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Internal friction of Fe–Mn–Si–Cr shape-memory alloy

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Abstract

Low-frequency internal friction and elastic moduli of Fe–Mn–Si–Cr shape-memory alloy were measured as a function of temperature from 120 K to 500 K. Two peaks appear in the internal friction curve on cooling and two other peaks on heating. Two of them occur around the phase transformation, and the other two are supposed to be related to the antiferromagnetic transformation. The elastic moduli (square of frequency) show a stepwise change, rather than the steep minimum observed in shape-memory alloys that undergo thermoelastic martensitic transformation. The effect of cooling/heating rate and of frequency was investigated and a conformity with Delorme's model was confirmed except for the modulus defect behaviour.

1. Introduction

Since the discovery of the shape-memory effect in the Au–Cd alloy by Chang and Read in 1951 [1], many alloys such as Ni–Ti, Cu–Zn–Al and Cu–Al–Ni have been reported to show this peculiar effect, which is caused by the martensitic transformation in the alloy. It has been reported that the thermoelastic martensitic transformations – both forward and reverse – in these shape-memory alloys are accompanied by internal friction peaks and the modulus defect (frequency anomaly). Reports on the behaviour of internal friction peaks and the modulus defect are not perfectly consistent with each other and they are, in general, very complicated, depending not only on the authors but on the measurement parameters and the history of the specimen, either thermal or mechanical.

It is almost certain that the internal friction peaks are directly connected with the martensitic or reverse transformations. Therefore investigation of the elastic and anelastic characteristics of shape-memory alloys should improve our knowledge of transformation mechanisms.

Martensitic transformations in iron-based alloys are usually non-thermoelastic and have been considered disadvantageous for the occurrence of the shape-memory effect. But the shape-memory effect has been reported recently in some iron-based alloys, such as Fe–Pd [2], Fe–Pt [3], Fe–Ni–Ti–Co [4] and Fe–Mn–Si [5]. In iron-based shape-memory alloys, martensites with a very large thermal hysteresis are formed. Although these martensites are not typically thermoelastic as in non-iron-based alloys, they possess the property of growing or shrinking by boundary motion to some degree, too.

In this work, internal friction and the modulus were investigated in the alloy Fe–Mn–Si–Cr, which has recently been developed and put into practical use [6]. The martensites of this alloy are non-thermoelastic, and the shape-memory effect is achieved by the reverse transformation of the stress-induced martensites by heating above the A_f temperature. In thermoelastic martensites such as Ni–Ti, the deformation of the alloy is due to deformation twinning or to the motion of martensite boundaries, and the deformed alloy recovers its former shape by heating above the A_f temperature. Therefore, the mechanism of the shape-memory effect in the alloy Fe–Mn–Si–Cr is somewhat different from that in Ni–Ti and others. How this difference manifests itself in the mechanical behaviour is the point of interest in the present work. Another point of interest is the effect of the antiferromagnetic transformation of this alloy on the mechanical characteristics.

The aims of this paper are to describe the results of internal friction and elastic moduli measurements as a function of temperature from 100 to 500 K, which show various behaviours, and to discuss these results in connection with the martensitic transformation and with the antiferromagnetic property of the alloy.

2. Experimental details

The specimens were prepared by induction furnace melting using high-purity iron, manganese, silicon and chromium. The chemical composition of the alloy is

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shown in Table 1. The ingot, of width 15 cm, was heated to 1423–1473 K, soaked at the same temperature for 1 h, and then hot-rolled to a thickness of 3 mm. The hot-rolled sheet was cold-rolled to the final thickness of 1 mm. Specimens for internal friction measurement were cut from the cold-rolled sheet to the size of 110×4×1 mm after annealing at 873 K for 30 min.

Internal friction measurements were made during thermal cycling between 100 and 500 K. The cooling and heating rate was mostly 2 K min^{-1}, but for the investigation of the effect of cooling/heating rate, several higher rates were adopted in some measurements. The measurements were made on a low-frequency inverted pendulum of Kê type (Sinku-Riko IFM-1500L). The calculation of internal friction and the recording of data were completely automatic; the internal friction and frequency versus temperature were plotted by a desktop computer. The resolution in the results was quite good, as is seen in Fig. 1.

The electrical resistivity was measured on the same specimen by the d.c. four-probe method. Néel temperature T_N was determined by a vibrating-sample magnetometer.

3. Results and discussion

3.1. Results on the as-quenched specimen

Figure 1 shows the internal friction Q^{-1} and the modulus (the square of the frequency f^2 is used instead) of the specimen, which was quenched after annealing at 873 K for 30 min (the "as-quenched" specimen). The cooling curve presents two internal friction peaks: we call the lower-temperature one at 238 K peak C_1, and the higher-temperature one at 275 K, peak C_2. On heating from the lowest temperature a peak appeared at the temperature corresponding to the C_1 peak, which we call the H_1 peak, but no peak appeared corresponding to C_2. A very large sharp peak was observed at 406 K (H_2 peak). Q^{-1} decreased gradually by holding the specimen at 450 K and reached a constant value (background value). No peak appeared on cooling down from 450 K at the temperature corresponding to the H_2 peak.

The modulus changed stepwise at temperatures corresponding to the C_1 (H_1) and H_2 peaks. These modulus defects will be called the C_1 step, and so on. Such a large stepwise temperature variation of the modulus is quite different from the case of thermoelastic shape-memory alloys, in which the modulus shows a sharp minimum near the phase transition temperature [7, 8].

TABLE 1. Chemical composition of the specimen (mass %)

Mn	Si	Cr	C	N	P	S	Fe
28.18	6.04	5.03	0.005	0.0027	0.004	0.007	balance

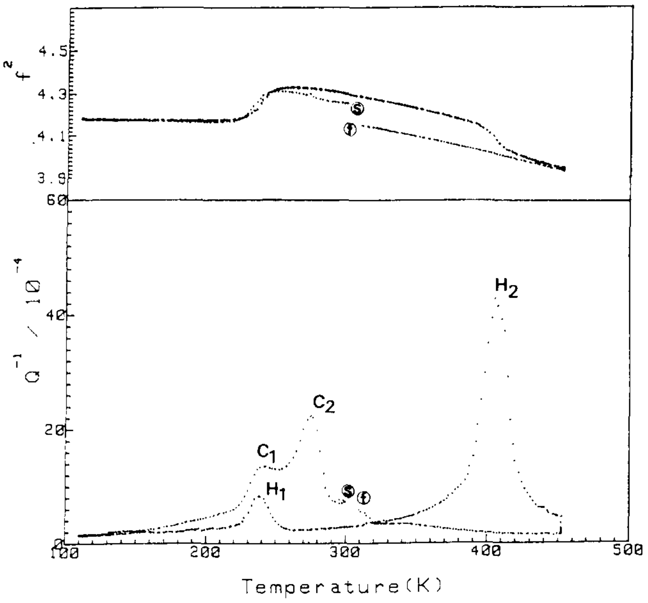

Fig. 1. Internal friction Q^{-1} and square of frequency f^2 of as-quenched specimen. Temperature cycle of measurement begins at s and finishes at f.

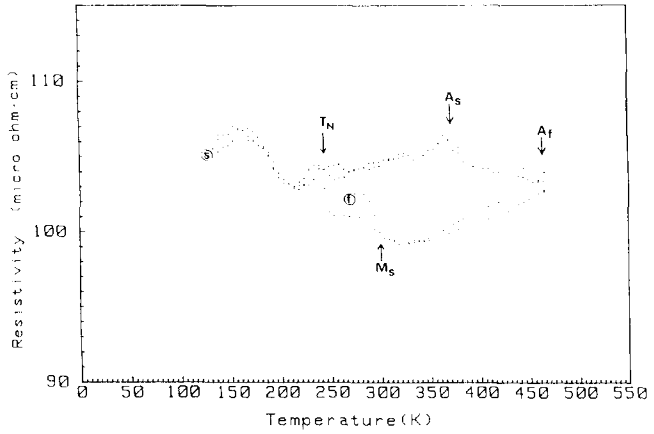

Fig. 2. Electrical resistivity. Measurement was done during two temperature cycles continuously.

The change in f^2 divided by f^2, $\Delta f^2/f^2$, was 0.029 and 0.038 for the H_2 and C_1 steps respectively. These values are compared with the internal friction peak height corrected for the background, 0.0042 and 0.0006 respectively. If the internal friction peak is of a relaxation type it is expected that $\Delta f^2/f^2$ is equal to twice the peak height. Clearly, this is not the case.

3.2. Correspondence between internal friction peak and the phase change

Figure 2 shows the result of resistivity measurement while cycling temperature twice from 120 to 460 K. From this $A_s=370$ K, $A_f=460$ K (or perhaps higher) and $M_s=300$ K were determined. M_f is not determined clearly. Electrical resistivity behaves rather anomalously below T_N, which was determined as 243 K by a magnetic measurement.

It is obvious that the peak H_2 corresponds to the reverse transformation. The fact that Q^{-1} decreased during holding at 450 K (Fig. 1) suggests that the reverse transformation has not yet finished at that temperature. The C_2 peak is considered to correspond to the martensitic transformation. This peak has a long tail towards the lower-temperature side, which shows that the transformation continues down to perhaps lower temperature than our measurement limit. Peaks C_1 and H_1 are different in nature from the other two because they appear at nearly the same temperature on cooling and heating. From their peak temperature they are presumed to originate from the antiferromagnetic transformation.

3.3. *Effect of annealing and straining*

Results of measurement on the specimen slowly cooled to room temperature after annealing at 1273 K are shown in Fig. 3(a). C_2 diminishes and its lower-temperature side decreases very slowly, not reaching the background value even at the lowest temperature of measurement. C_1 and H_1 disappeared. On reheating, the H_2 peak was higher and steeper than for the as-quenched specimen, but the peak temperature increased by 14 K.

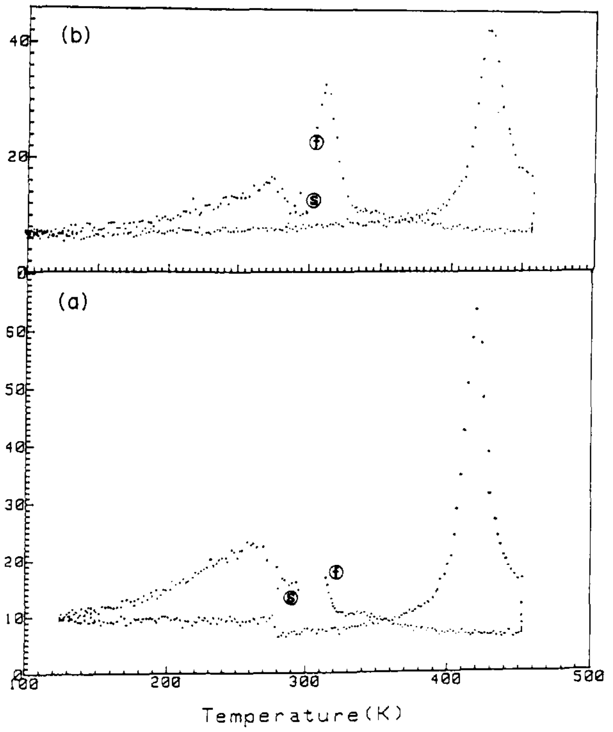

Fig. 3. Internal friction Q^{-1} of (a) annealed and slowly cooled specimen, and (b) of the specimen given 1% tensile strain after annealing.

Figure 3(b) is the result for the same specimen after 1% tensile strain was given. The heights of both C_2 and H_2 decreased and H_2 also shifted to higher temperature compared with the as-quenched specimen. It is suggested that the start of the reverse transformation was retarded by the strain. By holding the specimen at 460 K, Q^{-1} decreased gradually to the background value. This decrease of internal friction by fixing the temperature was observed in all measurements (Fig. 1). On further cooling, C_2 appeared but its shape was quite different from that observed before heating, and was similar to the as-quenched specimen, while the peak temperature was shifted to 310 K, higher than the as-quenched specimen.

It is supposed that peaks C_1 and H_1 are connected with the antiferromagnetic transformation, because they appeared around the Néel temperature; nonetheless, the precise mechanism is still unknown. Moreover, the disappearance of these peaks by the thermomechanical treatment is not understood. A further investigation is needed concerning this unsolved problem.

3.4. *Effect of cooling/heating rate*

The peak height was increased by increasing the temperature-change rate. When the heating rate was 5 K min^{-1}, the height of the H_2 peak corrected for the background was 113×10^{-4}, 2.7 times the value in Fig. 1, for which the heating rate was 2 K min^{-1}. The internal friction peaks observed in connection with most thermoelastic martensitic transformations were reported to become higher when the cooling/heating rate was increased. Delorme [9] derived the result that the internal friction of the preferential growth or reorientation of the martensite under the applied alternating stress is proportional to the cooling/heating rate dT/dt and is inversely proportional to the frequency f. The result of the present work is consistent with Delorme's model in this respect.

By changing the frequency from 2 Hz to 3 Hz the height of the H_2 peak decreased from 42×10^{-4} to 24.5×10^{-4}, the ratio being 0.58. The frequency dependence nearly conformed with Delorme's model, too.

3.5. *Modulus defect*

The most striking contrast between the present results and those on Ni–Ti and other thermoelastic martensites is the behaviour of the modulus near the temperature of the phase transformation. Instead of the generally reported sharp minimum associated with the phase transformation, in the Fe–Mn–Si–Cr alloy we observed a large and highly reproducible stepwise change. According to Delorme's model, a frequency change, not a minimum, of the size $\Delta f/f=Q^{-1}/2$ is expected. The $\Delta f/f$ value obtained in this work was several times larger than the internal friction peak height. A more reasonable explanation is the difference in the moduli of both phases. Estimating the martensite fraction of the alloy cooled down to the lowest temperature as 20–30% (depending on the cooling rate, thermal and mechanical history, etc.), it was derived from the modulus defect $\Delta f^2/f^2 = 0.029$ that the rigidity of the martensite phase is 10–13% larger than that of the parent phase. The value of $\Delta f^2/f^2$ depended neither on $\mathrm{d}T/\mathrm{d}t$ nor on frequency, which supports the above explanation. The temperature dependence of yield stress of this alloy is almost linear, but the gradient changes abruptly at the temperature M_s, being below M_s nearly twice as large as above M_s [6]. Such a behaviour of the yield stress is consistent with the supposition stated above that the rigidity of the martensite phase is higher than that of the parent phase.

4. Summary

In this paper we have observed four internal friction peaks in an iron-based shape-memory alloy Fe–Mn–Si–Cr, two on cooling and two on heating. Two peaks, C_2 and H_2, were due to martensitic and reverse martensitic transformations, respectively. The cooling/heating rate and frequency dependence of the peak height nearly conformed with Delorme's model. Corresponding to the peak, a stepwise modulus defect was observed, which was inconsistent with the Delorme's model and was explained by the difference in the moduli of both phases. Two other peaks around the Néel temperature were presumed to occur by the antiferromagnetic transformation but the mechanism of the stepwise modulus change that occurred in the same temperature range is not yet understood.

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