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Variation in transformation hysteresis in pure cobalt with transformation cycles

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Abstract

Details of the transformation in pure cobalt were measured by a calorimetric method in order to clear the transformation cycle dependence of the transformation behaviour. Effects of transformation cycles are discussed on the basis of the generation and rearrangement of transformation-induced defects.

Keywords: Cobalt; Martensitic transformation; Thermal hysteresis; Transformation temperature; Lattice defects

1. Introduction

The equiatomic nickel–titanium alloy shows a shape memory effect which is caused by a martensitic transformation. Its transformation behaviour is sensitive not only to compositional variation [1–5] and applied stress [6] but also to transformation cycles [7–13]. Repetition of the transformation influences the transformation temperature and the stability of each phase in NiTi. The effect of transformation cycles is taken to be attributable to defects such as dislocations introduced with the transformation [11,14], because the martensitic transformation of NiTi depends markedly on the change in inner state. Although materials such as NiTi, NiAl, AgCd, AuCd, Cu–Al–Ni, etc. show the martensitic transformation and shape memory [15], the transformation cycle dependence of their transformation behaviours has not yet been satisfactorily elucidated.

On the other hand, it is well known that pure cobalt shows the martensitic transformation from the α phase of h.c.p. structure of the β phase of f.c.c. structure near 700 K and this structural change facilitates the generation of stacking faults during the transformation. Although most shape memory alloys have an ordered lattice, a shape memory effect in cobalt is also reported to accompany its transformation in spite of it being a pure element [16,17]. The intrinsic property of a modification of the transformation behaviour caused by repeated transformations is important in understanding the relation between the transformation mechanism and structural defects in shape memory alloys.

So far, many investigations on pure cobalt as one of the basic materials have been performed, but the effect of transformation cycles has not yet been adequately elucidated. Recently the author investigated the behaviour of the $\alpha \rightarrow \beta$ transformation in cobalt during transformation cycles and found that the endothermic peak due to the $\alpha \rightarrow \beta$ transformation shifts to the high temperature side [18], although the temperature of the endothermic peak of the transformation in NiTi from the low temperature phase (monoclinic) to the high temperature phase (CsCl) [1] decreases with increasing transformation cycles [19–21]. In the present work, details of the transformation in cobalt were measured by a calorimetric method in order to reveal the characteristic behaviours of $\alpha \rightleftharpoons \beta$ transformation temperatures with thermal hysteresis.

2. Experimental procedures

A commercial plate of cobalt (purity 99.9%) 1 mm in thickness was cold rolled to 0.5 mm and a specimen was cut off the rolled plate. The specimen was annealed at 1273 K in a vacuum of 10^{-4} Pa in order to remove the influence of cold rolling and cutting. Measurement

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of the transformation behaviour was performed at a thermal cycle rate of 17×10^{-2} K s^{-1} using a differential scanning calorimeter (DSC) for up to 30 cycles.

3. Experimental results and discussion

The results of the calorimetric measurement of the endothermic ($\alpha\rightarrow\beta$ transformation) and exothermic ($\beta\rightarrow\alpha$ transformation) behaviours during thermal cycling are shown in Figs. 1 and 2 respectively. The endothermic peak shifts to the high temperature side with increasing number of thermal cycles as shown in Fig. 1. Moreover, the peak becomes sharper, which implies that thermal cycles facilitate the progress of the transformation in cobalt, in contrast with the thermal cycle dependence of the transformation in NiTi [14,21]. Regarding the transformation in cobalt, it is thought that because of the high transformation temperature, the rearrangement of defects introduced by the transformation is helpful for further progress of the transformation. The tendency to become sharper is also observed in the $\beta\rightarrow\alpha$ transformation as shown in Fig. 2. However, the exothermic peak of the $\beta\rightarrow\alpha$ transformation shifts to the low temperature side. The onset points of the peaks, which correspond to the start temperature of each transformation, are summarized in Fig. 3 as a function of the number of transformation cycles. The temperature width between the start temperatures of the $\alpha\rightleftharpoons\beta$ transformations displays a marked increase from 40 to 75 K over 30 cycles as shown in Fig. 3. Such an enlargement of the thermal hysteresis implies a change in inner state which is attributable

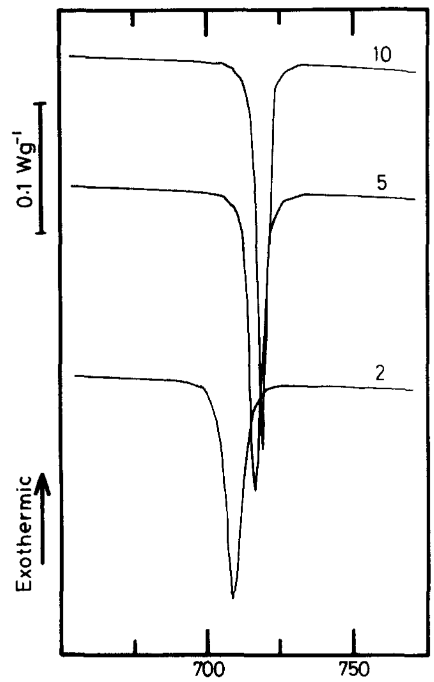

Fig. 1. Endothermic behaviour showing the $\alpha\rightarrow\beta$ transformation in cobalt during heating. The numbers correspond to the number of transformation cycles.

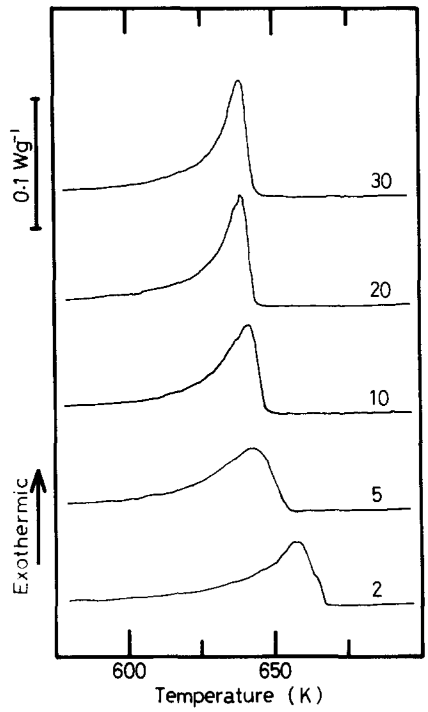

Fig. 2. Exothermic behaviour showing the $\beta\rightarrow\alpha$ transformation in cobalt during cooling. The numbers correspond to the number of transformation cycles.

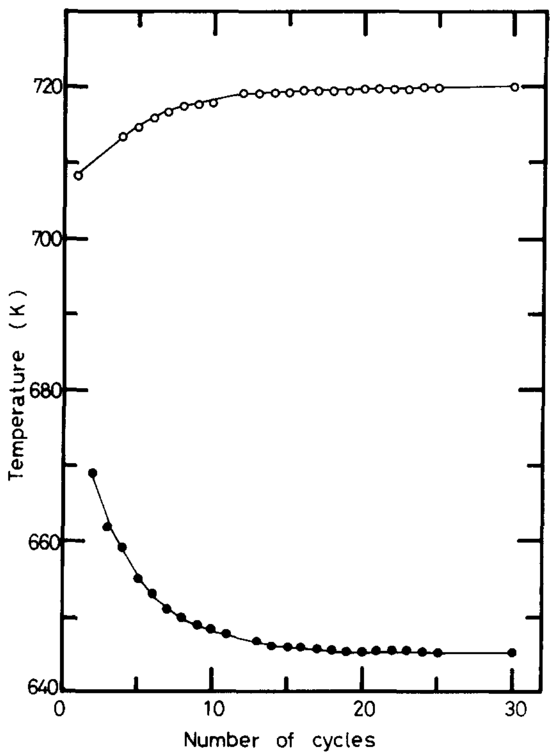

Fig. 3. Temperatures of $\alpha\rightarrow\beta$ (O) and $\beta\rightarrow\alpha$ (●) transformations as a function of the number of cycles.

to the increase in lattice defects induced by the transformation, i.e. the increase in non-chemical free energy such as strain energy and surface energy of a phase boundary [18]. Therefore the transformation behaviour of cobalt during thermal cycling depends on the generation and rearrangement of transformation-induced defects.

Although the transformations in cobalt and NiTi are sensitive to the presence of defects, because the transformation behaviours depend strongly on the repetition of the transformation, the shift in the transformation temperature of cobalt from the low temperature phase to the high temperature phase is opposite to that of NiTi during transformation cycling. Such a transformation behaviour of cobalt, rather than that of NiTi, is considered as a typical phenomenon due to the increase in non-chemical free energy which is obstructive in starting the transformation. The difference between the effects of transformation cycles on cobalt and NiTi may be attributed to differences in crystal structure and in the microstructure of defects such as dislocations and stacking faults or to the presence of some disorder in the atomic arrangements of NiTi. For a better understanding of the transformation cycle effect, detection of the transformation-induced defects is required by measurements of transmission electron microimages and physical properties.

4. Conclusions

The transformation behaviour of pure cobalt depends markedly on the thermal history of the transformation, and the hysteresis between $\alpha \rightleftharpoons \beta$ transformation temperatures increases as the transformation is repeated. The change in the transformation behaviour of cobalt with transformation cycles is considered as a phenomenon which is based on the increase in non-chemical free energy, and lattice defects play an important role in such a transformation behaviour. Moreover, with increasing number of transformation cycles, the calorimetric peak becomes sharper, which is attributable to the rearrangement of lattice defects generated by the transformation.

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