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Formation of a Nanoscale hcp Structure by Crystallization of an Amorphous $Co_{91}Zr_7B_2$ Alloy*

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Synopsis

A mostly single hcp phase with grain sizes ranging from 3 to 10 nm was found to form as a metastable phase in the crystallization process of an amorphous $Co_{91}Zr_7B_2$ alloy. The temperature range, in which the nanoscale hcp structure forms, extends from 800 to 900 K and the further heating above 900 K causes the phase transition to ε-Co + $Co_{23}(Zr,B)_6$. No distinct grain growth in the hcp structure is seen in the temperature range of 800 to 900 K. The hcp phase has a lattice parameter of a=0.2507 nm and c=0.4066 nm which is slightly different from that of pure ε-Co presumably because of the dissolution of Zr and B. The $Co_{91}Zr_9$ amorphous alloy crystallizes directly to a mixed phase of ε-Co + cubic $Co_{23}Zr_6$ with a large grain size of about 0.4 μm through a polymorphic-type crystallization mode. It is therefore concluded that the addition of a small amount of boron is essential for the formation of the nanoscale hcp structure.

I. Introduction

It has recently been found that a bcc structure with nanoscale grain size forms by crystallization of an amorphous phase in Fe-Si-B-Nb-Cu[1], Fe-Zr-B[2] and Fe-P-C-Cu-Ge-Si[3] systems and the nanoscale bcc alloys exhibit good soft magnetic properties. Among these alloy systems, the Fe-Zr-B system is particularly important because the bcc phase is formed in the simple ternary system without additional copper and niobium elements and the resulting high iron concentration causes an appearance of the highest saturation magnetization in the nanoscale bcc alloys[4]-[7]. We have previously reported[8] that the crystallization of a $Co_{90}Zr_{10}$ amorphous alloy occurs through the simple process of amorphous to ε-Co + cubic $Co_{23}Zr_6$ and there is no

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hcp single phase field. However, it is highly expected from the similarity of alloy compositions between Co-Zr-B and Fe-Zr-B alloys that a nanoscale hcp structure forms in the crystallization process of Co-Zr-B amorphous alloys. Little has been known about the crystallization behavior of Co-Zr-B ternary amorphous alloys. This paper is intended to examine the crystallization behavior of a $Co_{91}Zr_7B_2$ amorphous alloy and to investigate the possibility that the nanoscale hcp structure forms in Co-Zr-B system.

II. Experimental Procedure

An alloy ingot with composition $Co_{91}Zr_7B_2$ was produced by arc melting a mixture of pure Co, Zr and B in an argon atmosphere. The subscripts are assumed to be those of the unalloyed pure elements, since the weight loss during the arc melting was as small as 0.2 mass %. A rapidly solidified ribbon with a cross section of about 0.02 x 1 mm^2 was produced in an argon atmosphere by a single-roller melt spinning method in which the copper roller with a diameter of about 200 mm is rotated at a circumferential speed of 42 m/s. The as-quenched sample was subjected to heating for 3.6 ks at various temperatures ranging from 720 to 930 K inside a vacuum-sealed quartz tube, followed by water quenching. As-quenched and annealed structures were examined by X-ray diffractometry using Cu Kα radiation and transmission electron microscopy (TEM). The decomposition behavior upon continuous heating at a rate of 0.17 K/s was also examined by differential scanning calorimetry (DSC), X-ray diffractometry and TEM.

III. Results

Figure 1 shows the DSC curve of the amorphous $Co_{91}Zr_7B_2$ alloy, along with the result of an amorphous $Co_{91}Zr_9$ alloy. As is evidenced from the X-ray diffraction pattern shown in Fig. 2, the sharp exothermic peak with a maximum at 807 K for the Co-Zr binary alloy is due to the polymorphic precipitation of hcp Co and cubic $Co_{23}Zr_6$ and the broad exothermic peak with a maximum at 906 K corresponds to the further decomposition of the hcp Co phase to ε-Co and $Co_{23}Zr_6$ phases. The polymorphic precipitation accompanying a large growth rate of the precipitates is also confirmed from the bright-field electron micrograph and the electron diffraction pattern shown in Fig. 3. The grain size of the hcp Co phase is about 0.4 μm and the periodic arrangement of the reflection spots corresponding to $Co_{23}Zr_6$ indicates

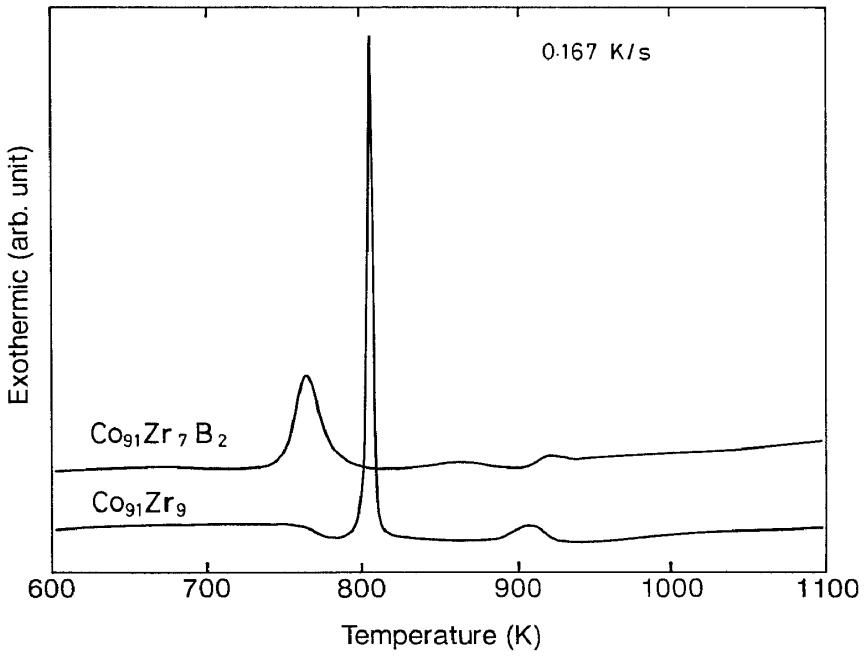

Fig. 1 Differential scanning calorimertic (DSC) curves of amorphous $Co_{91}Zr_9$ and $Co_{91}Zr_7B_2$ alloys.

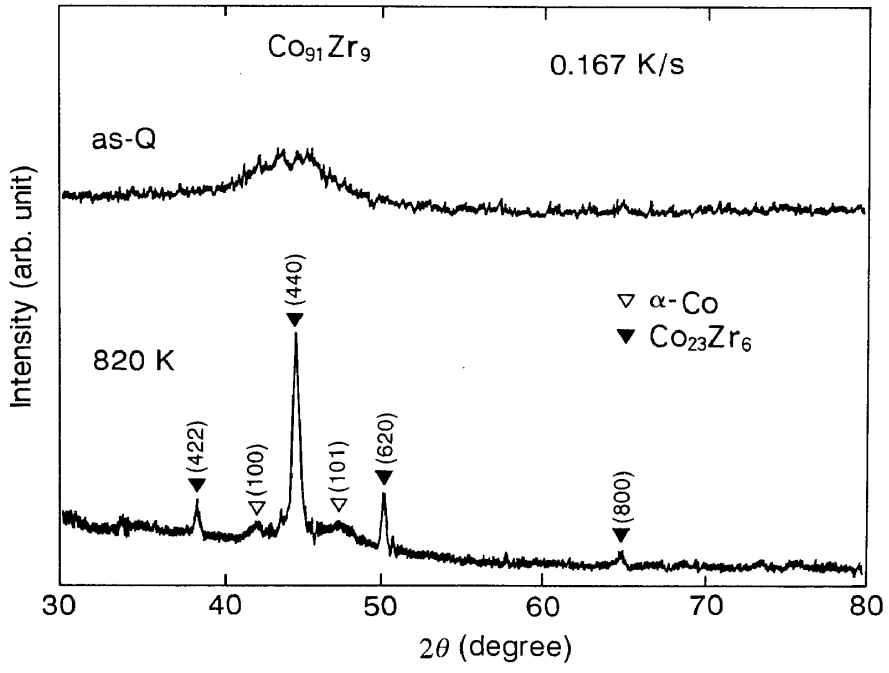

Fig. 2 X-ray diffraction patterns of an amorphous $Co_{91}Zr_9$ alloy in an as-quenched state (a) and heated up to 820 K (b).

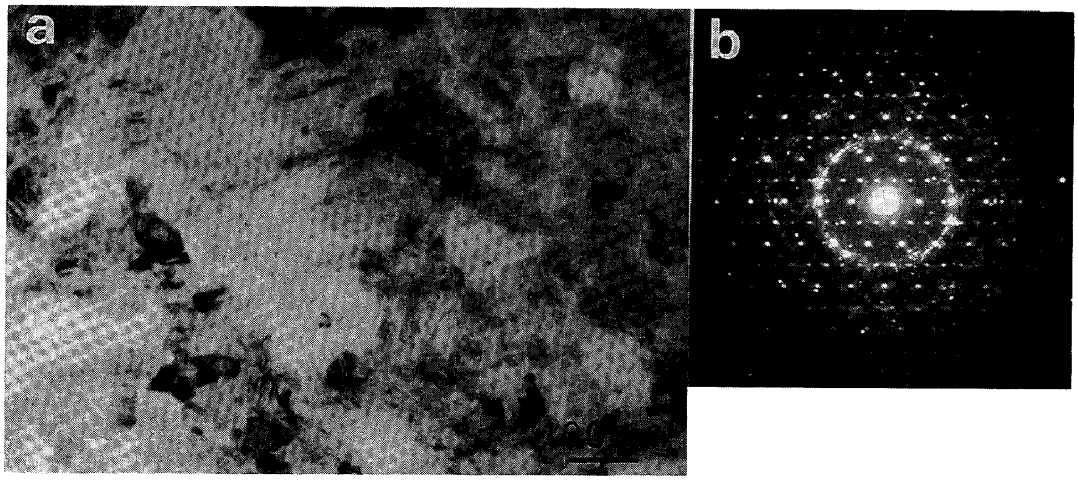

Fig. 3 Bright-field electron micrograph (a) and selected area diffraction pattern (b) of an amorphous $Co_{91}Zr_9$ alloy heated up to 820 K.

that the compound also has a rather large particle size. It is thus said that no nanoscale hcp structure is formed in the crystallization process of the binary $Co_{91}Zr_9$ alloy. On the contrary, the replacement of Zr by 2 at% B causes a significant change in the exothermic reaction due to crystallization as shown in Fig. 1. That is, an exothermic peak, which is broader as compared with the first exothermic peak for the Co-Zr alloy, is seen in the range of 730 to 800 K, indicating that the crystallization takes place in the rather wide temperature range. Thus, the crystallization temperature of the Co-Zr-B alloy decreases because of the decrease in zirconium content resulting from the replacement of zirconium by boron. In addition, another exothermic peak with low intensity is seen in the high temperature range of 905 to 938 K. In order to examine the structural change corresponding to the two exothermic peaks, X-ray diffractometry analysis was made for the samples heated up to 720, 820 and 930 K at a heating rate of 0.17 K/s which is the same as that for the DSC measurement.

Figure 4 shows the X-ray diffraction patterns of the $Co_{91}Zr_7B_2$ alloy in the as-quenched and heated states. The as-quecnhed sample consists only of a halo peak revealing the formation of an amorphous phase. The sample heated up to 820 K corresponding to the temperature

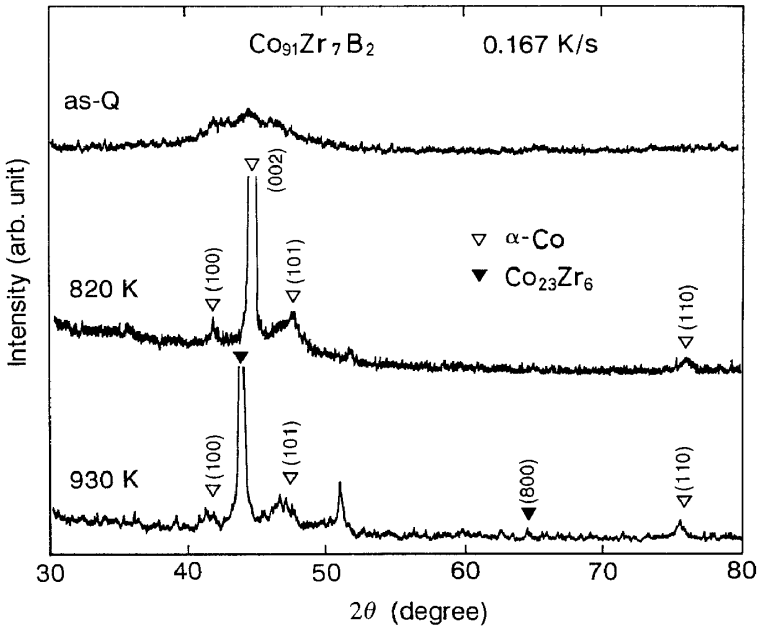

Fig. 4 X-ray diffraction patterns of an amorphous $Co_{91}Zr_7B_2$ alloy in an as-quenched state (a) and heated up to 820 K (b) and 920 K (c).

just above the first exothermic peak shows diffraction peaks consisting only of an hcp structure with lattice parameters of a=0.2507 nm and c=0.4066 nm and no broad peaks due to an amorphous structure are seen. In comparison with that for pure ε-Co, the a value is hust the same while the c value is slightly smaller. The difference is presumably due to the simultaneous dissolution of zirconium nd boron elements. The sample heated up to 930 K just above the second exothermic peak is composed of a mixed structure of hcp Co and cubic $Co_{23}Zr_6$. The further increase of heating temperature causes an increase in the peak intensity of $Co_{23}Zr_6$, indicating a grain growth of the compound. No appreciable peaks of Co_3B and Co_2B are observed in the entire heating temperature range and there is no appreciable solubility of boron into ε-Co in an equilibrium state. Accordingly, the small amount of boron seems to have been dissolved into the $Co_{23}Zr_6$ phases.

The microstructure of the mostly single hcp-Co phase and the coexistent hcp-Co and cubic $Co_{23}(Zr,B)_6$ phases was examined by TEM for the $Co_{91}Zr_7B_2$ samples heated up to the temperatures just above the first- and the second exothermic peak. Figures 5 and 6 show bright- and dark-field electron micrographs and a selected area diffraction pattern of the $Co_{91}Zr_7B_2$ samples heated up to 820 and 930 K,

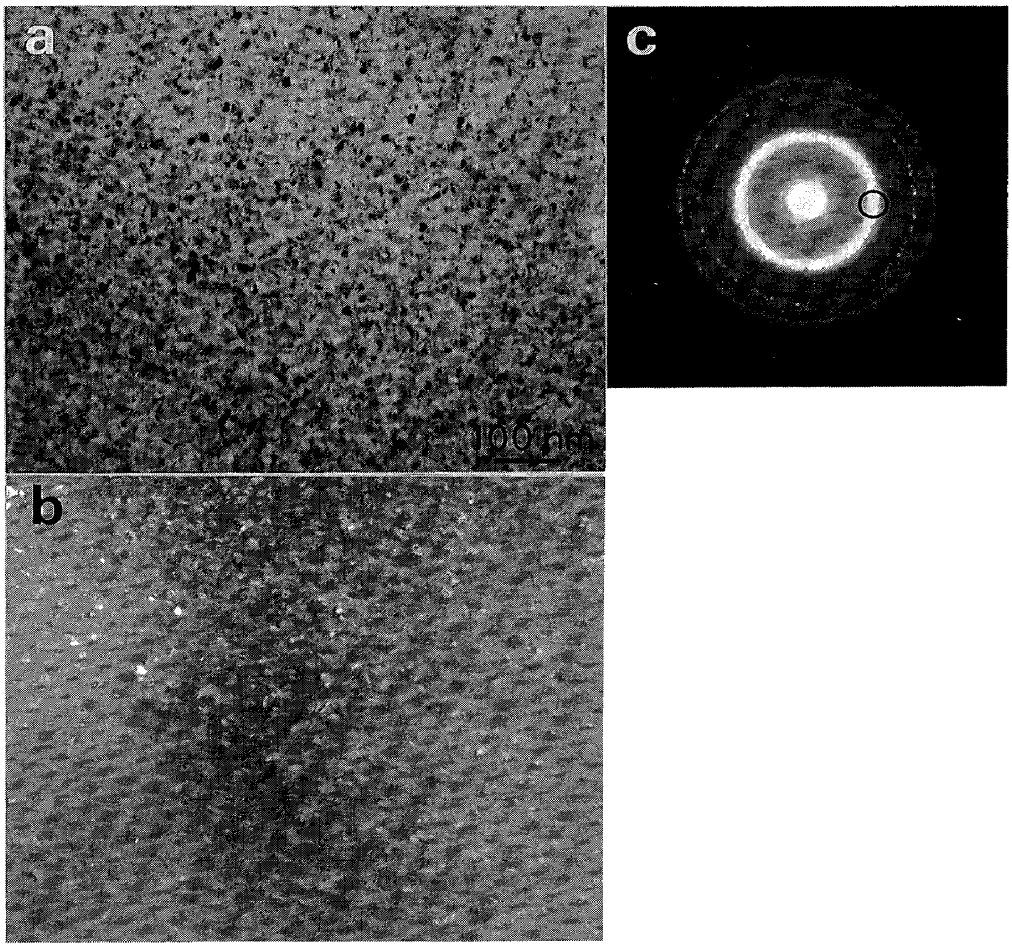

Fig. 5 Bright- and dark-field electron micrographs (a and b) and selected area diffraction pattern (c) of an amorphous $Co_{91}Zr_7B_2$ alloy heated up to 820 K. The open circle in Fig. 5 (c) represents the position and size of an aperture used to take the dark-field micrograph.

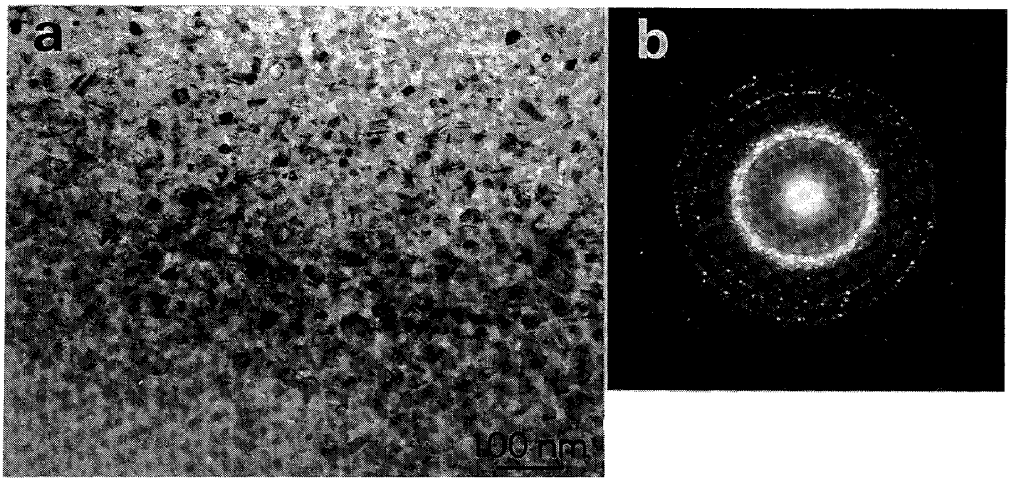

Fig. 6 Bright-field electron micrograph (a) and selected area diffraction pattern (b) of an amorphous $Co_{91}Zr_7B_2$ alloy heated up to 930 K.

respectively. The electron diffraction pattern (Fig. 5 (c)) taken from the sample heated up to 820 K consists only of reflection rings which can be identified as an hcp phase with lattice parameters of a=0.25 nm and c=0.406 nm. As seen in the dark-field electron micrograph (Fig. 5 (b)) taken from the reflection (100), (002) and (101) rings of the hcp phase, the hcp phase appears to have an ellipsoidal morphology and the particle size and interparticle spacing are as small as 7 nm and 10 nm, respectively. This result indicates clearly that a nanoscale hcp structure is formed through crystallization of the Co-Zr-B amorphous phase. In addition, Fig. 6 shows that the coexistent ε-Co and $Co_{23}Zr_6$ phases obtained by heating up to 930 K also have a very fine mixed structure with grain and/or particle sizes ranging from 10 to 30 nm. The formation of the fine structure for the sample heated up to 930 K indicates that the nanoscale grain of the hcp Co phase has a high resistance against the grain growth over a wide temperature range of about 100 K. Furthermore, Fig. 5 (c) reveals the existence of a diffuse halo ring, in addition to the reflection rings of the hcp Co phase, suggesting that the crystallization to the nanoscale hcp Co phase is not completed and a small amount of amorphous phase remains along the boundary of the nanoscale hcp Co phase. The residual existence of the

amorphous phase containing solute contents more than the nominal solute content is thought to cause the suppression of grain growth of the nanoscale hcp Co phase. The feature of the nanoscale structure is very similar to that[2] for the nanoscale bcc structure formed in Fe-Zr-B system. It is thus concluded that the low- and high-temperature exothermic peaks are due to the structural changes from amorphous to hcp phase and from hcp to ε-Co + $Co_{23}(Zr,B)_6$ phases, respectively. It should be noticed that the mostly single hcp phase with a nanoscale grain size is obtained in the wide temperature interval of 100 K between the first and the second exothermic peaks.

The possibility that the mostly single hcp phase forms by isochronal annealing for 3.6 ks was also examined for the $Co_{91}Zr_7B_2$ amorphous alloy, because of an engineering importance of the heat treatment. As an example, Fig. 7 shows the bright- and dark-field electron micrographs and the selected area diffraction pattern of the $Co_{91}Zr_7B_2$ amorphous alloy annealed for 3.6 ks at 720 K corresponding to the temperature just below the first exothermic peak. As similar for the microstructure (Fig. 5) in the $Co_{91}Zr_7B_2$ sample heated up to 820 K, the annealed structure consists of a mostly single hcp phase and the grain size is also as small as about 7 nm. In the case of isochronal annealing for 3.6 ks, a similar nanoscale hcp structure was confirmed to form in the temperature range of 690 to 840 K. In the comparison with the temperature range obtained by the continuous heating treatment, the temperature interval remains almost constant, though the temperature range shifts to a lower temperature side. It is therefore said that the mostly single hcp structure with nanoscale grain sizes is easily formed in the wide heat treatment condition by choosing the appropriate alloy composition.

IV. Discussion

It is important to discuss the reason for the useful effect of boron on the formation of the nanoscale hcp structure in the Co-Zr-B alloy. It is shown in Figs. 1 to 3 that the crystallization of the $Co_{91}Zr_9$ amorphous alloy takes place through the single process consisting of the simultaneous precipitation of ε-Co and cubic $Co_{23}Zr_6$. The replacement of zirconium by 2 at% B causes the slight decrease in the onset temperature for the precipitation of the hcp Co phase as well as the drastic increase in the precipitation temperature of the $Co_{23}Zr_6$ compound. These changes indicate that the suppression of the precipitation of the $Co_{23}(Zr,B)_6$ compound by the dissolution of boron causes the appearance of the wide phase field of the nanoscale

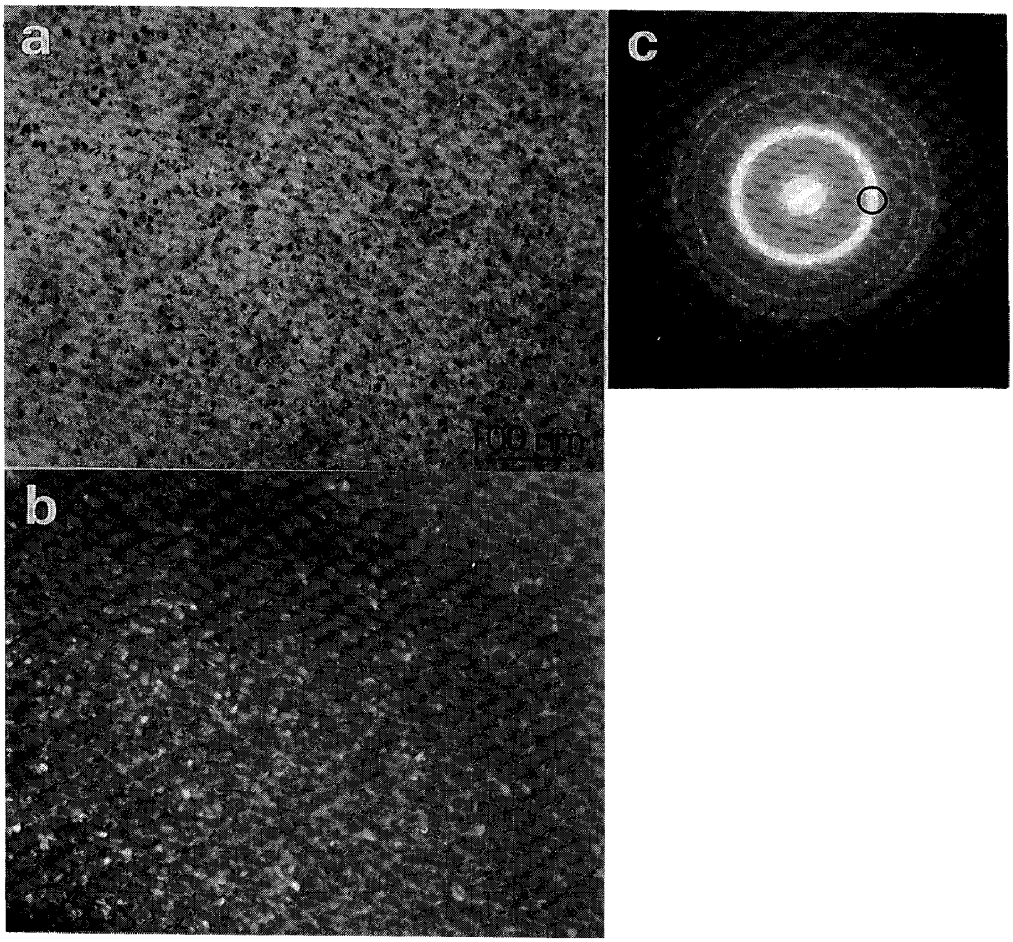

Fig. 7 Bright- and dark-field electron micrographs (a and b) and selected area diffraction pattern (c) of an amorphous $Co_{91}Zr_7B_2$ alloy annealed for 3.6 ks at 720 K. The open circle in Fig. 7 (c) represents the position and size of an aperture used to take the dark-field micrograph.

hcp phase. Considering that there is no solubility limit of boron element into ε-Co phase in an equilibrium state[9], the additional boron element must diffuse preferentially into the $Co_{23}Zr_6$ compound. This implies that the precipitation of the $Co_{23}(Zr,B)_6$ compound requires a significant diffusion of boron. The necessity of the diffusion of boron which is in a strong bonding state against the other constituent elements causes the retardation of the precipitation of $Co_{23}(Zr,B)_6$, leading to the appearance of the wide phase field of the hcp structure.

Furthermore, as similar for the formation of the nanoscale bcc structure in Fe-Si-B-Nb-Cu[1] and Fe-Zr-B[2] alloys, the residual existence of an amorphous phase with high thermal stability is also thought to be important for the formation of the nanoscale hcp structure. The redistribution of boron to the remaining amorphous phase resulting from the precipitation of the primary hcp phase enhances the thermal stability of the amorphous phase and allows the residual existence of the amorphous phase at high temperatures well above the precipitation temperature of the hcp phase. Consequently, the retardation of the grain growth of the nanoscale hcp phase is presumably because of the necessity of the redistribution of boron from the primary hcp phase to the remaining amorphous phase.

V. Conclusion

We have examined the possibility that a nanoscale hcp structure is formed in the crystallization process of Co-based amorphous alloys. By examining the crystallization behavior of a $Co_{91}Zr_7B_2$ amorphous alloy in comparison with that of a $Co_{91}Zr_9$ amorphous alloy, a nanoscale hcp phase with grain sizes of 3 to 10 nm was found to form in the wide temperature range of 800 to 900 K only for the Co-Zr-B alloy. The temperature range corresponds to the temperature interval between the first- and the second-exothermic peaks on the DSC curve measured at a heating rate of 0.17 K/s. The further heating above the second exothermic peak causes the decomposition of the nanoscale hcp phase to a mixed structure of ε-Co + cubic $Co_{23}Zr_6$. On the other hand, the $Co_{91}Zr_9$ amorphous alloy has a polymorphic-type crystallization process in which coexistent hcp Co and cubic $Co_{23}Zr_6$ phases precipitate simultaneously at a rather large growth rate in a narrow temperature range of 790 to 815 K. It is concluded from these results that the existence of boron plays an important role in the formation of the nanoscale hcp structure.

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