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Effect of thermal cycling on as-quenched and aged nickel-rich Ni–Ti alloy

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The effect of Ni_4Ti_3 precipitates on the structure and transformation sequences in Ni–49%Ti alloy has been investigated using internal friction, electrical resistivity and electron microscopy studies. It has been confirmed that in the alloy without precipitates the transformation occurs following the sequence B2 → R → M on cooling and M → B2 on heating with easily distinguished peaks on the internal friction curves and typical behaviour of the electrical resistivity, while the presence of the precipitates brings about complicated internal friction curves indicating either the appearance of two types of martensite or the transformation sequence: B2 → B2 + R → B2 + M → M.

1. Introduction

Ni–Ti alloys are best known and most technologically important shape memory materials, however, a number of different problems remain to be solved and the alloys still attract a good deal of interest. One of the difficulties concerns the transformation characteristics of Ni–Ti. The alloys exhibit so-called "premartensitic transition" which precedes the martensitic transformation and reveals in an electrical resistivity increase, extra reflection in electron diffraction patterns, additional peaks on DTA and international friction curves and other effects [1–5]. According to recent investigations [6, 7] the transformation sequence upon cooling is as follows: B2 → I(incommensurate phase) → R(commensurate phase) → M. This sequence, however, depends strongly on the composition and treatment of the alloy studied.

Recently, the effects of thermal cycling on the premartensitic and martensitic phenomena have been widely investigated. According to Miyazaki *et al.* [8] a shift of M_S was observed in the solution-treated alloys (irrespective of nickel content) while the transformation temperatures for aged nickel-rich alloys remained unchanged during cycling. These results were obtained for the alloys cycled up to 100 cycles at most. The effect of more thermal cycling up to 10000 times was examined by Tadaki *et al.* [9] in aged nickel-rich alloys. They showed that so-called "incomplete cycling" i.e. cycling causing only B2↔R transformation did not bring any changes in the transformation temperatures and structure of the alloy studied while the complete cycling (B2↔M) significantly affected both M_S and T_R temperatures, M_S being lowered whereas T_R was raised considerably.

The present work has been conducted to compare the transformations behaviour and the structure of the cycled, nickel-rich alloy with and without precipitates. Thus samples of the alloy were thermally cycled in the same conditions either directly after solution treatment or after solution treatment and aging and then examined by means of internal friction, electrical resistivity measurements and electron microscopy studies.

2. Experimental procedure

A Ni–49% Ti alloy, the preparation procedure of which was described earlier [5], was used in these experiments. The specimens in the form of strips 1 mm thick were solution treated at 700 °C for 15 min in argon atmosphere and quenched into methanol of -50 °C. A part of the specimens was then aged at 500 °C for 1 h. Subsequently, the specimens were cycled in the temperature range between -70 and $+60$ °C so that B2↔M transformations took place.

The transformation temperatures and their changes during cycling have been examined by the internal friction and electrical resistivity measurements. The internal friction measurements were conducted during cycling on a plate of $30 \times 10 \times 1$ mm^3 using an acoustic relaxator with the logarithmic decrement of damping. The speed of heating and cooling used was $2°\,\mathrm{min}^{-1}$. The electrical resistivity curves were recorded during cycling using a Diesselhorst compensator produced by "Tettex". The microstructural changes of the cycled alloy have been studied at room temperature by TEM observations. The JEM 200B (Jeol) electron microscope operating at 20 kV was used.

3. Results

The structure of the as-quenched material was confirmed to be the B2 ordered parent phase. Scarcely single dislocations were observed in the solution-treated sample (Fig. 1). In the aged sample fine, lenticular particles of rhombohedral Ni_4Ti_3 phase [5] occurred (Fig. 2).

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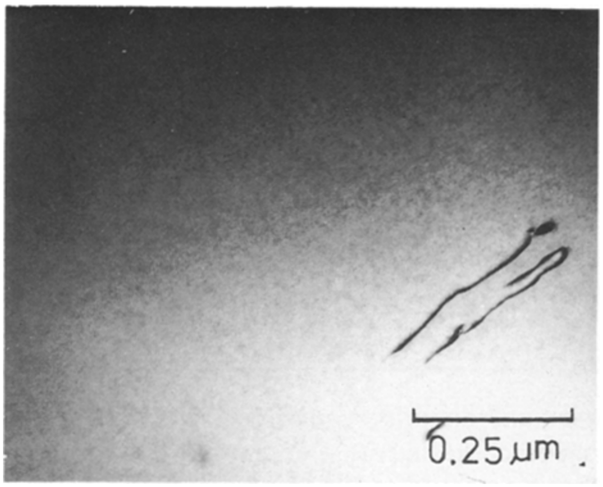


Figure 1 The structure of the quenched alloy.

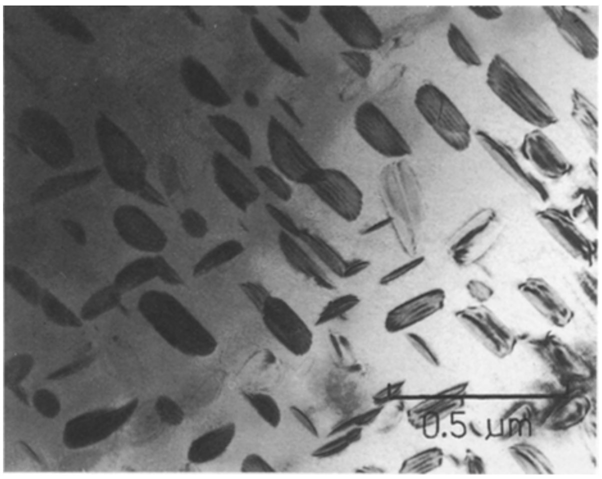


Figure 2 Ni_4Ti_3 precipitates in the alloy aged at $500\,°C\,h^{-1}$.

3.1. Effect of cycling on kinetics and structure of the as-quenched alloy

Figs 3 and 4 show internal friction and electrical resistivity curves for as-quenched samples subjected to the thermal cycling up to 100 times. On the internal friction curves obtained during cooling a strong peak corresponding to the martensitic transformation occurs. It shifts slightly towards lower temperatures with cycling (Fig. 3a). In the initial cycles apart from this main peak two additional, small peaks arise. One of them occurring just before the martensitic transformation can be connected with R-phase formation. It shifts towards higher temperatures with cycling. An origin of the second one, occurring in the range of parent phase will be discussed later.

The electrical resistivity of the sample increases gradually with cooling up to the maximum, then it drops quickly (Fig. 4a). This fall of the electrical resistivity occurs exactly at the temperature of the martensitic transformation peak on the internal friction curves. During heating only one, wide peak is observed on electrical resistivity curves (Fig. 4b), whereas on the internal friction curves there is one peak corresponding to the transformation and the other one occurring in the range of the parent phase (Fig. 3b). A

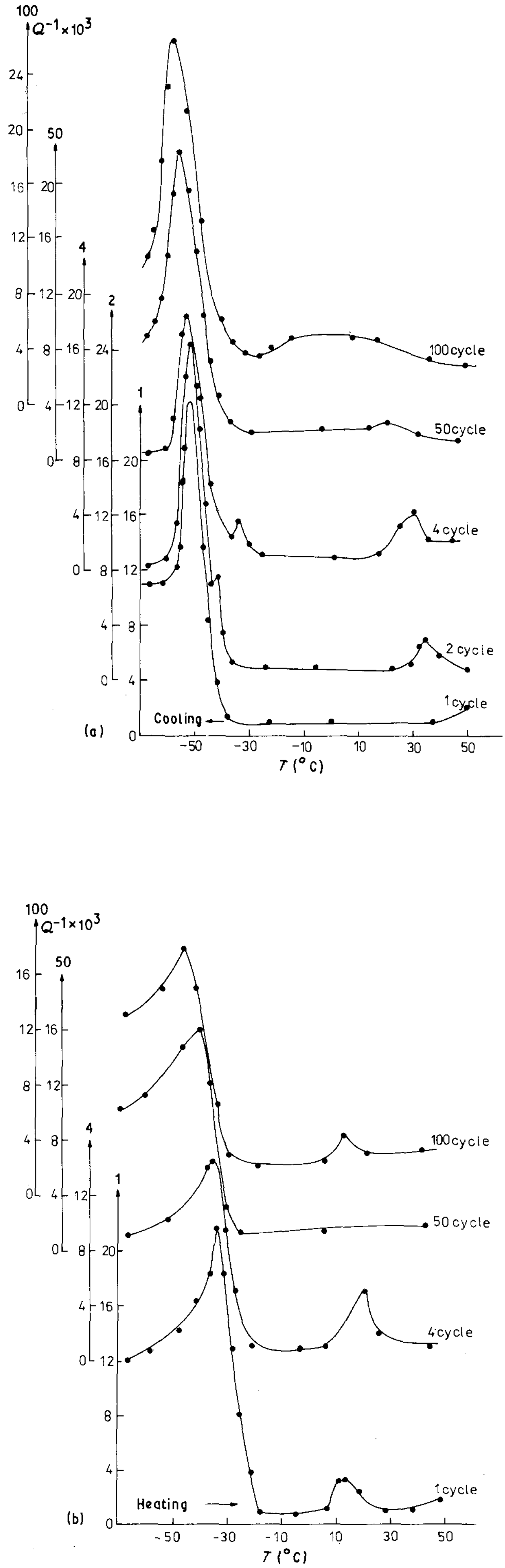
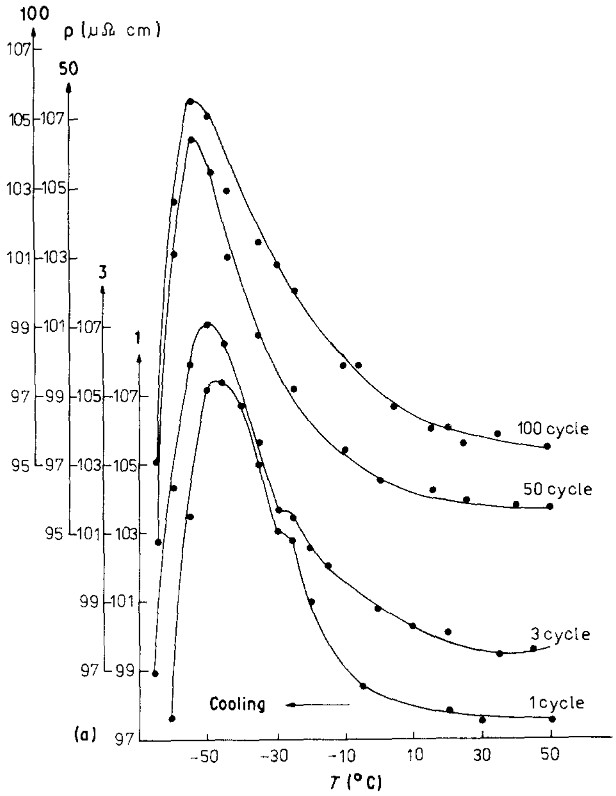


Figure 3 Internal friction curves for the quenched alloy. (a) on cooling, (b) on heating.



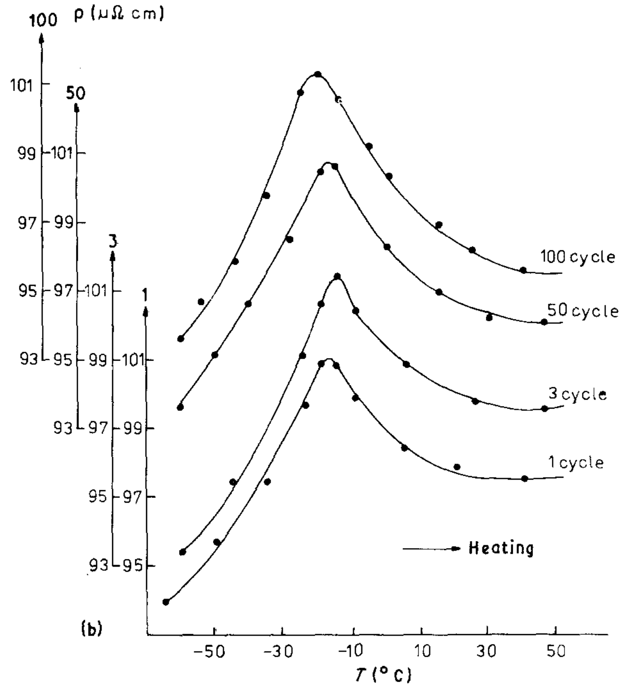


Figure 4 Electrical resistivity curves for the quenched alloy (a) on cooling (b) on heating.

slope of the transformation peak is small from the lower temperatures side and very high from the higher temperatures side. It also shifts towards lower temperatures with cycling.

Microstructural changes accompanied with the cycling are shown in Fig. 5. Dislocations have been generated in the first few cycles. They form arrays of parallel or semi-parallel lines (Fig. 5a) or in some regions they occur in rows (Fig. 5b). Slip traces are often visible in the matrix background (Fig. 5c).

Another substructural features that develop with cycling are linear vestigal ridges (Fig. 5d). We have not seen them after a single thermal cycle as the other authors did in copper-based alloys [11], but they appear in the sample after three cycles and become more numerous and sharply defined as the number of transformation cycles increases (Fig. 5e, f).

3.2. Effect of cycling on kinetics and structure of aged alloy

Figs 6 and 7 show internal friction and electrical resistivity curves for specimens aged at 500 °C for 1 h and then subjected to the thermal cycling. On the internal friction curves recorded during cooling three distinct peaks are observed for the first few cycles (Fig. 6a). This changes with increasing cycling into two effects. During heating also either two or three effects are visible (Fig. 6b).

The electrical resistivity measurements do not show these distinct effects. During cooling the resistivity starts to increase significantly at the temperature about 10 °C (this temperature increases with cycling) and falls again at the temperature about − 20 °C (this temperature decreases with cycling) (Fig. 7a). During heating there is one, wide peak observed on the electrical resistivity curves (Fig. 7b).

The structure of the alloy subjected to the thermal cycling does not differ much from this before cycling. The only visible effect of cycling is generation of some number of dislocations in the initial cycles (Fig. 8). They form low-angle boundaries (Fig. 8a) or interact with precipitates by Orowan mechanism (Fig. 8b). Even high numbers of cycling does not bring about any substantial changes in the microstructure of the alloy (Fig. 8c and d).

4. Discussion

It is to be noted that in aged specimens the M_s temperature increases significantly (of about 40 °C) comparing with the solution-treated specimen. This may be accounted for by the depletion of solute nickel atoms in the matrix accompanying the precipitation of Ni_4–Ti_3 particles. Similar behaviour of M_s in aged nickel-rich alloys has been observed [9, 12] while a slight decrease of M_s after aging has also been observed [2, 8]. The latter, however, dealt with the specimens aged at 400 °C, i.e. containing fine coherent particles. In this case the depletion of solute nickel atoms should be much smaller and the back stresses around precipitates much higher. This could lead to the depression of M_s.

The increase in M_s comparing with the solution-treated sample is much larger than that in A_s. This is probably because the particles are too large to act as obstacles impending the movement of R–M interfaces [9].

Thermal cycling of the Ni–Ti alloy brings about the lowering of M_s temperatures in both solution-treated and aged specimens. In the solution-treated specimen this decrease is slow but continuous, while in the aged specimen the first few cycles cause significant change

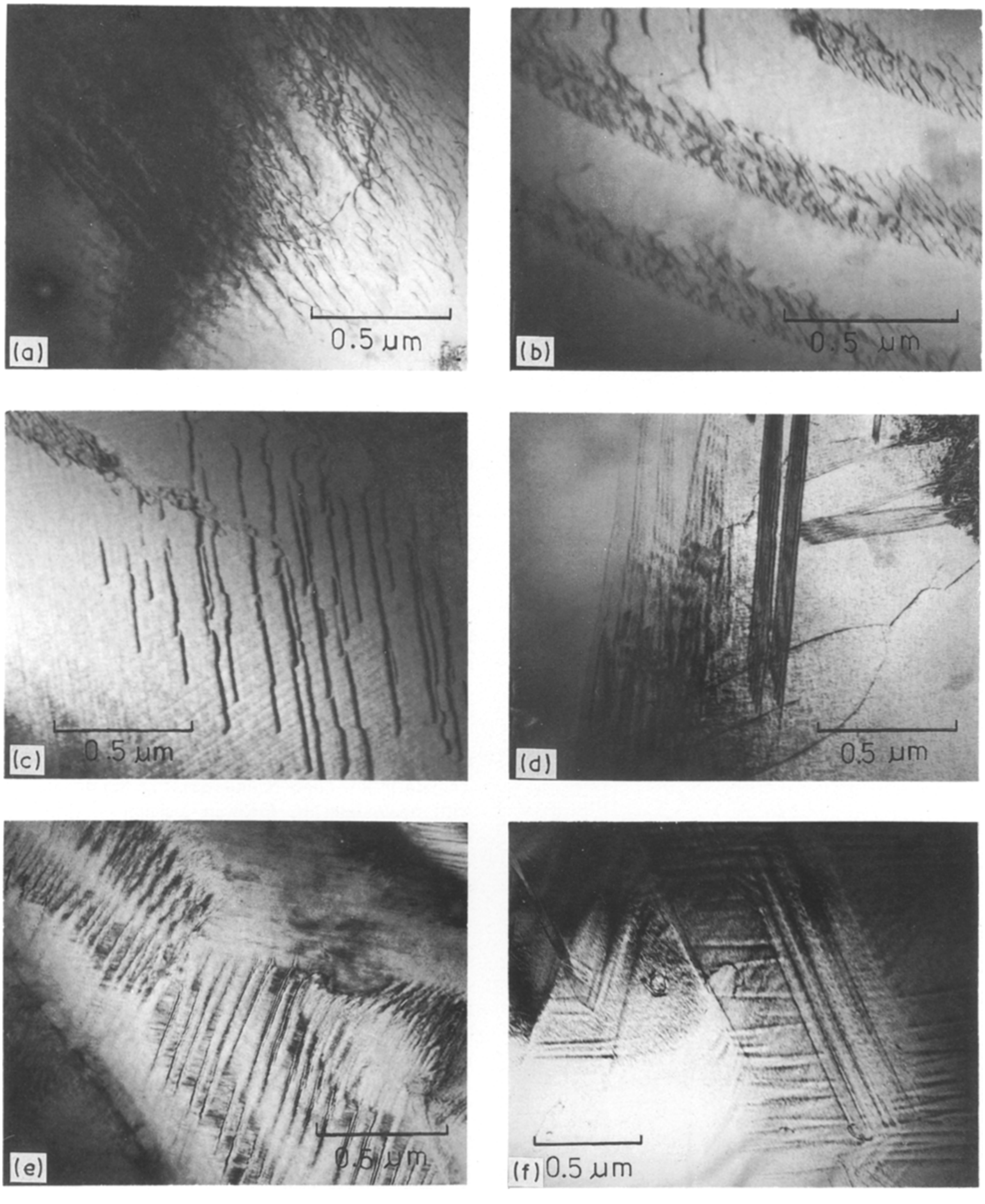


Figure 5 Structure of the quenched alloy after (a) 1, (b, c) 3, (d) 10 and (e, f) 50 thermal cycles.

of M_s, then it stabilizes for the next dozen cycles and drops again after 100 cycles. This behaviour of M_s could be ascribed to the generation of dislocations during cycling. This is supported by the microstructural observation from which it can be seen that the density of defects increases during cycling in the solution-treated specimen, while in the aged sample some dislocations arise in the first few cycles but they hardly move and the structure of the alloy remains practically unchanged. According to Tadaki *et al.* [9] the martensitic transformation accompanied by a positive volume change may be assisted by the tensile stress fields. Thus, if these fields are relaxed by the introduction of dislocations then the M_s is lowered, which hold true in the case of our supersaturated specimen.

It is a well known fact that in addition to the composition of the alloys, heat treatment is also an important factor which affects the transformation temperatures and sequences. In the case of the alloy studied the transformation behaviour of the solution-treated specimen differs from that of the aged speci-

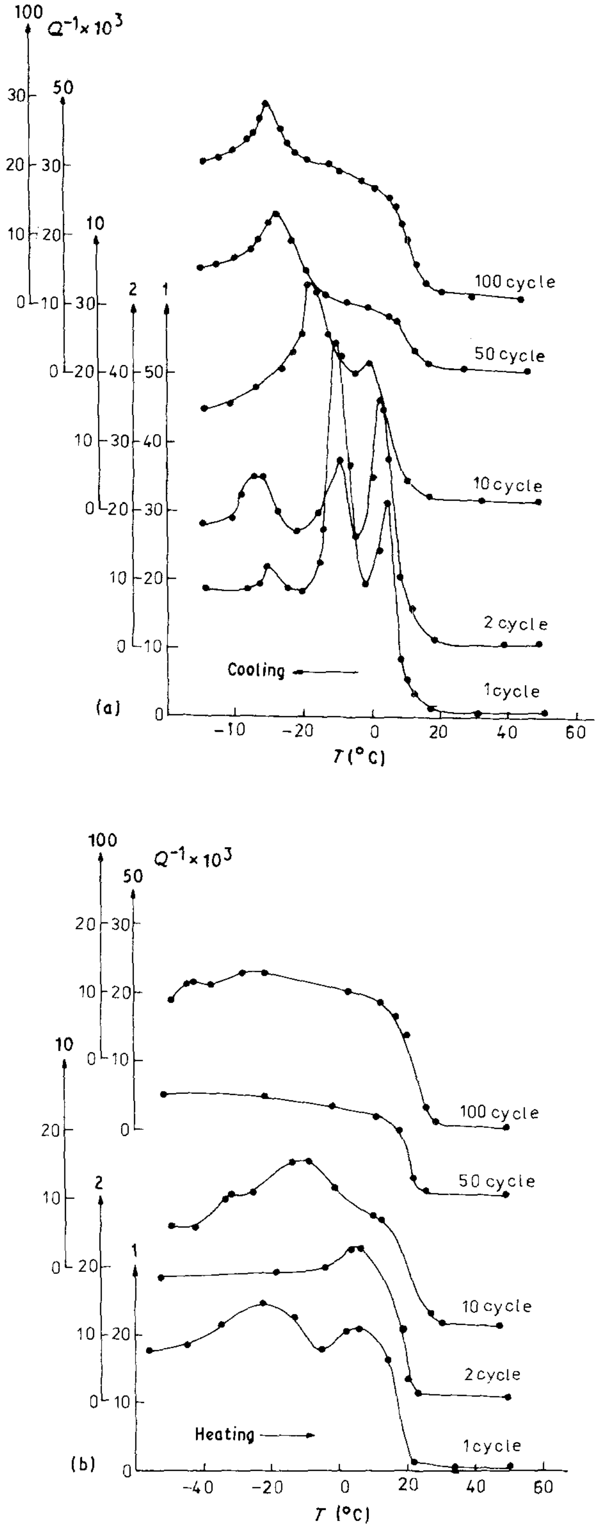


Figure 6 Internal friction curves for the aged alloy. (a) on cooling, (b) on heating.

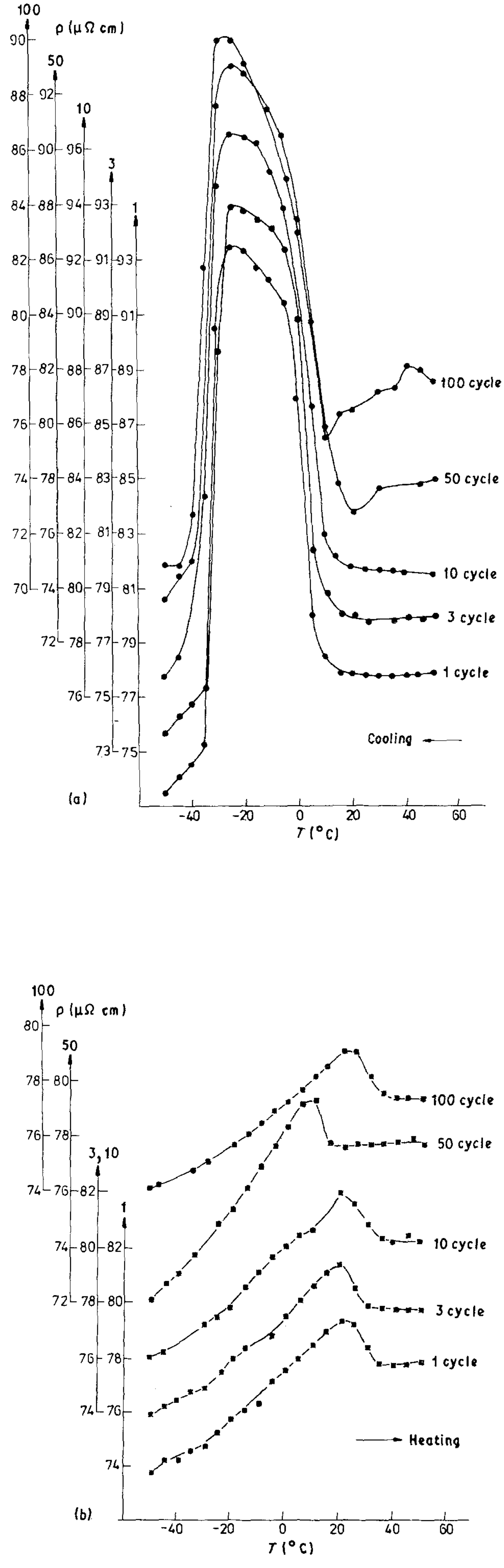


Figure 7 Electron resistivity curves for the aged alloy. (a) on cooling, (b) on heating.

men in which a complicated transformation sequence is observed (Fig. 6). On the internal friction curves obtained for the solution-treated specimen on cooling an additional peak, prior to the martensitic transformation one, occurs indicating that in this alloy the R-transition is well separated from the martensitic transformation. The T_r temperature increases with cycling which is in accordance with the results of Tadaki *et al.* [9]. This separate peak is not visible on curves obtained on heating. Thus in the supersaturated alloy the transformation sequences are as follows:

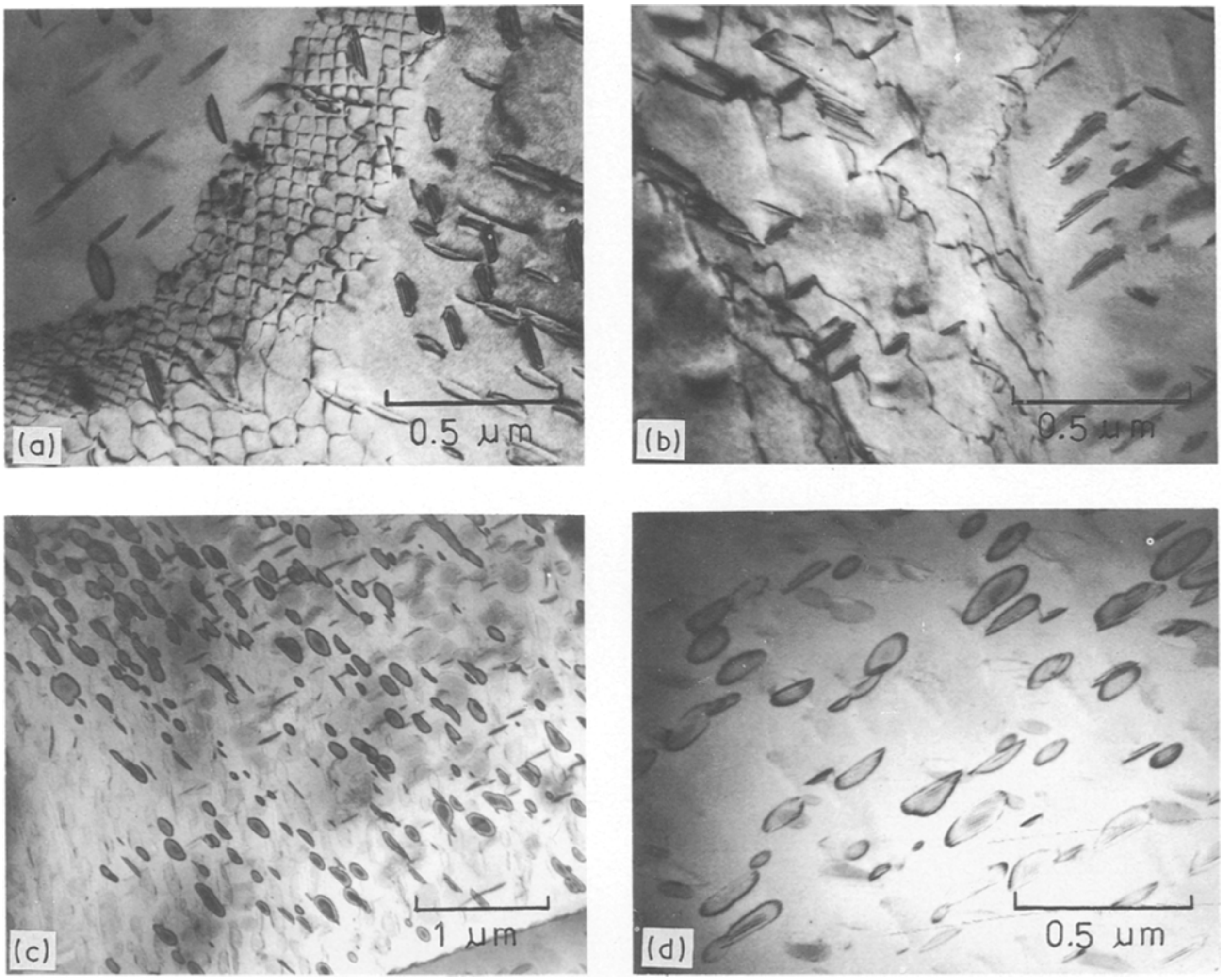


Figure 8 Structure of the aged alloy after (a, b) 3, (c) 10 and (d) 50 thermal cycles.

B2 → R → M on cooling and M → B2 on heating (although it is not clear whether on heating there is a single transformation or the reverse M → R and R → B2 transitions do not overlap).

The situation becomes more complicated in aged specimens for which on the internal friction curves three distinct peaks are observed for the first few cycles on cooling. In further cycling these peaks overlap causing a broad spectrum with a distinguished peak and an obscure second one on the higher temperatures side of the curve (Fig. 6). To make the explanation easier we drew on the same diagrams the changes of the electrical resistivity and internal friction for 1st, 10th, 50 and 100 cycle (Fig. 9). Now, it is easy seen that the first internal friction peak (counting from the higher temperatures side) corresponds to the increase in electrical resistivity and the last internal friction peak arises at the temperature of the sudden drop of the electrical resistivity. Thus, the first one could be described as the R-transition and the last one as the martensitic transformation. There is a problem of the middle peak, the origin of which is not clear from our experiments. It can be caused by the formation of two martensite phases, which have been suggested by some authors [13–15]. In this case the middle and the last peaks would appear due to formation of these two martensite phases. There is also another possible way to explain the three peaks on the internal friction curves. In the case of inhomogeneity of an alloy only a part of the specimen could undergo the R transition so that the two farther peaks would be caused one by R → M and the other by B2 → M transformations. Anyhow, it can be seen that with cycling these processes overlap and the first two become inferior to the last martensitic peak.

Finally, we would like to say a few words about the small peak arising on the internal friction curves obtained for the supersaturated alloy. It occurs at the temperature range much higher then M_s or A_f (of about 60 °C) thus it cannot be due to thermally activated martensitic transformation. It could be caused by the measuring stress but such peaks were observed very close to the transformation peak, usually as a part of it [16]. We think that the peak considered is caused by damping of dislocations which are induced during cycling as is seen from the electron microscopy studies.

5. Conclusions

The conclusions are as follows.

(1) The transformation sequences in nickel-rich Ni–Ti alloy which do not contain any precipitates are as follows: B2 → R → M on cooling and M → B2 on

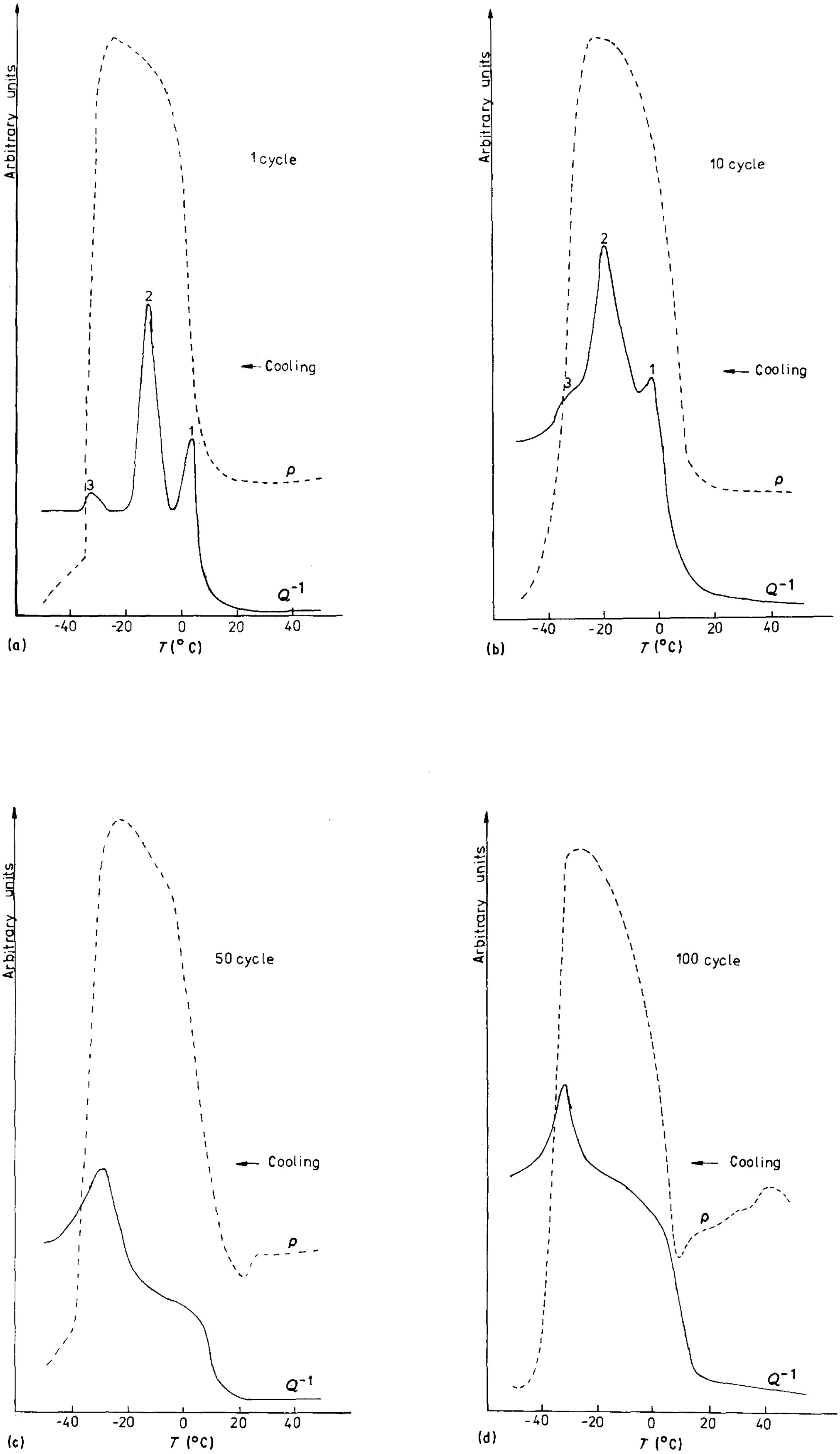


Figure 9 Comparison of the electrical resistivity (– – –) and internal friction (——) curves obtained on cooling for the aged alloy after (a) 1, (b) 10, (c) 50 and (d) 100 cycles.

heating. The thermal cycling up to 100 cycles brings about the lowering of the transformation temperatures.

(2) Precipitates occurring in the aged alloy cause all the transformation temperatures to rise and a complicated transformation behaviour appears.

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