The effect of chemical composition on enthalpy and entropy changes of martensitic transformations in binary NiTi shape memory alloys

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ABSTRACT

In the present research work the binary NiTi alloys with various compositions in the range of 50.3–51 at.% Ni were used. Samples have been annealed at 850 °C for 15 min and then quenched in water. In order to characterize transformation temperatures and enthalpy changes of the forward and the reverse martensitic transformation, Differential Scanning Calorimetric (DSC) experiments were performed. The enthalpy and entropy changes as a function of Ni atomic content have been thermodynamically investigated. Results show that enthalpy and entropy changes of martensitic transformation decrease when Ni atomic content increases. The variation of enthalpy and entropy of martensitic transformation with Ni content in binary NiTi alloys were explained by thermodynamic parameters and electron concentration of alloy (e/a) respectively.

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1. Introduction

The NiTi shape memory alloys, due to unique properties such as super elastic and shape memory effect, have many applications in different fields. The shape memory effect is based on a thermoelastic reversible martensitic transformation. On cooling the high temperature phase austenite with B2 structure, transforms to the low temperature phase martensite with monoclinic (B19′) structure. The reverse transformation (martensite to austenite) occurs during heating. The temperature hysteresis in binary NiTi alloys in direct and reverse martensitic transformation is about 20–30 °C. The conventional compositions of NiTi alloys have 50–51 at.% Ni. It is well known that Ni content has main influence on transformation temperatures. The changes of M_S and M_P temperatures are plotted as a function of Ni atomic content in Fig. 1 [1].

The condition of local balance between chemical and non-chemical forces in martensitic transformation is thermo elastic behavior. This condition is reached at the interfaces which are moving at a given temperature, during both direct and reverse transformation. Growth and shrinkage of the martensite plates in thermo elastic balance take place in a well defined sequential order; it means that the plates formed first during cooling are the last ones to disappear during heating.

The chemical forces arise from the difference in Gibbs free energy between austenite and martensite phases. The origin of chemical forces is the different atomic structure of austenite and martensite. Non-chemical forces have two main contributions. The first one is the need to accommodate the transformational shape and volume changes. When a shape memory alloy undergoes a martensitic phase transformation, equivalent shear direction occurs and the twinnings form and elastic energy is saved in the specimen. During the reverse transformation, the twinnings decay (detwinning) and elastic energy releases. The second contribution is the energy dissipated in the specimen as internal work during the transformation. The internal work is mainly devoted to overcome frictional barriers opposing interfacial motion, either during heating or cooling the samples [2–7].

Salzbrenner and Cohen [8] used the Eq. (1) for indicating the relative contributions of transformation heat.

$$\Delta H_{net.} = \Delta H_{ch.} + \Delta H_{el.} + \Delta H_{fr.} \tag{1}$$

$\Delta H_{net.}$ is the net enthalpy change that is achieved by the DSC curve, $\Delta H_{ch.}$ is the chemical enthalpy, $\Delta H_{el.}$ is the enthalpy change associated with the strain energy of the transformation and $\Delta H_{fr.}$ arises from the production of internal interfaces during transformation [8].

The measurement of enthalpy and entropy changes in martensitic transformation of NiTi alloys and the effect of composition on enthalpy and entropy changes have received considerable attention in the last years. Therefore, in the present study the influence of

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Ni atomic content on enthalpy and entropy changes in martensitic transformation of NiTi alloys have been investigated.

2. Materials and methods

In this work, the binary NiTi alloys with different compositions in the range of 50.3–51 at.% Ni were purchased from Memory Metals, Weil am Rhein. Samples with masses in the range of 20–50 mg were prepared by wire cut from cylindrical rods of 1 m length and 13 mm diameter. Samples have been annealed at 850 °C for 15 min and then quenched in water. In order to determine the characteristic temperatures and enthalpy changes of the forward and the reverse martensitic transformation, DSC experiments (type 2920 CE from TA instruments) were performed. DSC samples were heated up to 100 °C, where they were held for 3 min. Then the DSC measurements started by cooling the specimens down to −100 °C with a cooling rate of 10 °C min⁻¹. At −100 °C the samples were again held for 3 min and then heated up to 100 °C with a heating rate of 10 °C min⁻¹.

3. Results and discussion

The equilibrium temperatures of martensitic transformation can be calculated by the Eq. (2) below.

$$T_o = \frac{M_S + A_f}{2} \qquad (2)$$

The enthalpy changes of the forward and the reverse martensitic transformation can be achieved by measuring the area of cooling and heating curves of DSC results. The entropy changes of martensitic transformation can be calculated by the Eq. (3) as follows:

$$\Delta S = \frac{\Delta H_{ave.}}{T_o} \qquad (3)$$

The transformation temperatures and all calculated values of equilibrium temperatures, enthalpy and entropy changes of martensitic transformations are presented in Table 1.

The enthalpy changes of forward and reverse martensitic transformation as a function of Ni atomic composition is shown in Fig. 2. Fig. 2 shows that in binary NiTi alloys, the enthalpy changes of forward and reverse martensitic transformation decrease with increase of Ni atomic composition.

The reason of the decrease in enthalpy changes with increase of Ni atomic composition can be explained by thermodynamic parameters. Thermodynamic parameters can be divided into two categories; chemical and non-chemical forces. The origin of chemical forces is the different atomic structure of austenite and martensite phases.

Non-chemical forces arise from two main different contributions:

- The first one is the need to accommodate the transformational shape and volume changes. If accommodation takes place elastically; the associated elastic energy is stored in the specimen during the transformation from austenite to martensite, and reversibly recovered during the reverse transformation. Therefore this contribution opposes the forward transformation and promotes the reverse one. Elastic accommodation of the transformational shape and volume changes is a necessary and sufficient condition for the thermoelastic behavior.
- The second contribution is the energy dissipated in the specimen as internal work during the transformation. The internal
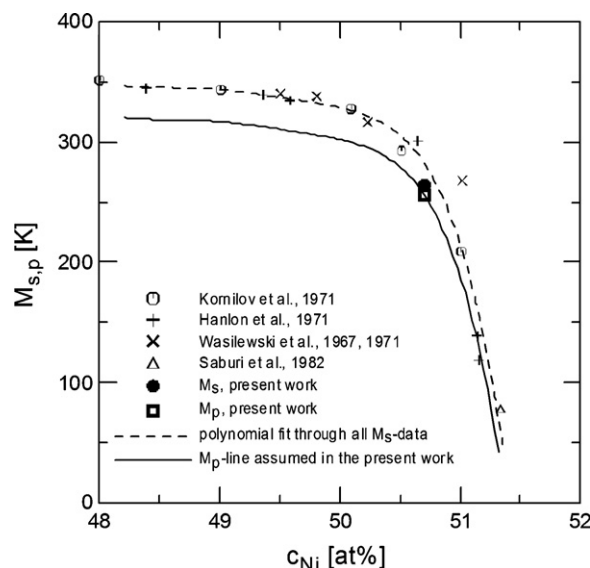

Fig. 1. Variation of M_S and M_P temperatures as a function of Ni atomic content in binary NiTi alloys.
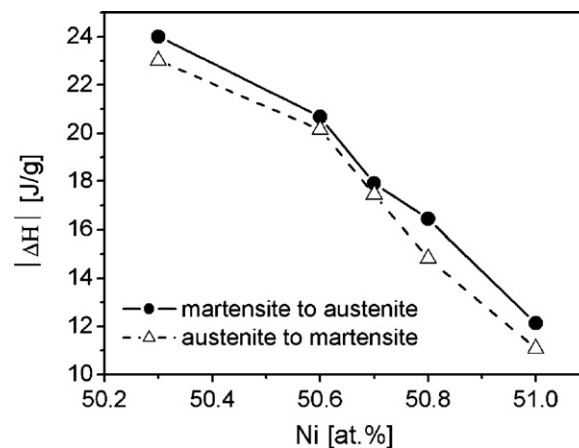

Fig. 2. Enthalpy changes of forward and reverse martensitic transformation as a function of Ni atomic content in binary NiTi shape memory alloys.

work is mainly devoted to overcome frictional barriers opposing the interfacial motion, either during heating or cooling the samples. This contribution represents the irreversible part of the non-chemical energies and is responsible for the thermal hysteresis observed in many thermoelastic transformations.

The temperature hysteresis is due to the presence of irreversible contributions of non-chemical free energy change [7–9].

The equation of elastic strain energy is as follows:

$$\phi_E = \frac{E_A + (\xi_1 + \xi_2)\Delta E}{2\rho} \left[\varepsilon - (\xi_1 - \xi_2)\beta \right]^2 + \frac{\gamma}{2\rho}\varepsilon'^2 \qquad (4)$$

Table 1
The values of equilibrium temperatures (K), enthalpy changes (J/g) of forward and reverse martensitic transformation and entropy changes (J/g K) of martensitic transformation for binary NiTi shape memory alloys with different Ni content.

Alloy (%Ni)	M_S	M_f	A_S	A_f	T_o	$\Delta H_{A \to M}$	$\Delta H_{M \to A}$	$\Delta H_{ave.}$	ΔS
50.3	314.6	279	308.2	353.2	333.9	−23.01	24.01	23.51	70.4
50.6	279.1	240.2	271.7	309.2	294.15	−20.14	20.67	20.405	69.4
50.7	266.2	237	263.3	296.8	281.5	−17.45	17.91	17.68	62.8
50.8	251.2	221.5	249.8	278.4	247.55	−14.83	16.44	15.635	63.2
51	216.7	174.2	215.8	257.8	237.25	−11.08	12.13	11.605	48.9