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THE DETERMINATION OF GRAIN BOUNDARY SEGREGATION PROFILES IN BORON CONTAINING AUSTENITIC STAINLESS STEELS USING TEM, AP AND IAP

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Résumé Nous avons utilisé simultanément la microscopie électronique par transmission, la microscopie ionique à effet de champ, la sonde atomique et la microscopie à désorption pour étudier la ségrégation des joints de grains en deux aciers inoxydables austénitiques contenant du bore. Les profils de la ségrégation de B, Mo, Ni et Fe sont présentés. Il est montré qu'en combinant des techniques, les profils de concentration peuvent être déterminés avec une haute résolution spatiale quelle que soit l'orientation des joints de grain.

Abstract A combination of transmission electron microscopy (TEM), field-ion microscopy (FIM), atom-probe (AP), and imaging atom-probe (IAP) has been used to study grain boundary segregation in two boron containing austenitic stainless steels. Segregation profiles for B, Mo, Ni, and Fe are presented. It is shown that, by the use of a combination of techniques, concentration profiles can be determined with high spatial resolution regardless of the grain boundary orientation.

Introduction

The properties of materials are often considerably affected by the local chemical composition at their phase and grain boundaries. Changes in the chemical composition at interfaces can be caused either by equilibrium or by non-equilibrium processes and the width of the affected zone can vary from a few to several hundreds of atomic planes. In order to understand these processes it is necessary to know both the intergranular structure and the chemical composition on a fine scale.

B is a highly grain boundary active element, often added in small concentrations (10-30 wt. ppm) to austenitic stainless steels, that tends to segregate to grain boundaries mainly by a non-equilibrium process. The understanding of this process has, however, so far been hindered by the lack of detailed quantitative grain boundary compositional information. Therefore, the FIM-AP and IAP techniques, with their ability of giving qualitative and quantitative information for all elements with near atomic spatial resolution, have been used to investigate the non-equilibrium segregation of B in two austenitic stainless steels.

Material and specimen preparation

The two steels, one Mo-free with composition (wt.%):

0.0023 B, 0.02 C, 17.4 Cr, 13.2 Ni, 1.80 Mn, 0.62 Si, 0.01 Mo, balance Fe,

and one Mo-containing with:

0.0040 B, 0.02 C, 17.5 Cr, 13.2 Ni, 1.76 Mn, 0.55 Si, 2.62 Mo, balance Fe,

had, after heat treatments, a final grain size of more than 100 μm . A well controlled specimen preparation technique, using pulsed electropolishing combined with TEM (1), was thus needed to prepare specimens with a grain boundary sufficiently close to the specimen tip.

Method of analysis

A combination of TEM, FIM-AP, and IAP was used to determine grain boundary concentration profiles. The profiles were constructed from successive AP point analyses (Fig. 1 (right)), each containing 500-1000 ions. The perpendicular distances from the grain boundary to the probed volumes were determined from the FIM images using the usual magnification formula: $M=R/r\cdot\beta$, where R is the tip to screen distance, r the tip radius, and β the image compression factor. In order to do this accurately each specimen was characterized with TEM before and after AP analysis and the tip symmetry, the inclination angle of the grain boundary, and the tip radius perpendicular to the grain boundary were determined. The IAP was used as a complement to the AP making it possible to separate smooth concentration changes from discontinuous changes.

Results and discussion

Tip radius

The curvature usually varies significantly over the field evaporated surface of FIM specimens prepared from pure metals (2,3). However, a much smaller crystallographic influence on the local radius was found for the two highly alloyed steels studied here (Fig. 2). The radius determined by TEM could therefore in most cases be used without introducing significant errors. A disturbance of the curvature (on a scale readily detectable with TEM) was, however, found when the intersecting grain boundary was nearly parallel to the specimen surface.

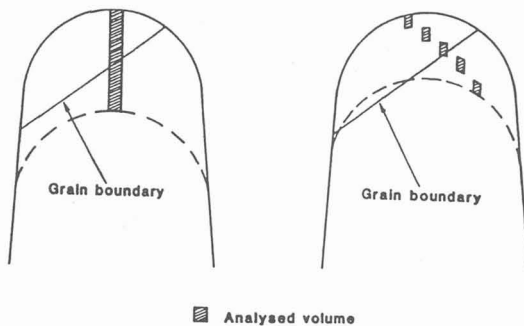


Fig. 1. Determination of a concentration profile across a grain boundary by (left) the continuous profile method and by (right) the point analysis method.

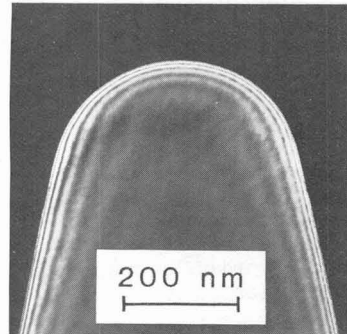


Fig. 2. TEM darkfield micrograph showing a specimen from the Mo-free steel analysed at 19 kV. The field evaporated endform closely resembles a hemisphere.

Grain boundary concentration profiles

The distribution of B, Mo, Ni and Fe, after three different heat treatments, were chosen to exemplify the method used to determine concentration profiles. The materials were first homogenised by a solution treatment, 15 min at 1250°C, before the final heat treatment and cooling.

Heat treatment 1 (HT1)

The Mo containing steel was quenched rapidly from 1250°C to room temperature with an average cooling rate of 530°C/s in the temperature interval 1250 - 500°C. Two specimens were analysed and the AP concentration profiles were in very good agreement both

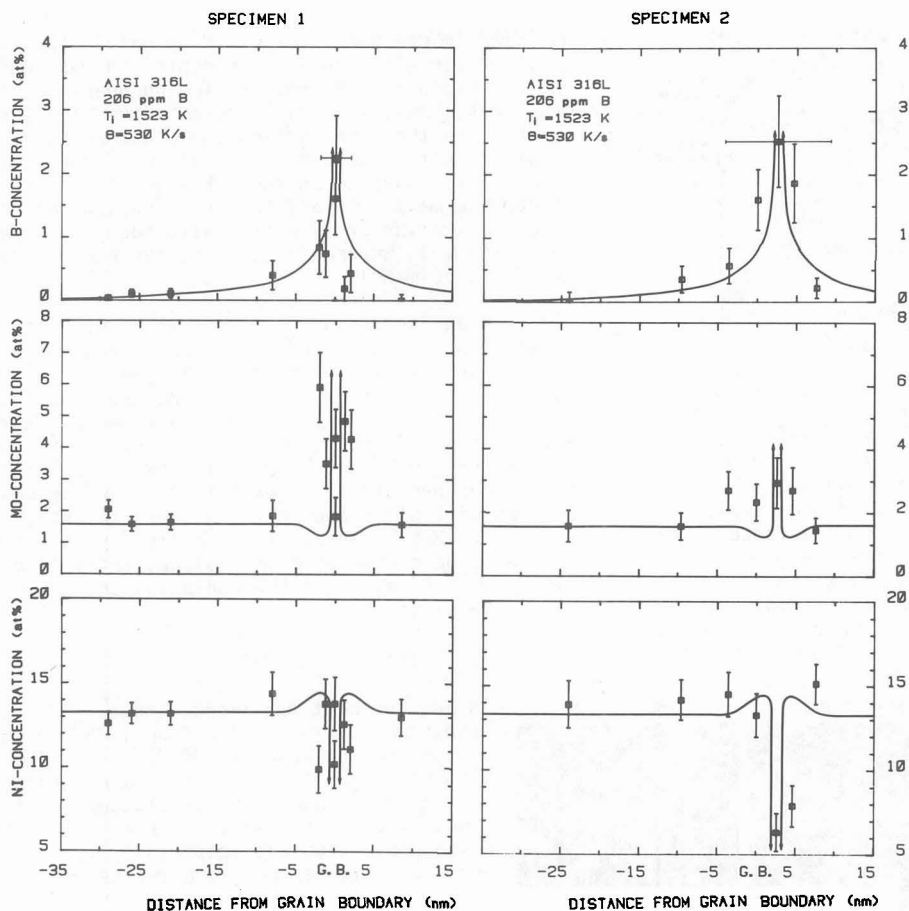


Fig. 3. AP concentration profiles for B, Mo and Ni obtained from Specimens 1 and 2 from the Mo-containing steel rapidly quenched from 1250°C (HT1). The full line represents a common concentration profile as derived from TEM, AP, and IAP data from both specimens. Note for Specimen 2 the difference between the position of the grain boundary as determined above and as defined by the FIM image (bottom scale). "Distance error bars", as defined in Fig. 4, are given for one data point in each B profile.

qualitatively and quantitatively (Fig. 3). Mo and Ni showed no significant changes from their bulk concentration values except when the probe hole covered some part of the grain boundary. B, on the other hand, showed a rather smooth non-equilibrium type of concentration profile with a measured peak value of 2.5 at.% at the grain boundary.

The grain boundaries were decorated in the FIM image and therefore easily detected. This contrast was associated with the localized increase in Mo concentration detected by AP. A similar decoration of grain boundaries by Mo has been found for the same material after other heat treatments (4) (see also HT2) and also in a low alloyed Mo-containing steel (5) and seems thus to be a common effect in Mo-containing steels.

An unexpected effect, probably connected with the influence of the intersection angle between tip surface and grain boundary on the local radius, was found in the IAP images (Fig. 5). Specimen 1, where the intersection angle was small ($\sim 0^\circ$), gave

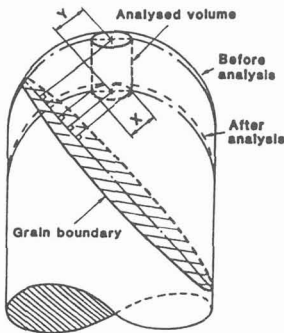


Fig.4. The spatial resolution perpendicular to a grain boundary of an analysis depends on the inclination of the boundary plane and also on the size of each analysed volume. A "distance error bar" therefore gives the sum of the shift, normal to the g.b. plane, of the centre of the probed area and its diameter projected on the g.b. plane normal.

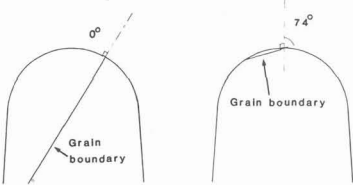
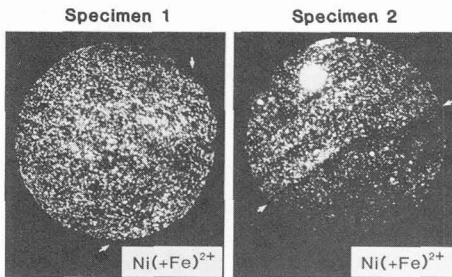


Fig. 5. $Ni(+Fe)^{2+}$ IAP micrographs of specimens 1 and 2 from the rapidly quenched Mo-containing steel (HT1). The accompanying drawings show position and inclination angle of each g.b. The arrows in the micrographs mark the positions of the g.b.'s. The bright spot in the second micrograph is an instrumental artefact caused by a lit up channel in the image intensifier. The image streaking is mainly due to the non-uniform magnification of an unsymmetrical specimen.

Ni^{2+} IAP images where the boundary was in practice undetectable although a clear depletion was found in the corresponding AP profile. The boundary in specimen 2 was, however, clearly seen in the Ni^{2+} IAP image. Here the intersection angle was much larger ($\sim 74^\circ$). A difference in the position of the grain boundary as observed in the FIM image and as determined from maximum B and Mo concentrations in the AP concentration profiles was also found for specimen 2 (Fig.3), whereas no such difference was detected for specimen 1.

Although an increased Mo concentration was detected at the grain boundary using AP, no corresponding increase was seen in the Mo^{2+} IAP images (Fig.6). This was due to two effects. Firstly, Mo appeared both as $2+$ and $3+$ ions at the grain boundary whereas almost only Mo^{2+} was found in the matrix. Unfortunately the Mo^{3+} signal could not be used to obtain useful Mo IAP images because of a low intensity and because of overlap with Ni^{2+} . Secondly, in order to obtain meaningful Mo^{2+} images, it was necessary to evaporate a large number of atomic planes which lead to a significant movement of the non-axial boundary during analysis.

Heat treatment 2 (HT2)

In another heat treatment, the same Mo-containing steel was cooled from $1075^\circ C$ with an average cooling rate of $27^\circ C/s$. Also in this case, a grain boundary imaged in the FIM, was decorated and signs of clustering at the boundary could be seen. A sharp increase in Mo concentration was measured (Fig. 7) when parts of this feature were analysed.

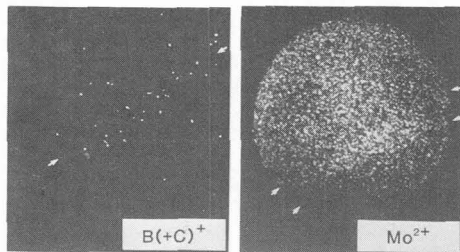


Fig. 6. IAP micrographs from the rapidly quenched Mo-containing steel (HT1). The arrows show the position of the grain boundary during analysis of B and the starting (upper) and final (lower) positions during analysis of Mo. The $B(+C)^+$ image clearly shows the segregation of B to the grain boundary region whereas no significant effect of the g.b. can be seen in the Mo^{2+} image.

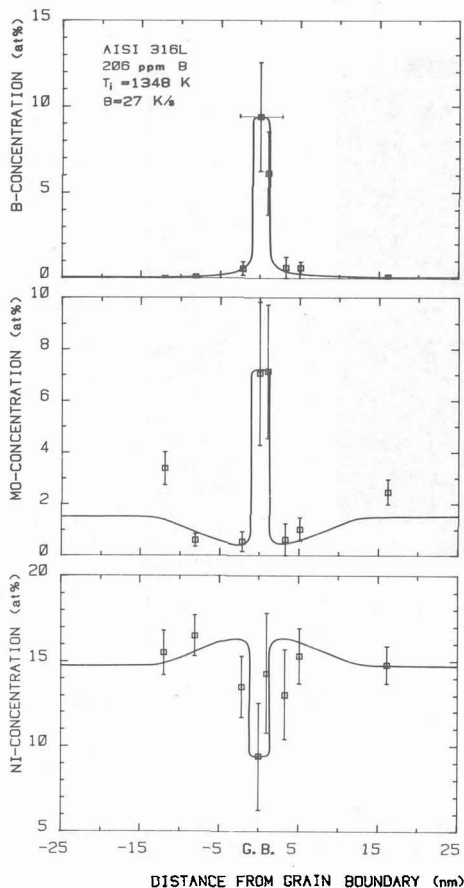


Fig. 7. AP concentration profiles for B, Mo, and Ni from the Mo-containing steel cooled with 27°C/s from 1075°C (HT2). The full line shows the profile as derived from TEM, FIM-AP, and IAP data. A typical "distance error bar" is given for one data point in the B profile.

The IAP results were qualitatively in very good agreement with the AP results (Fig.8). B showed a sharp increase at the boundary with a tail of decreasing concentration, this was seen both for B⁰ and B²⁺. The depletion of Ni was also clearly seen. A lower intensity at a boundary can, however, also be due to a locally higher magnification (6-10) and the contrast might therefore be partly due to this effect. As for HT1 it was not possible to image the increase in Mo concentration at the boundary.

Heat treatment 3 (HT3)

The Mo-free steel was cooled very slowly from 1250°C (0.3°C/s) to 750°C and then quenched in water. The main segregation effects in this material were similar to those of the Mo-containing: Fe was depleted and B enriched at the boundary (Fig.9). The changes were, however, more localized and smaller. Neither the small relative change in Fe concentration nor the B enrichment could be detected with certainty in the IAP images. The detection of B was complicated by the appearance of B both as B⁺

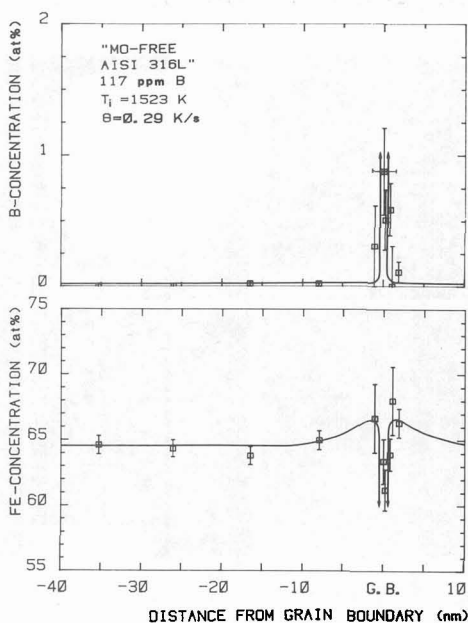


Fig. 9. AP concentration profiles for B and Fe from the Mo-free steel cooled with 0.3°C/s from 1250°C to 750°C and then rapidly quenched to room temperature (HT3). The full line shows the profile as derived from TEM, FIM-AP, and IAP data. A typical "distance error bar" is given for one data point in the B profile.

A somewhat different B concentration profile compared to HT1 was found, consisting of a smooth profile of approximately the same width as after HT1 plus a localized sharp increase to almost 10 at.% at the boundary. The narrow zone with increased B and Mo concentrations was depleted in Ni and an increased Ni concentration near the boundary was measured (Fig. 7).

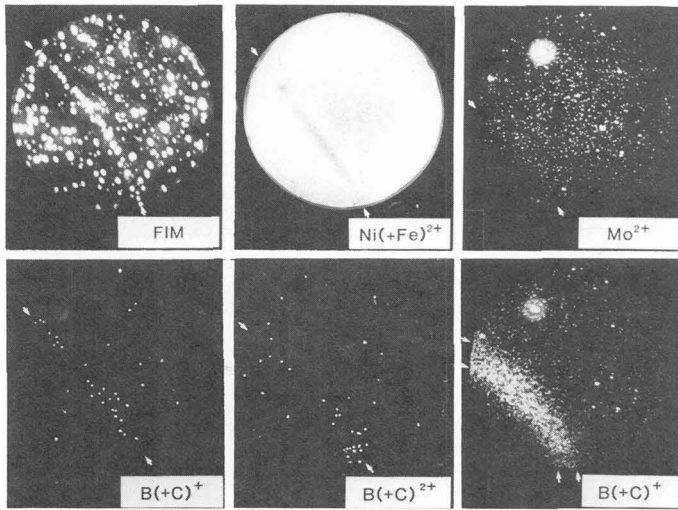


Fig.8. FIM and IAP micrographs of a grain boundary in the Mo-containing steel cooled with 27°C/s from 1075°C (HT2). The decoration of the grain boundary is clearly seen in the FIM micrograph. No increase in Mo concentration was found with the IAP although the depletion of Ni and enrichment of B are clearly seen. The position of the grain boundary during IAP analysis is indicated with arrows. The bright spot in two of the IAP micrographs is due to a lit up channel in the image intensifier.

and B^{2+} and by difficulties to separate the B and C signals, so that an initially small B signal was further reduced and superimposed on a small but not insignificant C signal.

The earlier interpretation of Mo as the contrast giving element at grain boundaries in the Mo-containing steel was supported since no decoration of the boundary was found in this case.

Conclusions

- o The AP point analysis method, combined with TEM, FIM, and IAP, has been used to determine grain boundary segregation profiles in two B containing steels.
- o Results are presented and discussed for B, Mo, Ni, and Fe.
- o TEM showed no significant changes in the radius over the field evaporated surface except at intersecting grain boundaries that were nearly parallel to the surface.
- o The contrast from grain boundaries in IAP images varies with the angle between the grain boundary plane and the specimen surface.
- o A very good agreement was found between profiles determined from grain boundaries with different inclination angles.

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References

1. HENJERED, A. and NORDEN, H., J. Phys. E: Sci. Instrum. 16 (1983) 617.
2. MÜLLER, E.W. and TSONG, T.T., "Field Ion Microscopy" New York, Elsevier, (1969).
3. LOBERG, B. and NORDEN, H., Arkiv för Fysik 39 (1968) 383.
4. KARLSSON, L., ANDREN, H.-O. and NORDEN, H., Scr. Met. 16 (1982) 297.
5. BACH, P.W. and VERBRAAK, C.A., "Proc. 27th IFES", Tokyo (1980) 254.
6. SOUTHON, M.J., BOYES, E.D., TURNER, P. J. and WAUGH, A. R., Surf. Sci. 53 (1975) 554.
7. WAUGH, A.R. and SOUTHON, M.J., Surf. Sci. 68 (1977) 79.
8. WAUGH, A.R. and SOUTHON, M.J., Surf. Sci. 89 (1979) 718.
9. WAUGH, A.R., PAETKE, S. and EDMONDS, D.V., Metallurgy 14 (1981) 237.
10. PAETKE, S. and WAUGH, A.R., Proc. "Solid to Solid Phase Transformations" Pittsburgh 1981, The Metallurgical Society, AIME (1982) 769.