain boundary region (Fig.3). The distribution of boron is quite different from that of the specimen after normal heat-treatment. The microstructure of same field is given in Fig.4 Comparing Fig.3 and Fig.4 it is found that the track density is high at these grain boundaries where $M_{23}C_6$-type carbide has precipitated, but it is low where

MC carbide exists.Although the amount of $M_{23}C_6$ at the grain boundary is relatively small but the width of high density region is about 3-4 times that obtained after normal heat-treatment. It is inferred that in this case a part of boron has migrated to the grain boundary regions and has segregated there in the atomic form.

Fig.4
Microstructure of same field as Fig.3 x300

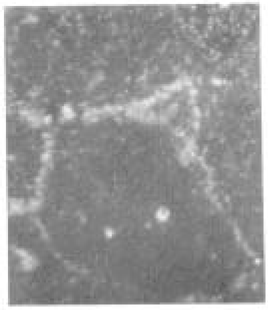

Fig.5
Autoradiograph 816°C 8000hr dark field x300

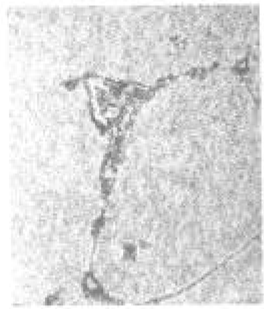

Fig.6
Microstructure of same field as Fig.5 x300

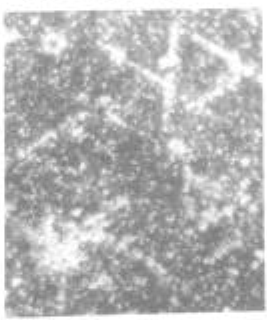

Fig.7
Autoradiograph 816°C 8000hr dark field x300

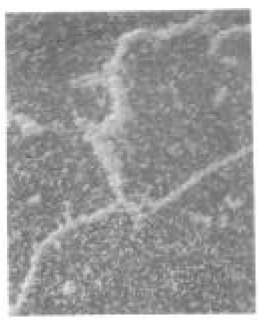

Fig.8
Autoradiograph 860°C 3000hr dark field x300

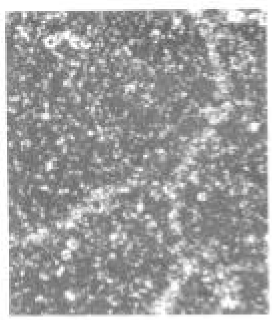

Fig.9
Autoradiograph 860°C 10000hr dark field x300

After ageing at 816°C for 8000hrs the boron near the grain boundary region is no longer in the atomic form. Instead, most of boron is concentrated in the precipitated phase at grain boundaries and also within the grains. The precipitate within the grains has a definite crystallographic orientation with the matrix(Fig.5,Fig.7). Microstructure (Fig.6) indicates that the carbide reaction $MC+\gamma - \gamma'+$

$M_{23}C_6$ occurs on the surface of the carbide MC. As a result of this reaction, the surface is roughened and surrounded by particles $M_{23}C_6$. Boron concentrates in the surface layer which is $M_{23}C_6$ phase converted from the MC particles.

The autoradiograph and microstructure of specimens after 860 C 3000 and 10000hrs ageing are shown in Fig.8,9, 10. In Fig.8 the boron tracks have merged with each other and can not be resolved. The grain boundaries look very thick. It seems that the degree of decomposition of MC has increased and a greater amount $M_{23}C_6$ precipitates has produced. After 860°C 10000hrs ageing $M_{23}C_6$ particles agglomerate into rather massive block (Fig.9,10).

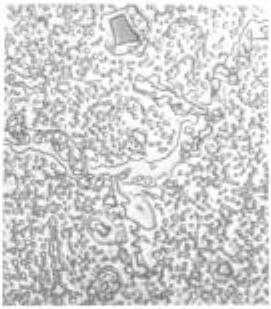

Fig.10 Microstructure 860°C 10000hr x1020

Fig.11 Fractograph of 650°C impact test, 650°C 5000hr ageing x900

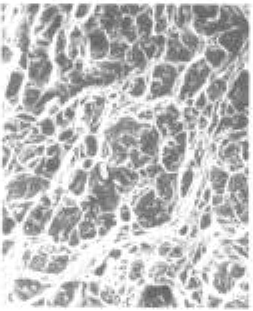

Fig.12 Fractograph of 650°C impact test, 8000°C 3000hrs ageing x225

By using scanning electron microscope,X-ray and chemical analyses of electrolytically extracted carbide residues it was possible to reveal that the carbide precipitated at the grain boundaries and within the grains is $(CrCoMo)_{23}(CB)_6$, containing boron 0.0011%-0.0013%(wt%). Its lattice parameter is 10,70Å. The increase in lattice parameter suggestes that more carbon atoms were replaced by boron in the carbide $M_{23}(CB)_6$. This replacement resulted an increase in quantity of $M_{23}(CB)_6$ and also in its stability. These results are in agreement with previous works (4,5). Most of boron was concentrated in the $M_{23}C_6$-type carbide and at the carbide/matrix interface, only very small amount of boron was retained in the matrix in the atomic form.

DISCUSSION

1. From experimetal results it has been found that boron generally was segregated at the grain boundaries; within the grains, as the borocarbide phase $M_{23}(CB)_6$ and at carbide /matrix interface and when specimens were exposed to various temperature for different periods of time, the location of distribution and the form of boron changed as described previously. When carbide $M_{23}C_6$ has been pricipitated, the redistribution of boron is eventually controlled by the presence of $M_{23}C_6$-type carbide. High concentration of boron occurs wherever $M_{23}C_6$ carbide is precipitated, consequently, changing number of $M_{23}C_6$ particles and carbide/matrix interface will certainly cause redistribution of boron. In cast superalloy grain size of the matrix does not change during heat-treatment,but the particle size of carbides does. The total carbide/matrix interface was changed to a greater extent than total grain boundaries of matrix. O.A. Bannax and others had reported that in Cr-Mn austenitic steel at 800°C on the average the surface of carbides was about 7 times greater than the surface of austenitic grains(3). Therefore change of carbide/matrix interfacial area probably has an important effect on the boron distribution. The segregation of boron to grain boundaries and on surface of carbides supplied boron atoms required for the formation of carbide $M_{23}(CB)_6$, also promoted the degeneration of MC to $M_{23}(CB)_6$. This can also be derived from the data of chemical analyses of electrotically extracted carbide residues and the relative intensity of X-ray diffraction of these carbides. (For example, at 650°C, 1000hrs ageing the amount of MC is 0.3%, $M_{23}(CB)_6$-0.15%, but at 860°C 3000hrs ageing MC-0.22%$M_{23}(CB)_6$ - 0.4%(wt%).

2. The alloy exhibits relatively low ductilities when primary MC carbide takes a coarse morphology. The specimen with a fractograph shown in Fig.11 is an example of the large MC particles originally in the fracture surface. Its 650°C high-temperature impact strength was only of a value of 0.263J/mm^2. But as a result of boron segregation on the surface of MC particles, more $M_{23}(CB)_6$ particles were formed

from degeneration of MC. It takes the form of a ring and is encased in γ'. The remaining MC appears to be smaller and situates in the center of the ring (Fig.6,10). It can thus eliminate a portion of brittleness arisen from presence of large MC particles. This can modify the fracture characteristics of the grain boundaries and improve the high-temperature ductility of the alloy. For example, the differences in toughness are reflected in the marked difference in the fracture mode. The fracture of the ageing specimen at 860°C 3000hrs was almost entirely ductile (650°C high-temperature impact strength 0.572J/mm^2), no large brittle MC particles was found (Fig.12). Whereas ageing specimen at 650 C 5000hrs contains considerable amount of large brittle MC particles (Fig.11). In effect it is due to the MC changed into smaller, the presence of $M_{23}(CB)_6$ particles and γ' enveloping them, the ductility of grain boundary was improved.

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