Direct characterization of boron segregation at random and twin grain boundaries*

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Boron distribution at grain boundaries in hot-deformed nickel is directly characterized by the time-of-flight secondary ion mass spectrometry. The segregations of boron are observed at both the random and twin grain boundaries. Two types of segregations at random grain boundaries are observed. The first type of segregation has a high intensity and small width. Its formation is attributed to the incorporating of dislocations into the moving grain boundaries. The second type of segregation arises from the cooling induced segregation at the dislocations associated with the grain boundaries. The segregation at twin boundary is similar to the second type of segregation at random grain boundaries.

Keywords: boron segregation, recrystallization, twin boundary, SIMS

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1. Introduction

Grain boundaries (GBs) are interfaces between grains in polycrystalline material. They are always the initiators of the slip, crack, and corrosion, so they play essential roles in deformation, intergranular crack, and intergranular corrosion behavior of materials.[1–3] The properties of materials can be significantly improved by increasing useful GBs and reducing detrimental GBs, which is the aim of the widely studied grain boundary engineering (GBE).[4,5] For example, by increasing the proportion of twin boundaries (TB), the intergranular corrosion resistance of the polycrystalline material has been remarkably improved.[5–7] The properties of materials can also be affected by the solute elements segregated at the GBs.[8–10] Nie *et al*.[11] found that the segregated solute elements exert a pinning effect on TBs, and hence strengthening the material. The addition of boron to nickel-based superalloys leads to a significant increase of high temperature creep resistance, and this is always attributed to the GB strengthening effect of boron or borides at GBs.[12–14]

Boron is commonly added to alloys to strengthen the GBs.[12,15] It was first used to increase the hardenability of steel, and the remarkable effect is attributed to the non-equilibrium segregation of boron at GBs.[16,17] The segregation of boron has been systematically studied by the particle tracking autoradiography (PTA) based on ^{10}B fission reaction.[18–20] The results show that the segregation of boron is sensitive to the thermal mechanical history of the material.[17,21–24] However, the spatial resolution of PTA is 2 μm,[22] which brings uncertainties into the results.

Given the small atomic mass and trace addition of boron, the characterization of boron has always been difficult in experiments. Apart from PTA, the widely used techniques are the three-dimensional atom probe (3DAP) and secondary ion mass spectrometry (SIMS). The 3DAP is one of the most powerful techniques for achieving good quantitativity and high spatial resolution. The segregations of boron at prior austenite GBs and the TBs have been characterized in detail using 3DAP.[25,26] However, it is difficult to obtain systematical results of segregation for the extreme small analysis volume of 3DAP. Moreover, the systematic results are important for the segregation of boron, which is sensitive to the thermal and mechanical history of the material.

SIMS has been widely used to analyze the composition of solid surfaces due to its high sensitivity and acceptable spatial resolution. In this technique, the secondary ions are sputtered out of the sample surface and introduced into the mass spectrometer, in which the mass/charge ratio of the ion can be measured to determine the elemental composition. Several researches of boron characterization by SIMS have been reported. Hwang *et al*.[27] and Huang *et al*.[28] studied the segregation behavior of boron at GBs in steel and Ni–Fe–Cr-based alloys using SIMS. Their results indicate that the heat treatment parameters significantly affect the segregation of boron.

The exploitation of the advantages of boron segregation at GB requires full knowledge of its behavior and mechanism. Although the effects of heat treatment have been studied suf-

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ficiently, the effect of mechanical treatment must be clarified. Given that deformation and recrystallization are the two basic processes during the alloy production, the study of their effects on boron segregation is instructive. In this study, the time-of-flight SIMS (TOF-SIMS) is used to characterize the segregation of boron at different GBs in nickel after hot deformation.

2. Materials and experiments

The material used is high-purity nickel with the addition of 0.0056-wt% B and 0.051-wt% Nb. Cylindrical specimens each with a diameter of 10 mm and a length of 12 mm are heated to 1150 °C at a rate of 10 °C/s and maintained for 15 min. Subsequently, the specimens are cooled down to 1100 °C, 1000 °C, 900 °C, 800 °C, and 700 °C at a rate of 2 °C/s, respectively. Subsequently, the specimens are deformed with a 20% reduction of its height at a strain rate of 2 s^{-1}, and then cooled down to 600 °C at a rate of 2 °C/s and finally quenched in water. The cylindrical specimen is cut into two semi-cylinders along the centreline and a 2-mm thick slice is cut off parallel to the cut face. The sections along the centreline of the cylinders are mechanically polished for subsequent analysis.

The samples are then etched with a solution of 40% glacial acetic acid, 40% nitric acid, and 20% deionized water to reveal the GBs. The microstructures are observed by an optical microscope, and the GBs involved are marked with the same method used in our previous work.[29] Long and straight random GBs and TBs are marked with Vickers hardness indentation. And the samples are then mechanically polished again to eliminate etched layer while maintaining the clarity of the indentations.

SIMS measurements are conducted on a TOF-SIMS 5-100 system (ION-TOF GmbH, Germany). As the samples are polished again, the position of GBs should be determined with the aid of the indentations. The measured areas on the GB are first sputtered by argon ion to obtain a clean surface. Bismuth ion Bi^{3+} is used as a primary ion beam, and the beam size is estimated to be 200 nm.

3. Results and discussion

The microstructures of the samples obtained by an optical microscope are shown in Fig. 1. The figure shows that evident recrystallizations occur in the samples deformed at 1100 °C, 1000 °C, and 900 °C, and the grain sizes are approximately 200 μm. In the samples deformed at 800 °C and 700 °C, no evident recrystallizations appear, and the deformed grains remain extremely huge.

The analyzed random GBs of all the samples are indicated by long white arrows in Fig. 1. Annealing twins are always thin laminas and easy to be identified from Fig. 1 due to their prominent morphologies.[30] In Fig. 1(b), three twins are indicated by short red arrows and similar twins can also be observed in other samples.

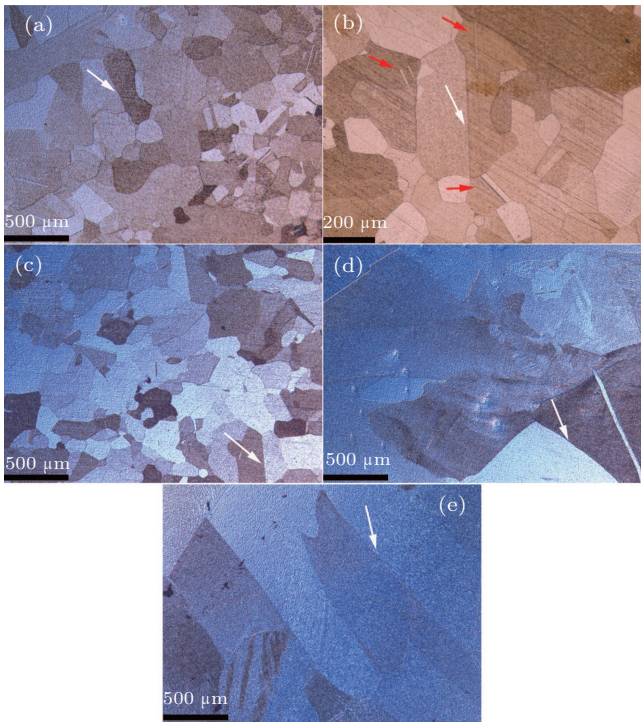


Fig. 1. (color online) Microstructures of the samples with the to-be-measured random grain boundaries indicated by long white arrows. Deformed temperature: (a), 1100 °C; (b), 1000 °C; (c), 900 °C; (d), 800 °C; (e), 700 °C. Three annealing twins are indicated by short red arrows in panel (b) to illustrate their morphological characteristics.

The random GBs and the boron distribution characterized by SIMS are shown in Fig. 2. The results show two types of segregations: one is that the segregations happen in the sample deformed at 1100 °C (Fig. 2(a1)) and the other is that the segregations occur in the sample deformed at 700 °C (Fig. 2(e1)). The intensity of the former is greater than that of the latter, and the width of the former is smaller than that of the latter. In the samples that deformed at 1000 °C and 800 °C, both types of segregations are observed and are indicated in Fig. 2 by red and white arrows, respectively.

The annealing TBs analyzed and boron distribution characterized by SIMS are shown in Fig. 3. The boron segregations at TBs appear in the samples deformed at 1100 °C, 1000 °C, 800 °C, and 700 °C. Unlike the segregations at random GBs, the segregations at TBs in samples deformed at different temperatures are almost the same; except that the width of segregation increases with the decrease of temperature.

The width of segregation is related to the time needed for the dislocations to incorporate into the moving GBs and is important for understanding the mechanism of boron segregation.[22] Figure 4 shows the widths of the two types of boron segregations at random GBs and the segregation at TBs. The widths of all the segregations increase with the decrease of deformation temperature.

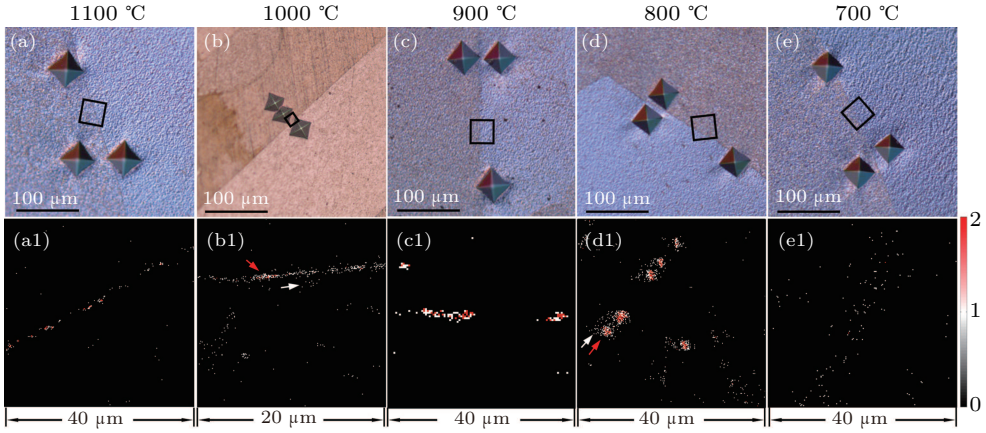


Fig. 2. (color online) Microstructures of the analyzed random GBs (row 1) and boron distribution characterized by SIMS (row 2) in the samples deformed at different temperatures. The marked random grain boundaries are shown in Fig. 1 by long white arrows. The two types of segregations are indicated by red and white arrows, respectively in Figs. 1(b) and 1(d). The possible measured areas are shown by black rectangles in the optical microscope images in row 1.

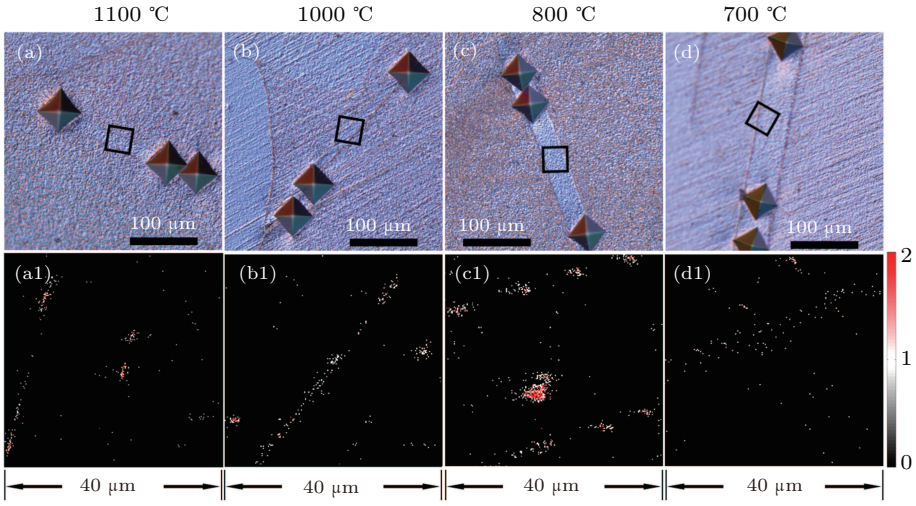


Fig. 3. (color online) Microstructures of the analyzed TBs (row 1) and boron segregations characterised by SIMS (row 2) in the samples deformed at different temperatures. The possible measured areas are shown by black rectangles in the optical microscope images in row 1.

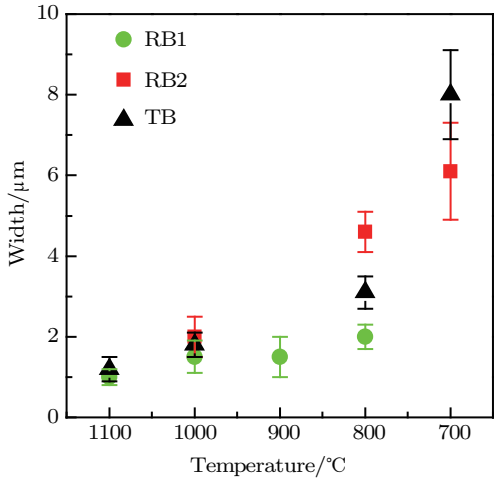


Fig. 4. (color online) Widths of the segregations at different GBs against the deformation temperature. RB1 and RB2 are the two types of segregations at random GBs, and TB is the segregation at TBs.

The theory of non-equilibrium segregation of boron states[8,17,22,24] that the cooling process and movement of GBs may both lead to the segregation of boron. When cooling from a high temperature, the supersaturated vacancies in the material may diffuse to the GBs and dislocations. The vacancy–boron complex mechanism suggests that the vacancy flux leads to the diffusion of boron to the dislocations and GBs. Given that GBs and dislocations are sinks of vacancy, the vacancies will annihilate and boron will segregate there.[17] The movement of GBs leads to the dislocations together with the segregated boron on them incorporating into GBs,[22] which induces the segregation of boron at moving GBs.

In this work, the samples are first cooled down at a rate of 2 °C/s, during which the boron segregates at GBs and dislocations.[24] In the samples deformed at 1100 °C, 1000 °C, and 900 °C, recrystallizations occur after the hot deformation. According to the segregation mechanism proposed by Jahazi and Jonas,[22] the incorporation of dislocations into the moving boundaries induces the segregation. Given that the entrance of dislocations increases the distortion and thickness of GBs, GBs cannot immediately change their structures. The time required for GBs to incorporate into the dislocations af-

fects the width of the segregation at moving GBs.[22] The incorporating time required will increase with the decrease of deformation temperature. Therefore, the width of the first type of segregation also increases as shown in Fig. 4. This type of segregation is also observed in the sample deformed at 800 °C, in which no evident recrystallization occurs. This result indicates that the dislocations may enter into GBs significantly even in samples without recrystallization.

The second type of segregation occurs in samples deformed at 1000 °C, 800 °C, and 700 °C. This type of segregation may be induced by the hot deformation and cooling process. Given that GBs are obstacles and traps of dislocations, the deformation leads to the dislocations significantly increasing along the GBs, which was directly observed by Elkajbaji and Thibault–Desseaux[31] by using a high-resolution electron microscopy. The dislocations that cannot enter into the GBs will pile up there and become the associated dislocations. The cooling processes before and after the hot deformation enable the boron to keep diffusing to the GBs and their associated dislocations (vacancy sinks), where boron segregations occur. Therefore, the large width of the second type of segregation can be attributed to the segregations at the associated dislocations.

Annealing twins are always observed in nickel and considered as stable structures due to their low energies.[32] The formation of annealing twins has important relations with the movement of GBs, i.e., the recrystallization and the growth of the grains.[30] After the formation of the annealing twins, the structures of the TBs will not undergo evident changes during the deformation or the recrystallization[33] and no evident dislocations will enter into the TBs. Therefore, the segregations of boron at TBs are similar to the second type of segregation at random GBs, which are mainly attributed to the cooling and deformation processes. Therefore, the widths of the segregations at TBs are similar to those of the RB2s as shown in Fig. 4.

4. Summary

Boron segregations at random GBs and TBs are directly characterized by TOF-SIMS in hot deformed nickels. Two types of segregations are observed on random GBs. The first type, which has high intensity and small width, is attributed to the incorporation of dislocations into the GBs, whereas the second type is related to the cooling and deformation processes. The segregations at TBs are similar to the second type of segregation. The widths of all the segregations increase with the decrease of deformation temperature.

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