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Short Communication

Diffusion of Boron on Superplastic Duplex Stainless Steel

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Abstract

It is well known that duplex stainless steels having refined grain, structure exhibit superplasticity. In this paper, the diffusion of boron in the superplastic duplex stainless steels has been investigated. Boron diffuses through the interior of the grains in superplastic duplex stainless steels. On the other hand, in case of normal duplex stainless steel having the same chemical concentration, boron mainly diffuses along the grain boundaries and does not diffuse through the interior of the grains. Investigations using Auger electron microscopy for super plastic duplex stainless steels revealed, the Cr concentration is much higher than Fe concentration in boron diffused areas. These results indicate that superplasticity activates diffusion into the interiors of grains. Further, it seems that boron preferentially reacts with Cr rather than Fe. Moreover the distribution of Fe and Cr is changed by the diffusion of boron.

Keywords alloys, diffusion, experimental study, iron alloys, microstructure

1. Introduction

Studies on the special properties of materials, such as superplasticity, superconductivity, magneto-volume anomaly, so-called Invar and Elinvar anomaly, etc., are very important for the development of materials science and technology.[1,2]

Recently, many studies have been conducted on superplasticity and its applications.[1,3-7] An experimental study has been reported that the elastic constant C′ of the superplastic Ti-based alloy is smaller than another alloy.[1] C′ is the elastic constant along [110] directions while C_{44} is the elastic constant along [100] directions. And, it can be defined as $C' = ½(C_{11}\text{-}C_{12})$ where C_{11}, C_{12}, and C_{44} are the three constants of the standard stress strain matrix for cubic symmetry. Further, a first-principle calculation performed by Souvatzis et al. revealed that C′ is very sensitive to the density of state (DOS) and led to superplasticity.[3]

A duplex stainless steel with the concentration listed in Table 1 shows superplastic behavior after certain thermal and mechanical treatments. This superplastic stainless steel alloy has been found, after appropriate thermal and mechanical treatment, to be a fine-grained two-phase alloy with one phase (α) being a body centered cubic (BCC) phase and the other phase (γ) being a face-centered cubic (FCC) phase. The onset of superplastic behavior was determined as 1273 K. Currently duplex stainless steels are month the common "Fe-based" superplastic materials.

Our research group had previously investigated the superplastic flow/diffusion bonding[8] and diffusion coating of carbon on superplastic alloy surfaces under compressive stress; these processes are responsible for superplasticity.[9,10] In this study, the diffusion of B into superplastic duplex stainless steel has been investigated. Further, diffusion of B into the normal duplex stainless steel made by casting having the same chemical concentration was investigated and compared with the superplastic duplex stainless steel.

2. Experiments

2.1 Preparation of Superplastic Duplex Stainless Steel

The chemical composition of the duplex stainless steel, which initially does not show superplasticity (NDS), is listed in Table 1. NDS conversion to the superplastic duplex stainless steel (SDS) results from a refinement of grain size by means of the following process. First, to obtain a BCC single-phase alloy, the original stainless steel was annealed at 1573 K for 1 h and then quenched in water. The alloy was then rolled to a thickness that was 25% of that of the original steel. The rolled alloy was next annealed at 1273 K to precipitate small FCC grains in a BCC matrix. The net result of this procedure was the formation of a very fine-grain duplex stainless steel. This SDS steel exhibits superplasticity at 1273 K. Diffraction peaks of the BCC and FCC phases were confirmed by x-ray diffraction (XRD) measurements, as shown in Fig. 1.

2.2 Boronizing Method

The surfaces of the samples (dimensions: 16 × 8 × 8 mm^3) were polished until their roughness became 0.32 μm. The polished surfaces (16 × 8 mm^2) were buried in fine boron powder in a boat and annealed at 1273 K for 8 h in an evacuated Tammann tube. The average grain diameter of SDS steel is approximately 5 μm. On the other hand, average grain diameter of NDS is approximately 10 μm.

Table 1 Composition list of sample

	Fe	C	Si	Mn	P	S	Ni	Cr	Mo
Composition (wt.%)	69.046	0.02	0.36	0.08	0.027	0.007	5.43	23.8	1.23

2.3 Analysis Method

The chemical concentration map of the cross sections of the boronized surfaces was obtained by using Auger electron spectroscopy (AES). Further, XRD measurements were performed to examine the boronized surfaces.

3. Results and Discussion

The chemical composition maps of B obtained by means of AES for both specimens are shown in Fig. 2. The presence of B in the surface layer can be confirmed in both samples. Further, the thickness of the boronized layer of both samples is approximately the same. In the case of NDS, B appears to exhibit a network-type distribution. Considering this observation, the grain boundary diffusion was mainly observed in NDS. However, in SDS, B does not exhibit a network-type distribution. It appears to diffuse into the interior of the grains. This result indicates that the diffusion type of SDS is different from that of NDS having the same mean chemical concentration. This difference can be attributed to the effect of superplasticity on diffusion phenomenon. In the superplastic state, several paths, such as dislocation, become active. Further, C′ may decrease with the appearance of the superplastic state, as has been predicted theoretically for some alloys.[3]

The chemical composition maps of Cr, Fe, and B in the boride layer in SDS obtained by means of AES are shown in Fig. 3. Cr and B exist in the same area. In addition, the Cr concentration is higher than that of Fe in the B diffused area. In both the BCC and the FCC phases, the Fe concentration is higher than that of Cr before boronization treatment. Considering these results, B diffuses into the interior of the grain and Fe is driven out of the grain. The XRD patterns of the boronized surfaces of SDS are shown in Fig. 4. The diffraction pattern of the boronized SDS surface would indicate that this occurs because of the generation of Cr_2B, and this result corresponds to the result of AES shown in Fig. 3. These

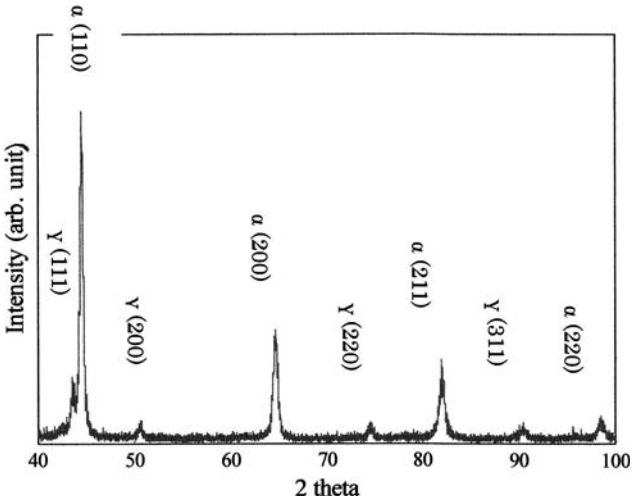


Fig. 1 X-ray diffraction patterns of SDS

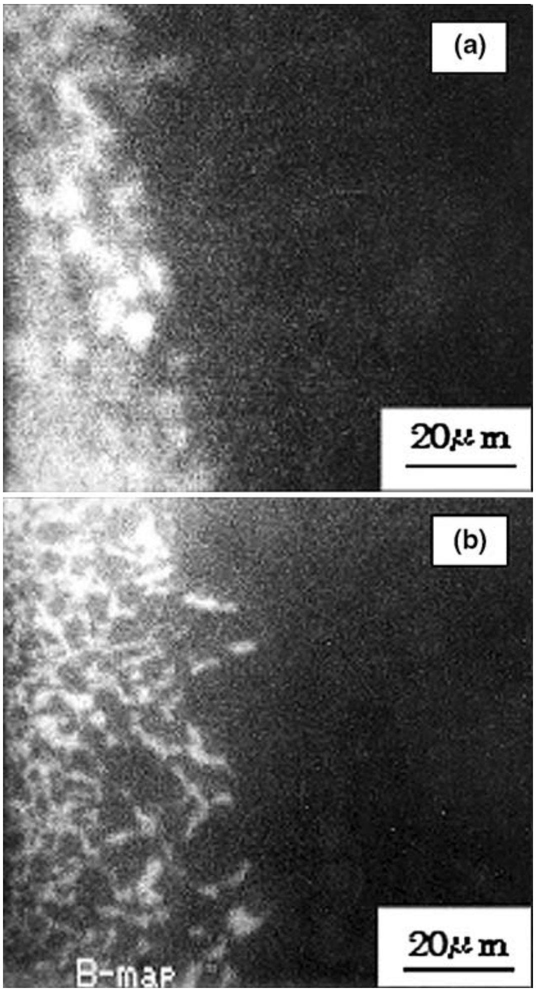
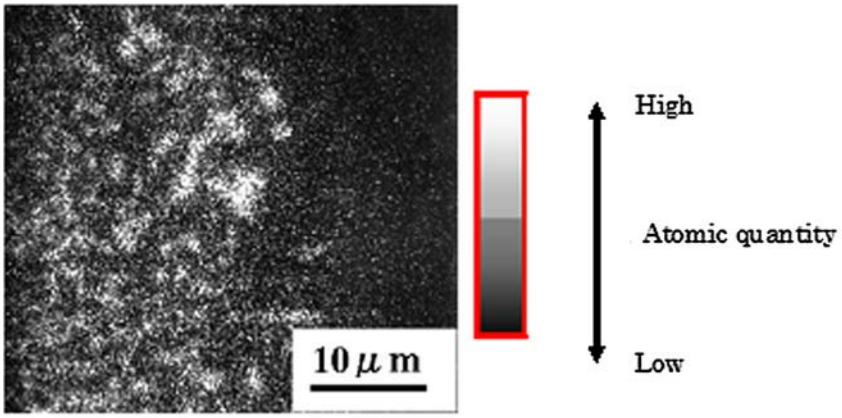
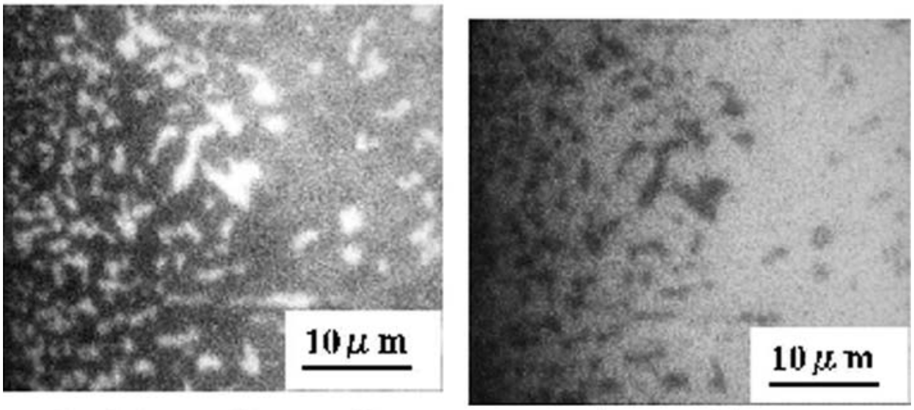


Fig. 2 Distribution maps of B of the cross sections of both specimens obtained by means of AES: (a) SDS and (b) NDS



Chemical composition map of B



Chemical composition map of Cr

Chemical composition map of Fe

Fig. 3 Chemical composition maps of Cr, Fe, and B in the boride layer in SDS obtained by means of AES

phenomenons could be considered to the effect of superplasticity on diffusion phenomenon. The view that superplasticity leads to the observed diffusion anomaly is based upon the following reasoning.

C′ is small in Ti-based superplastic alloys,[1] and a theoretical calculation also predicts a low value of superplastic materials.[3] Therefore, if a low-valued C′ is a characteristic of superplastic materials, the shear anisotropy will be high, and energy minimization will predict that grain boundary orientations in fine-grained material will prefer a dominance of boundaries oriented to favor [110] shear directions. Then with cognizance of the fact that a low shear modulus will lead to a low elastic limit, superplastic deformation with grain boundary sliding is implicit. Such grain boundary sliding during the recrystallization process which accompanies the annealing of the present two-phase material would be expected to carry impurity atoms, in the present case B, rapidly through the dynamically forming grain boundary network. Therefore, even after plastic flow ceases during the post-anneal equilibration, the grain boundaries provide a short circuit path for much faster diffusion than through bulk material. Thus, with the highly stable Cr_2B to tie down the B once it diffuses from a grain boundary into an adjacent grain, this sequence seems a plausible model for the experimental observations.

4. Conclusion

Superplasticity activates the diffusion of B. B appears to diffuse into the interior of the grain and drives out Fe from the grain. This phenomenon cannot be observed in nonsuperplasitc stainless steel having the same overall chemical concentration.

The form of the concentration map reveals the generation of Cr boride, which has a stronger bonding energy than Fe-Cr-Ni. Further, the generation of Cr boride can be considered to drive out Fe from the grain.

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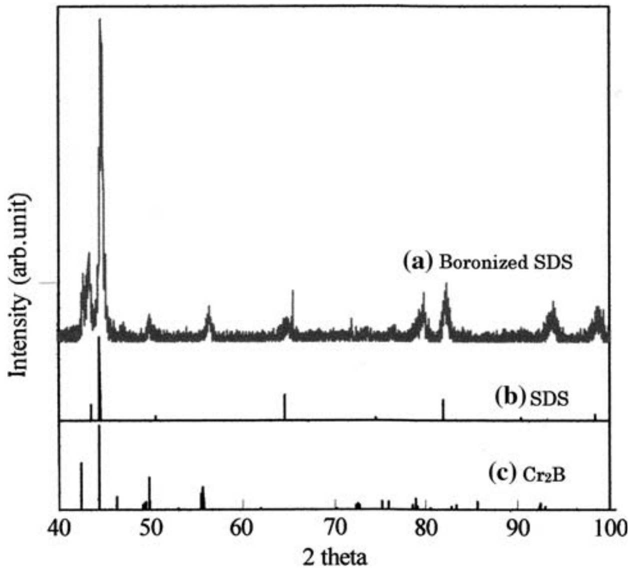

Fig. 4 XRD patterns of boronized superplastic duplex stainless steel. (a) Observed x-ray diffraction pattern from boronized SDS. (b) and (c) Peak positions for SDS and Cr_2B, respectively

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