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The distribution of boron in stainless steels as revealed by a nuclear technique

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SYNOPSIS

Additions of boron have been found to increase the hot workability of stainless steels. Boron forms complex chromium-iron borides, primarily at grain boundaries but also on delta-ferrite stringers. This paper describes how a nuclear technique based on the track-etch method was used to distinguish between borides and chromium carbides on grain boundaries and to investigate the distribution of boron in stainless steels. The method was found to be sensitive for boron, and made it possible for boron precipitates to be identified on grain boundaries and interphase boundaries.

SAMEVATTING

Toevoeging van boron by austenitiese vlekvryestaal verbeter die warmverwerkbaarheid. Boron kan egter komplekse chroom-yster boriedes op korrelgrense sowel as in delta-ferriet stringe vorm. Hierdie referaat beskryf hoe auto-radiografie gebruik is om die voorkoms en verspreiding van boron te bepaal en te kan onderskei tussen boried en karbied presipitate op die korrelgrense en interfase grense. In dié tegniek word spore, gelaat deur alfa-deeltjies, gebruik om die posisies van boron vas te stel. Die tegniek is sensitief en spesifiek vir boron.

Introduction

Boron is added to high-alloy austenitic stainless steels such as AISI 310, AISI 316, and AISI 317 to improve the hot workability. It also has a beneficial effect if added to duplex ferritic–austenitic stainless steels such as AISI 318 (UNS S31803).

Boron (up to 60 p.p.m.) does not affect the hot- or cold-rolling characteristics of AISI 201 and AISI 304 steels. However, the presence of even 10 p.p.m. of boron alters the microstructure of annealed AISI 201. When conventional mill-processing parameters are used, it is most difficult to obtain a microstructure free of grain-boundary boride phases[1].

An addition of boron improves the low-temperature ductility of stainless steels but also lowers the nil-ductility temperature. The higher the boron content, the stronger is this effect. Keown[2] has given a good description of these effects. Fig. 1 shows the decrease in nil-ductility temperature for type 316 from approximately 1350°C (curve A, 9 p.p.m. of boron) to 1200°C (curve D, 170 p.p.m.), although the low-temperature ductility, measured as percentage reduction in diameter, has increased. From Fig. 1 it is apparent that there is an optimum amount of boron for both a high nil-ductility temperature and a good low-temperature ductility range (curves B and C, 40 to 90 p.p.m. of boron).

Boron is also used to increase the creep properties of oxidation-resisting steels and stainless steels used at elevated temperatures[3]. The addition of about 50 p.p.m. leads to an increase in the mean stress-to-rupture life by a factor of 3 or an increase in stress to failure in 10 000 hours of up to 25 per cent.

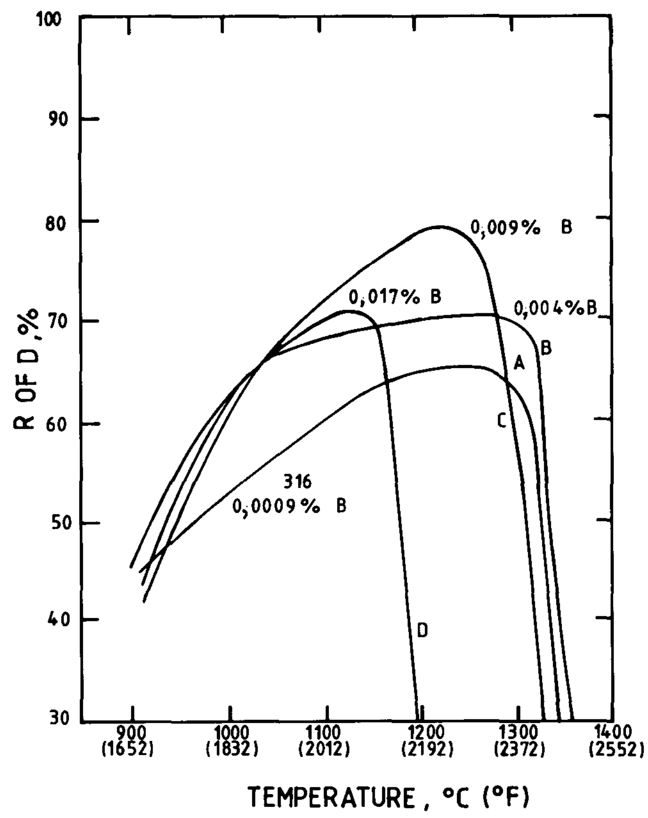

Fig. 1—The effect of boron additions on the hot ductility of type 316 stainless steel as a function of temperature[2] (R of D = reduction of diameter)

It was found recently that boron has a beneficial effect (normally in combination with some titanium—typically 0,015 per cent) on controlling a surface defect known as

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TABLE I

EFFECT OF BORON ON THE MEAN VALUE OF STRESS TO RUPTURE IN 10 000 HOURS FOR TYPE 316[3] (N/mm^2)

Stress to rupture, N/mm^2					
600°C		650°C		700°C	
No boron	Boron	No boron	Boron	No boron	Boron
171	191	108	128	66	82

edge slivers. This is probably due to its effect on hot ductility and hot workability[4] (Fig. 2). Boron strengthens the grain boundaries or hinders the segregation of elements that cause embrittlement or hot shortness. It also reduces grain-boundary diffusion.

Boron segregates strongly to grain boundaries in austenitic stainless steels as a borocarbide, $M_{23}(CB)_6$, and one could expect it to modify the resistance to intergranular corrosion. Moskowitz *et al.*[5] found that, although boron in solid solution is beneficial, precipitated boron may be detrimental. Boron should preferably be present as the boronitride. In molybdenum-bearing steels, $M_{23}(CB)_6$ could be a complex carboboride[6], $(Fe, Cr, Mo)_{23}(C,B)_6$.

Goldschmidt[7] has shown that the solubility limit of boron in an 18Cr–15Ni steel containing less than 100 p.p.m. of carbon is 95 p.p.m., and that the precipitating phase is the boride $(Fe,Cr)_2B$, which may form a eutectic of low melting point with the gamma phase at temperatures between 1150 and 1225°C, depending on the composition of the base metals and the segregation.

It is quite possible for boron to be picked up from refractories and from teeming or casting powders. After the melting–refining process, boron is retained if the oxygen potential is low and deoxidants (reducing agents) and inoculants have been added.

Fig. 3 shows a portion of the phase diagram for an 18Cr–15Ni stainless steel. The solubility of boron[7] is about 60 p.p.m. in austenitic steels at solution heat-treatment temperatures of 1050°C. Since 304 and 316 stainless steels are solution heat-treated above 1040°C, it should be no problem for the boron to be brought into solid solution. However, the segregation of boron towards the grain and interphase boundaries probably occurs during cooling (or aging) since borides are often visible on grain boundaries.

It is often difficult to optically distinguish between boron and carbide precipitates (sensitization), and the track-etch technique was therefore developed to assist in the identification of the types of precipitates on grain boundaries.

The track-etch technique is based on the creation of narrow regions of intense damage caused by the passage of heavy ionizing particles through a dielectric, i.e. through most insulating materials. What happens is that, when the ion is travelling through the dielectric, it primarily interacts with the electrons belonging to the atoms or molecules within the dielectric. In this process, electrons are either excited to a higher energy level or ejected from their parent atom, and then themselves act in the same manner, i.e. they interact with other electrons. Thus, the ionizing particle alternately loses some of its own electrons and captures electrons from the medium. This purely Coulomb interaction is responsible for the slowing down of the moving particles and eventually for the damage (tracks) induced in the bombarded material. The damage tracks can be revealed and made visible

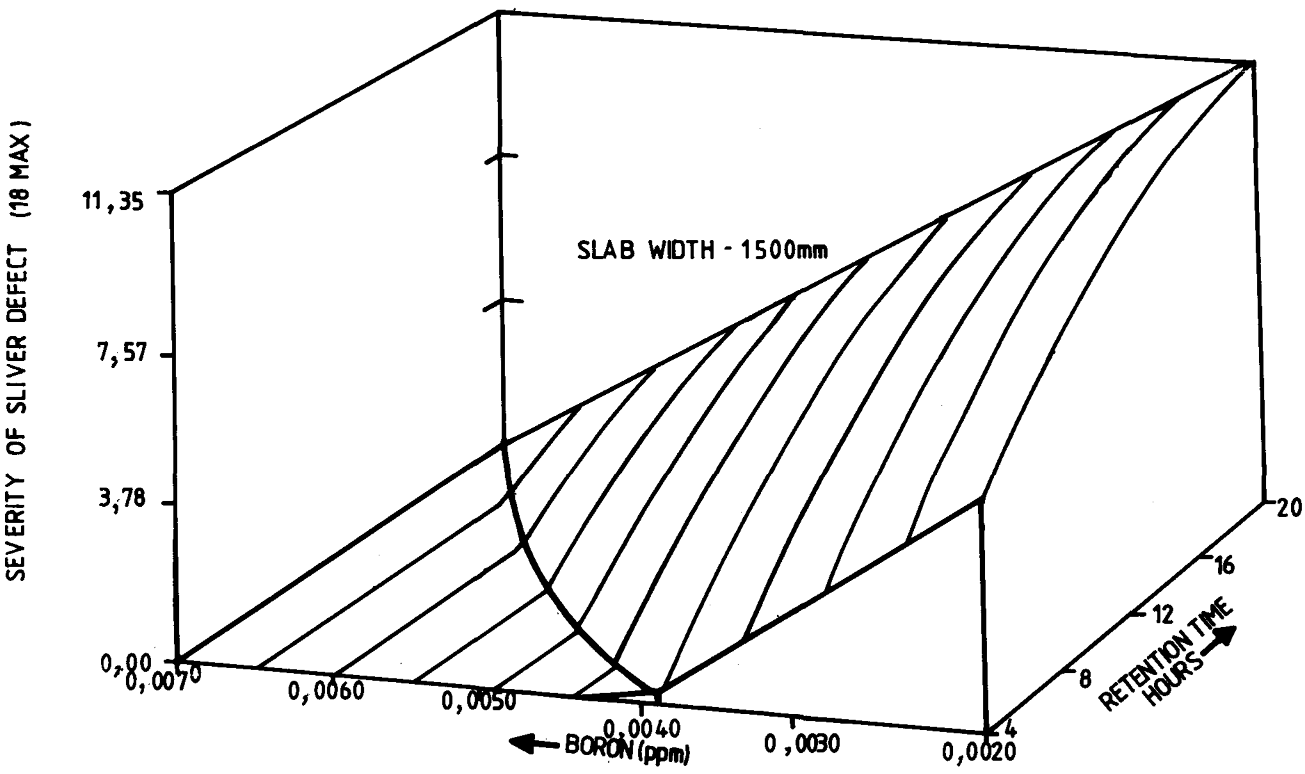

Fig. 2—The effect of boron content and retention time on the incidence of slivers in type 316 stainless steel[4]

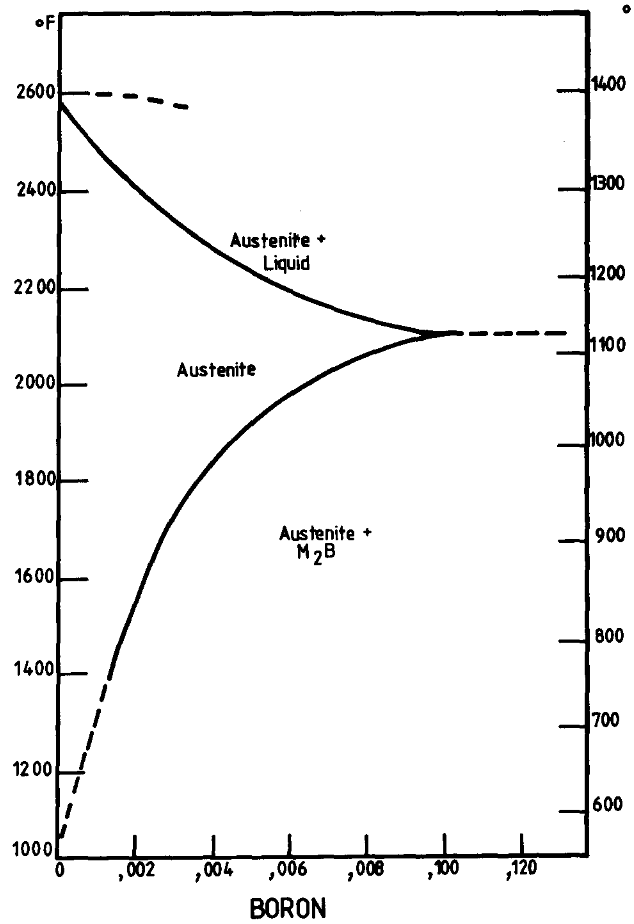

Fig. 3—The solubility of boron in 18Cr-15Ni stainless steels (in percentages by mass)

under an ordinary optical microscope when they have been treated with a suitable chemical reagent that rapidly and preferentially attacks the damaged regions.

The reason why boron is sensitive to this analysis is that boron contains 20 per cent of the isotope ^{10}B, which has an extremely high cross-section (3800 barns) for the capture of slow neutrons according to the reaction $^{10}B(n,\alpha)^7Li$, while all the other elements normally found in steel have rather low capture cross-sections. It is the tracks caused in a suitable insulating material (detector) by the alpha-particles emitted in the above-mentioned reaction that are used to map the distribution of boron in steel.

The track density is directly proportional to the concentration of boron in a steel specimen as can be seen from the expression[8]

$$\rho = N\sigma\Phi tR,$$

where ρ = track density (cm^{-2})
N = concentration of ^{10}B (cm^{-3})
σ = reaction cross-section (cm^2)
Φ = neutron flux ($cm^{-2}\cdot s^{-1}$)
t = exposure time (s)
R = range of alpha particle in detector (cm).

Experimental Procedure

Several specimens of austenitic stainless steel were prepared for standard optical metallographic assessment and neutron irradiation. Table II shows the chemical compositions of the steels investigated.

For the neutron irradiation, the specimens were prepared by standard metallographic polishing procedures. Films of cellulose nitrate were pressed onto the polished surfaces of the specimens, being moistened with methyl acetate to ensure intimate contact. This contact is extremely important to the achievement of acceptable microscopic 'images' of the boron atoms. If there is any space between the film and the metal surface—even a fraction of a millimetre—the resolution of the image can deteriorate so dramatically that interpretation of the image on the film becomes impossible. The composite metal and films were irradiated for 5 seconds in one of the neutron beam ports of the Safari-1 reactor at Pelindaba with a flux of 7,5 × 10^{12} neutrons per second per square centimetre. After irradiation, the films were stripped from the metal and etched for 4 minutes in a 10 per cent solution of sodium hydroxide at 60°C, which made the tracks visible for microscopic examination.

The following etchants were used for the optical metallography:

(1) ammonium persulphate to bring out the structure of the grain boundaries and precipitates (carbides or borides);
(2) 40 per cent potassium hydroxide to bring out the stringers of delta ferrite in the rolled material and the interdendritic delta ferrite in the cast structure.

Results

The photomicrographs shown in Figs. 4 to 10 compare

TABLE II
CHEMICAL COMPOSITIONS OF STEELS INVESTIGATED
(All the results are given in percentages by mass)

Specimen marked	Heat	Type	C	S	P	Mn	Si	Mo	Cr	Ni	B	N	δ–Fe
65B	620 962	304	0,041	0,011	0,027	1,26	0,37	0,17	18,34	9,10	0,0015	0,044	4,3
61	73 036	304	0,040	0,014	0,031	1,23	0,61	0,19	18,34	9,22	0,0005	0,027	6,5
169	73 213	304	0,041	0,026	0,021	1,18	0,55	0,11	18,31	9,18	0,0005	0,028	6,0
625	73 625	316L	0,028	0,009	0,029	1,10	0,55	2,05	16,58	10,29	0,0026	0,033	4,7
76866	76 866	317L	0,029	0,015	0,026	1,58	0,34	3,03	18,58	12,33	0,0036	0,060	6,0
82-232	611 487	304	0,042	0,017	0,022	1,37	0,45	0,17	18,11	9,24	0,0005	0,031	4,3

δ–Fe = Delta ferrite, which was calculated from the formula

$$\delta\text{–Fe} = \frac{1}{0,45}\,[1,4(Cr + Mo + 1,5\ Si + 0,5Nb + 2,4Ti) - Ni - 30(C+N) - 0,5\ Mn - 12,5]$$

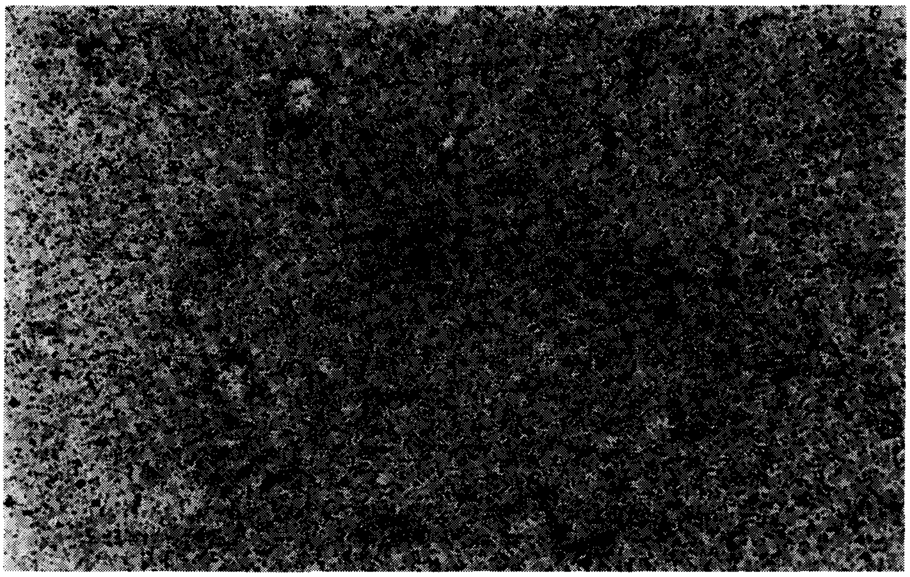

Fig. 4—Track-etch showing boron segregated in interdendritic delta ferrite (cast structure). Specimen 625, × 170

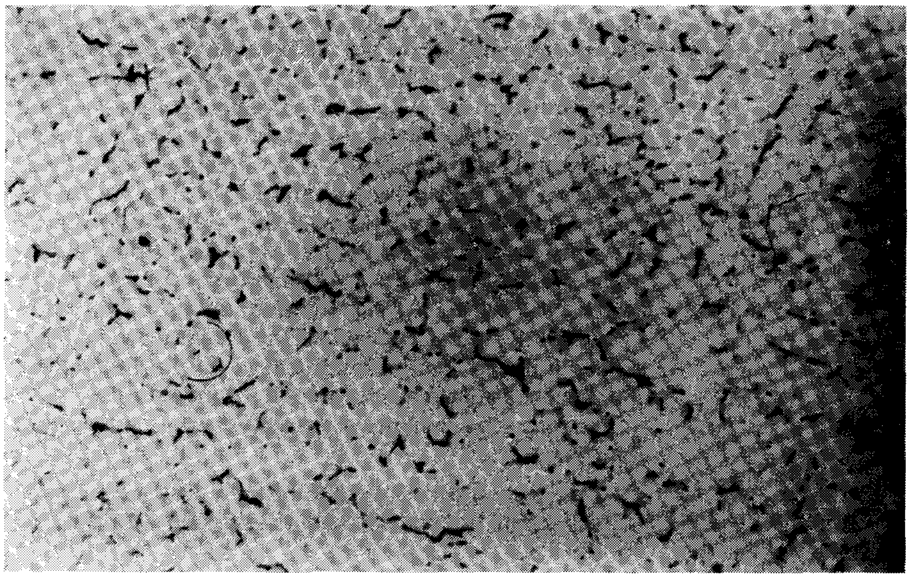

Fig. 5—Potassium hydroxide etch showing interdendritic delta ferrite (cast structure). Specimen 625, × 160

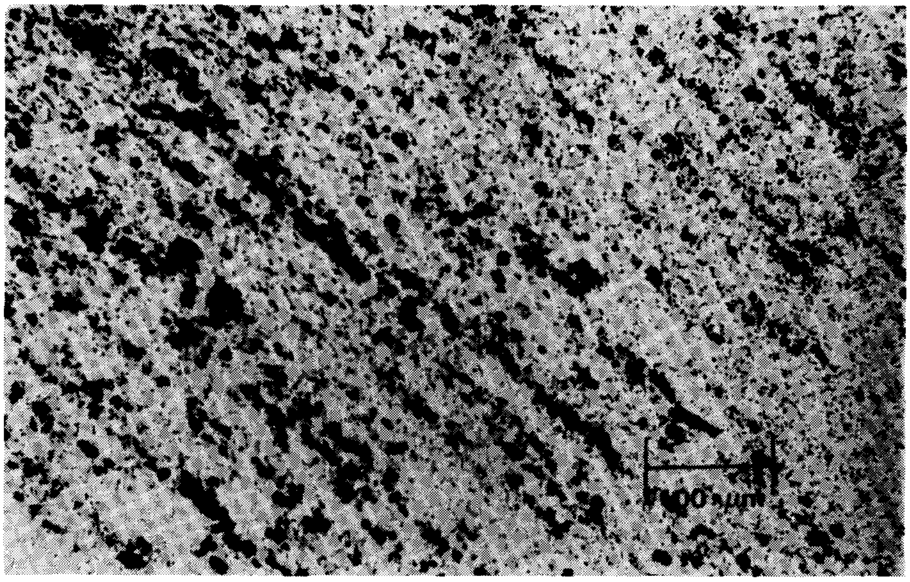

Fig. 6—Track-etch showing boron segregated in delta-ferrite stringers (hot-rolled and annealed structure). Specimen 76 866, × 170

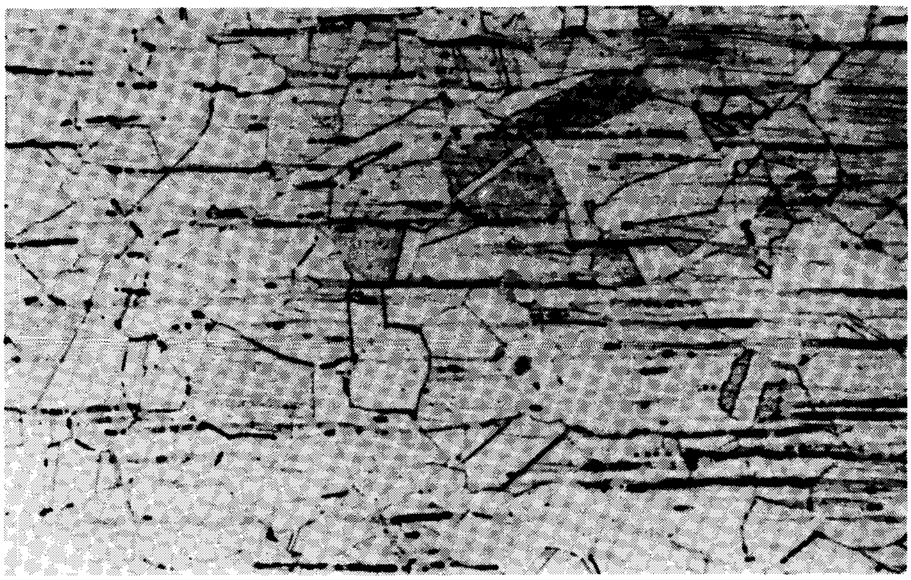

Fig. 7—Ammonium persulphate etch showing boride precipitates mainly in delta-ferrite stringers. Specimen 76 866, × 256

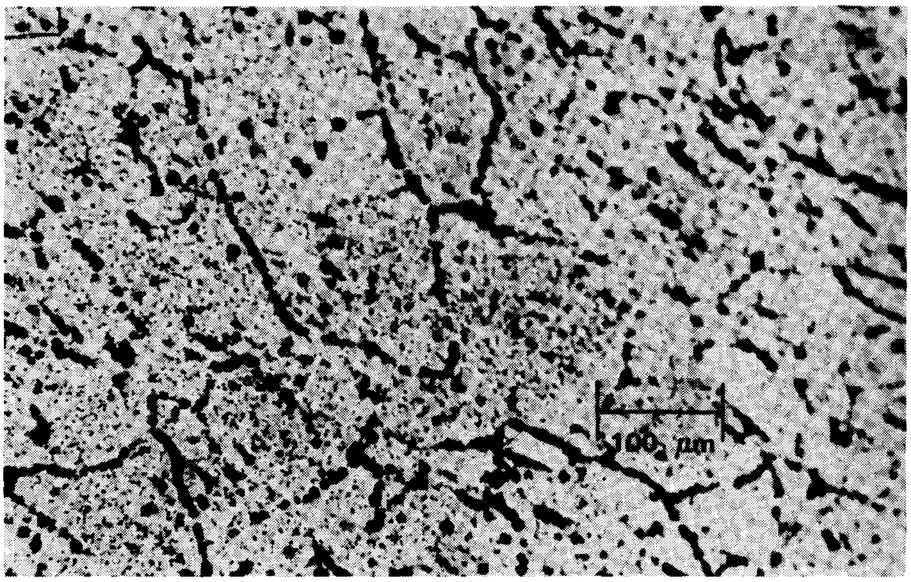

Fig. 8—Track-etch showing boron segregation on grain boundaries. Specimen 65B, × 170

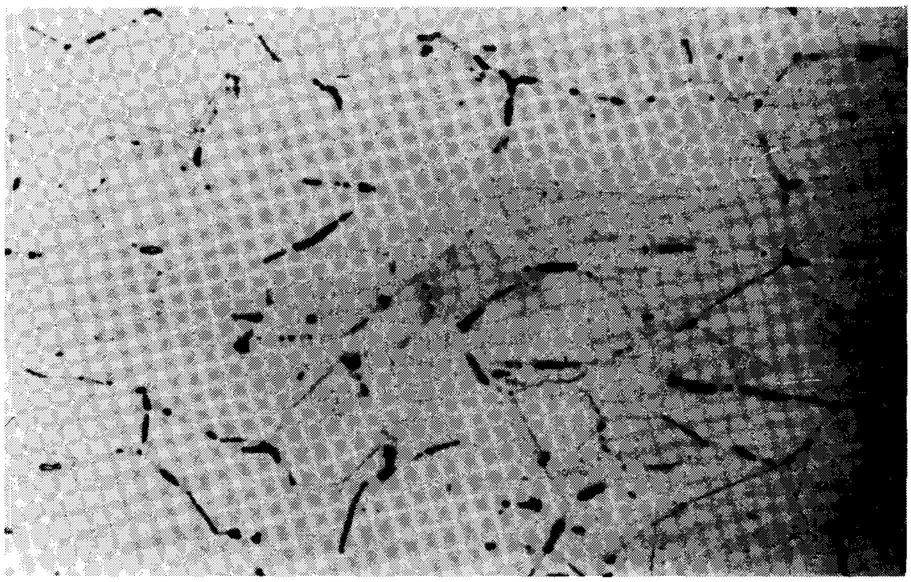

Fig. 9—Ammonium persulphate etch showing borides on grain boundaries. Specimen 65B, × 256

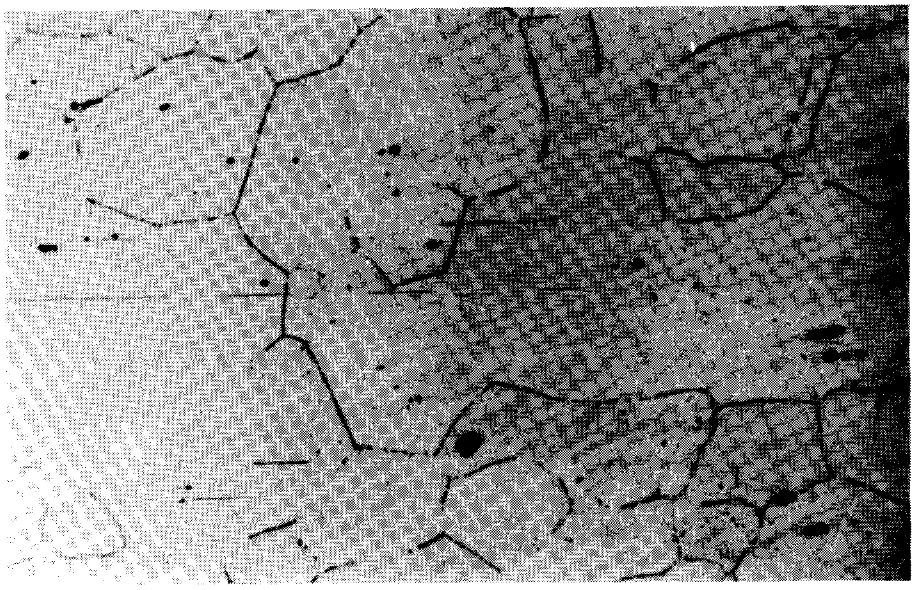

Fig. 10—Ammonium persulphate etch showing true sensitization, i.e. chromium carbides on grain boundaries. Specimen 82-232 after a sensitization heat treatment, × 256

the microstructures with the boron images obtained by the track-etch method. It should be noted that they are not necessarily of the same area or to the same magnification.

Of special interest is the continuous network of carbides shown in Fig. 10, as against the 'pockets' or discontinuous network ('necklace') of boride particles in Fig. 9.

Discussion

Cameron and Morral[9] found that the solubility of boron is higher in austenite than in ferrite at the invariant temperature, thus proving that the reaction is eutectoid in nature, i.e. $\gamma \rightarrow Fe_2B + \alpha$.

Figs. 6 and 7 show boron-rich precipitates in ferrite stringers, and Figs. 8 and 9 show the boron concentrated mainly in the interdentritic delta-ferrite phase. All four photographs tend to prove that the solubility of boron in the alpha (or delta) phase is lower than in the gamma phase.

Helium may be formed by the transmutation of the ^{10}B isotope during irradiation in a reactor, and precipitates as small bubbles that produce premature intergranular failure and embrittlement of austenitic steels in high-temperature tensile and creep rupture tests[10]. Background images are present, which are believed to be caused mainly by the alpha tracks from the $^{17}O(n,\alpha)\,^{14}C$ reaction taking place in the cellulose-nitrate film itself or the helium bubbles as described above, or both.

Additions of boron to stainless steels occasionally result in the appearance of a grain-boundary precipitate in the annealed structure of the finished product. This precipitate appears when the steel cools too slowly from the annealing temperature. A water quench is thus necessary if the product is heavy section plate. In type 316, the molybdenum retards the precipitation of borides. Boron does not appear on the grain boundaries at quenching rates greater than some critical value between 50 and 500°C per second[6]. Thomas and Henry[11] have indicated that solubility decreases rapidly with temperature and becomes negligible below about 900°C.

In Huey tests (with boiling 65 per cent nitric acid) conducted for 164 hours[12], the progressive penetration averaged 0,01 mm per month (standard 0,015 mm per month). Thus, it appears[12] that the boride type of grain-boundary precipitate does not adversely affect the intergranular corrosion resistance of boron-containing 304.

Tests with 10 per cent oxalic acid (ASTM A262–A) were used in the present work in the determination of the resistance to intergranular corrosion of all the steel samples showing boron precipitation on the grain boundaries. In all instances, the steel passed the test. It can thus be concluded that the resistance to intergranular corrosion of an austenitic stainless steel is not adversely affected by boron contents of 40 p.p.m. or less.

Conclusions

(1) The main advantage of the track-etch method for the detection and, particularly, imaging of boron are that it is virtually insensitive to beta, gamma, or proton radiation; it is specific for boron; and it lends itself to the mapping of the boron distribution in a metallographic section.
(2) It is possible to distinguish between boron precipitation and the precipitation of any other element.
(3) Boron precipitates preferentially on grain boundaries and interphase (alpha–gamma) boundaries, or both, in hot-rolled plates.
(4) In the cast structure, boron segregates towards the interdendritic delta-ferrite phase during cooling of the slab.
(5) The solubility of boron in Fe–Ni–Cr alloys is low[7].
(6) Boron contents of more than 90 p.p.m. may introduce hot shortness in 304 and 316 steels[2].
(7) Intergranular corrosion in 304 and 316 steels is not impaired by boron contents of up to 40 p.p.m.

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