ENTHALPY AND HEAT CAPACITY OF TITANIUM BASED ALLOYS

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Abstract

Light metal alloys, as aluminium- and titanium based alloys, are of great interest to aerospace industry but thermodynamic information, mainly heat capacity, is often missing.

Then we measured on heating the heat content of seven industrial titanium alloys from room temperature to 600°C with the help of a high-temperature Calvet calorimeter (drop method). Their heat capacities were deduced by derivation of the enthalpy with respect to temperature. The departures from Kopp-Neuman law were calculated.

Introduction

Thermodynamic information on light metal alloys, as titanium-based alloys, is very scarce. Since such solid alloys are of great interest to aerospace industry, a better knowledge of their thermophysical properties is needed in order to develop previsional models as well as to promote their industrial applications. Then it is the aim of this work to provide experimental data on these alloys, especially from the point of view of their heat capacity.

Experimental

The enthalpy variations from room temperature to T, $\Delta H(T) = H(T)-H(25)$, were measured on heating by a drop method using a high temperature ($T<1000°C$) Calvet calorimeter. The method used was already described [1]. At

each given temperature, the measurements were repeated about ten times by dropping small samples (40–80 mg, 25°C) of alloy into the calorimetric cell at T.

Then the thermal effect, $\Delta H(T)$, corresponding to each drop is the following:

$$\text{Ti-alloy } (25°C) \rightarrow \text{Ti-alloy } (T/°C)$$
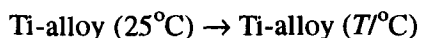
The calibration of the apparatus was performed by dropping some (about five) small quantities of certified N. B. S. α-alumina, the enthalpy of which is well known [2].

The titanium-based alloys were provided by the Mannesmann Research Institute (Stuttgart, Germany). Their chemical analysis is given in Table 1. The purity of pure titanium, purchased by Koch-Light, was better than 99.99 mass%.

Table 1 Chemical analysis of the alloys investigated (mass %)

	B1	E1	E3	G11	E2A	G10	I1
Ti	89.78	86.02	92.60	85.04	89.42	89.49	76.05
Al	6.03	5.6	4.9	5.78	6.36	6.34	3.1
V	4.09	5.4		<0.01	4.08	3.90	14.8
C	0.032	0.015	0.010	0.066	0.026	0.024	0.024
Fe	0.10	0.52	2.5	0.05	0.14	0.27	0.15
N	0.013	0.013	0.01	0.035	0.015	0.015	0.019
O	0.14	0.19	0.13	0.24	0.166	0.235	0.11
Sn		1.9		3.85			2.9
Cu		0.56					
Si				0.35			
Mn				0.05			
Zr				3.47			
Nb				1.03			

Results

In order to check the consistency of our experimental determinations we measured the enthalpy variation of pure titanium in the same range of temperature as for the alloys. The results are given in Table 2 and shown in Fig. 1. As it can be seen they agree well with the values selected by Hultgren et al. [3].
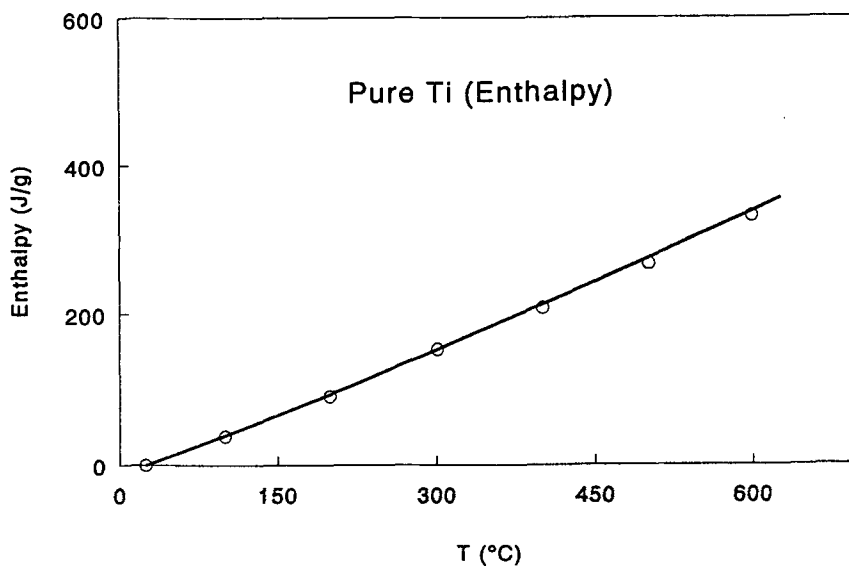
The experimental enthalpy variations of the seven alloys investigated are shown in Figs 2 to 8 with respect to temperature. The corresponding data are

Table 2 Heat content of pure titanium (experimental results)

$T/^\circ C$	$H/J\cdot g^{-1}$	$\sigma/J\cdot g^{-1}$	$T/^\circ C$	$H/J\cdot g^{-1}$	$\sigma/J\cdot g^{-1}$
100	38.9	0.3	401	208.2	3.6
199	92.1	0.5	501	267.3	4.8
301	153.6	1.7	599	331.9	4.5

Table 3 Heat content of the B1 sample (experimental results)

$T/^\circ C$	$H/J\cdot g^{-1}$	$\sigma/J\cdot g^{-1}$	$T/^\circ C$	$H/J\cdot g^{-1}$	$\sigma/J\cdot g^{-1}$
98	40.6	0.4	300	155.0	5.1
99	41.5	1.2	347	186.6	4.3
100	40.9	0.4	348	185.9	4.0
152	70.0	0.4	350	189.1	3.6
197	96.5	0.5	394	212.9	4.9
198	96.8	0.8	401	219.0	4.2
199	97.7	0.9	456	253.3	6.9
200	97.6	1.7	503	283.0	5.9
249	126.9	0.6	551	315.4	3.5
250	127.5	0.6	602	356.8	7.0
299	157.4	0.5			

Fig. 1 Heat content variation with respect to temperature of pure titanium. Each experimental point corresponds to the mean value of about ten measurements. The solid line was taken from Ref. [3]

given respectively in Tables 3 to 9. They differ only slightly at high temperature from that of pure titanium since they contain at least 75 mass% of titanium.
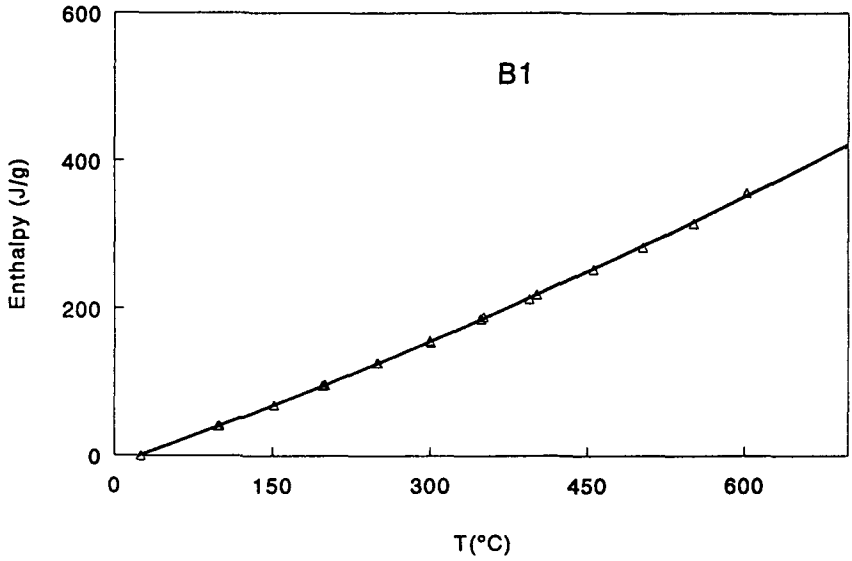

Fig. 2 Heat content variation with respect to temperature of B1 sample. Each experimental point corresponds to the mean value of about ten measurements
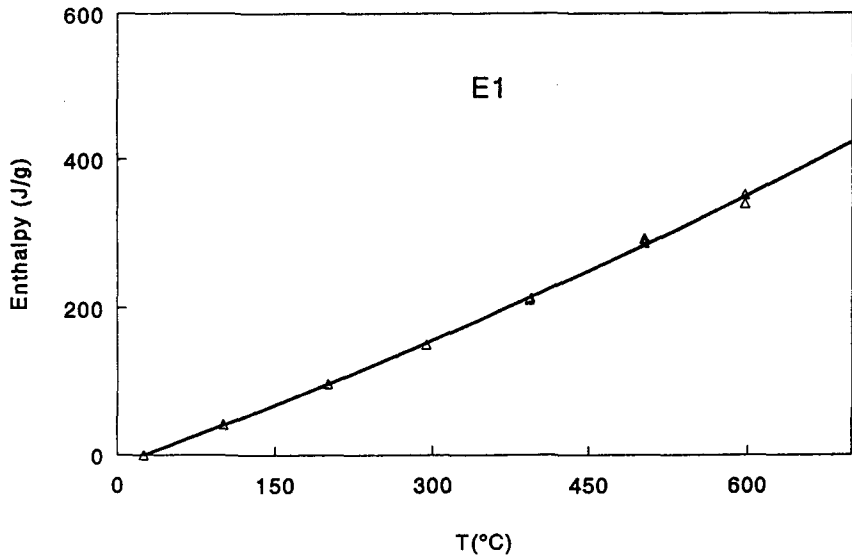

Fig. 3 Heat content variation with respect to temperature of the E1 sample. Each experimental point corresponds to the mean value of about ten measurements
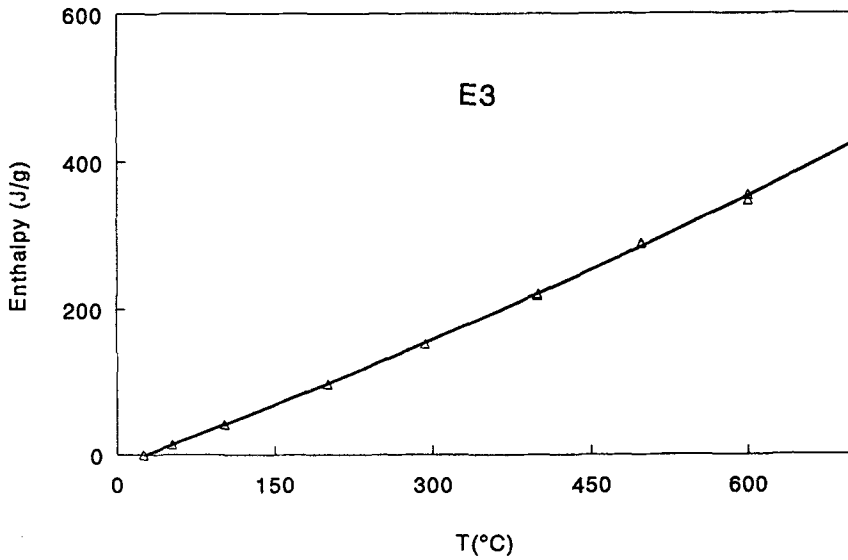
Fig. 4 Heat content variation with respect to temperature of the E3 sample. Each experimental point corresponds to the mean value of about ten measurements
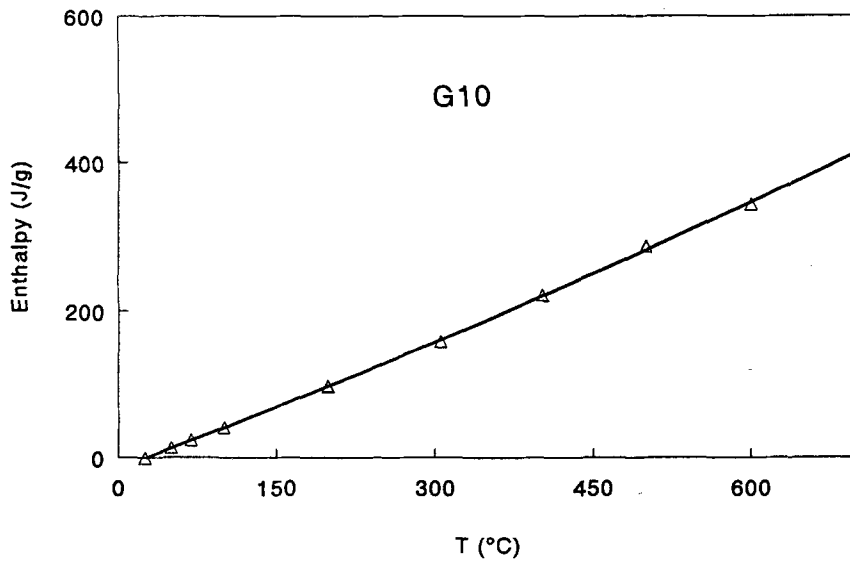

Fig. 5 Heat content variation with respect to temperature of the G10 sample. Each experimental point corresponds to the mean value of about ten measurements
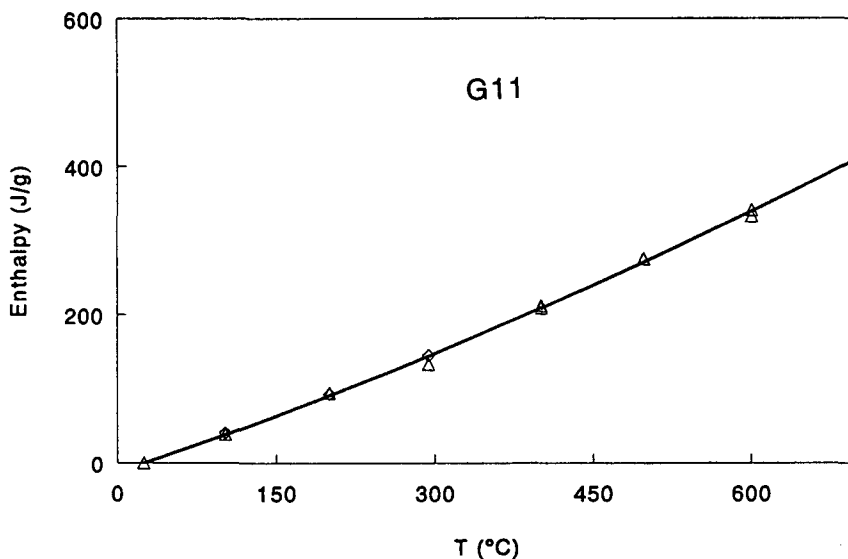
Fig. 6 Heat content variation with respect to temperature of the G11 sample. Each experimental point corresponds to the mean value of about ten measurements. The rhombi correspond to measurements after annealing for two hours at 200°C
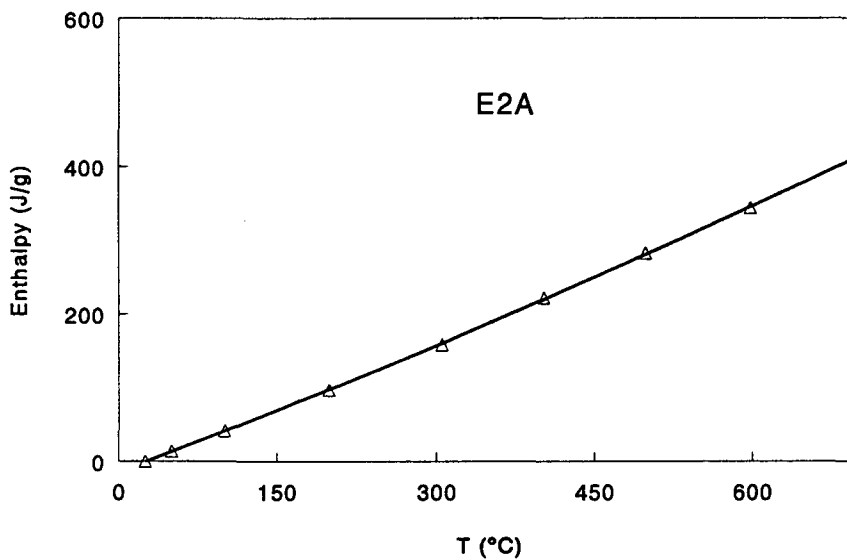

Fig. 7 Heat content variation with respect to temperature of the E2A sample. Each experimental point corresponds to the mean value of about ten measurements
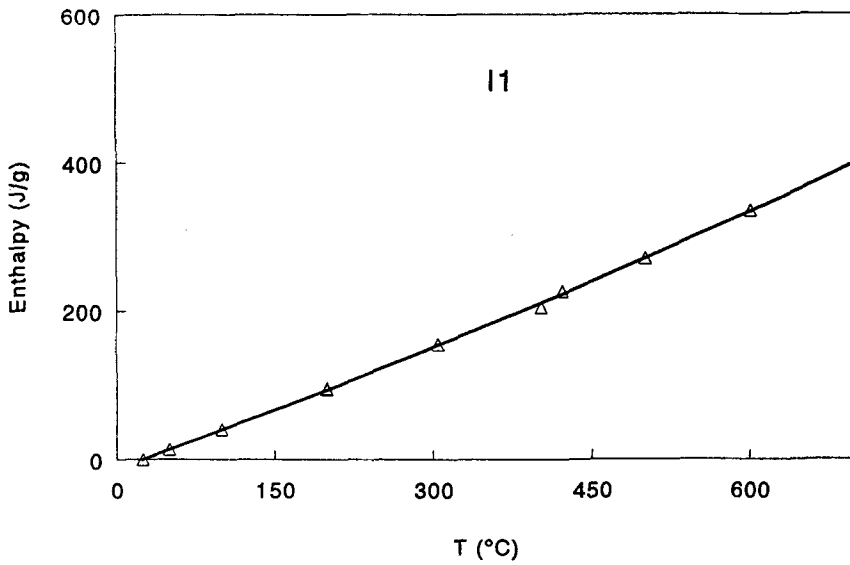
Fig. 8 Heat content variation with respect to temperature of the I1 sample. Each experimental point corresponds to the mean value of about ten measurements
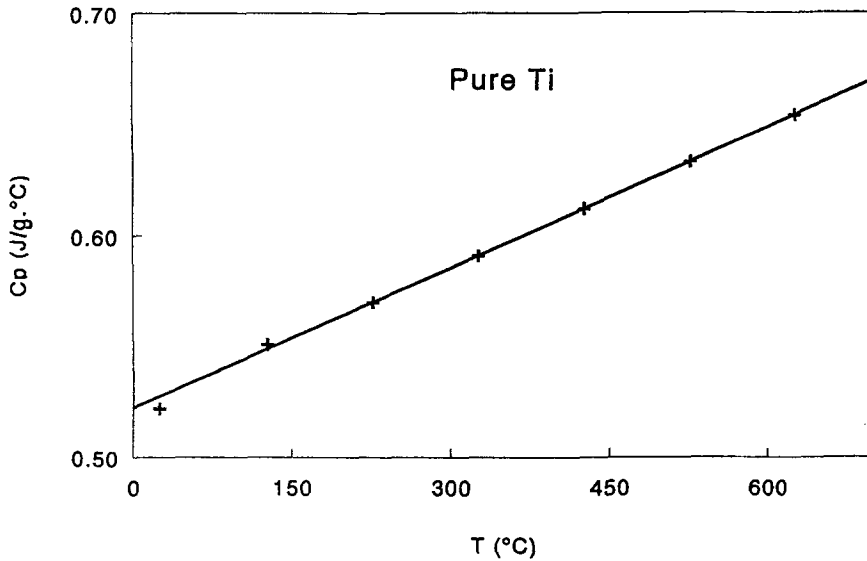

Fig. 9 Heat capacity of pure titanium with respect to temperature. The crosses were taken from [3]. The solid line corresponds to a linear fitting of the crosses

Table 4 Heat content of the E1 sample (experimental results)

$T/°C$	$H/J\cdot g^{-1}$	$\sigma/J\cdot g^{-1}$	$T/°C$	$H/J\cdot g^{-1}$	$\sigma/J\cdot g^{-1}$
101	41.7	0.1	393	211.0	3.4
101	41.5	0.3	394	213.7	4.9
103	43.5	0.1	502	288.7	5.7
200	97.3	0.2	502	294.4	4.1
200	96.7	0.2	597	352.9	2.5
294	150.4	0.9	597	340.8	4.7
294	150.3	0.5			

Table 5 Heat content of the E3 sample (experimental results)

$T/°C$	$H/J\cdot g^{-1}$	$\sigma/J\cdot g^{-1}$	$T/°C$	$H/J\cdot g^{-1}$	$\sigma/J\cdot g^{-1}$
52	14.0	0.1	400	218.5	6.7
102	41.8	0.2	498	290.0	6.4
200	97.4	0.2	498	288.8	5.2
294	151.8	0.9	600	355.4	6.0
400	220.2	4.3	600	348.0	4.2

Table 6 Heat content of the G11 sample (experimental results)

$T/°C$	$H/J\cdot g^{-1}$	$\sigma/J\cdot g^{-1}$	$T/°C$	$H/J\cdot g^{-1}$	$\sigma/J\cdot g^{-1}$
102	39.5	1.5	401	290.5	3.8
102	39.3	0.8	498	276.3	4.1
200	93.2	2.5	498	275.1	2.3
294	133.7	3.4	600	340.8	5.9
401	212.2	3.1	600	332.8	3.7

Table 7 Heat content of the E2A sample (experimental results)

$T/°C$	$H/J\cdot g^{-1}$	$\sigma/J\cdot g^{-1}$	$T/°C$	$H/J\cdot g^{-1}$	$\sigma/J\cdot g^{-1}$
50	13.7	0.2	402	222.2	5.8
100	41.2	0.3	498	282.2	11.0
199	97.0	0.4	598	344.0	5.6
305	159.0	0.7			

Table 8 Heat content of the G10 sample (experimental results)

$T/°C$	$H/J·g^{-1}$	$\sigma/J·g^{-1}$	$T/°C$	$H/J·g^{-1}$	$\sigma/J·g^{-1}$
50	13.3	0.2	199	98.0	0.2
69	24.3	0.6	305	158.8	0.9
100	41.7	0.3	402	221.6	3.0
199	98.1	0.2	500	287.0	2.9
199	97.3	0.4	600	343.8	8.3
199	98.8	0.3			

Table 9 Heat content of the I1 sample (experimental results)

$T/°C$	$H/J·g^{-1}$	$\sigma/J·g^{-1}$	$T/°C$	$H/J·g^{-1}$	$\sigma/J·g^{-1}$
50	13.3	0.2	199	96.2	0.2
50	13.6	0.1	305	154.4	0.6
100	40.1	0.3	402	204.8	4.8
199	94.1	0.6	501	271.0	3.1
199	94.1	0.3	601	335.1	11.7

Table 10 Heat content and heat capacity of the B1 sample (smoothed values)

T/K	$H/J·g^{-1}$	$C_p/J·g^{-1}·deg^{-1}$	T/K	$H/J·g^{-1}$	$C_p/J·g^{-1}·deg^{-1}$
300	2.4	0.525	600	173.1	0.613
325	15.6	0.533	625	188.5	0.620
350	29.0	0.540	650	204.1	0.627
375	42.6	0.547	675	219.9	0.635
400	56.3	0.554	700	235.8	0.642
425	70.3	0.562	725	252.0	0.649
450	84.4	0.569	750	268.3	0.657
475	98.8	0.576	775	284.8	0.664
500	113.3	0.584	800	301.5	0.671
525	127.9	0.591	825	318.4	0.679
550	142.8	0.598	850	335.4	0.686
575	157.8	0.606	875	352.6	0.693

We used a second order polynomial for the seven alloys investigated. Indeed, the crosses in Fig. 9 correspond to the C_p data of pure Ti taken from Hultgren *et al.* [3] and the solid line corresponds to the C_p data obtained by

parabolic fitting of the enthalpy values of the same authors (i.e. linear fitting of the heat capacity). As can be seen, they are in good agreement with the direct data (except near 0°C), which confirms the validity of our simplified mathematical treatment.

The corresponding C_p data are shown in Figs 10–16 and given in Tables 10 to 16. They lead to the following equations:

Alloy B-1

$$H(T/°C) - H(25°C) / J \cdot g^{-1} = -11.710 + 0.51735 \, T + 0.000146 \, T^2$$
$$C_p \, (T/°C) / J \cdot K^{-1} \cdot g^{-1} = 0.51735 + 0.000292 \, T$$

Alloy E-1

$$H(T/°C) - H(25°C) / J \cdot g^{-1} = -13.255 + 0.52154 \, T + 0.000145 \, T^2$$
$$C_p \, (T/°C) / J \cdot K^{-1} \cdot g^{-1} = 0.52154 + 0.000290 \, T$$

Alloy E-3

$$H(T/°C) - H(25°C) / J \cdot g^{-1} = -14.356 + 0.53658 \, T + 0.000129 \, T^2$$
$$C_p \, (T/°C) / J \cdot K^{-1} \cdot g^{-1} = 0.53658 + 0.000258 \, T$$

Alloy G-11

$$H(T/°C) - H(25°C) / J \cdot g^{-1} = -12.363 + 0.48425 \, T + 0.000170 \, T^2$$
$$C_p \, (T/°C) / J \cdot K^{-1} \cdot g^{-1} = 0.48425 + 0.000340 \, T$$

Alloy E-2A

$$H(T/°C) - H(25°C) / J \cdot g^{-1} = -14.152 + 0.54520 \, T + 0.000094 \, T^2$$
$$C_p \, (T/°C) / J \cdot K^{-1} \cdot g^{-1} = 0.51520 + 0.000186 \, T$$

Alloy I-1

$$H(T/°C) - H(25°C) / J \cdot g^{-1} = -12.167 + 0.51139 \, T + 0.000108 \, T^2$$
$$C_p \, (T/°C) / J \cdot K^{-1} \cdot g^{-1} = 0.51139 + 0.000216 \, T$$

Alloy G-10

$$H(T/°C) - H(25°C) / J \cdot g^{-1} = -14.278 + 0.54895 \, T + 0.000088 \, T^2$$
$$C_p \, (T/°C) / J \cdot K^{-1} \cdot g^{-1} = 0.54895 + 0.000176 \, T$$

The same fitting applied to pure titanium yields the following expressions:

$$H(T/°C) - H(25°C) / J \cdot g^{-1} = -13.183 + 0.52261 \, T + 0.000105 \, T^2$$
$$C_p \, (T/°C) / J \cdot K^{-1} \cdot g^{-1} = 0.52261 + 0.000210 \, T$$

In Figs 10 to 16, we put also the heat capacity values according to additivity (open squares) and the corresponding deviations to the Kopp and Neumann law

(open circles). The heat contents of pure solid components were taken from [4]. For tin, we had to extrapolate its C_p values from its melting point up to 600°C. We took into account only metallic additives, neglecting oxygen, nitrogen, hydrogen and carbon impurities. As can be seen the departures from additivity are very low. The maximum corresponds to the G-11 sample at 600°C (+5.8%).

In case of G-11 sample, we also measured the heat content after annealing at 200°C for about 2 h (see diamond symbols in Fig. 5). There is no significant difference.

Table 11 Heat content and heat capacity of the E1 sample (smoothed values)

T/K	$H/J\cdot g^{-1}$	$C_p/J\cdot g^{-1}\cdot deg^{-1}$	T/K	$H/J\cdot g^{-1}$	$C_p/J\cdot g^{-1}\cdot deg^{-1}$
300	0.9	0.529	600	172.8	0.616
325	14.3	0.537	625	188.3	0.624
350	27.8	0.544	650	204.0	0.631
375	41.5	0.551	675	219.8	0.638
400	55.3	0.558	700	235.9	0.645
425	69.4	0.566	725	252.1	0.653
450	83.6	0.573	750	268.5	0.660
475	98.0	0.580	775	285.1	0.667
500	112.6	0.587	800	301.9	0.674
525	127.4	0.595	825	318.8	0.682
550	142.3	0.602	850	335.9	0.689
575	157.5	0.609	875	353.3	0.696

Table 12 Heat content and heat capacity of the E3 sample (smoothed values)

T/K	$H/J\cdot g^{-1}$	$C_p/J\cdot g^{-1}\cdot deg^{-1}$	T/K	$H/J\cdot g^{-1}$	$C_p/J\cdot g^{-1}\cdot deg^{-1}$
300	0.2	0.544	600	174.9	0.621
325	13.9	0.550	625	190.5	0.627
350	27.7	0.556	650	206.3	0.634
375	41.7	0.563	675	222.2	0.640
400	55.9	0.569	700	238.3	0.647
425	70.2	0.576	725	254.5	0.653
450	84.7	0.582	750	270.9	0.660
475	99.3	0.589	775	287.5	0.666
500	114.1	0.595	800	304.3	0.673
525	129.1	0.602	825	321.1	0.679
550	144.2	0.608	850	338.2	0.685
575	159.5	0.615	875	355.4	0.692

Table 13 Heat content and heat capacity of the G11 sample (smoothed values)

T/K	$H/J\cdot g^{-1}$	$C_p/J\cdot g^{-1}\cdot deg^{-1}$	T/K	$H/J\cdot g^{-1}$	$C_p/J\cdot g^{-1}\cdot deg^{-1}$
300	0.8	0.493	600	164.2	0.595
325	13.3	0.502	625	179.2	0.604
350	25.9	0.510	650	194.4	0.612
375	38.8	0.519	675	209.8	0.621
400	51.9	0.527	700	225.4	0.629
425	65.2	0.536	725	241.3	0.638
450	78.7	0.544	750	257.3	0.646
475	92.4	0.553	775	273.6	0.655
500	106.3	0.561	800	290.0	0.663
525	120.5	0.570	825	306.7	0.672
550	134.8	0.578	850	323.6	0.680
575	149.4	0.587	875	340.8	0.689

Table 14 Heat content and heat capacity of the E2A sample (smoothed values)

T/K	$H/J\cdot g^{-1}$	$C_p/J\cdot g^{-1}\cdot deg^{-1}$	T/K	$H/J\cdot g^{-1}$	$C_p/J\cdot g^{-1}\cdot deg^{-1}$
300	0.6	0.550	600	174.2	0.607
325	14.5	0.555	625	189.4	0.611
350	28.4	0.560	650	204.8	0.616
375	42.4	0.564	675	220.2	0.621
400	56.6	0.569	700	235.8	0.626
425	70.9	0.574	725	251.5	0.630
450	85.3	0.579	750	267.3	0.635
475	99.8	0.583	775	283.2	0.640
500	114.5	0.588	800	299.3	0.644
525	129.2	0.593	825	315.4	0.649
550	144.1	0.597	850	331.7	0.654
575	159.1	0.602	875	348.1	0.658

Finally, Figs 17 and 18 enable to compare our results on the B-1 and I-1 samples with those of Ziegler and Mullins [5] quoted by Touloukian and Buyco in their compilation [6]. As can be seen, the agreement is not so bad although Ziegler and Mullins did not use a linear dependence of C_p vs. T. Moreover, the composition of their alloy was not exactly the same as for our samples (5.89 mass% Al and 3.87 %V instead of 6.03 and 4.09 for B-1 and 2.75 %Al and 14.95 %V instead of 3.1 %Al and 14.8 %V for I1 respectively).

Table 15 Heat content and heat capacity of the G10 sample (smoothed values)

T/K	H /J·g^{-1}	C_p /J·g^{-1}·deg^{-1}	T/K	H /J·g^{-1}	C_p /J·g^{-1}·deg^{-1}
300	0.6	0.554	600	174.6	0.607
325	14.5	0.558	625	189.9	0.611
350	28.5	0.563	650	205.2	0.615
375	42.6	0.567	675	220.6	0.620
400	56.9	0.571	700	236.2	0.624
425	71.2	0.576	725	251.8	0.629
450	85.6	0.580	750	267.6	0.633
475	100.2	0.585	775	283.5	0.637
500	114.9	0.589	800	299.5	0.642
525	129.7	0.593	825	315.6	0.646
550	144.5	0.598	850	331.8	0.651
575	159.5	0.602	875	348.1	0.655

Table 16 Heat content and heat capacity of the I1 sample (smoothed values)

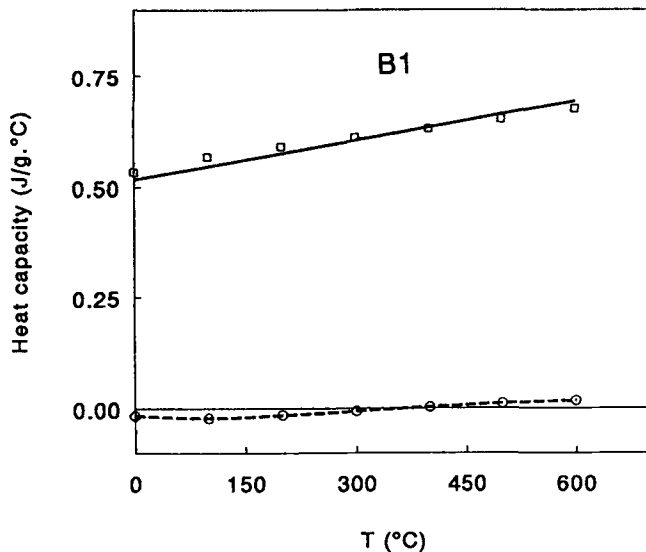| T/K	H /J·g^{-1}	C_p /J·g^{-1}·deg^{-1}	T/K	H /J·g^{-1}	C_p /J·g^{-1}·deg^{-1}
300	1.7	0.517	600	166.6	0.582
325	14.7	0.523	625	181.2	0.587
350	27.9	0.528	650	196.0	0.593
375	41.1	0.533	675	210.9	0.598
400	54.5	0.539	700	225.9	0.604
425	68.1	0.544	725	241.1	0.609
450	81.7	0.550	750	256.3	0.614
475	95.5	0.555	775	271.8	0.620
500	109.5	0.560	800	287.3	0.625
525	123.6	0.566	825	303.0	0.631
550	137.8	0.571	850	318.9	0.636
575	152.1	0.577	875	334.8	0.641

Fig. 10 Heat capacity (solid line) and departures from additivity (dotted line and open circles) of the B1 sample with respect to temperature. The open squares were calculated assuming additivity
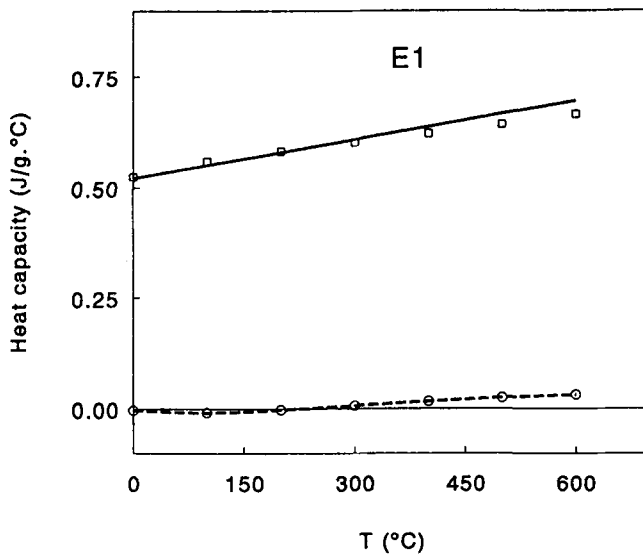

Fig. 11 Heat capacity (solid line) and departures from additivity (dotted line and open circles) of the E1 sample with respect to temperature. The open squares were calculated assuming additivity
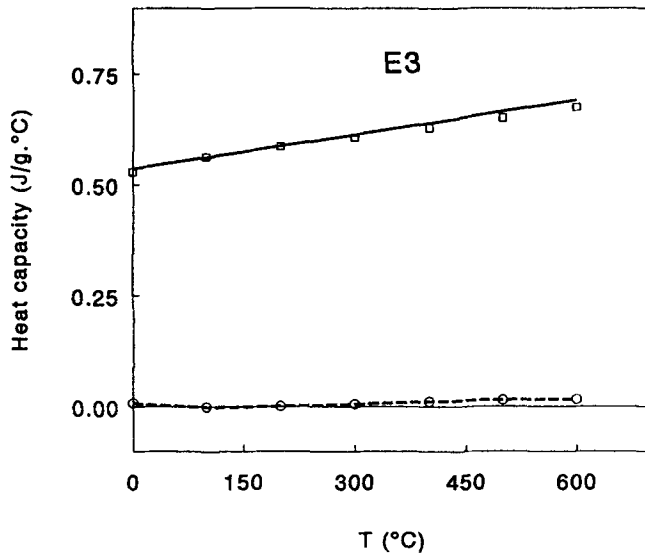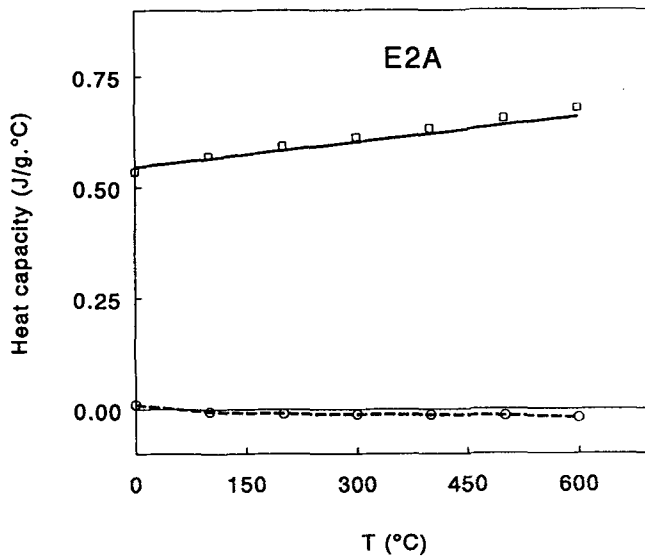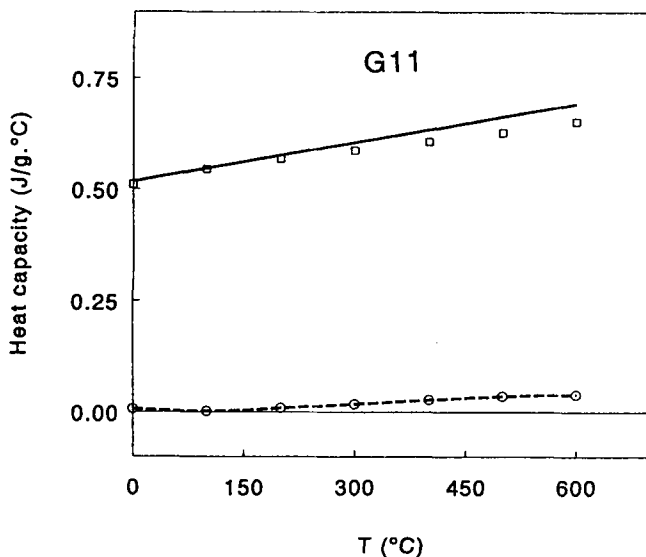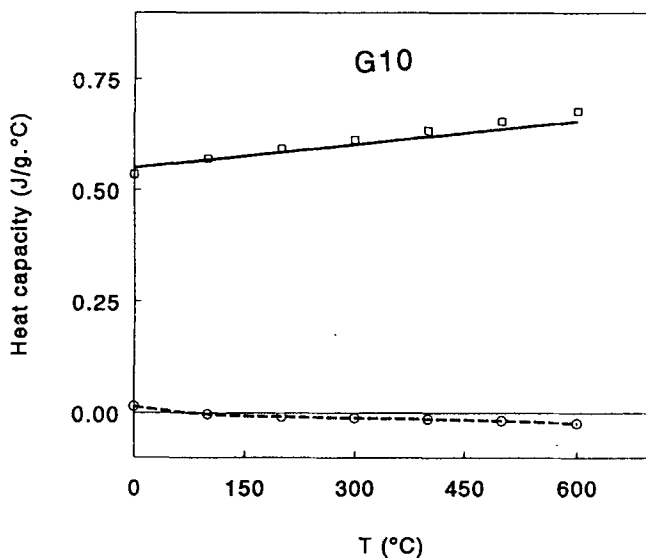
Fig. 12 Heat capacity (solid line) and departures from additivity (dotted line and open circles) of the E3 sample with respect to temperature. The open squares were calculated assuming additivity

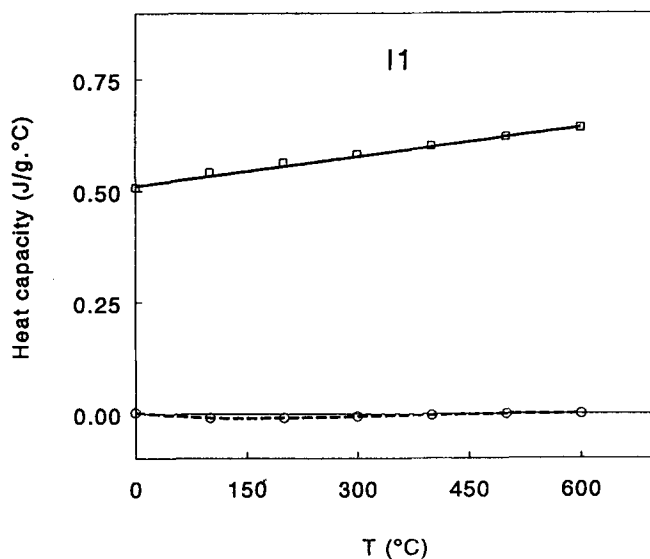

Fig. 13 Heat capacity (solid line) and departures from additivity (dotted line and open circles) of the E2A sample with respect to temperature. The open squares were calculated assuming additivity

Fig. 14 Heat capacity (solid line) and departures from additivity (dotted line and open circles) of the G11 sample with respect to temperature. The open squares were calculated assuming additivity

Fig. 15 Heat capacity (solid line) and departures from additivity (dotted line and open circles) of the G10 sample with respect to temperature. The open squares were calculated assuming additivity

Fig. 16 Heat capacity (solid line) and departures from additivity (dotted line and open circles) of the I1 sample with respect to temperature. The open squares were calculated assuming additivity
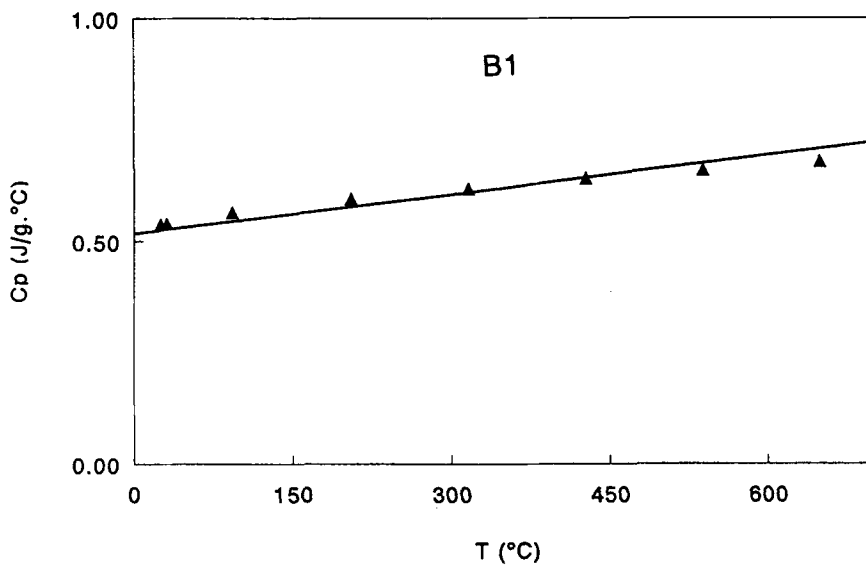

Fig. 17 Heat capacity of the B1 sample with respect to temperature. Solid line: this work, solid points: according to [5]
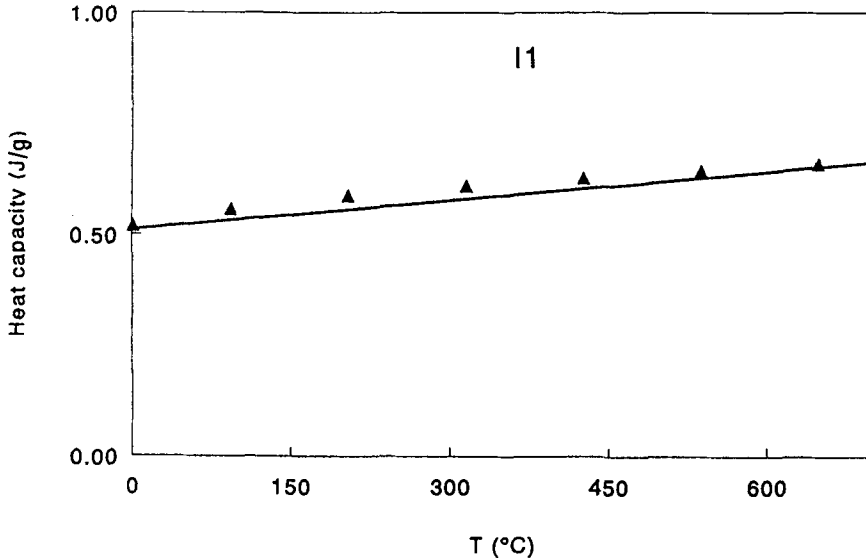
Fig. 18 Heat capacity of the I1 sample with respect to temperature. Solid line: this work, solid
points: according to [5]

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Zusammenfassung — Leichtmetallegierungen auf Aluminium- und Titanbasis sind von großem Interesse für die Raumfahrtindustrie, oft fehlen jedoch thermodynamische Angaben, insbesondere zur Wärmekapazität.
Mit Hilfe eines Hochtemperatur Calvet-Kalorimeter (drop-method) bestimmten wir von Raumtemperatur bis zu 600°C die Enthalpie von sieben verschiedenen Titanlegierungen. Die Wärmekapazitäten wurden aus der Enthalpie nach der Temperatur abgeleitet. Es wurde eine Abweichung vom Kopp-Neumannschen Gesetz berechnet.