Differential Scanning Calorimetry Study on Transformations in a $\text{Ni}_{47}\text{Ti}_{50}\text{Fe}_3$ Alloy

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The transformations of a $\text{Ni}_{47}\text{Ti}_{50}\text{Fe}_3$ alloy (submitted to a preliminary solution treatment at 1273 K or to an ageing at 673 K following the solution treatment specified above) have been examined by means of differential scanning calorimetry. The B2-R-phase transformation distinct from the R-phase-B19' transformation has been investigated.

The heat flow during both direct steps and reverse ones has been followed during some complete thermal cycles and enthalpy changes have been deduced for each step. No clear difference which discriminates different thermal treatments has been found, except for a slight shift of the martensitic transformation on the temperature scale. Enthalpy changes here found are compared with literature results.

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I. Introduction

NiTiFe is one of the oldest ternary system of the NiTiX family, known from the early days since the exploitation of shape memory properties⁽¹⁾.

Interest has grown during the years for this system, due to the large separation on the temperature scale between the transformations of the B2 parent phase (*P*) to the rhombohedral phase (*R*) and the R-phase to the B19' martensitic phase (*M*), introduced by a few percent of Fe⁽²⁾. This allowed to investigate thoroughly the R-phase separately from martensitic phase and to settle that the former is not a precursory phase of martensite⁽³⁾. Similarly the role of R-phase on the mechanical properties of NiTiFe has been clarified⁽⁴⁾.

All the published data, however, are always related to static properties only: moreover, few data are known as concerns the enthalpy change connected with the above mentioned transformations in this system⁽²⁾⁽⁴⁾⁽⁵⁾. The transformations are here investigated in a $\text{Ni}_{47}\text{Ti}_{50}\text{Fe}_3$ (at%) alloy, either in a solution treated condition or in an aged state, examining the heat exchange during the transformations.

The enthalpy changes as deduced from heat scans are followed as a function of *P*↔*M* thermal cycling and are compared and contrasted with the results obtained in literature on either the *R*→*M* or the *P*→*R* transformation.

II. Experimental

A $\text{Ni}_{47}\text{Ti}_{50}\text{Fe}_3$ alloy (nominal composition) has been

investigated (wire 0.9 mm in diameter), submitted to different heat treatments:

(1) Solution treatment at 1273 K (3.6 ks) followed by quenching into iced water (IQ), (specimens labeled A).

(2) Ageing at 673 K (3.6 ks) and IQ, after treatment (1) (specimens labeled B).

Heat flow vs. temperature measurements were performed with a Perkin-Elmer DSC7 PCLab differential scanning calorimeter (DSC), at a scanning rate of 0.17 K/s. The range of investigated temperatures was from 93 K to 293 K.

Transformation temperatures were determined by the slope-baseline intersection method; enthalpy changes were calculated by the Perkin-Elmer software package. The heat flow of the transformations has been followed during some complete *P*-*R*-*M* cycles.

III. Results

Figure 1 shows a complete *P*-*R*-*M* thermal cycle (A specimen): a wide separation in temperature can be seen between the *P*↔*R* and *R*↔*M* steps, as expected.

Figures 2 and 3 show, respectively, the direct *R*→*M* and the reverse *M*→*R* transformations, during the first four complete thermal cycles, for two typical specimens, solution treated (A), and aged (B). Except for a slight shift on the temperature scale, due to the different preliminary heat treatment, similar heat flow profiles and a similar shift as a consequence of cycling are found in both cases. The same applies for the reverse *M*→*R* transformations, though the shift on the temperature scale due to the different heat treatment is absent.

The heat exchange during the *R*→*M* step involves a narrow range of temperatures, typically 2–3°C, whilst during the reverse *M*→*R* step the heat exchange takes

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Fig. 1 Thermal scans during a complete M - R - P cycle for a typical solution treated specimen.

Fig. 2 Thermal scans related to the $R \rightarrow M$ step, during complete P - M cycles: A) solution treated specimen; B) aged specimen.

Fig. 3 Thermal scans related to the $M \rightarrow R$ step corresponding to the cycles depicted in Fig. 2.

place in a wider range, typically 15°C .

A consistent shift towards lower temperatures can be appreciated for the martensite start temperature (M_s) on cooling, consequent to complete P - R - M cycles, chiefly during the first cycle. The heat flow profile during the direct $R \rightarrow M$ transformation is also fairly affected by thermal cycling, whilst slight changes can be appreciated in the heat flow during the reverse $M \rightarrow R$ transformation.

As concerns P - R step, the transformation temperature

Fig. 4 Enthalpy changes connected with the $R \rightarrow M$ step of $\text{Ni}_{47}\text{Ti}_{50}\text{Fe}_3$, compared with the previous result⁽⁴⁾ obtained from Clausius-Clapeyron relationship on similar alloys. Results obtained on the $R \rightarrow M$ step of NiTi alloys are also given⁽⁶⁾⁽⁷⁾.

onsets, both direct and reverse, are insignificantly affected by complete thermal cycling; the heat flow of the transformation does appear nor slightly modified as well with cycling. This applies to all the specimens examined.

Measured enthalpy changes and transformation temperatures during both the $P \rightarrow R$ and $R \rightarrow M$ transformations, on cooling and heating, are quoted in Table 1; the enthalpy changes during the $R \rightarrow M$ transformations are plotted as a function of the onset transformation temperature in Fig. 4. The enthalpy change calculated by Otsuka from the Clausius-Clapeyron relationship during the stress-induced $R \rightarrow M$ transformation on the same alloys⁽⁴⁾ is also therein given. The measured $R \rightarrow M$ enthalpy changes previously obtained⁽⁶⁾⁽⁷⁾ on some NiTi alloys are just reported for comparison.

IV. Discussion

Results here obtained on both $P \rightarrow R$ and $R \rightarrow M$ transformations consequent to thermal cycling show features similar to the ones detected on NiTi alloys⁽⁶⁾⁽⁸⁾.

Both transformation temperatures and enthalpy changes generally decrease with cycling as concerns $R \rightarrow M$ transformation; as concerns $P \rightarrow R$ transformation, no shift is found for T_R , whilst the enthalpy change slightly decreases with cycling. The slight shift in transformation temperatures consequent to ageing agrees with the literature results on NiTiFe⁽⁴⁾.

The $P \rightarrow R$ transformation heat flow looks insensitive to thermal cycling; on the contrary, the modification in the $R \rightarrow M$ transformation heat flow with thermal cycling is unexpected, particularly for the solution treated specimens, in the light of the results obtained on the NiTi alloys⁽⁹⁾.

The stepwise heat flow of the $R \rightarrow M$ transformation might be ascribed to a spread in onset temperatures between different martensitic variants, induced by internal constraints. Actually, a stress-induced martensitic variant has a specific critical "onset-stress", related to its own Schmid factor⁽¹⁰⁾: the existence of microstructural internal stress fields and/or a texture in the specimen might

Table 1 Enthalpy changes and transformation temperatures of *P-R* and *R-M* transformations in solution-treated (A) and aged (B) specimens.

Specimen	Cycle	$M_s(R-M)$ (K)	$M_f(R-M)$ (K)	$A_s(M-R)$ (K)	$A_f(M-R)$ (K)	$T_r(P-R)$ (K)	$T_r(R-P)$ (K)	$\Delta H(R \rightarrow M)$ (J·mol ⁻¹)	$\Delta H(M \rightarrow R)$ (J·mol ⁻¹)	$\Delta H(P \rightarrow R)$ (J·mol ⁻¹)	$\Delta H(R \rightarrow P)$ (J·mol ⁻¹)
A1	1	—	—	—	—	256.20	—	—	—	162.26	—
	2	107.30	104.80	181.00	196.50	256.60	259.50	94.16	152.15	158.54	147.90
	3	104.80	100.60	181.30	196.40	256.20	259.40	110.66	151.09	155.88	145.77
	4	104.10	98.30	180.50	196.30	256.40	259.40	101.61	147.90	144.70	139.92
A2	1	127.00	123.70	180.80	197.30	256.20	259.30	128.21	195.24	182.48	157.47
	2	120.70	118.40	180.10	196.60	256.00	259.20	125.02	182.48	170.77	152.68
	3	117.50	114.40	178.90	196.50	256.40	259.40	128.21	189.72	167.05	151.62
	4	115.80	113.10	178.70	196.90	256.20	258.90	122.36	194.18	158.54	151.62
A3	1	125.50	123.00	180.30	195.50	255.90	258.40	151.62	196.31	196.84	169.71
	2	120.70	117.50	179.80	195.10	255.50	258.20	143.11	191.52	177.69	161.73
	3	117.80	113.50	177.50	194.80	255.60	258.20	143.11	192.58	171.30	159.07
	4	113.00	110.10	178.30	194.20	255.50	258.20	133.53	169.18	160.13	158.54
A4	1	115.00	112.80	180.40	194.80	255.40	258.20	116.51	177.69	169.71	153.22
	2	109.70	107.50	180.00	194.70	255.30	258.10	112.78	172.90	156.94	146.83
	3	107.50	104.30	179.80	194.40	254.90	258.00	110.12	163.86	151.62	144.70
	4	104.00	101.40	178.00	194.10	255.20	257.90	102.14	161.20	144.70	140.98
B1	1	113.80	108.70	179.80	193.90	255.60	258.50	83.52	128.74	158.54	146.83
B2	1	125.90	114.20	179.70	195.10	256.10	258.70	111.40	179.82	189.92	170.24
	2	120.40	110.20	179.70	194.90	255.30	258.60	121.83	167.05	184.07	163.32
	3	116.80	107.00	178.90	194.40	255.90	258.60	113.85	158.54	165.45	156.41
	4	115.50	105.40	179.70	193.90	255.80	258.50	111.72	144.70	159.60	161.73
B3	1	119.80	112.50	180.30	194.20	255.60	258.60	93.10	148.96	148.96	143.11
	2	115.50	109.50	179.40	194.40	255.30	258.50	95.76	135.13	145.77	140.98
	3	110.70	107.30	179.60	193.50	255.40	258.40	92.57	132.47	140.45	135.66
	4	116.10	110.30	178.30	193.30	255.30	258.30	89.91	128.74	133.00	132.47
B4	1	126.60	122.80	179.00	195.30	256.00	258.60	142.63	200.56	187.80	172.37
	2	119.60	116.80	179.40	194.70	255.80	258.50	140.98	195.24	179.28	164.92
	3	117.90	113.00	177.10	194.10	255.80	258.40	128.74	179.28	168.64	155.88
	4	115.60	110.80	178.30	193.90	255.70	258.30	130.90	175.56	158.00	156.94

act as a kinetic barrier to the growth up of specific variants, requiring different undercooling to be settled.

The prompt character of the *R*→*M* transition in comparison to the *M*→*R* transition (2–3°C against 15°C), is supported by both the above picture and the intrinsic features of the martensitic thermoelastic transformations, which involve, in the *M*→*R* step, the shrinking of martensitic plates and not the renucleation of the high temperature phase. Similar results have already been obtained on thinner NiTi wires subjected to similar heat treatments⁽¹¹⁾.

The enthalpy changes involved in both *P-R* and *R-M* steps look of the same order of magnitude, as found by Matsumoto and Honma⁽²⁾, though lower in absolute value.

The *R*→*M* enthalpy change calculated by Otsuka *et al.*⁽⁴⁾ is higher than the ones here obtained: in that case, however, the stress-induced martensite was settled, with specific variants most probably involved. In the present case thermal martensite is obtained, with equioriented martensitic variants settled, as far as the previous thermomechanical treatment affords.

The different values can therefore be explained by the different driving force to obtain martensite⁽¹²⁾. The different M_s onset temperatures of the material in-

vestigated given by Ref. (4), might be ascribed to the different methodology adopted to detect it; in Ref. (4) M_s is detected by electrical resistance measurements, in this case M_s is deduced from DSC curves. The M_s values here obtained are within the range 100–132 K, where the limits are deduced from extrapolation of the curves critical stress to induce martensite vs. deformation temperature given respectively in Figs. 7b, 6b of Ref. (4).

V. Conclusions

The *P-R* and *R-M* thermally activated transformations in a Ni₄₇Ti₅₀Fe₃ alloy, both direct and reverse, have been investigated by differential scanning calorimetry measurements. The heat flows of the *P*↔*R* transformation both direct and reverse, and the *M*→*R* transformation, are deemed insensitive to thermal cycling. On the contrary, *R*→*M* heat flow during direct transformation is fairly affected by thermal cycling, with a consistent shift in onset transformation temperatures as a function of cycles.

Both solution treated and aged specimens have similar heat flows during the *R*→*M* transformations, though at slightly different temperatures.

The evaluated enthalpy changes during the different

steps, *P-R* and *R-M*, appear of the same order of magnitude, as found in the previous investigations⁽²⁾.

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