IDENTIFICATION OF AN ORDERED HEXAGONAL BeFe PHASE

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Abstract - The complementary techniques of atom probe field-ion microscopy and transmission electron microscopy have been employed to identify an ordered equiatomic BeFe phase in the iron-beryllium system. This phase was observed to form in a Fe- 25 at. % Be alloy after aging at 650°C for 4 h.

INTRODUCTION

The iron-beryllium system has been the subject of numerous phase transformations studies because of the suggested presence of a tricritical point in the Fe-rich portion of the phase diagram.^[1-16] The equilibrium phase diagram indicates that the α solid solution decomposes into a hexagonal (C14) FeBe₂ phase and α -ferrite. Previous transmission electron microscopy and atom probe field-ion microscopy studies of the iron-beryllium system have revealed a low temperature miscibility gap within which phase separation of the solid solution α -ferrite occurs.^[8-16] During aging within this gap, the α -ferrite decomposes to produce a crystallographically-aligned two-phase mixture of a body-centered cubic α' -ferrite and a B2-ordered phase. Upon further aging, a B32-ordered equiatomic FeBe phase forms at the expense of the triaxially-aligned modulated microstructure.^[9,10] Both B2 and B32 crystal structures are ordered body-centered cubic lattices.

Although the evolution of the modulated microstructure has been characterized in detail, little attention has been focussed on the aging behavior of these alloys above the miscibility gap. In this investigation, the microstructural development which occurs during aging at 650°C has been examined by atom probe field-ion microscopy and transmission electron microscopy.

EXPERIMENTAL

The material used in this investigation was an Fe-25 at. % Be alloy that was solution annealed at 1100°C for 0.5 h prior to isothermal aging at 650°C for 4 h. This temperature is above the low temperature miscibility gap. Thin foil specimens were examined in Philips EM430T, EM400T, and JEOL 200CX electron microscopes. All atom probe investigations were performed in the ORNL energy-compensated APFIM.^[17] The error bars quoted for all atom probe compositional determinations are for 2 standard deviations. The field-ion micrographs were recorded with neon as the imaging gas and specimen temperatures of between 50 and 70 K. Both electron diffraction patterns and field-ion micrographs were computer-simulated to facilitate the identification of complex structures.^[18,19]

RESULTS AND DISCUSSION

After aging at 650°C, the microstructure of the alloy consisted of three phases: ferrite, a metastable B32 FeBe phase, and an unidentified phase. A transmission electron micrograph of the general microstructure is shown in Fig. 1. The B32-ordered phase was characterized by a generally mottled appearance which consisted of a locally aligned, very fine substructure as shown in Fig. 2. No such features were observed in the unidentified phase. The unidentified phase was detected throughout the ferrite matrix. This phase produced high quality images in the field-ion microscope. Field-ion micrographs of this phase and the ferrite matrix are shown in Fig. 3.

A hexagonal structure was deduced from the field-ion micrograph, Fig. 4, because of the 6-fold symmetry of the most prominent pole (i.e., the (0001) pole). Successive basal planes were observed to alternate between bright and dim contrast as shown in Fig. 5. This imaging behavior is indicative of an ordered lattice.

Detailed TEM examination of this phase revealed the presence of anti-phase boundaries (APBs) and numerous stacking faults. Both types of substructural features are visible in the dark field electron micrograph shown in Fig. 6. APBs were also directly observed in the field-ion images as demonstrated in Fig. 7. The presence of APBs also indicates an ordered structure. Atom probe microchemical analysis of this phase yielded a composition of Fe-51.2 $\pm$ 1.2 at. % Be indicating an equiatomic Be-Fe intermetallic compound. Furthermore, atom probe analysis revealed that successive (0001) planes alternated in composition between iron and beryllium. After this aging treatment at 650°C, 2.7 $\pm$ 0.6 at. % Be remained in solution in the ferrite matrix.

Based upon the TEM, FIM and AP data presented above, three ordered hexagonal structures are possible for the unidentified phase. These three structures are B_h (WC), B4 (ZnS), and B8 (NiAs). The stacking sequence of the B_h and B8 crystal structures differ only in the position of the "B" atoms. In the B_h structure, the stacking sequence along the [0001] direction is abababab..., whereas the B8 structure has an abacabac... sequence where b and c sites are occupied by "B" atoms (note the difference as to whether Fe or Be atoms occupy the a sites; BeFe denotes Be on the a sites and FeBe denotes Fe on the a sites). The B4 structure has an abcdabed... stacking sequence where b and d sites are occupied by "B" atoms and a and c sites are occupied by "A" atoms.

In order to distinguish these crystal structures, selected area electron diffraction patterns (SADP) were obtained. The fine scale of the microstructure precluded the acquisition of patterns from only the hexagonal phase. Therefore, a complicating contribution from the ferrite matrix was always present. The lattice parameter a_0 was determined from the analysis of SADPs to be approximately 0.42 nm with a c/a of ≈ 1.66 . A [0001] pattern obtained from this hexagonal phase which is superimposed on the [011] ferrite zone is shown in Fig. 8. A [1121] pattern from the hexagonal phase is shown in Fig. 9. Corresponding simulated electron diffraction patterns for these two zones are presented in Fig. 10 for the possible crystal structures. The relative intensities of the (1100) and (1120) reflections in the [0001] SADP indicated that the phase may be B8-ordered BeFe. The B_h structure can be eliminated on the basis of the geometry of the [2110] electron diffraction pattern since the c/a for the B_h structure should be half of the value for the B4 and B8 structures. The subtle differences in the intensity of the reflections in the [1211], [2119], [1216] and [2423] zones indicates that the structure is most consistent with B8-ordered BeFe.

The equilibrium $FeBe_2$ phase was reported to have a C14 hexagonal structure based upon x-ray diffraction data obtained by Misch^[1] with $a_0 = 0.4212$ nm and $c/a = 1.626$ with 12 atoms per unit cell. These values are very similar to those determined in this investigation. Although the C14 structure produces similar electron diffraction patterns to the B8 structure, the prominence of the poles in the field-ion images and the measured composition further support the B8 structure. Unfortunately, only limited data are available to substantiate the C14 observation. It is possible that the previously identified C14-ordered phase is in fact the B8-ordered BeFe phase.

CONCLUSIONS

Aging at 650°C has resulted in the formation of an additional phase in an Fe-25 at. % Be alloy. APFIM has revealed that the composition of this phase is equiatomic BeFe. Both FIM and TEM techniques have shown that this phase has an ordered hexagonal structure. The analysis of field-ion micrographs and electron diffraction patterns with the equiatomic composition indicate that the crystal structure of this BeFe phase is B8.

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Fig. 1. Transmission electron micrograph of the Fe-25 at. % Be alloy aged at 650°C for 4h. Note the presence of ferrite, B32-ordered FeBe, and the unidentified phase (?).

Fig. 2. Dark-field transmission electron micrograph of the B32-ordered FeBe formed during aging at 650°C.

Fig. 3. Neon field-ion micrographs of the (a) unidentified phase and (b) ferrite.

Fig. 4. Field-ion image which illustrates the 6-fold symmetry about the (0001) pole in the unidentified phase.

Fig. 5. Alternating brightly- and dimly-imaging rings present at the (0001) pole. Atom probe chemical analysis confirmed that these planes alternated between Fe and Be.

Fig. 6. Dark-field electron micrograph of the equiatomic phase which contains numerous stacking faults and APBs.

Fig. 7. Neon field-ion micrographs of APBs in the hexagonal ordered phase.

Fig. 8. Selected area electron diffraction pattern obtained from the unidentified phase and ferrite. The $[0001]$ zone of unidentified phase is superimposed on the $[011]$ ferrite pattern.

Fig. 9. $[1121]$ selected area electron diffraction pattern obtained from the unidentified phase.

Fig. 10. Computer simulated [0001] SADP for the (A) B8-ordered FeBe, (B) B4, (C) B8-ordered BeFe, (D) B_h and [1121] SADP for the (E) B8-ordered FeBe, (F) B4, (G) B8-ordered BeFe, and (H) B_h.