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Permanent deformation of (Co, Ni)Zr intermetallic compounds through phase transformation

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(Co, Ni)Zr intermetallic compounds, which have B_f structure at room temperature and B2 structure at elevated temperatures, were heated and cooled repeatedly in the temperature range between room temperature and 1223 K. This process produced the large permanent deformation in $Co_{30}Ni_{20}Zr_{50}$. Permanent elongation by as much as 0.2 to 0.3% per cycle was observed for the specimen parallel to the columnar structure, which grew from the bottom to the top of the button ingot, and permanent shrinkage by as much as 0.2% per cycle was observed for the specimen perpendicular to the columnar structure. For example, permanent elongation of about 30% was obtained after 93 cycles of the heating and cooling process in the former specimen, but no permanent elongation nor shrinkage was observed in the specimen parallel and perpendicular to the columnar structure for $Co_{36}Ni_{14}Zr_{50}$. The latter alloy had a different preferred orientation of the columnar structure from the former. These facts show that the crystal orientation influenced the permanent deformation caused by this transformation.

1. Introduction

CoZr is an intermetallic compound with B2(CsCl) structure and exhibits no phase transformation even at temperatures as low as liquid nitrogen temperature [1]. On the other hand, NiZr is an intermetallic compound with B_f(CrB) structure. Both compounds have been reported to have no composition range of zirconium [2]. The substitution of nickel for cobalt is therefore expected to cause phase transformation from B2 to B_f structure. $Co_{40}Ni_{10}Zr_{50}$ showed phase transformation as the temperature decreased to liquid nitrogen temperature, and the reverse transformation at about 373 K as the temperature increased from liquid nitrogen temperature [3].

(Co, Ni)Zr is an intermetallic compound which is composed of groups VIII and IVa elements in the Periodic Table, and NiTi, which is a famous shape-memory alloy, consists of elements of the same groups as (Co, Ni)Zr. The shape-memory effect of NiTi results from the martensitic transformation as the temperature falls, and the reverse transformation as it rises. Thus, it is interesting to examine the phase transformation behaviour of (Co, Ni)Zr intermetallic compounds. In this work, (Co, Ni)Zr, which showed phase transformation above room temperature, was examined macroscopically using a thermal extensometer and large permanent deformation was found when $Co_{30}Ni_{20}Zr_{50}$ was heated and cooled cyclically in the temperature range from room temperature to 1123 K.

2. Experimental procedure

The materials used for melting were electrolytic cobalt flakes (99.90 wt %), electrolytic nickel (Ni + Co > 99.95 wt %) which was induction melted in vacuum, and non-consumable arc-melted sponge-zirconium. $Co_{30}Ni_{20}Zr_{50}$ and $Co_{34}Ni_{16}Zr_{50}$ were non-consumable arc-melted and button ingots of 100 g were obtained; 100 g Fe–15 wt % Ni was also arc melted to compare with (Co, Ni)Zr. The weight loss of an ingot was less than 0.03 wt % and therefore chemical analysis was not carried out. (Co, Ni)Zr ingots were annealed at 1173 K for 180 k sec in vacuum followed by machining to specimens with a height of 9 mm and a cross-sectional area of $2.3 \times 2.3\,mm^2$ for thermal expansion measurement. Both the annealed and the as-melted ingots had grains elongated from the bottom to the top of the button ingots. Then, the height direction of the specimen was chosen to be parallel or perpendicular to the elongated direction of the grains. As-melted Fe–Ni alloy was machined to specimens with the same geometry.

Thermal expansion was measured using a Formaster (Fuji Denpa Co.) in which a specimen was heated and cooled in vacuum with induction heating. The heating rate of the specimen was 950 K/3 min to 950 K/24 min, and the specimen was cooled naturally from 1223 K to room temperature or at cooling rates of 950 K/3 min to 950 K/24 min. Both the heating and cooling rates of 950 K/6 min were mainly used when heating and cooling were cyclically repeated in the temperature range from room temperature to 1223 K.

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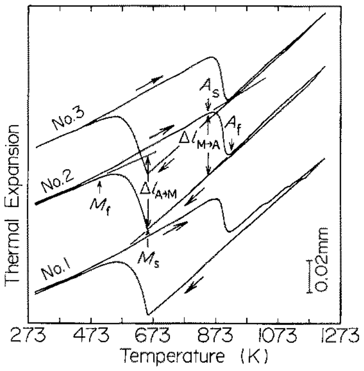

Figure 1 Dilatometric heating and cooling curves for the 85-70 specimen (⊥) parallel to the columnar structure of Fe–15 wt % Ni.

3. Experimental results

Fig. 1 shows examples of the temperature dependence of thermal expansion for the longitudinal specimen of Fe–15 wt % Ni which was machined parallel to the direction of elongated grains. Little permanent deformation was observed when the specimen was heated and cooled repeatedly. When various transformation temperatures, i.e. austenite-start temperature, A_s, finish temperature, A_f, martensite-start temperature, M_s, and finish temperature, M_f, were defined as shown in Fig. 1, $A_s = 848\,K$, $A_f = 923\,K$, $M_s = 656\,K$ and $M_f = 503\,K$. The change in specimen length, $\Delta l_{M\to A}$ caused by austenitic transformation was about 0.039 mm, and $\Delta l_{A\to M}$ caused by martensitic transformation was about 0.046 mm, i.e. the change in specimen length was large, although little permanent deformation was obtained.

Fig. 2 shows the relationship between temperature and thermal expansion for the longitudinal specimen of $Co_{30}Ni_{20}Zr_{50}$ (no. 85-58). The shrinkage of the specimen, which was caused by the transformation from the low-temperature phase (B_f structure) to the high-temperature phase (B2 structure) on heating, was small compared with its expansion caused by the transformation from B2 to B_f structure. This trend never changed in 93 cycles of the heating and cooling process. It was also unchanged when the specimen was heated at rates of 950 K/3 min to 950 K/24 min, and when it was cooled naturally or at the rate of 950 K/3 min to 950 K/24 min. A large permanent elongation of 0.2 to 0.3% was, therefore, obtained at room temperature by each heating and cooling process. The fact that the difference between the A_s and A_f temperatures was larger compared to that in the Fe–15 Ni alloy indicates that the transformation from B_f to B2 structure proceeded gradually with increasing temperature.

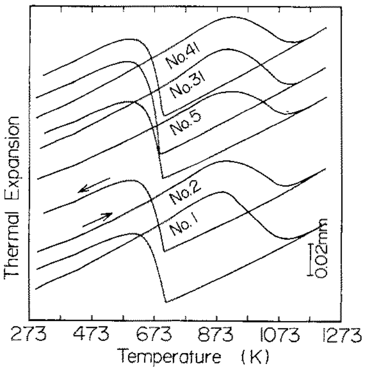

Figure 2 Dilatometric heating and cooling curves for the specimen (⊥) parallel to the columnar structure of $Co_{30}Ni_{20}Zr_{50}$ (no. 85-58).

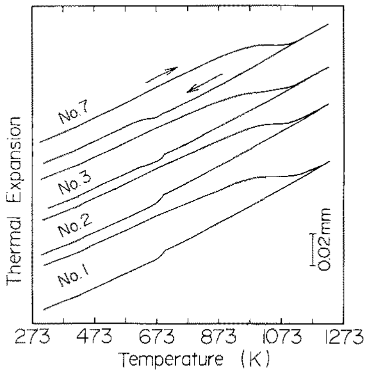

Figure 3 Dilatometric heating and cooling curves for the specimen (∥) perpendicular to the columnar structure of $Co_{30}Ni_{20}Zr_{50}$ (no. 85-58).

Fig. 3 shows examples of a similar relationship for the transverse specimen of $Co_{30}Ni_{20}Zr_{50}$ (no. 85-58) which was machined perpendicular to the direction of the elongated grains. The shrinkage of the specimen, which was caused by the transformation from B_f to B2 structure on heating was smaller compared with that shown in Fig. 2. The specimen showed not expansion but shrinkage, when it was cooled, that is, when it transformed from B2 to B_f structure. The shrinkage of the specimen on cooling changed to expansion when the heating and cooling process was repeated several times as shown in Fig. 3, although its expansion was very small. Thus, a large permanent shrinkage of about 0.2% was obtained on each heating and cooling process.

Fig. 4 shows examples of a similar relationship for the transverse specimen of another $Co_{30}Ni_{20}Zr_{50}$ (no. 85-69). The specimen showed not shrinkage but expansion as in the longitudinal specimen, when it transformed from B2 to B_f structure on cooling. This behaviour of the transverse specimen was different from that of specimen 85-58. However, its expansion was smaller than that of the longitudinal specimen and, consequently, permanent shrinkage was obtained after the heating and cooling process. Fig. 5 shows the elongation per cycle which was caused by the

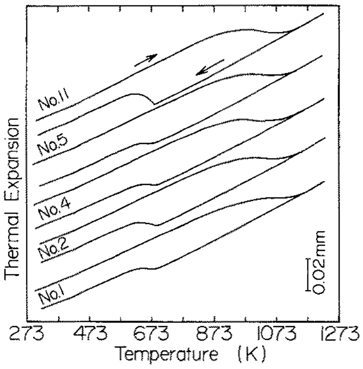

Figure 4 Dilatometric heating and cooling curves for the specimen (∥) perpendicular to the columnar structure of $Co_{30}Ni_{20}Zr_{50}$ (no. 85-69).

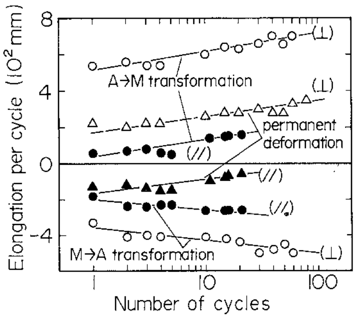

Figure 5 Elongation which was caused by the transformation during the heating and cooling process for $Co_{30}Ni_{20}Zr_{50}$ (no. 85-69). A → M transformation: transformation from B2 to B_f. M → A transformation: transformation from B_f to B2.

transformations on the heating and cooling process for 85-69 specimens. The permanent elongation per cycle increased and the permanent shrinkage per cycle decreased with increasing numbers of heating and cooling cycles, although both the elongation and the shrinkage per cycle, which were caused by transformations, increased with increasing number of cycles.

Fig. 6 shows some examples of similar relationships for the longitudinal specimen of $Co_{34}Ni_{16}Zr_{50}$ (no. 85-68). The transformation temperatures from B_f to B2 structure on heating and from B2 to B_f structure on cooling were lower than those for $Co_{30}Ni_{20}Zr_{50}$. Permanent deformation was not observed after the heating and cooling process, although the change in specimen length, which was caused by transformations on heating or on cooling, was relatively large. Fig. 7 shows a similar relationship for the transverse specimen of $Co_{34}Ni_{16}Zr_{50}$. The specimen had a remarkably smaller change in length caused by transformations, than had the longitudinal one. In the transverse specimen, no permanent shrinkage nor elongation was observed. Fig. 8 shows the elongation per cycle which was caused by transformation in the heating and cooling process for 85-68 specimens. The change of elongation per cycle for the longitudinal specimen was not observed, but the shrinkage per cycle for the transverse specimen increased with increasing number of cycles, although permanent deformation was not obtained for either specimen.

Fig. 9 shows the specimen configurations after the heating and cooling process for $Co_{30}Ni_{20}Zr_{50}$ (no. 85-58). The longitudinal specimen had considerably larger elongation and the transverse one had the larger shrinkage. A characteristic feature showing the deformation along elongated grain boundaries was observed on the specimen surfaces. Permanent elongation and permanent shrinkage were observed parallel and perpendicular to the direction of the elongated grains, respectively. In specimen 85-69, the specimen shapes after the heating and cooling process were macroscopically similar to specimen 85-58. Fig. 10 shows the transverse cross-section for the longitudinal specimen 85-69 after the heating and cooling process. The shrinkage in the transverse direction of the longitudinal specimen was not symmetrical and the crystal orientation of the grains might affect the permanent deformation. On the processed specimen surfaces of $Co_{34}Ni_{16}Zr_{50}$, a similar characteristic feature was also observed, although no permanent deformation was obtained after heating and cooling.

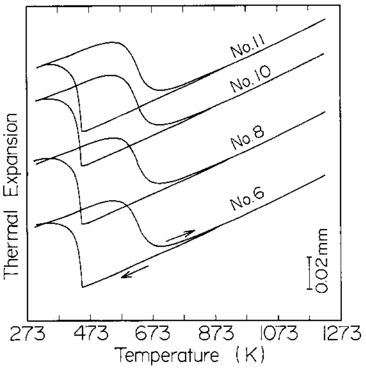

Figure 6 Dilatometric heating and cooling curves for the specimen ($\perp$) parallel to the columnar structure of $Co_{34}Ni_{16}Zr_{50}$ (no. 85-68).

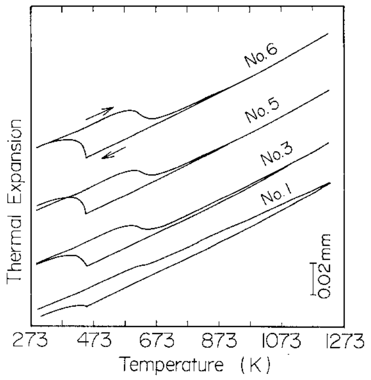

Figure 7 Dilatometric heating and cooling curves for the specimen ($\parallel$) perpendicular to the columnar structure of $Co_{34}Ni_{16}Zr_{50}$ (no. 85-68).

4. Discussion

4.1. Some examples of permanent deformation caused by phase transformation

When a rod specimen is rapidly cooled from elevated temperatures, as in water-quenching, a temperature gradient exists from the cooled surface to the centre of the specimen, depending on its thermal conductivity. Thus, when the specimen is cooled through the transformation temperature, phase transformation occurs gradually from the surface to the centre of the specimen, depending on the temperature gradient. The surface layer which is transformed earlier at a nominal critical temperature deforms its neighbouring region plastically, when the transformed region has a higher

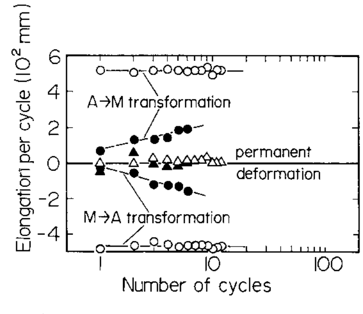

Figure 8 Elongation which was caused by the transformation during the heating and cooling process for $Co_{34}Ni_{16}Zr_{50}$ (no. 85-68); (○, △) $\perp$ direction, (●, ▲) $\parallel$ direction.

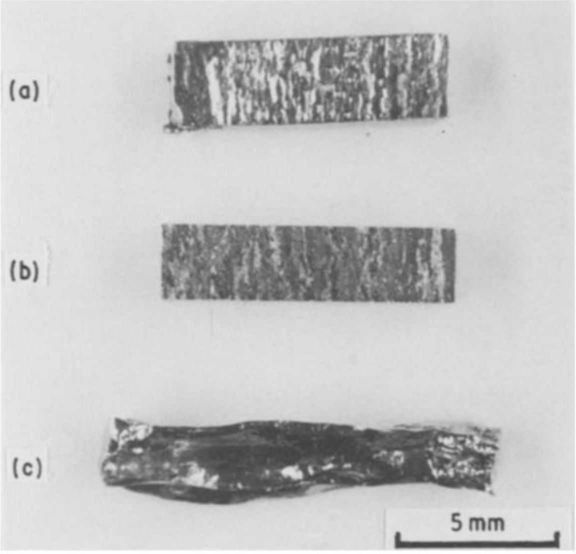

Figure 9 Configurations of specimens after the heating and cooling process for $Co_{30}Ni_{20}Zr_{50}$ (no. 85-58): (a) specimen perpendicular to the columnar structure after 21 cycles; (b) as-cast specimen perpendicular to the columnar structure; (c) specimen parallel to the columnar structure after 93 cycles

strength than the untransformed one. Next, the plastically deformed region is transformed later with decreasing temperature. This process is repeated from the surface to the centre of the specimen as the temperature falls. Consequently, permanent deformation is obtained when the specimen is rapidly cooled through the transformation temperature. One example of this type of permanent deformation was observed for iron. Iron has a transition temperature between alpha and gamma phases at 1183 K. When a rod specimen was rapidly cooled from a high temperature, permanent elongation was observed, depending on the cooling rate. The elongation was very small, and an elongation of 0.5% and 0.8% was obtained, when the heating and cooling process was repeated 10 and 30 times, respectively [4–6]. The other example is for uranium, which has alpha–beta and beta–gamma transformations with increasing and decreasing temperature. Permanent shrinkage of the specimen was observed in the case of alpha–beta transformation and permanent elongation was obtained in the case of beta–gamma transformation. The total change in specimen length was less than 1%, when the heating and cooling process was repeated 50 times, although permanent deformation increased with increasing graphite content [7].

Permanent deformation caused by phase transformation is also observed, when the specimen has a microstructure which has a laminated composition distribution, parallel to the direction of the specimen length. One example was observed for a maraging steel which was cold rolled by 70% followed by annealing. Permanent shrinkage and elongation as large as 0.2% per cycle was obtained for the specimens parallel and perpendicular to the rolling direction, respectively, when the specimens were cyclically heated and cooled through the transformation temperature. This fact was interpreted as follows: the specimen had a laminated microstructure which was arrayed parallel to the rolling direction by the heavy cold rolling, and the laminated structure had different transformation temperatures from austenite to martensite phase. When the specimen was cooled from temperatures above the austenite transformation temperature, one part of the specimen was first transformed to martensite phase and resulted in a large expansion parallel to the laminated direction. The neighbouring part was, therefore, deformed plastically by the transformed part, followed by transformation to the martensite phase and expansion parallel to the laminated direction. This process was repeated with decreasing temperature and, consequently, a large permanent deformation was obtained, when the specimen was heated and cooled cyclically [8].

The other example was observed for the laminated plate which was composed of maraging steels with different transformation temperatures from austenite to martensite phase. Permanent elongation and

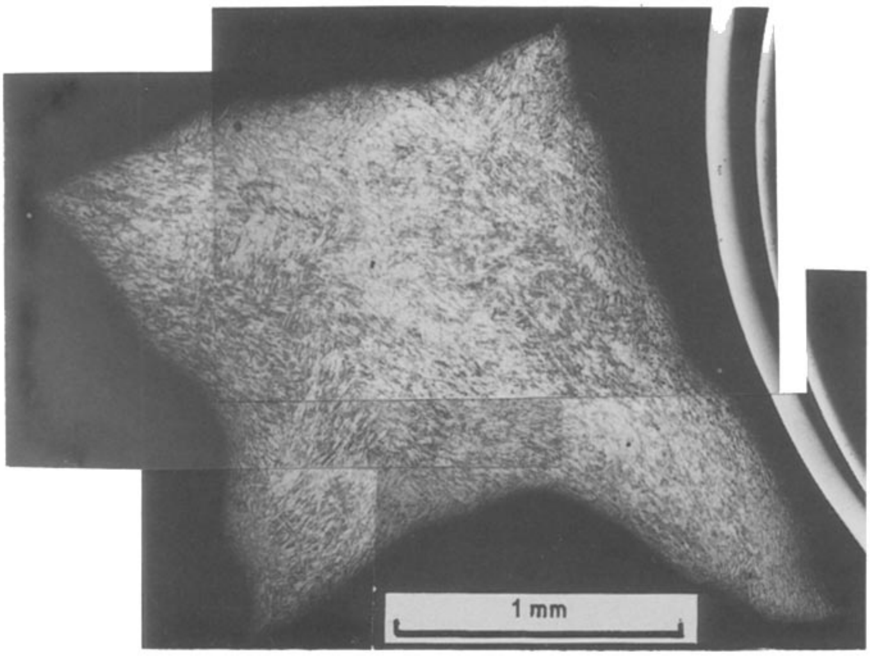

Figure 10 Transverse cross-section of $Co_{30}Ni_{20}Zr_{50}$ (no. 85-69) after 80 cycles of the heating and cooling process.

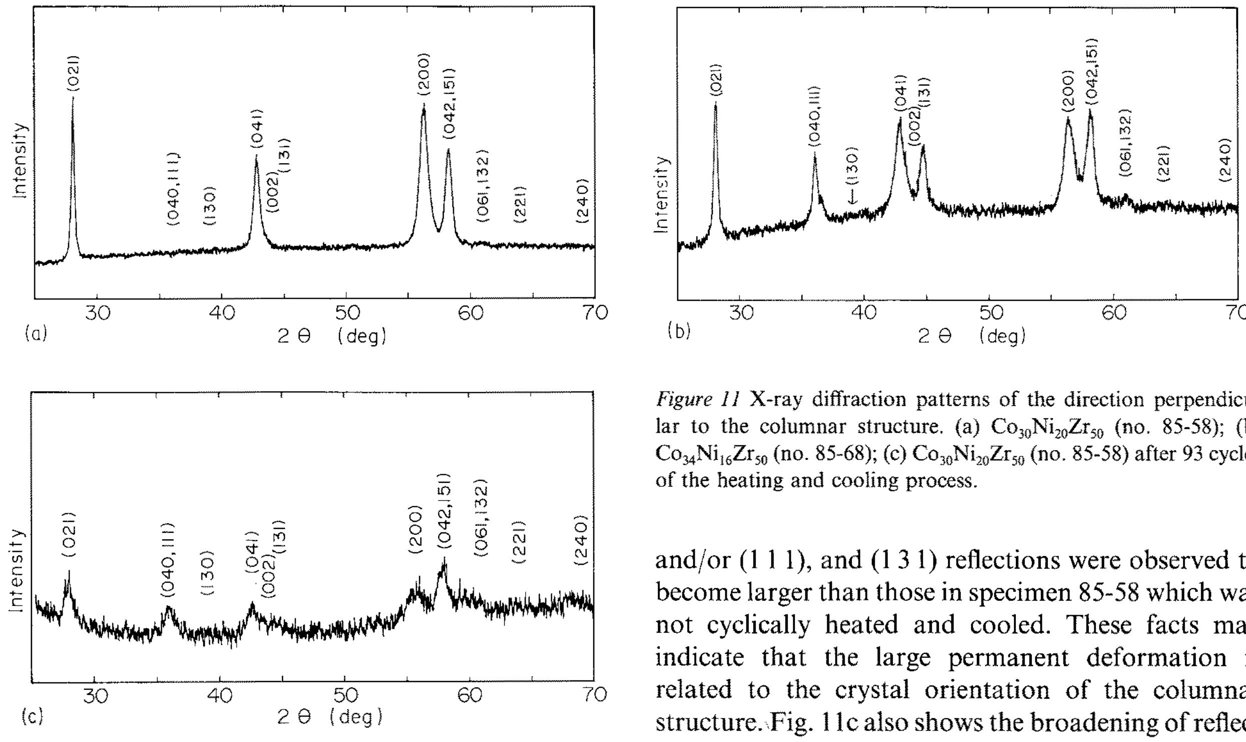

Figure 11 X-ray diffraction patterns of the direction perpendicular to the columnar structure. (a) $Co_{30}Ni_{20}Zr_{50}$ (no. 85-58); (b) $Co_{34}Ni_{16}Zr_{50}$ (no. 85-68); (c) $Co_{30}Ni_{20}Zr_{50}$ (no. 85-58) after 93 cycles of the heating and cooling process.

shrinkage as large as 0.3% per cycle were obtained for the specimens parallel and perpendicular to the laminated direction, respectively, when the specimen was heated and cooled cyclically [9].

4.2. Comparison between the reports and the experimental results

The linear analysis of the compositions was carried out for the as-cast Fe–15 wt % Ni used in this experiment, using an electron probe micro-analyser. The probe was scanned on the transverse cross-section of the longitudinal specimen. Although iron and nickel were observed not to be mixed uniformly and a composition gradient was seen along the radial direction of the specimen, no permanent deformation was found after the heating and cooling cycle. Meanwhile, in $Co_{30}Ni_{20}Zr_{50}$, no composition gradient was observed, although it showed a large permanent deformation after the heating and cooling process. Thus, it was concluded that permanent deformation of $Co_{30}Ni_{20}Zr_{50}$ was not caused by the inhomogeneous distribution of alloying elements.

The columnar structure of the specimens may not affect the permanent deformation explicitly, because both Fe–15 wt % Ni and $Co_{34}Ni_{16}Zr_{50}$ showed no large permanent deformation. Second phases such as $CoZr_2$, Co_2Zr, etc., were observed in both $Co_{34}Ni_{16}Zr_{50}$ and $Co_{30}Ni_{20}Zr_{50}$. Thus, second phases have no influence on the permanent deformation caused by the transformation.

Fig. 11 shows the X-ray diffraction pattern (copper target and nickel filter) of the transverse cross-section of the columnar structure for (Co, Ni)Zr. In $Co_{30}Ni_{20}Zr_{50}$ (0 4 0) and/or (1 1 1), and (1 3 1) reflections were hardly observed (Fig. 11a) or had a low intensity. In $Co_{34}Ni_{16}Zr_{50}$ these reflections had a relatively high intensity (Fig. 11b). Fig. 11c shows the X-ray diffraction in $Co_{30}Ni_{20}Zr_{50}$ (no. 85-58) which was given 93 cycles of heating and cooling. (0 4 0) and/or (1 1 1), and (1 3 1) reflections were observed to become larger than those in specimen 85-58 which was not cyclically heated and cooled. These facts may indicate that the large permanent deformation is related to the crystal orientation of the columnar structure. Fig. 11c also shows the broadening of reflection peaks, considered to be caused by plastic deformation during the heating and cooling process.

Fig. 12 shows the microstructures of the longitudinal specimen of $Co_{30}Ni_{20}Zr_{50}$ (no. 85-69) which was given 80 cycles of heating and cooling. The microstructure of the longitudinal cross-section was observed to be the cast structure elongated parallel to the direction of permanent elongation. In the microstructure of the transverse cross-section, the elongated cast structure was also observed (see also Fig. 10).

The large permanent deformation is considered to be caused by the large distortion of lattice structure from B2 to B_f at the martensitic transformation. Fig. 13 shows the change in lattice structure which is considered to be caused by the transformation from B2 to B_f structure. The (0 1 1) plane of the B2 structure is considered to agree with the (0 0 1) plane of the B_f structure. A large elongation is expected in the ⟨0 1 0⟩ direction of B_f and a shrinkage is also expected perpendicular to the ⟨0 1 0⟩ direction of B_f, when the ⟨1 1 1⟩ direction of B2 transforms to the ⟨0 1 0⟩ direction of B_f. The untransformed parts adjacent to transformed regions are also deformed plastically because of the good ductility of B2 [1, 3, 10] and the high strength of B_f [3], when the martensitic transformation from B2 to B_f occurs inhomogeneously, e.g. because of the non-uniform distribution of temperature throughout the specimen. Then, the plastically deformed regions are transformed from B2 to B_f and this process is repeated, which may result in the large permanent elongation and shrinkage.

This mechanism for the large permanent deformation may not always explain the difference between the behaviours of $Co_{34}Ni_{16}Zr_{50}$ and $Co_{30}Ni_{20}Zr_{50}$, although this difference may result from that of the preferred orientation as shown in Fig. 12. In order to clarify the orientation effect on the permanent deformation, further experiments will be required for (Co, Ni)Zr single crystals with various orientations and various nickel contents.

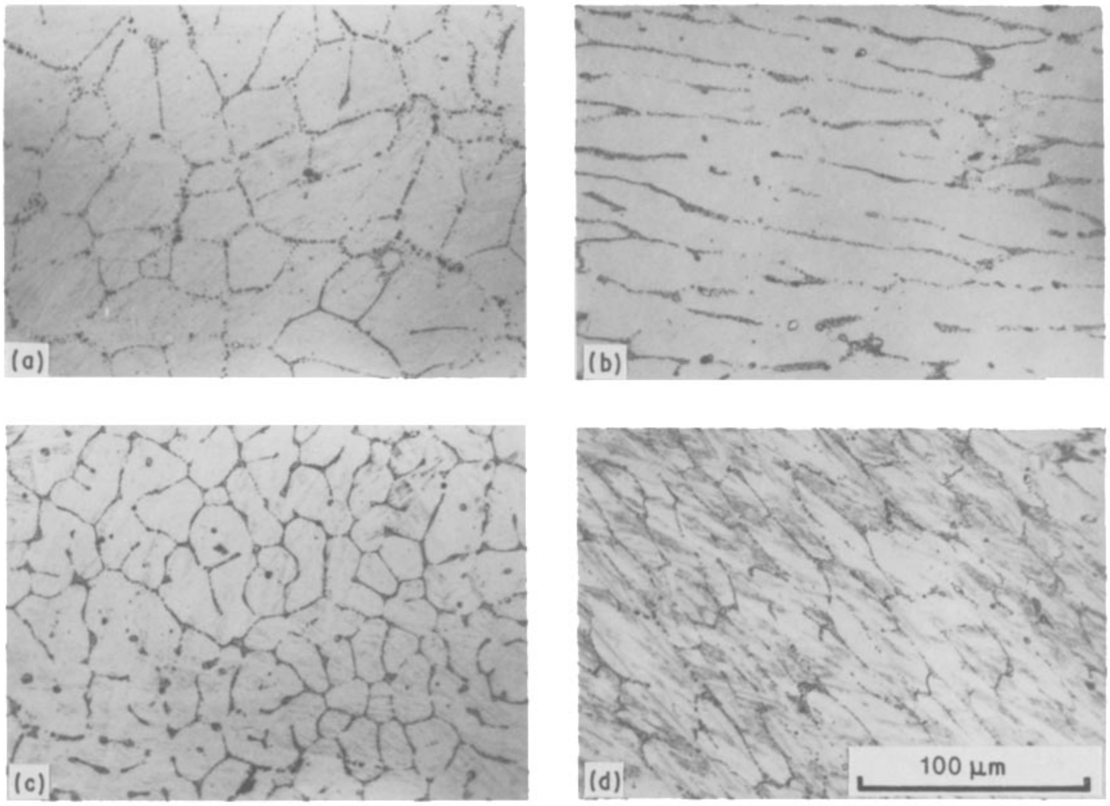

Figure 12 Microstructures of $Co_{30}Ni_{20}Zr_{50}$ (no. 85-69) after the heating and cooling process. Longitudinal cross-sections (a) as-cast and (b) after 80 cycles, and transverse cross-sections (c) as-cast and (d) after 80 cycles.

5. Conclusion

(Co, Ni)Zr intermetallic compounds, which have B_f structure at room temperature and B2 structure at elevated temperatures, were heated and cooled repeatedly in the temperature range from 1223 K to room temperature. This process produced a large permanent deformation in $Co_{30}Ni_{20}Zr_{50}$. This was caused by larger deformation at the transformation from B2 to B_f on cooling than that occurring from B_f to B2 on heating. Permanent elongation as large as 0.2 to 0.3% per cycle was observed for the specimen parallel to the columnar structure, which grew from the bottom to the top of the button ingot, and permanent shrinkage as large as 0.2% per cycle was observed for the specimen perpendicular to the columnar structure. For example, a permanent elongation of about 30% was obtained after 93 cycles of the heating and cooling process in the former specimen, but no permanent elongation nor shrinkage was observed in the specimens parallel and perpendicular to the columnar structure for $Co_{34}Ni_{16}Zr_{50}$. The latter alloy had a different preferred orientation of the columnar structure from the former. These facts indicate that the crystal orientation influenced the permanent deformation caused by this transformation.

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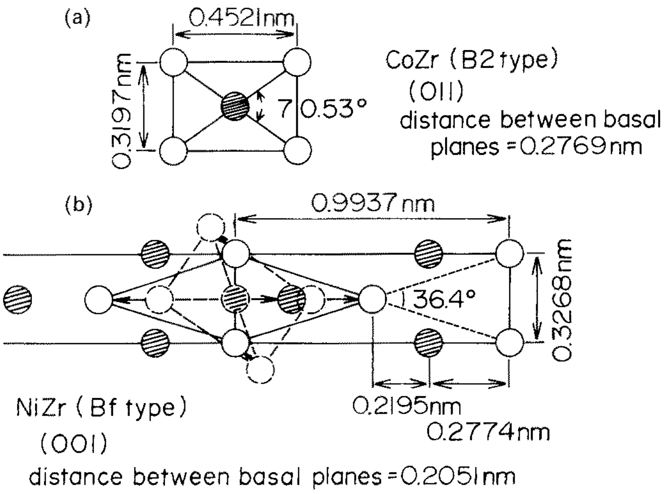

Figure 13 Structure change from B2 to B_f structure. (a) B2 structure, and (b) B_f structure.

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