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Enthalpy Increment Measurements from 4.5 K to 350 K and the Thermodynamic Properties of the Titanium Silicide Ti_5Si_3(cr)

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Enthalpy increments for Ti_5Si_3(cr) were measured from 4.5 K to 350 K with an adiabatic calorimeter. From a representation of these measurements the enthalpy relative to 0 K, the entropy, and the heat capacity of Ti_5Si_3(cr) to 350 K were calculated. Values of the Debye temperature, Θ_D, and the coefficient for the heat capacity of the conduction electrons, γ_{el}, were determined from the model. Thermodynamic properties for formation from the elements at 298.15 K were also given. Our previous value of Θ_D for $TiSi_2$ was revised due to improvement in the method of representation.

Introduction

This contribution is part of a continuing program of determination of the thermodynamic properties of metal−silicide materials, in general, and the titanium silicides, in particular. The present work provides new thermodynamic measurements and thermodynamic functions for Ti_5Si_3(cr). The measurements are enthalpy increments measured for small differences in temperature, on the order of 1.5 K to 5 K, with an adiabatic calorimeter. The entropy, enthalpy relative to 0 K, and the heat capacity of Ti_5Si_3 to 350 K were calculated from these measurements.

Experimental Section

Ingots of Ti_5Si_3 were produced by means of arc melting in a titanium gettered, argon atmosphere (Feder et al., 1993; Grosman and Cotts, 1993). Mass differences between the ingots and the starting materials were negligible. The titanium and silicon used in sample preparation were of high purity, <0.01 and <0.005 mol % metallic impurities, respectively. Pieces of each Ti_5Si_3 ingot were finely powdered in an acetone medium. Glass slides were coated with a thin layer of Vaseline petroleum jelly, and the powder was sprinkled onto the slide. X-ray diffraction analysis was performed in a standard $\theta-2\theta$ geometry using Cu Kα radiation. The observed lattice parameters, $a = (0.7454 \pm 0.001)$ nm and $c = (0.5150 \pm 0.001)$ nm, were consistent with previous observations (0.7465 nm, 0.5162 nm from Pietrokowsky and Duwez, 1951; 0.7448 nm, 0.5114 nm, from Nowotny et al., 1959). Chemical analysis, performed by LECO Corp., on selected samples indicated that the ingots contained <600 ppm O_2, <200 ppm C, <50 ppm N_2, and <2 ppm H_2.

Selected, relatively large pieces of ingots were cut and polished for optical microscope analysis. Optical micrographs revealed grain sizes between (0.5 and 1.0) mm, primarily of single phase. The level of contamination by secondary phases was estimated to be between 0.7% and 0.9% by mass. X-ray diffraction, electron dispersion spectroscopy, and scanning electron microscopy were used to determine the stoichiometry of the contaminating phases. The contaminating phases consisted of Ti_3Si and Ti_5Si_4. The maximum effect on the thermodynamic properties of Ti_5Si_3 that results from this amount of secondary phase is discussed below. The Ti_5Si_3 ingots were lightly crushed and separated by particle size by means of a 20 mesh sieve. Pieces of the ingots larger than 20 mesh were used to load the calorimeter.

The calorimetric apparatus has been described previously (Archer, 1995). The loaded calorimeter was evacuated and then approximately 8 kPa (300 K) of helium was sealed in the calorimeter. The mass of Ti_5Si_3 used for the measurements was 9.7609 g and corresponded to approximately 37% of the internal volume of the calorimeter. The density of Ti_5Si_3 was calculated from the X-ray data to be 4.32 $g\cdot cm^{-3}$. The formula weight was taken to be 323.656 $g\cdot mol^{-1}$. The measured enthalpy increments of the filled calorimeter were converted into enthalpy increments for Ti_5Si_3 by subtraction of the enthalpy increment for the empty calorimeter and for the small differences in amounts of helium and vacuum grease between the empty and filled calorimeters. The enthalpy increments were corrected for the small systematic biases in the calorimetric system using the equations

$$\epsilon\Delta H_m = -[\{(T_2 + T_1)/2\} - 100\ \mathrm{K}]0.00001\ \mathrm{K}^{-1}\ \Delta H_m \qquad (T_1 > 100\ \mathrm{K}) \quad (1)$$

$$\epsilon\Delta H_m = -0.0025\Delta H_m \qquad (T_2 < 13.8\ \mathrm{K}) \quad (2)$$

where T_2 and T_1 are the larger and the smaller of the two temperatures for the enthalpy increment, respectively, and $\epsilon\Delta H_m$ is the correction added to the substance's enthalpy increment, ΔH_m. The origin of these corrections has been described previously (Archer, 1995).

Results and Discussion

The measured enthalpy increments for Ti_5Si_3 are given in Table 1. Above 50 K, the measurements are expected to be uncertain by no more than (0.05 to 0.1)%, dependent

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[†] Certain commercial materials and suppliers are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by either the U.S. Government or the National Institute of Standards and Technology nor does it imply that the equipment or materials identified are necessarily the best available for the purpose.

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Table 1. Enthalpy Increment Measurements for Ti_5Si_3(cr)

T_1/K	T_2/K	$\Delta H_m(T_1 \rightarrow T_2)$/J·mol^{-1}	σ^a	δ^b	T_1/K	T_2/K	$\Delta H_m(T_1 \rightarrow T_2)$/J·mol^{-1}	σ^a	δ^b
302.1004	307.0967	906.247	0.1	−0.07	5.801	7.628	0.2061	U	−6.89
307.0881	312.0952	912.964	0.1	−0.06	7.607	9.472	0.3115	4	−0.26
312.0812	317.0940	918.485	0.1	−0.05	9.455	11.196	0.3913	4	0.51
317.0738	322.0850	923.177	0.1	0.02	11.187	13.315	0.6356	5	−1.04
322.0592	327.0811	928.724	0.1	−0.04	13.2800	15.3856	0.8867	3	1.27
327.0481	332.0628	931.381	0.1	−0.04	15.3625	17.6324	1.3197	2.5	−0.09
332.0219	337.0487	937.515	0.1	−0.04	17.6210	19.9043	1.880	2.5	−0.32
336.9994	342.0360	943.496	0.1	0.01	19.9079	22.2751	2.769	2.5	−0.11
341.9795	347.0114	946.389	0.1	0.03	22.2682	24.8871	4.384	0.6	0.62
346.9451	349.4694	476.032	0.1	0.02	24.8745	27.3414	5.673	0.6	−1.12
301.5712	306.5685	906.079	0.1	−0.06	27.3165	29.9109	8.351	0.5	0.96
306.5609	311.5688	912.832	0.1	−0.04	29.8862	32.5019	11.281	0.5	−0.01
311.5552	316.5718	918.675	0.1	−0.06	32.4773	35.1810	15.415	0.5	−0.03
316.5519	321.5652	922.393	0.1	−0.06	35.1547	37.9009	20.236	0.3	0.18
321.5389	326.5638	928.927	0.1	−0.03	37.8789	40.6812	26.008	0.3	0.10
326.5298	331.5471	932.021	0.1	0.02	40.6615	43.5238	32.888	0.2	0.16
331.5060	336.1360	863.084	0.1	−0.03	43.5072	46.4041	40.587	0.2	0.44
336.0878	340.7167	866.438	0.1	0.02	4.387	5.803	0.1251	6	2.08
340.6615	345.3047	872.132	0.1	0.01	5.808	6.875	0.1185	5	−1.35
345.2422	349.8813	874.590	0.1	0.04	6.852	8.779	0.2873	4	0.74
79.3733	82.4911	172.410	0.1	−0.07	8.783	10.644	0.3726	4	−1.34
82.4902	85.6452	186.591	0.1	−0.03	10.610	12.686	0.5778	5	1.19
85.6431	88.8260	200.366	0.1	−0.05	12.693	14.8461	0.8246	4	0.44
88.8227	92.0033	212.227	0.1	−0.06	14.8213	17.0098	1.1603	2.5	−0.24
91.9990	95.2048	225.921	0.1	−0.04	16.9982	19.3153	1.731	2.5	−0.74
95.1996	98.3975	237.213	0.1	0.00	19.3064	21.6579	2.505	2.5	−0.53
98.3918	101.6063	250.064	0.1	0.01	21.6386	24.0792	3.673	0.6	−0.08
101.5998	104.8181	261.890	0.1	0.05	24.0531	26.5308	5.178	0.6	−0.08
104.8109	108.0376	273.708	0.1	0.03	26.5014	29.0563	7.353	0.6	0.07
108.0296	111.2538	284.395	0.1	0.03	29.0267	31.6597	10.272	0.5	−0.36
111.2452	115.0135	345.838	0.1	0.03	31.6308	34.3204	14.020	0.5	−0.29
115.0041	118.7776	360.041	0.1	−0.08	34.2923	37.0233	18.573	0.3	0.04
118.7671	122.5317	373.163	0.1	0.03	36.9958	39.7929	24.118	0.3	−0.08
122.5215	126.3017	387.918	0.1	0.03	39.7668	42.6197	30.554	0.2	−0.30
126.2908	130.0729	400.920	0.1	0.03	42.5945	45.4789	37.810	0.2	−0.15
130.0616	133.8497	413.877	0.1	0.01	45.4381	48.3877	46.448	0.1	−0.13
133.8382	137.6205	425.240	0.1	0.01	48.3614	51.3436	55.671	0.1	0.00
137.6081	141.4065	438.015	0.1	−0.14	51.7198	54.6825	65.847	0.1	0.19
141.3934	145.1885	450.041	0.1	0.14	54.6566	57.7090	77.761	0.1	0.01
145.1746	148.9779	461.242	0.1	0.00	57.6841	60.7610	89.095	0.1	−0.01
148.9631	152.7565	470.509	0.1	0.02	60.7325	63.8426	101.255	0.1	−0.04
152.7414	156.5468	481.98	0.1	0.01	63.8146	66.9440	113.462	0.1	−0.07
156.5313	160.3326	491.085	0.1	−0.01	66.9205	70.0631	125.883	0.1	−0.02
160.3164	164.1156	499.961	0.1	−0.03	70.0399	73.2066	139.027	0.1	0.01
164.0992	167.9039	509.789	0.1	0.00	43.2822	46.6967	47.763	0.1	0.04
167.8870	171.6943	518.096	0.1	−0.13	46.6707	49.5995	49.636	0.1	−0.01
171.6770	175.4740	525.606	0.1	−0.01	49.5766	52.5782	59.808	0.1	−0.02
175.4561	179.2598	534.251	0.1	−0.06	52.5534	55.5781	69.883	0.1	−0.08
179.2406	183.0316	540.508	0.1	0.02	55.5538	58.5984	80.607	0.1	−0.04
183.0108	186.8111	548.900	0.1	−0.03	58.5748	61.6392	92.735	U	0.90
186.7894	190.5867	555.881	0.1	0.02	61.6224	64.7244	104.382	0.1	0.07
190.5649	194.3615	562.446	0.1	0.00	64.7020	67.8359	117.037	0.1	−0.04
194.3384	198.1347	569.009	0.1	0.00	67.8139	70.9561	129.477	0.1	0.11
198.1109	203.0967	756.874	0.1	0.00	70.9345	74.1021	142.570	0.1	0.02
203.0742	207.6240	699.401	0.1	−0.06	74.0807	77.2658	155.540	0.1	−0.09
207.5986	212.1418	707.283	0.1	0.03	77.2443	80.4343	168.538	0.1	0.12
212.1183	216.6727	716.548	0.1	−0.04	80.4130	83.6158	181.567	0.1	0.05
216.6481	221.6308	792.760	0.1	−0.03	83.5951	86.7968	193.896	0.1	0.05
221.6049	226.5821	800.501	0.1	−0.05	86.7762	89.9939	207.067	0.1	−0.01
226.5546	231.5279	808.297	0.1	−0.04	89.9613	94.7485	330.692	0.1	0.05
231.4985	236.4695	816.138	0.1	−0.01	93.7897	98.2604	327.456	0.1	−0.07
236.4387	241.4030	823.532	0.1	0.09	98.2510	102.6867	347.667	0.1	0.09
241.3715	246.3390	830.790	0.1	0.02	102.6770	107.1512	372.024	0.1	−0.03
246.304	251.2689	837.355	0.1	0.01	107.1390	111.6189	393.694	0.1	−0.03
251.2321	256.2004	844.518	0.1	−0.02	111.6066	116.0888	414.194	0.1	−0.07
256.1606	261.1326	851.691	0.1	−0.02	116.0745	120.5675	435.387	0.1	0.03
261.0895	266.0672	858.880	0.1	−0.03	120.5525	125.0636	455.852	0.1	−0.06
266.0222	270.9853	863.300	0.1	0.07	125.0475	129.569	475.992	0.1	0.07
270.9380	275.9093	869.723	0.1	−0.02	129.5538	134.0741	493.190	0.1	−0.02
275.8589	280.8243	874.199	0.1	−0.04	134.0570	138.5874	511.359	0.1	−0.02
280.7704	285.7408	880.533	0.1	−0.03	138.5699	143.1085	528.851	0.1	0.00
285.6835	290.6612	887.608	0.1	0.03	143.0908	147.6339	544.824	0.1	−0.06
290.6004	295.5724	891.483	0.1	0.01	147.6156	152.1640	560.660	0.1	−0.04
295.5081	300.4709	894.826	0.1	0.03	152.1451	156.6837	574.510	0.1	0.07
300.4028	305.3768	901.311	0.1	0.00	156.6642	161.2168	590.065	0.1	0.06
4.462	5.867	0.1225	6	−0.83	161.1976	165.7484	602.738	0.1	0.01

Table 1 (Continued)

T_1/K	T_2/K	$\Delta H_m(T_1 \rightarrow T_2)$/J·mol^{-1}	σ^a	δ^b
165.7287	170.2794	615.090	0.1	−0.03
170.2584	174.8046	626.469	0.1	−0.03
174.7833	179.3375	639.887	0.1	0.10
179.3164	183.8695	650.504	0.1	0.06
183.8476	188.3989	660.637	0.1	0.04
188.3754	192.9310	671.190	0.1	0.02
192.9069	197.4661	681.522	0.1	0.05
197.4416	201.9921	689.244	0.1	0.03
201.9664	206.5236	698.942	0.1	0.01
206.4968	211.0491	706.514	0.1	0.00
211.0215	215.5698	713.740	0.1	−0.03
215.5454	220.0906	720.925	0.1	−0.04
220.0655	224.6058	727.573	0.1	−0.03
224.5797	229.1175	734.462	0.1	0.00
229.0901	233.6296	741.745	0.1	0.03
233.6011	238.1432	748.697	0.1	0.03
238.1137	242.6595	755.739	0.1	0.04
242.6285	247.1635	759.532	0.1	−0.03
247.1299	251.6710	766.590	0.1	0.00
251.6357	256.1796	772.641	0.1	−0.01
256.1423	260.6784	777.021	0.1	0.02
260.6390	265.1829	783.716	0.1	0.03
265.1407	269.6747	787.103	0.1	0.03
269.6296	274.1754	793.316	0.1	−0.07
274.1270	278.6639	796.509	0.1	−0.07
278.6126	283.1589	803.397	0.1	0.01
283.1054	287.6500	807.670	0.1	0.03
287.5810	292.1373	814.097	0.1	0.03
292.0764	296.6238	817.388	0.1	0.12
296.5626	301.1032	819.716	0.1	0.06
301.0372	305.5706	821.959	0.1	0.02
305.5006	310.0239	824.543	0.1	0.10
309.9495	314.4838	830.037	0.1	0.08

[a] σ is the percentage uncertainty assigned to the observation for the purposes of the least-squares calculation. A "U" indicates that observation was not included in the least-squares calculation. [b] δ is the percentage difference of the calculated enthalpy increment from that observed.

upon the particular temperature. These uncertainty values were based on the previous measurements of enthalpy increments for calorimetric reference materials (Archer, 1995), the present reproducibility, and the percentage of the total measured enthalpy increment that was due to the Ti_5Si_3 sample. Below 50 K, the results must be considered less accurate, partly due to limits in accuracy of platinum resistance thermometer temperature scales below 50 K and partly due to an unfavorable percentage of the total measured enthalpy being due to the titanium silicide sample. The contribution of the Ti_5Si_3 to the total measured enthalpy increment was a minimum of 9% near 20 K and increased in percentage with both increasing and decreasing temperatures from 20 K. The sample contributed 25% of the total enthalpy increment for the lowest temperature measurement. The increasing contribution of Ti_5Si_3 to the total enthalpy increment for temperatures less than 20 K is a result of Ti_5Si_3 possessing a much larger contribution to the molar enthalpy from the conduction electrons than does copper, which comprised the bulk of the calorimeter.

Thermodynamic properties for Ti_5Si_3 were calculated from a least-squares representation using a cubic-spline method described previously (Archer, 1992, 1995).

Briefly, a function $f(T)$ was used, where

$$f(T) = [T\{(C_{p,m} - \gamma_{el}T)/C_p^\circ\}^{-1/3} - bT]/T^\circ \qquad (3)$$

and where T was temperature, T° was 1 K, $C_{p,m}$ was the molar heat capacity, C_p° was 1.0 J·K^{-1}·mol^{-1}, γ_{el} was the coefficient for the contribution to the heat capacity of the conduction electrons, and b was a coefficient arbitrarily chosen to be 0.14 for the present case. The function $f(T)$ of eq 3 was fitted with a cubic spline using polynomials of the form

$$f(T) = a_i(T - T_i)^3 + b_i(T - T_i)^2 + c_i(T - T_i) + d_i \quad (4)$$

where the subscript i refers to the polynomial that contains the specified value of T and spans the temperature range T_i to T_{i+1}. A particular (T_i, d_i) pair is referred to as a "knot". It can be shown that if it is assumed that the effective Debye temperature is independent of temperature near 0 K, then the first derivative of the spline of eq 4 should be $-b$ at 0 K. A "natural spline" end condition (*i.e.* second derivative equal to 0) was imposed at the highest temperature end knot. (For the purpose of calculation: $T_{i+1} > T > T_i$). The end condition imposed at the lowest temperature knot was a value of $-b$ (−0.14) for the first derivative. The calculated heat capacity was thus

Table 2. Least-squares Estimated Knot Positions and γ_{el} for Ti_5Si_3

T_i/K	d$_i$
0	26.8162
12	24.0122
20	19.9402
26	17.4274
32	15.3461
40	13.5055
55	11.5598
75	10.3005
100	9.5842
130	9.3085
180	9.5363
240	10.3967
300	11.5355
380	13.2766

$\gamma_{el}/C_p^\circ = 0.015\,602$ K^{-1}

$$C_{p,m}/C_p^\circ = \left(\frac{T}{T^\circ f(T) + bT}\right)^3 + \gamma_{el}T/C_p^\circ \qquad (5)$$

Equation 5 was integrated numerically to obtain the enthalpy. The model was determined by fitting the measured enthalpy increments with a nonlinear least-squares program. The estimated square root of the variance for the least-squares procedure was calculated from twice the irreproducibility for a full calorimeter determination and the percentage of the observed enthalpy due to the Ti_5Si_3 sample. These values, given in Table 1, actually corresponded approximately to a 95% confidence interval rather than the square root of the variance. Representation of the experimental results, over the full range of temperature, required 14 variable values for the knot positions and the variable γ_{el}. The fitted equation yielded an estimate of the Debye temperature of approximately (670 ± 50) K and a value of γ_{el}/C_p° of 156×10^{-4} K^{-1} ±~5%. The least-squares estimated knot positions (the T_i, d_i pairs) are given in Table 2, and calculated thermodynamic properties are given in Table 3.

In our previous representation of the thermodynamic properties of $TiSi_2$ (Archer et al., 1995), we did not impose the first derivative of $-b$ at the 0 K knot. In order to rectify that, calculations were performed as described previously with the exception that the first derivative of the spline at the lowest temperature knot (0 K) was assigned the value of $-b$. No change in the previously tabulated thermodynamic properties of $TiSi_2$ resulted from the resulting change in the lowest temperature knot positions. However, the Debye temperature at 0 K did change, as would be expected, to (725 ± 50) K.

Table 3. Thermodynamic Properties of Ti_5Si_3(cr) Calculated from Eqs 4 and 5

T/K	$C_{p,m}$/J·K^{-1}·mol^{-1}	$H_m(T) - H_m(0\ K)$/kJ·mol^{-1}	S_m/J·K^{-1}·mol^{-1}
5	0.085	0.000	0.080
10	0.212	0.001	0.174
15	0.459	0.003	0.300
20	0.992	0.006	0.496
25	2.005	0.013	0.815
30	3.752	0.027	1.322
35	6.382	0.052	2.087
40	9.801	0.092	3.154
45	13.980	0.152	4.542
50	18.810	0.233	6.260
55	24.146	0.340	8.300
60	29.862	0.475	10.644
65	35.823	0.640	13.268
70	41.910	0.834	16.145
75	48.048	1.059	19.246
80	54.195	1.314	22.543
85	60.29	1.601	26.012
90	66.28	1.917	29.628
95	72.12	2.263	33.369
100	77.79	2.638	37.213
110	88.56	3.470	45.139
120	98.49	4.406	53.276
130	107.57	5.437	61.524
140	115.87	6.555	69.804
150	123.40	7.752	78.059
160	130.22	9.021	86.245
170	136.38	10.354	94.328
180	141.95	11.746	102.28
190	146.99	13.192	110.10
200	151.55	14.685	117.75
210	155.69	16.221	125.25
220	159.46	17.797	132.58
230	162.91	19.409	139.74
240	166.06	21.055	146.75
250	168.99	22.730	153.58
260	171.68	24.434	160.27
270	174.18	26.163	166.79
280	176.50	27.917	173.17
290	178.65	29.692	179.40
298.15	180.29	31.155	184.38
300	180.65	31.489	185.49
310	182.51	33.305	191.45
320	184.25	35.139	197.27
330	185.87	36.989	202.96
340	187.38	38.856	208.54
350	188.79	40.737	213.99

As stated above, optical microscopy of the measured material indicated the presence of a small amount of phases other than the Ti_5Si_3 phase. We make the following observations: (1) This level of phase impurity is borderline detectable in our X-ray analysis. (2) Elemental analysis gives no information regarding which phases are present in a sample. Thus, performance of only elemental analysis and an X-ray pattern determination, as has been done for most of the other thermodynamic studies of metal silicides, could not have ruled out the existence of secondary phases at the (0.1 to 1)% level in those studies. As such, the measurements for other transition-metal silicides may have contributions from secondary phases present in unknown amounts, comparable to these orders of magnitude.

We made an estimate of the magnitude of the error in our thermodynamic values for Ti_5Si_3 that could result from the presence of the secondary phase. For the purposes of this estimate we considered the worst-case scenario as follows: If one assumed that there were two secondary phases, $TiSi_2$ and Ti, in amounts that totaled 1% and which agreed stoichiometrically with the original ratio of titanium to silicon, the resultant errors in the measured enthalpy increments would be 0.4% at 10 K, 0.3% at 40 K, 0.15% at 100 K, 0.06% at 200 K, and 0.04% at 300 K. The resulting error in the entropy for 300 K would be about 0.1%. This was the worst-case scenario because we considered the case of one of the impurities to be uncombined element, in this example, pure titanium. The silicides of titanium have Debye temperatures significantly larger than that of either pure silicon or titanium. The smaller Debye temperature for titanium, as compared to a titanium silicide, resulted in a larger calculated contribution to the total heat capacity of the specimen, as compared to a titanium silicide impurity, at low temperatures. This is the source of the increasing error with decreasing temperature calculated above. If the above calculation had been performed using only titanium silicides as the impurities, the calculated errors would have been smaller still, especially at low temperatures.

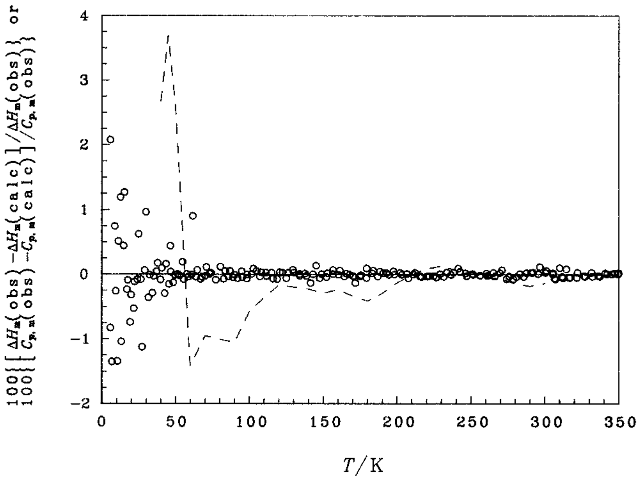

Figure 1. Differences from the fitted model, in percent: (○) the present results; (- -) the heat-capacity values from Sychev et al. (1980).

We believe the contaminating phases to be Ti_5Si_4 and Ti_3Si. We based this on the various examinations (discussed above) performed on pieces of the ingots used for the present measurements, and also on similar examinations of poorly annealed ingots. The remaining titanium and/or silicon (remaining from the deviation of Ti_5Si_4 and Ti_3Si from the 5 to 3 stoichiometric ratio of titanium and silicon used to prepare the specimen) would be present within the homogeneity range of Ti_5Si_3. The maximum deviations these impurities can cause on the stoichiometry of the Ti_5Si_3 phase were estimated also. For example, if one assumed the contaminating phase were entirely Ti_5Si_4 then the resulting titanium mole fraction in the Ti_5Si_3 phase would have been 0.6257 rather than the nominal 0.625, a rather small difference. All of these calculations considered, we expected the total uncertainty in the heat capacity and entropy of Ti_5Si_3, introduced by the impurity phases, to be smaller than the values calculated in the previous paragraph.

The differences of the present measured values from the least-squares estimated model are shown in Figure 1. The root-mean-square difference of the present measurements from the fitted model was approximately 0.05% for temperatures greater than 50 K. Also shown in Figure 1 are the differences of the heat capacity values given by Sychev et al. (1980) from the model. The differences of Sychev et al.'s values from the model, and thus also from the present measurements, become progressively worse as the temperature decreased from 60 K. At 15 K, Sychev et al.'s lowest reported temperature, their heat capacity value is twice that calculated from the model.

The large differences of Sychev et al.'s (1980) heat capacity values from the model were partly responsible for large differences of their Debye temperature, (495 ± 4) K, and γ_{el}/C_p°, (200 ± 16) × 10^{-4} K^{-1}, from the present values of (670 ± 50) K and 156 × 10^{-4} K^{-1}, respectively. These differences are similar to those found for a comparison of Sychev et al.'s values with others for V_5Si_3. Sychev et al. compared their values of the Debye temperature and γ_{el}/C_p° for V_5Si_3 with values given by Ryder (1963). For V_5Si_3, Sychev et al. obtained (558 ± 7) K for the Debye temperature whereas the value cited from Ryder was (660 ± 50) K. Our value of the Debye temperature for $TiSi_2$, (725 ± 50) K, was similar to the value that Gottlieb et al. (1993) obtained for VSi_2 from their heat capacity measurements from (0.1 to 7.5) K, (665 ± 10) K. Our present value of Debye temperature for Ti_5Si_3 is similar to that obtained by Ryder for V_5Si_3 but is in disagreement with the value obtained by Sychev et al. In other words, the heat capacity values from Sychev et al. are larger than our values for Ti_5Si_3 and are also larger than Ryder's values for V_5Si_3.

It is now generally accepted, but apparently not by all, that the Debye temperature, as calculated from thermal property measurements, usually begins to diverge from a constant value for $(\Theta_D/T) < 50$. This rule of thumb indicates that one would obtain a reasonable value for the Debye temperature for Ti_5Si_3 from measurements of the thermal properties only for $T < 13$ K. Because the initial deviation of the Debye temperature from constancy is for it to decrease with increasing temperature, values obtained from measured temperatures greater than 13 K necessarily would be smaller than those obtained for measured temperatures significantly below 13 K. It was thus expected that Sychev et al.'s value for the Debye temperature should have been smaller than the present value, even if their measurements did not show large differences at their lowest temperatures from the present measurements. Thus, the above comparisons of Debye temperatures from Sychev et al.'s work must be viewed with some caution because his lowest temperature measurements were for temperatures greater than the helium boiling point, 13.8 K, and so must be averages over the temperature region that contained the initial decline of Θ_D with respect to temperature. Because of the previous demonstrations of the accuracy of the present calorimetric system (Archer, 1995), we believed the present thermodynamic values to be more accurate than those from Sychev et al.

Combination of the present 298.15 K entropy with the reference values of the entropies of titanium and silicon (Chase et al., 1985) gives an entropy of formation of −25.88 $J\cdot K^{-1}\cdot mol^{-1}$ for 298.15 K. Schlesinger (1990) recommended the value −579.2 $kJ\cdot mol^{-1}$ for the 298.15 K enthalpy of formation, taken from Maslov et al. (1978). Combination of these two values gives a 298.15 K Gibbs energy of formation of −571.5 $kJ\cdot mol^{-1}$. The uncertainty of this value is estimated to be about 30 $kJ\cdot mol^{-1}$.

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