Cp Measurements on the Shape Memory Alloy Ni-52Ti

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Introduction

As yet, some investigations on the specific heat as well as on the enthalpy of trans-formation of shape memory alloy NiTi have been carried out (1 – 4). The published values of the enthalpy of transformation are 1297 J mol^{-1} (1), 1300 J mol^{-1} (2), 1548 ± 84J mol^{-1}(3), and 1688 to 2075 J mol^{-1}(4). At the martensitic transforma-tion temperature M_s in the region of the austenitic phase the specific heat is given as $C_p = 23.703$ J mol^{-1}K^{-1}+0.0098385 J mol^{-1}K^{-2}T(4). All these experiments were carried out using a differential thermal analyzer (DTA). The difference of the results reported in the literature may be due to incomplete martensitic transformation as well as to the low accuracy of DTA. The transformation temperature M_s is found to be 115°C at the composition Ni-52at.%Ti (5). Lohmann (6) measured the tempera-ture dependence of the change of deformation with different states of external stress for a Ni-Ti alloy and he discovered some stepwise transformation. This observation was explained by Hornbogen (7). The main point of his theory is that this step-wise transformation from austenite to lenticular martensite proceeds in subsequent generations, the size of the martensitic volume parts of each subsequent generation on step being smaller then the prior one. In addition, a generation formed later on needs more undercooling. This phenomenon shall be investigated with the aid of C_p measurements. If the different generations should be separated in their transforma-tions the cooling resp. heating must be done according to Lohmann (6) slowly, e.g. 0.01Ks^{-1}.
In the present paper, a stepwise heating resp. cooling is applied on a DSC (differen-tial scanning calorimeter). After every heating resp. cooling, it is waited for a new equilibrium state. The measurement of a reference curve and a calibration measure-ment is carried out together with the measurement within one experiment with the same calorimeter parameters. Each single measurement for one C_p value corresponds with a measurement of enthalpy and is evaluated by integration using a computer. The baseline necessary for this operation is constructed by spline functions. The advantages of this method are: (i) There is no influence of the speed of heating resp. cooling, therefore e.g. M_s is measured more precisely in comparison with a conven-tional DSC. (ii) The rate of heating resp. cooling may be chosen as it is suitable. Measuring the enthalpy of martensitic transformation, the method described by Dud-dek et al. (8) does not give a reference curve. This method uses a repetition of
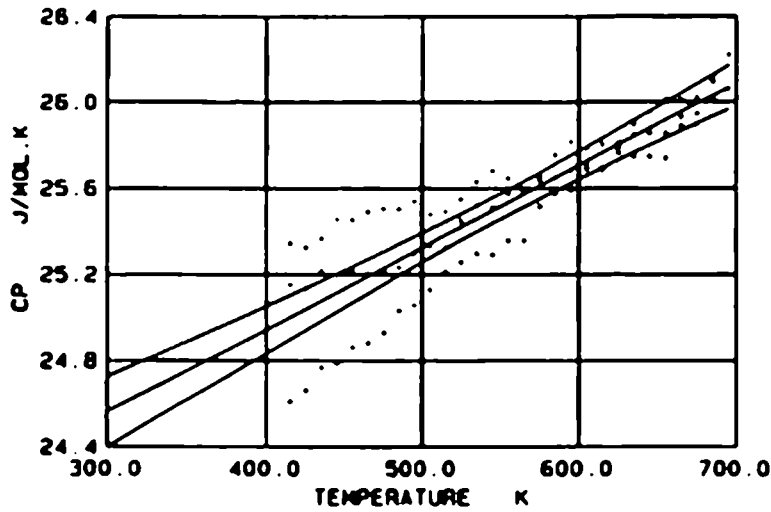
Figure 1: Specific heat of Ni-52Ti in the austenitic range, measured points, fitted linear curve and confidence interval

heating, but the re-transformation cannot be suppressed by this procedure in the case of the martensitic transformation. Therefore, a virtual baseline to determine the enthalpy is needed. In the present paper a C_p function is described in the form $C_p = a + bT$. This function is determined by measurements in the region of the austenitic phase.

Experimental Method

The rate of heating resp. cooling was 0.02 K s^{-1}. The isothermic time of the steps amounted to 180 s. Thus, an effective mean rate of 0.005 K s^{-1} resulted. In order to get appropriate resolution of the temperature a temperature interval of 1 K was chosen. High purity (99.999%) argon with a pressure of 1.5 10^5 Pa was used as protective gas. The measured temperatures of martensitic and austenitic transformation were in the range from 355 to 300 K and from 340 to 390 K, respectively. The C_p measurement for the determination of the reference curve was carried out in the range from 410 to 700 K. Since in the range from 410 K to M_s a deviation from linearity is observed this part of the measurement may not be used for the extrapolation of the reference curve. This deviation may be due to pre-martensitic transformation. Results of the measurements are depicted in Fig. 1. In addition, a confidence interval with a probability of 95% is plotted. The function determined is $C_p = 23.412$J mol^{-1}K^{-1} + 0.00038786 J mol^{-1} K^{-2}T. M_{sx}, M_{fx}, A_{sx}, and A_{fx} may be determined by application of the tangent rule, the suffix x describes different generations. The enthalpies of transformation of different generations were determined by the peak area with the following equation

$$S_x = h_x \cdot w_x \qquad \text{Equ.1}$$

where h_x = height and w_x = width of half value. In Fig. 2 the determination of A_{sx} and A_{fx} is shown. The broken lines resulted by the assumption of symmetric peaks. M_{sx} and M_{fx} may be determined accordingly. In consequence, T_{0x} may be evaluated as
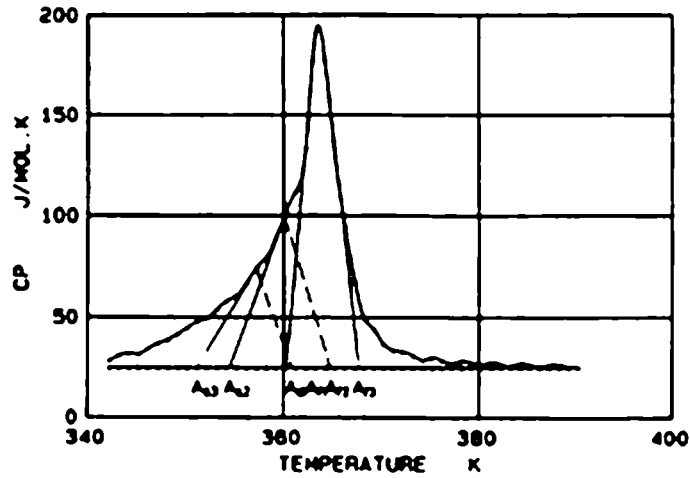
$$T_{0x} = (M_{sx} + A_{sx})/2 \qquad \text{Equ.2}$$

Figure 2: Specific heat of Ni-52Ti during the transformation martensite to austenite, mean heating rate 0.005 K s^{-1}. Determination of A$_s$ and A$_f$.

SN	C	M_{s_1}	A_{s_1}	M_{s_2}	A_{s_2}	M_{s_3}	A_{s_3}	M_{f_1}	A_{f_1}	M_{f_2}	A_{f_2}	M_{f_3}	A_{f_3}
1	i		361		359		347		368		363		359
1	i		361		354		351		368		365		361
1	i		359		353		350		368		364		362
1	ii	338		336		330		328		324		320	
1	ii	338	361	332	357	330	352	327	369	323	366	318	364
1	iii	337	364	332	359	331	356	326	374	322	370	318	365
1	iii	337	364	333	359	330	355	326	372	322	368	318	364
2	iii	348		341		338		336		333		330	
2	ii		364		361		357		378		373		370
AV(i,ii)	338	361	334	356	330	350	328	368	324	365	319	363
AV(iii)	337	364	333	359	331	356	326	373	322	369	318	365

Table 1: The points of transformation, SN = sample number, C = cooling way, temperatures in K, AV(C) = average value with indicated cooling way.

Different heat treatments resp. pre-treatments were applied: (i) The sample was cooled from the region of austenite into the region of martensite with a cooling rate of 0.005 K s^{-1}. (ii) The cooling rate for the same procedure amounted to 1.3 K s^{-1}. (iii) The sample was cooled from the region of austenite into the region of martensite with a cooling rate of 1.3 K s^{-1} and after this it was immediately quenched in liquid nitrogen.

	T_{0_1}	T_{0_2}	T_{0_3}	ΔT_1	ΔT_2	ΔT_3
AV(i,ii)	349.5	345	340	11.5	11	10
AV(iii)	350.5	346	343.5	12.5	13	12.5

Table 2: Average values of T_0 and ΔT.

SN	C	ΔH_t	h_1	w_1	ΔH_1	f_1	h_2	w_2	ΔH_2	f_2	h_3	w_3	ΔH_3	f_3
1	ii	1130	138	5.0	690	46.0	59	6.0	354	23.6	24	5.0	120	8.0
1	ii	1120	135	5.5	743	49.5	39	4.5	176	11.7	23	6.0	138	9.2
1	iii	1160	120	4.5	660	44.0	59	5.5	325	21.6	34	6.0	204	13.6
2	iii	1380	161	6.0	966	66.6	58	4.0	232	16.0	27	4.0	108	7.4
AV(1)					664	46.5			284	19.0			154	10.3

Table 3: Enthalpy of martensitic phase transformation estimated for different generations, h in kJ mol^{-1}K^{-1}, w in K, ΔH in J mol^{-1}, f in %, AV(1) average value of sample 1.

SN	C	ΔH_t	h_1	w_1	ΔH_1	f_1	h_2	w_2	ΔH_2	f_2	h_3	w_3	ΔH_3	f_3
1	i	1350	191	3.5	669	44.6	112	2.0	224	14.9	29	6.0	174	11.6
1	i	1370	170	3.5	595	39.7	92	5.5	595	39.7	50	5.0	250	16.7
1	i	1450	165	4.5	743	49.5	92	5.5	595	39.7	64	6.0	384	25.6
1	ii	1360	178	4.0	712	47.5	78	4.5	372	24.8	54	6.5	351	23.4
1	iii	1480	185	5.0	925	61.7	88	5.5	484	32.3	50	4.5	225	15.0
1	iii	1500	197	4.0	788	52.5	71	4.5	320	21.3	40	4.5	180	12.0
2	ii	1450	138	6.0	828	57.1	59	6.0	354	24.4	34	6.5	221	14.9
AV(1)					739	49.3			432	28.8			261	17.4

Table 4: Enthalpy of austenitic phase transformation estimated for different generations, h in kJ mol^{-1}K^{-1}, w in K, ΔH in J mol^{-1}, f in %, AV(1) average value of sample 1.
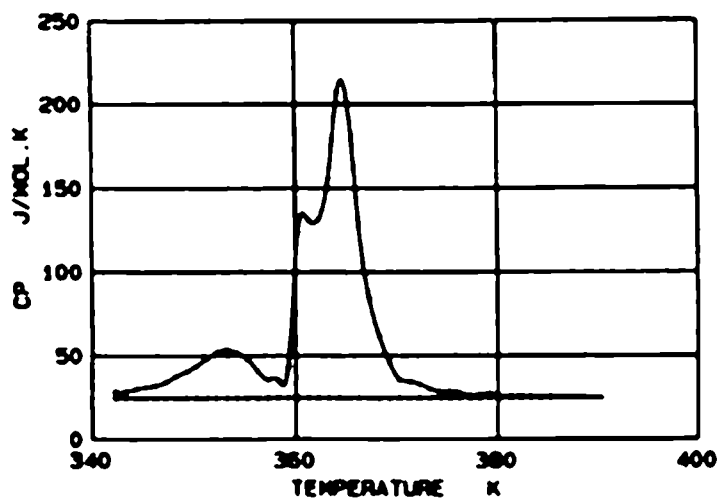

Figure 3: Specific heat of Ni-52Ti during the transformation martensite to austenite, mean heating rate 0.005 K s^{-1}. This special example may be taken as a proof of transformation in generations

Results and Discussion

Tables 1 to 4 show the results of C_p measurements. It can be concluded from Table 1 that different samples exhibit different temperatures M_s, A_s, M_f, and A_f. In addition, there are differences concerning these temperatures for the same sample. The cooling rates (i) and (ii) produce small differences only, but the quenching in liquid nitrogen (iii) produces the following differences: M_{ss} is lower and A_{ss} is higher. I. e., the sample quenched in liquid nitrogen needs more Gibbs energy to form the new phase. An assumed reason is that thermal stress does not favour the phase transition. The influence of internal stresses and of the structure of distribution of dislocations on $\Delta T = T_0 - M_s$ is discussed by Jost and Hornbogen (9). In this paper obstructing as well as favouring influence of stress is explained. Another observation is that different generations exhibit nearly the same temperature differences ΔT (See Table 2). I. e., the surface energy plays the same rôle for both directions of phase transition. The Gibbs energy of the phase transition is given by

$$\Delta G = \Delta G_V \cdot V + \Delta \sigma \cdot S \qquad \text{Equ.3}$$

where ΔG_V is the Gibbs energy per volume, V transformed volume per mole, $\Delta \sigma$ Gibbs surface energy and S change in molar surface. Later generations have a larger ratio surface to volume. Therefore, they need more volume Gibbs energy for transformation, i. e., $M_{s,s+1} < M_{ss}$. Since ΔT_z of different generations is nearly the same, the ratio surface to volume is only dependent on differences of T_{0s}. Table 3 and Table 4 give the enthalpies of phase transition of different generations. The phase transformation is not complete, therefore the maximum value is taken as a total enthalpy. The enthalpies of transformation of sample 1 and sample 2 are 1500 and 1450 J mol^{-1}, respectively. These values are within the scatter of the values published in the literature (1 - 4). If the enthalpy of different generations is divided by the total enthalpy the relative fractions of the different generations are nearly given. The means of these values show that the fraction of the first generation for the two directions of phase transition is nearly the same (40.5 and 49.3%). Beginning with the second generation a difference is observed. The formation of austenite is usually complete. The formation of martensite is not complete, beginning with the second generation due to the following reason: It is possible that the size within one generation is not equal and that the obstruction for the formation of small martensite plates is too large. Small martensite plates cannot be formed simultaneously with large ones, but they are formed later on, i. e., at lower temperatures.
The fractions of different generations derived by the enthalpies of transformation correspond with those which can be derived by microscopic investigation (7). Small martensitic plates may be formed after a longer time (e. g. some days). A possible reason is that internal stresses may be transformed by a process of relaxation during this time. After that a smaller obstruction for the formation will exist.
A proof of the formation on martensite in generations is shown in Fig. 3. It may be seen, that different parts of the martensitic transformation need a different undercooling, too.

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