JOURNAL OF MATERIALS SCIENCE 24 (1989) 2587–2593

Calorimetric techniques for the evaluation of thermal efficiencies of shape memory alloys

A. P. JARDINE*
H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK

The latent heat and entropy changes of NiTi shape memory effect (SME) alloys have been evaluated by three different calorimetric techniques; adiabatic calorimetry, differential scanning calorimetry and a Clapeyron analysis of isothermal stress–strain data. It is found that these techniques provide consistent estimates for the enthalpy and entropy to within 20% for NiTi and noble metal SME alloys. From published thermodynamic data for SME alloys, thermal efficiencies were calculated based on an ideal SME heat engine cycle. It was found that NiTi provides the maximum thermal efficiency with the highest temperature transformation range.

1. Introduction

The phenomenon of the shape memory effect (SME), whereby a material will revert to its original shape after large deformations by heating, makes these materials interesting working media for heat engines exploiting low-grade thermal reservoirs. The thermal efficiencies of SME heat engines which are, therefore, of interest have been estimated from the entropies of transformation and the transformation temperatures of the alloys.

An ideal SME heat engine cycle has been described in detail elsewhere [1, 2] and has been summarized in the preceding paper [3]. Ahlers [4], Tong and Wayman [5] and Wollants *et al.* [1, 2] have generally agreed that the thermal efficiency for the ideal shape memory heat engine cycle can be given as

$$\eta_{\mathrm{th}} = \frac{\Delta H \Delta T_0}{T_0[C_p \Delta T_0 + \Delta H(\sigma)]} \qquad (1)$$

where C_p is the specific heat of the material and $\Delta T_0 = T_0(\sigma) - T_0$. Wollants *et al.* [1, 2] states that ΔH in the denominator of Equation 1 is a function of stress, given by

$$\Delta H(\sigma) = \Delta H T_0(\sigma)/T_0 \qquad (2)$$

The formulae derived by Ahlers [4] and Tong and Wayman [5] do not include this stress dependence in ΔH. According to Mukherjee [6], the change in ΔH can be considered negligible for the maximum stress considered here, i.e. just before plastic deformation.

The ideal SME heat engine cycle involves three assumptions that are not normally realized in practice. They are (a) that the SME alloy is single crystal, (b) that 100% conversion of austenite to martensite occurs and (c) that the equilibrium transformation temperature, T_0, is measurable. Assumptions (a) and (b) are interrelated in that 100% conversion is not likely to occur in polycrystalline alloys as the confined volume of the individual grains cannot expand to accommodate the volume expansion of growing martensitic plates. In noble metal SME alloy single crystals, 100% conversion can occur; however, this has never been reported for single-crystal NiTi. The fractional conversion of austenite to martensite is difficult to predict and will depend on grain size, ageing treatments, etc. By assuming (a) and (b), the maximum thermal efficiency will be calculated.

Salzbrenner and Cohen [7] have demonstrated that T_0 is fundamentally indeterminant, due to the inseparable elastic and thermal effects. Four stress-dependent transformation temperatures can be measured; M_s and M_f, the martensitic start and finish temperatures and A_s and A_f, the start and finish temperatures for austenite. T_0 is estimated as

$$T_0 = 1/2(M_s + A_s) \text{ or } 1/2(M_f + A_f) \qquad (3)$$

The transformation temperature region (TTR) is taken as $A_f - M_f$. Assuming that T_0 lies somewhere in the TTR, then if the TTR is near room temperature, for a hysteresis of say 30 K, the error in estimating T_0 using Equation 3 will be 3 to 5%. Hence the three assumptions will predict an upper limit to the thermal efficiency for a SME alloy.

The measurement of ΔH can either be directly by calorimetry or indirectly by using a Clapeyron analysis of isothermal stress–strain data. It is not obvious that these two techniques ought to agree; in DSC, $\Delta H^{M \to A}$ is measured with no applied stress, in a Clapeyron analysis $\Delta H^{A \to M}$ is measured from the variation of the stress required to induce the martensitic transformation (σ_c) with temperature.

The affect of stress (σ) on T_0 for one mole of material is described by the Clapeyron equation

$$\mathrm{d}P/\mathrm{d}T = \Delta H/(T_0 \Delta V) \qquad (4)$$

It applies to any change in which a volume increase, ΔV working against a confining pressure, P, is accompanied by an entropy increase, ΔS, ($= \Delta H/T_0$), and states the dependence of the equilibrium value of this pressure on temperature or, by inverting the

---

*Present address: Department of Material Science and Engineering, Cornell University, Ithaca, New York 14853, USA.

0022–2461/89 $03.00 + .12

expression, the dependence of equilibrium temperature on pressure. Here ΔS is the amount of entropy lost by relative immobilization of atoms during transformation and ΔV the associated volume increase.

Inverting the Clapeyron equation, and expressing the result in grams (hence we introduce the density ϱ), the stress coefficient with transformation temperature A_f or A_s is

$$d\sigma_{\max}/dA_s = \varrho\Delta S/\Delta\varepsilon \qquad (5)$$

Given the stress coefficient, the transformation temperature, A_f, is known at any stress given one value of $A_f(\sigma)$. The effect of uniaxial applied stress (σ) in forcing martensitic transformations to occur at higher temperatures can be expressed by inverting Equation 5.

$d\sigma \cdot \Delta\varepsilon$ is the tensor product of the stress forcing transformation to occur at higher temperatures and the strain generated by transformation. Note that Δ rather than d is used on the right-hand side of the equation. This is in line with usage of Clapeyron's equation in steam engine technology where only a proportion of the available water is instantaneously and uniformly converted into steam. Here, only a proportion of shape memory material is transformed from martensite to austenite. It is possible, although unlikely, that ΔS could be measured for 100% conversion of martensite to austenite. However, in polycrystalline working elements of a heat engine, it is evident that not all grains will be orientated for 100% conversion under the action of the applied stress. With a single-crystal working element it would, in principle, be possible to measure sufficient data to evaluate all nine equations in the tensor product of stress and strain. In practice, measurement of the largest strain produced by transformation under the action of, say, uniaxial tension (or pure shear) would have to suffice.

This paper first examines the equivalence of latent heat values for forward and reverse transformations obtained by differential scanning calorimetry (DSC) and the Clapeyron equation in NiTi and for some noble metal SME alloys. NiTi was examined as its stress–strain behaviour with temperature has been extensively researched and adiabatic calorimetry results are available from the accompanying paper [3]. Also, NiTi is a promising candidate for heat engine work as it is reasonably easy to set a hot shape and is fairly ductile. It is interesting to note that the latent heat ($\Delta H^{M\to A}$) for NiTi can range from being equal to being half that of the latent heat for Fe–Ni [8]. This is an impressive comparison as latent heat for transformation in Fe–Ni is large. Thus in NiTi, the large driving forces involved in the transformation allow more work to be done while transforming, thus increasing the efficiency of the transformation.

Finally, the upper limit to the thermal efficiencies at maximum loading (i.e. just before plastic deformation) are calculated for some SME alloys from Equation 1 using data taken from the literature.

2. Latent heat measurements

Table I gives the DSC latent heat measurements of polycrystalline NiTi from Jardine *et al.* [9]. The growth of a secondary peak ascribed to the R-phase with ageing at 400 and 450° C makes the latent heat data ($\Delta H^{M\to A}$) dependent on the ageing times.

Measured values of A_s and A_f are tabulated with the transformation temperature for B19 to the R-phase (denoted as T_R) and the latent heats for both transformations. Two values for $\Delta S^{M\to A}$ were calculated from $\Delta H(T_0) = \Delta S$ using A_s and A_f, respectively, for T_0. (Although T_0 is fundamentally indeterminant, it is bracketed somewhere between A_s and A_f on heating or M_s and M_f on cooling. Given a temperature difference of 30° C about a mean value of, say, 300 K, then the indeterminancy in T_0 is 5%, an acceptable error.) Finally a value for $\Delta S^{M\to R}$ is included. $\Delta S^{M\to A}$ is found to be $\sim 2.7\,\mathrm{J\,mol^{-1}\,K^{-1}}$ for 723 K with an increasing contribution from the R-phase and from 3.5 to $4.0\,\mathrm{J\,mol^{-1}\,K^{-1}}$ for the 673 K ageing.

These values agree well with the $\Delta S^{M\to A}$ values on polycrystalline stoichiometric NiTi reported by Melton and Mercier [10] using rapid pulse calorimetry. They report an enthalpy of transformation of $20.1\,\mathrm{J\,g^{-1}}$ with an A_s of 314 K and A_f of 341 K. This then provides an entropy of transformation of $3.3\,\mathrm{J\,mol^{-1}\,K^{-1}}$. This value is within the entropy value range established by either DSC or adiabatic calorimetric techniques. Other workers also get similar results. Wang *et al.* [11] reported an enthalpy of $1295\,\mathrm{J\,mol^{-1}}$, and Wasilewski *et al.* [12] reported an enthalpy of $1300\,\mathrm{J\,mol^{-1}}$.

Significantly higher values were reported by Berman *et al.* [13] who measured an enthalpy of transformation $\Delta H^{M\to A}$ of 1687 to $2075\,\mathrm{J\,mol^{-1}}$. The transformation temperature was 360 K, hence $\Delta S^{M\to A}$ was 4.68 to $5.86\,\mathrm{J\,mol^{-1}K^{-1}}$. High latent heats were also reported by Goo and Sinclair [14] who measured $\Delta H = 3.75\,\mathrm{J\,g^{-1}}$ for R → B2 at −14° C (259 K) so that $\Delta S = 0.0145\,\mathrm{J\,g^{-1}\,K^{-1}}$ and $\Delta H = 25.5\,\mathrm{J\,g^{-1}}$ for M → R at −110° C (163 K) so that $\Delta S = 0.1564\,\mathrm{J\,g^{-1}\,K^{-1}}$. Addition of these gives $\Delta S^{M\to A} = 0.1709\,\mathrm{J\,g^{-1}\,K^{-1}}$ ($9.1\,\mathrm{J\,mol^{-1}\,K^{-1}}$) for the overall martensite to austenite transformation. The consensus of results tends to support the values presented in Table I. There is also broad agreement between the latent heat values in the accompanying paper.

3. Clapeyron analysis

Isothermal stress–strain curves at various temperatures above M_s provide the variation of critical stress with temperature by measuring the stress (σ_c) at which a deflection is observed in the load-extension plot. Taking T_0 as the temperature at which austenite transforms to martensite at a stress σ_c, and using $\Delta S = \Delta H/T_0$ then from Equation 5

$$\frac{d\sigma_c}{dT} = \frac{\varrho\Delta S}{\Delta\varepsilon} \qquad (6)$$

The transformational strain is measured on a tensometer as the extension of the flat Luders-like region just after σ_c is reached. This region is more evident for single crystals than in polycrystalline material. Using single crystals of 50.6 at.% Ni–Ti wire, Miyazaki *et al.* [15] demonstrated that the strains observed with a stress–strain curve are dependent on

TABLE I Thermodynamic data from DSC. Latent heat data from Jardine *et al.* [9] are used to calculate $\Delta S^{M \to A}$. The two columns of numbers under $\Delta S^{M \to A}$ are generated by substituting A_s and A_f for T_0

A_s (K)	A_f (K)	T_R (K)	$\Delta H^{M \to A}$ (J mol^{-1})	ΔH^R (J mol^{-1})	$\Delta S^{M \to A}$ (J mol^{-1} K^{-1}) (1)	$\Delta S^{M \to A}$ (J mol^{-1} K^{-1}) (2)	ΔS^R (J mol^{-1} K^{-1})
723 K Anneal, M → A							
304.5	311.2	-	394	-	1.30	1.27	-
301.2	309.8	-	780	-	2.59	2.52	-
302.4	311.0	-	818	-	2.71	2.56	-
305.7	317.0	300.1	836	6.930	2.73	2.64	0.095
308.8	319.0	303.6	863	19.19	2.79	2.70	0.265
313.6	324.6	307.7	834	25.58	2.71	2.62	0.350
315.2	327.3	309.5	838	27.71	2.62	2.56	0.375
317.3	328.8	311.2	820	34.10	2.59	2.49	0.460
320.8	330.7	314.8	838	36.71	2.61	2.53	0.475
673 K Anneal, M → A							
301.8	310.0	310.8	1076	-	3.56	3.47	-
303.6	312.3	313.0	1074	-	3.53	3.43	-
302.7	316.1	312.6	1066	-	3.52	3.37	-
305.0	320.6	314.3	1121	-	3.67	3.49	-
307.3	325.6	314.7	1088	-	3.53	3.33	-
308.9	328.9	316.5	1166	-	3.77	3.55	-
312.0	334.8	318.7	1270	-	4.07	3.79	-

the orientation of the crystal with respect to the tensile direction.

The value for $\Delta\varepsilon$ is difficult to measure for polycrystalline material as all of these strain orientations are present to some degree. The stress–strain curve presents an average of all the strains present in the material. $\Delta\varepsilon$ may be estimated better for polycrystalline NiTi as the nearly uniaxial strain generated when a B2 unit cell transforms to a B19 martensitic unit cell. Both macroscopic and microscopic evaluations of $\Delta\varepsilon$ are considered.

3.1. Case I. Bulk matrix strain

Miyazaki *et al.* [16] measured the transformation strains for straight polycrystalline wire specimens of 50.6 at. % Ni–Ti and found that the transformational strain as measured from the extent of the Luders-like region of the stress–strain curve was 5%. In single-crystal aged specimens, the transformational strains for 50.5 at. % Ni–Ti (aged at 1273 K for 60 min, quenched and aged at 673 K for 60 min then quenched) were fairly uniform, regardless of crystal orientation. The transformational strains ranged from 3.8 to 5.9% near $\langle 1\,1\,0 \rangle_{B2}$ in solution-aged NiTi.

3.2. Case II. Microscopic strain

According to Michal and Sinclair [17] the largest strain generated during the transformation from austenite to martensite is parallel to a $\langle 1\,1\,0 \rangle$ direction in B2 and the strain calculated as $\Delta\varepsilon = 0.066$.

A strain value of 0.059 was the maximum observed by Miyazaki *et al.* [15] on 673 K aged 50.6 at. % Ni–Ti single crystals. Although Miyazaki *et al.* studied a slightly different composition material, it is unlikely that these values for $\Delta\varepsilon$ are significantly changed from NiTi. The value for $\Delta\varepsilon$ would seem to be in the range 5.9 to 6.6%. In the following calculations, $\Delta\varepsilon$ was taken as 0.059 as it was a measured value from tensile tests. Using $\varrho = 6.40 \times 10^3\,\mathrm{kg\,m^{-3}}$ (341.1 mol m^{-3}), the ΔS values for forward and reverse transformations are calculated and tabulated in Table II.

3.2. Stress–strain data from the literature

Miyazaki *et al.* [18] measured a linear region from $250\,\mathrm{K} < T < 325\,\mathrm{K}$ (i.e. above M_s) for the critical stress with temperature for near-stoichiometric single-crystal NiTi, from which values for $\mathrm{d}\sigma_c/\mathrm{d}T$ were calculated. Using the transformational strain of 0.058, the resulting values for ΔS are shown in Table II for the various heat treatments as listed by Miyazaki *et al.* With near stoichiometric compositions and ageing for 1 h at 673 K there was an improvement in the values of $\Delta S^{M \to A}$, although it would appear that ageing for 1 h at 1273 K plus quenching produced the best values. Suburi *et al.* [19] also performed tensile tests on 50.5 at. % Ni–Ti samples. Here it was found that ageing at 850 and 500° C for 1 h did not noticeably affect the gradient of the critical stress against temperature curve. Using the available data, the entropy change was calculated as 4.5 J mol^{-1} K^{-1}.

ΔS values obtained by a Clapeyron analysis of stress–strain curves with temperatures gave values consistent with those from DSC. They are also consistent with the adiabatic calorimetry values discussed in our accompanying paper. As the techniques are for the most part consistent, this implies the latent heats for M → A and A → M with stress transformations are nearly equal.

4. Comparison with other SME alloys

A comparison of the available ΔH and ΔS data from either calorimetry or Clapeyron experiments for different SME alloys was performed. Most of the data obtained were for noble metal single crystals. Frequently the authors neglected to include key data so estimates were made of some parameters. For example, ϱ was calculated on the basis of the high-temperature unit cell, $\Delta\varepsilon$ may be given by a different author, etc.

TABLE II Entropies of transformation as calculated from stress–strain data using the Clapeyron equation. The strain value used was $\Delta\varepsilon = 0.059$. Processing nomenclature: FC, furnace cooled; AC, air cooled; Q, quenched (e.g. 1273 1 Q implies 1 h anneal at 1273 K followed by quenching

Material, conditions	$\frac{d\sigma^{A\to M}}{dT}$ (MPa K^{-1})	$\frac{d\sigma^{M\to A}}{dT}$ (MPa K^{-1})	$\Delta S^{A\to M}$ (J mol^{-1} K^{-1})	$\Delta S^{M\to A}$ (J mol^{-1} K^{-1})	Reference
NiTi 500°C 1 FC	6.71	9.35	0.83	1.15	[9]
NiTi 500°C 1 AC	6.80	8.20	0.84	1.02	[9]
NiTi 500°C 1 Q	6.54	6.25	0.81	0.77	[9]
49.8 at. % Ni 1273 1 Q	8.0	–	3.70	–	[18]
49.8 at. % Ni 773 1 Q	7.50	14.7	3.70	1.82	[18]
49.8 at. % Ni 673 1 Q	4.14	7.94	1.91	0.980	[18]
51.6 at. % Ni 1273 1 Q → 673 1 Q	3.95	6.26	1.82	0.778	[18]
50.6 at. % Ni 1273 1 Q → 673 1 Q	4.51	7.08	2.08	0.875	[18]
50.1 at. % Ni 1273 1 Q → 673 1 Q	6.01	–	2.78	–	[18]
49.8 at. % Ni 1273 1 Q → 673 1 Q	6.77	–	3.13	–	[18]
50.4 at. % Ni 850°C 1 Q	9.80	–	4.53	–	[19]
50.4 at. % Ni 500°C 1 Q	9.80	–	4.53	–	[19]
51.3 at.% Ni 1000°C 1 Q	5.72	–	2.64	–	[19]
51.3 at. % Ni 700°C 1 Q	5.01	–	2.32	–	[19]
51.3 at. % Ni 600°C 1 Q	7.49	–	3.46	–	[19]
51.3 at. % Ni 500°C 1 Q	7.88	–	3.65	–	[19]
50.6 at. % Ni 1273 1 Q	6.57	6.57	3.23	3.23	[16]

The gram molecular weight for an alloy was calculated as the sum of the percentage weight of the constituent elements, in accordance with other workers in the field. The data assembled are the most complete set of thermodynamic values for SME alloys known to date.

4.1. Comparison with noble metal SME alloys

Noble metals SME single crystals differ from NiTi in that they can transform to an entirely martensitic single-phase body. Listed in Table III are the compositions of the alloys, the strain associated with the transformation, the latent heat as measured by DSC, the approximate T_0 value and the ΔS value as given from Equation 2. Also listed for each alloy (when available) is the variation of critical stress with temperature and the calculated entropy change from the Clapeyron equation. Finally, a reference(s) for the presented data is given.

It is first evident from examining Table III that the values for ΔS from either DSC or the Clapeyron equation are reasonably consistent for each alloy. It is also observed that these values tend to be in the range of 0.1 to 2 J mol^{-1} K^{-1}, which is lower than those for NiTi. The lowest values are for In–Tl alloys which are in the range 0.1 to 0.6 J mol^{-1} K^{-1}. Entropies of transformation for Au–Cd based alloys are generally in the range 0.6 to 1.4 J mol^{-1} K^{-1}, significantly better than those for InTl. The largest ΔS belongs to copper based alloys, both Cu–Al–Ni and Cu–Al–Zn have entropies of 1.75 to 2.25 J mol^{-1} K^{-1}. The T_0 values are all within the range 200 to 400 K and so correspondingly, the latent heats are also significantly smaller than NiTi.

The Clapeyron equation provides a good estimate of the transformational entropy values for noble metal SME materials. It is evident that these materials have consistently smaller transformational entropy and latent heats changes than NiTi. These alloys then are less desirable thermodynamically than NiTi as engine elements.

5. Thermal efficiency calculations for SME alloys

A comparison of the thermal efficiencies for SME alloy systems can be performed using Equation 1. This equation will be tested for NiTi using the data for the case of zero or small external load and the largest applied stress before plastic deformation for both NiTi and noble metal SME alloys. The estimation of ΔT_0 involves several assumptions. First, it was assumed that $T_0 = 1/2(M_s + A_s)$ or $1/2(M_s + A_f)$, depending on the available data for the alloy. This does introduce a small amount of inconsistency in the

TABLE III Thermodynamic data from the literature for the noble metal SME alloys. Comparison is available between ΔS values from DSC (ΔS_D) and the Clapeyron equation (ΔS_C). All compositions are in at. %. Due to the difficulty in comparing results, no errors are presented. Only tensile stresses are considered

Alloy	ε	ΔH ($\mathrm{J\,mol^{-1}}$)	T_0 (K)	ΔS_D ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	$d\sigma/dT$ ($\mathrm{MPa\,K^{-1}}$)	ΔS_C ($\mathrm{J\,mol^{-1}}$)	References
52.5Au–47.5Cd	0.038	364*	338	1.08	2.45		[20, 21*]
51.0Au–49.0Cd	0.038	439*	306	1.43	2.45		[20]
50.0Au–50.0Cd	0.038	406*	299	1.36	2.45		[20]
49.0Au–51.0Cd	0.038	414*	266	1.56	2.45		[20]
52.0Au–47.5Cd		255					[22]
52.0Au–47.5Cd		145	331	0.44			[23]
51.0Au–49.0Cd		170	304	0.56			[23]
26Au–29Cu–45Zn	0.06	195	340	0.57	3.04		[24]
26Au–28Cu–46Zn	0.05	157	308	0.51			[24]
26Au–27Cu–47Zn	0.05	157	270	0.58			[24]
26Au–26Cu–48Zn	0.06	153	252	0.61			[24]
50Au–2.5Ag–47.5Cd	0.044	–	315	1.00	2.1	0.999	[25]
50Au–2.5Ag–47.5Cd	0.044	–	305	1.00	2.1	0.999	[25]
47.5Au–5.0Ag–47.5Cd	0.043	318	278	0.81	2.2	1.02	[25]
26.5Au–26.5Ag–47.5Cd	0.020	162	152	1.06	4.7	1.01	[25]
20.0Au–32.5Ag–47.5Cd	0.016	157	183	1.05	3.5	0.858	[25]
20.0Au–32.5Ag–47.5Cd	0.024	184	140	1.34	4.2	1.08	[25]
17.5Au–35.0Ag–47.5Cd	0.020	170	120	1.41	4.6	1.21	[25]
5.0Au–47.5Ag–47.5Cd	0.010	100	151	0.66	4.1	0.446	[25]
84In–16Tl		92.3	403	0.230			[26]
83In–17Tl		80	386	0.207			[26]
82In–18Tl		69	374	0.184			[26]
81In–19Tl		74	361	0.205			[26]
80In–20Tl		62	346	0.179			[26]
79In–21Tl		90.5	331	0.273			[26]
78In–22Tl		40	318	0.126			[26]
78.0In–22.0Tl	0.0095		313		0.0252		[27]
79.0In–21.0Tl	0.0095		332		0.0226		[27]
79.3In–20.7Tl	0.0095		343		0.0316	0.0456	[28]
79In–21Tl	0.0095		333		0.025	0.036	[29]
78In–22Tl	0.0095		311		0.023	0.036	[29]
77In–23Tl	0.0055		290		0.019	0.084	[29]
76In–24Tl	0.0044		265		0.034	0.062	[29]
75In–25Tl	0.0061		230		0.012	0.057	[29]
74In–26Tl	0.0063		211		0.078	0.180	[29]
56.0Ag–44Cd	0.0744		233		1.96	2.89	[30]
55.0Ag–45Cd	0.0744		204		1.96	2.89	[30]
55.0Ag–45Cd	0.0744		196		0.725	1.36	[31]
60.0Cu–40.0Zn	0.17		140		0.096	1.296	[32]
63.8Cu–34.5Zn–1.6Sn	0.055		222		1.915	1.61	[33]
60.8Cu–39.1Zn	0.068		153		1.51		[34]
83.5Cu–14Al–2.5Ni		515	304	1.70			[37]
68.6Cu–27.6Al–3.8Ni	0.085		307		2.04	1.30	[35]
67.9Cu–16.0Al–16.1Zn			273		2.10	1.45	[36]
66Cu–25.3Al–9.1Zn	0.065	289	206	1.40	2.5	1.41	[37]
62.25Cu–36.0Zn–1.75Al	0.065		180		26		[38]

calculation but it is not likely to be serious. Secondly, we assume $dM_s/d\sigma = dA_{s,f}/d\sigma$ which is not a bad assumption for the noble metals or for NiTi. It is needed, as most authors only report $dM_s/d\sigma$ values. To calculate ΔT_0, we take

$$T_0(\sigma_{\max}) = 1/2[M_s(\sigma_{\max}) + A_s(\sigma_{\max})] \tag{7}$$

$$= 1/2[M_s + (dM_s/d\sigma)\sigma_{\max} + A_s + (dA_s/d\sigma)\sigma_{\max}] \tag{8}$$

$$= T_0 + (dM_s/d\sigma)\sigma_{\max} \tag{9}$$

Hence

$$\Delta T_0 = (dM_s/d\sigma)\sigma_{\max} \tag{10}$$

Due to the second assumption, M_s values can be substituted for any others of the start–finish temperatures. The values for ΔT_0 are then calculated from the observed temperature–stress diagram.

5.1. Fully stressed thermal efficiencies

The thermodynamic data of the preceding sections allow production of the definitive table of calculated thermal and Carnot efficiencies of these alloy systems. This is not a rigorous assessment of the data as there were approximations and assumptions required for the calculation to proceed. For example, in most cases C_p values were calculated from the Neumann–Kopp rule, after assuming that the Debye temperature of the alloy was below M_s. In all cases this was so. In addition, the value of $\sigma_{\max}$, the maximum applied stress to produce a martensitic transformation without introducing deformations, varies with temperature. The

TABLE IV Thermal efficiencies for noble metal SME alloys and NiTi are calculated using Equation 1 from published or derived thermodynamic data. Nomenclature identical to that used in Table II. The values for σ_{max} ($dA_f/d\sigma$) for ageings at 673 and 723 K are taken from Miyazakis *et al.* data [18] for 49.8 at. % Ni–Ti at 673 and 773 K, respectively

Material	T_0 (K)	$\sigma_m \frac{dA_f}{d\sigma}$ (K)	C_p ($J\,mol^{-1}\,K^{-1}$)	ΔH ($J\,mol^{-1}$)	η_{th} (%)	η_{car} (%)	Reference
Au–47.5Cd	338	95.3	26.69	368	3.56	–	[20]
Au–49.5Cd	330	77.5	17.99	443	5.67	–	[20]
Au–50.0Cd	299	73.2	18.04	410	4.55	–	[20]
Ag–45Cd	196	123.6	24.62	266	5.07	31.9	[31]
Ag–45Cd	204	120	24.59	589	9.79	41.6	[25]
Ag–44Cd	233	99.96	24.59	673	9.22	34	[25]
In–21Tl	333	29.71	28.03	12.0	0.127	–	[29]
In–22Tl	311	18.27	28.00	11.0	0.124	–	[29]
In–23Tl	290	21.04	28.05	24.3	0.287	–	[29]
In–24Tl	265	27.05	27.57	16.5	0.221	–	[29]
In–25Tl	230	53.99	27.30	13.1	0.207	–	[29]
In–26Tl	211	15.18	27.48	37.9	0.600	–	[29]
Au–29Cu–45Zn	340	27.41	29.72	195	1.55	13.2	[24]
Au–28Cu–46Zn	308	32.24	29.72	157	1.47	15.6	[24]
Au–27Cu–47Zn	270	19.35	29.73	157	1.54	8.89	[24]
Au–26Cu–48Zn	252	21.29	29.83	153	1.64	9.41	[24]
Au–2.5Ag–47.5Cd	315	50.92	27.82	315	3.02	15.8	[25]
Au–2.5Ag–47.5Cd	305	47.6	27.82	305	2.92	13.5	[25]
Au–32.5Ag–47.5Cd	183	64.35	25.94	110	2.17	28.0	[25]
Au–32.5Ag–47.5Cd	140	58.31	23.89	152	4.09	44.3	[25]
Au–47.5Ag–47.5Cd	151	43.6	22.95	67.4	1.82	22.0	[25]
Cu–16.1Zn–16.0Al	240	93.3	25.92	348	4.89	28.6	[36]
Cu–25.33Zn–9.11Al	206	90.71	23.85	289	5.24	31.9	[37]
Cu–27.6Al–3.8Ni	307	186.2	28.03	389	4.21	42.4	[35]
49.8 Ni–Ti 773 1 Q	297	40.8	25.55	541.5	4.6	–	[18]
49.8 Ni–Ti 673 1 Q	282	84.4	25.55	276.4	3.4	–	[18]
51.6 Ni–Ti	212	120	23.12	164.9	3.2	–	[18]
50.6 Ni–Ti	241	84.6	24.70	210.8	3.22	–	[18]
NiTi 723 1 FC	305	32	25.59	1870	7.5	13.6	[9]
NiTi 723 1 AC	293	37	25.59	1595	7.9	14.9	[9]
NiTi 723 1 Q	293	48	25.59	1200	8.1	16.4	[9]
NiTi aged 723 K	307	40.8	25.55	394	3.64	–	[9]
NiTi aged 723 K	305	40.8	25.55	780	5.72	–	[9]
NiTi aged 723 K	326	40.8	25.51	838	5.59	–	[9]
NiTi aged 673 K	305	84.4	25.59	1076	9.20	–	[9]
NiTi aged 673 K	323	84.4	25.59	1270	9.67	–	[9]

value of σ_{max} chosen was the largest presented by the authors. There were no estimates presented in the literature concerning the fraction of material transforming which is dependent on the sample history, etc. Hence these values contain significant scatter due to this lack of documentation.

$\Delta H^{M \rightarrow A}$ values tabulated in Table IV are either derived from the Clapeyron equation in Table III or from DSC measurements. Au–Cd and related alloy systems (Au–Ag–Zn) etc., typically have thermal efficiencies ranging from 2 to 6%, the exception being Ag–45.0Cd with a larger efficiency of 9%. In–Tl alloys have a small latent heat and so have a small thermal efficiency of 0.2%. β-phase brass alloys such as Cu–Zn–Al and Cu–Al–Ni have roughly equal thermal efficiencies of 4 to 5%.

NiTi has a large latent heat associated with its forward work-producing transformation which is roughly 1200 J mol^{-1} so that the calculated maximum thermal efficiency is 12%. This is a significant increase to that of the noble metals.

The two assumptions which allowed these calculations to proceed have an indeterminant error. In the case of NiTi at 10% efficiency the uncertainty was estimated as ~3%. In the case of Au–Cd the uncertainty was ~1.5%. Scatter in the efficiencies for one alloy are strongly dependent on the conditioning the material underwent before testing (e.g. observe the variation in latent heats in 50.6 at. % Ni–Ti in Table IV). These calculations should be treated as a general "rule of thumb" for comparing SME alloy performance.

6. Conclusions

The following points have been established about the martensitic transformation responsible from shape memory behaviour in NiTi.

1. The enthalpies of transformation in NiTi are large and are of the order of 1200 J mol^{-1} with a transformation temperature of 300 K, corresponding entropies of transformation are 3 to 4 J mol^{-1} K^{-1}. In noble metal SME alloys, the entropies are, at best, two times smaller than NiTi. At worst, as in the case of InTl, they are at least fifteen times smaller.

2. DSC and the Clapeyron equation provide similar results in evaluating the latent heats for NiTi. In noble metal SME alloys, there is also consistency between Clapeyron and calorimetric values for entropy and enthalpy changes.

3. The maximum thermal efficiency for NiTi ranges

from 7.5 to 10% for a transformation near 300 K, a factor of 2 better than that of Cu–Al–Ni or Cu–Al–Zn. A close rival is Ag–Cd with 9% efficiency transforming at ~ 150 K.

Acknowledgements

The author is grateful to the British Gas Corporation for a British Gas Scholarship, and also wishes to acknowledge technical assistance from Dr J. Sargent and Messrs H. Young and M. Gabb. This work was carried out under the supervision of Professor K. H. G. Ashbee.

References

1. P. WOLLANTS, M. DE BONTE and J. ROOS, *Z. Metallkde* **70** (1979).
2. *Idem, ibid.* **70** (1979) 113.
3. A. P. JARDINE, *J. Mater. Sci.* (1987).
4. M. AHLERS, *Scripta Metall.* **9** (1975) 7174.
5. H. C. TONG and C. M. WAYMAN, *Acta. Metall.* **22** (1974) 987.
6. K. MUKHERJEE, *Scripta Metall.* **14** (1980) 405.
7. R. J. SALZBRENNER and M. COHEN, *Acta Metall.* **24** (1980) 739.
8. G. KAUFMAN and M. COHEN, *Progr. Metal Phys.* **7** (1958) 197.
9. A. P. JARDINE, K. H. G. ASHBEE and M. BASSETT, *J. Mater. Sci.* (1987).
10. M. MELTON and O. MERCIER, *J. Appl. Phys.* **50** (1979) 5747.
11. F. E. WANG, W. J. BUEHLER and S. J. PICKART, *ibid.* **36** (1965) 3232.
12. R. J. WASILEWSKI, S. R. BUTLER, J. E. MANLON and D. WARDEN, *Met. Trans.* **2** (1971) 229.
13. H. A. BERMAN, E. D. WEST and A. G. ROZNER, *J. Appl. Phys.* **38** (1967) 4473.
14. E. GOO and R. SINCLAIR, *Acta Metall.* **33** (1985) 1717.
15. S. MIYAZAKI, S. KIMURA, K. OTSUKA and Y. SUZUKI, *Scripta Metall.* **18** (1984) 883.
16. S. MIYAZAKI, K. OTSUKA and Y. SUZUKI, *ibid.* **15** (1981) 287.
17. G. M. MICHAL and R. SINCLAIR, *Acta Crystallogr. B* **37** (1981) 1803.
18. S. MIYAZAKI, Y. OHMI, K. OTSUKA and Y. SUZUKI, Proceedings ICOMAT (Leuven), *J. de Phys.* **43** (1982) C4-255.
19. T. SUBURI, T. TATSUMI and S. NENNO, *ibid.* **43** (1982) C4-261.
20. N. NAKANISHI, T. MORI, S. MIURA *et al., Phil. Mag.* **28** (1973) 277.
21. N. NAKANISHI and C. M. WAYMAN, *Trans. AIME.* **227** (1963) 500.
22. J. INTRATER, L. C. CHANG and T. A. REED, *Phys. Rev.* **86** (1952) 598.
23. B. PREDEL, *Z. Metallkde* **55** (1964) 117.
24. S. MIURA, S. MAEDA and N. NAKANISHI, *Phil. Mag.* **30** (1974) 565.
25. S. MIURA, F. HORI and N. NAKANISHI, *ibid.* **A40** (1979) 661.
26. J. PATEL and S. AHMED, *Met. Sci.* **12** (1978) 147.
27. S. MIURA, T. ITO and N. NAKANISHI, *Scripta Metall.* **10** (1974) 87.
28. M. W. BURKHART and T. A. READ, *Trans. AIME* **197** (1953) 1516.
29. S. MIURA, M. ITO, K. ENDO and N. NAKANISHI, *Mem. Fac. Eng. Kyoto Uni.* **43** (1983) 287.
30. S. MIURA, T. MORI and N. NAKANISHI, *Scripta Metall.* **7** (1973) 697.
31. R. V. KRISHNAN and L. C. BROWN, *Metall. Trans.* **4** (1973) 423.
32. W. ARNEODO and M. AHLERS, *Acta Metall.* **22** (1974) 1475.
33. J. D. EISENWASSER and L. C. BROWN, *Metall. Trans.* (1972) 1359.
34. T. A. SCHROEDER and C. M. WAYMAN, *Acta Metall.* **27** (1979) 405.
35. K. OTSUKA, H. SAKAMOTO and K. SHIMUZU, *ibid.* **27** (1979) 585.
36. T. SABURI, Y. INADA, S. NENNO and N. HORI, Proceedings ICOMAT (Leuven), *J. de Phys.* **43** (1982) C4-633.
37. P. WOLLANTS, M. DE BONTE and J. ROOS, *Z. Metallkde* **70** (1979a).
38. H. POPS and N. RIDLEY, *Met. Trans.* **1** (1970) 2653.

Received 22 September 1987
and accepted 26 January 1988