Thermochimica Acta, 85 (1985) 187—190
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

DSC -ANALYSIS OF THERMOMECHANICALLY TREATED TINI SHAPE MEMORY ALLOY

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ABSTRACT

The martensitic transformation behaviour, after thermomechanical treatment of the TiNi-alloy with two-way shape memory, have been studied by differential scanning calorimetry. The results are correlated with electrical resistivity and electron microscopical observations. One heating and cooling cycle in the martensitic temperature range (-60/+70 °C) is recorded in order to separate the respective transformation processes involved. DSC curves of a series of sequential cycles illustrate the reversibility of the pre-martensitic structural change. Additionally, evidence is sought for the tetragonal lattice distortion which can occur in the austenitic lattice after heating up to 200 °C. All the observations showed that DSC is an important tool in the investigation of complex phase transitions.

INTRODUCTION

The Reversible Shape Memory Effect in TiNi alloys is a result of a martensitic transformation near ambient temperature which is accompanied by a shape change. Heating reverts the martensite to the high temperature phase thereby annihilating the shape change (1-4). The transformation is influenced not only by the composition but also by the internal stressfield of the specimen. The crystal structure of the phases involved in the transformation are well documented. However, the influence of successive thermal cycling as well as prior annealing temperatures on the transformation behaviour is not yet clarified (5,6). This paper presents DSC-measurements of the phase transitions occurring on thermal cycling of specimens annealed below 625 °C after cold rolling. The results are related to the substructure resulting from the thermomechanical treatment.

EXPERIMENTAL PROCEDURES

Specimens cold rolled 38% and annealed at 400, 500 and 600 °C with a cross-section of 2,5x2,5 mm were used for electrical resistivity measurements and electron microscopy.

0040-6031/85/$03.30

For the DSC-investigation the Du Pont model 1090 B Thermal Analyzer was used in combination with the model 912 dual sample DSC (7,8) provided with the "mechanical cooling accessory" for cyclic programmes. The software used for the evaluation of the thermogrammes were standard programmes as provided with the instrument; phenomena were calculated as melting events. Two point calibrations (9) were done at zero (water) and 156,6 °C (indium) for the temperature axis, while this method was also used for the quantification of the Y-axis (28,4 Joules per gr.). As the "cross talk" levels between the two samples in the DSC-cell were less than 0,5% they were neglected. The samples demonstrated a non reproducible behaviour during the first thermal cycle, therefore these measurements were omitted in this report.

RESULTS AND DISCUSSION

In figure 1 the broken line A represents the electrical resistivity versus temperature curve for a 500 °C annealed specimen. After a linear decrease on cooling the curve starts to increase and reaches a maximum at the martensite start temperature M_S. In the DSC-curve well separated peaks are observed on cooling. Clearly two separate transformations occur: austenite(A) to intermediate phase(R) and second intermediate phase to martensite(M). The start temperatures for the transformations can be accurately determined from the DSC-curves. Annealing at 600 °C reveals a double exothermic peak indicating a shift of the M_S-temperature towards the R-transformation. Only one endothermic peak is observed on heating in both the 500 °C and 600 °C annealed specimen with a shift to higher temperatures at 600 °C .

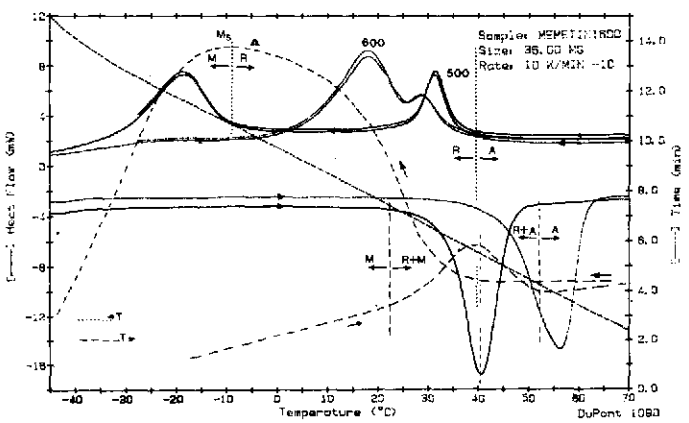

Fig. 1 DSC-curves of TiNi annealed at 500 °C and 600 °C.
Electrical resistivity of TiNi annealed at 500 °C. (A)

The start temperature difference of the martensite and R-phase is very small in both cases so that one peak is observed. The intermediate phase is unstable

at these temperatures and the reaction is continuous M-R-A. Fig. 2 illustrates the behaviour of a specimen annealed at 400 °C. Cooling down to -60 °C partial transformation to martensite has taken place. The heating part of the DSC curve shows a double peak suggesting two sequential reactions M-R and R-A. The second endotherm is related to the R-A transition phase as illustrated by the thermal cycle between 0 °C - 80 °C. Additionally a small endothermic reaction is observed when the specimen is heated from the martensitic state to 200 °C. (A and B) This reaction is ascribed to a gradual tetragonal distortion of the high temperature ordered b.c.c. phase which has been observed by X-ray diffraction in the past but was not verified by other techniques (5).

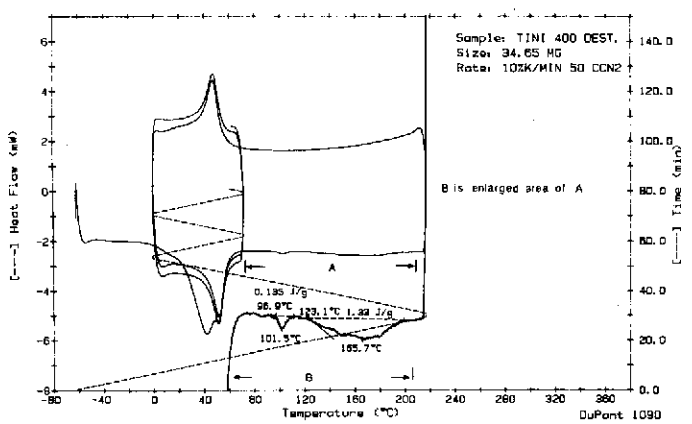

Fig. 2 DSC-curves of TiNI annealed at 400 °C after subsequent thermal cycles.

The stability of the intermediate phase is illustrated in fig. 3. Six subsequent cycles show the reversibility of the transformation with a very small hysteresis of 4 - 15 °C at 500 °C and 400 °C annealed specimens respectively.

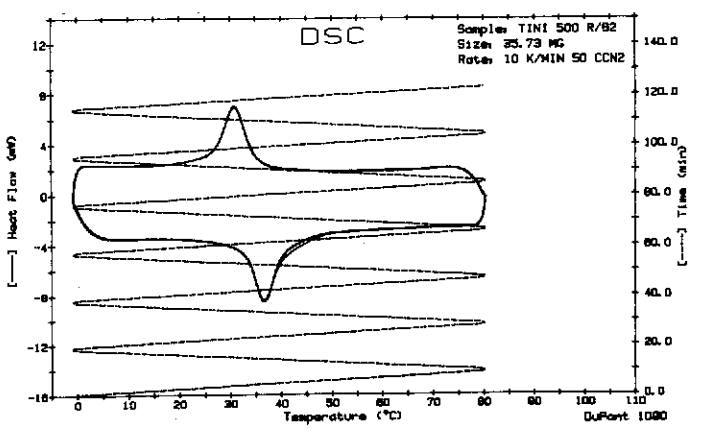

Fig. 3 Stability of the R-phase on thermal cycling TiNi annealed at 500 °C.

The electron micrographs of the samples annealed at 400, 500 and 600 °C are shown in fig. 4. At low temmperature annealing the deformation structure is still present. The austenitic structure is stabilized resulting in a low M_s temperature. The transformation temperature of the intermediate phase is relatively stable indicating that some dislocations needed for this transformation is already present in the deformed structure (a). At 500 °C the dislocation structure is mainly recovered but some early recrystallization has taken place in the more heavily deformed area's (b). The structure is less stable to the transformation shifting the M_s to higher temperatures. At 600 °C the structure is fully recrystallized (c). At the first thermal cycle the necessary dislocations for the A-R transformation are absent and a straight transformation to martensite occurs. After the first cycle these dislocations are created by the reverse transformation and the intermediate phase reaction appears as in fig. 1.

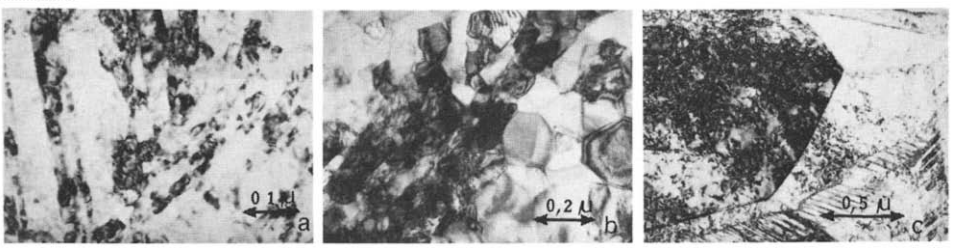

Fig. 4 Microstructure of specimens annealed at a) 400 °C b) 500 °C c) 600 °C.

The results described above show that the different phase transitions which occur in shape memory TiNi alloy can be observed and seperated by DSC. The observations on changes in transformation behaviour on annealing and the stability of the transition phases during subsequent thermal cycling in combination with structural information provide us a better understanding of the processes invloved in RSME. DSC is therefore a powerfull instrument for the study of martensitic phase transitions and for the detection of very weak transformation effects, as the tetragonal distortion of the high temperature phase.

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