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THE ENTHALPHY OF MIXING OF THE INTERMEDIATE PHASES IN THE SYSTEMS FeTi, CoTi, AND NiTi BY DIRECT REACTION CALORIMETRY

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ABSTRACT

The enthalphy of mixing of some intermediate phases in the systems FeTi, CoTi, and NiTi have been measured by direct reaction calorimetry between 1200 and 1500 K. The method is described, the results are given and compared with available data from diagram estimations and from earlier experimental work.

INTRODUCTION

Binary transition metal alloys show many intermediate phases which are of great interest both in industry and in the theoretical study of the solid state. However, there are so few data in the literature that calculations are often the only way of finding the order of magnitude of thermodynamic properties in these phases (see, for example, refs. 1—5). We have successfully studied the enthalpies of mixing of some phases in the systems FeTi, CoTi, and NiTi. In this paper, we report our method and our first results. We compare them with experimental (when possible) and computed data from the literature.

EXPERIMENTAL STUDY

Measuring technique

The powders of the two transition components are cold compressed in suitable proportions and then put in the calorimeter at a temperature, T_0, just below the melting point of the phase we want to obtain. The rise of temperature in the sample induces an alloying reaction and the enthalpy of mixing can be deduced from the heat of the reaction as the heat contents of the pure metals are tabulated [6,7]. Figure 1 shows the type of signal obtained.

Calorimeter

The calorimeter has been described earlier [8]. In these experiments, it works as a heat transfer calorimeter. The output signal is graphically

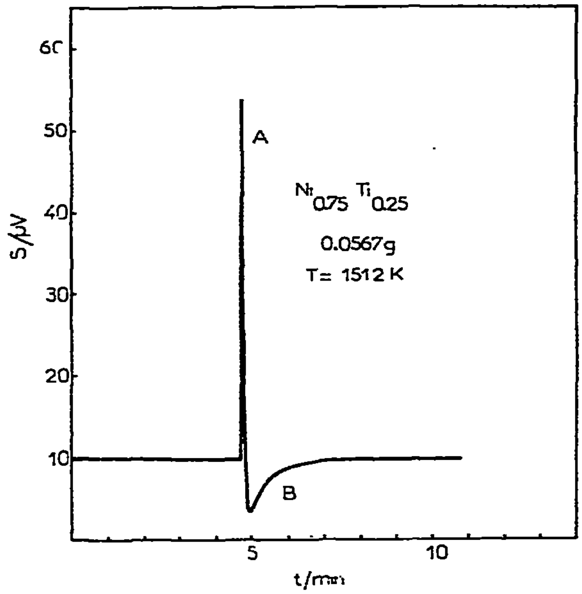

Fig. 1. Calorimetric signal. The calorimetric signal shows the two parts of the heat of reaction. The endothermic part (A) comes from the heat content of the sample between room temperature and crucible temperature and the exothermic part (B) shows that the absolute value of the heat of mixing is greater than the heat content. The reaction is completed within four minutes.

recorded and simultaneously integrated. Calibration is made with α-alumina cold samples which are introduced into the crucible alternatively with metallic samples. As calibration results do not vary during an experiment, the mean value is taken to interpret all the measurements. A check has been made by measuring the heat content of pure Ti in the same conditions. We found $H_{295K}^{1492K}(\mathrm{Ti}) = 39800$ J mole^{-1} ($\sigma = 1400$) compared with a tabulated value [6] of 39823 J mole^{-1}.

Sample preparation

The characteristics of pure metals are given in Table 1.

As powders of such fineness are very oxidizable, all the preparations are

TABLE 1

Characteristics of the pure metals

Metal	Manufacturer	Fineness (µm)	Purity (%)
Ti	Alfa Ventron	44	99
Fe	Koch Light	6–8	99
Co	Alfa Ventron	44	99.9
Ni	Alfa Ventron	1	99

made in a glove box under purified argon. The powders are cold compressed with a hand-powdered press, then the button is broken into pieces of about 0.1 gram which are weighed and put in individual boxes to permit their transport under argon to the calorimeter. Each sample is then removed from its box, comes into contact with the air but is immediately introduced into the vacuum-tight entrance lock of the calorimeter and put under argon (1 atm) in the crucible. This procedure avoids oxidization in the bulk of the samples. In each experiment, we repeat the same measurement three to five times and take the mean value. Only one phase is studied in each experiment to avoid reaction between two different compounds in the crucible.

TABLE 2

FeTi system

(a) $Fe_{0.5}Ti_{0.5}$ cubic (B2)

θ	Experiment: Mo anticathode				Ref. 9: Cu anticathode	
	hkl	*hkl* other phases	d_{hkl}	I/I_0	d_{hkl}	I/I_0
6.9	100		2.952	2		
8.35		002 Ti_2O	2.442	1		
8.54		110 Fe_2Ti	2.388	2		
8.96		101 Ti_2O	2.277	3		
9.27		103 Fe_2Ti	2.201	4		
9.5		Ti		~1		
9.76	110		2.092	100	2.097	100
10.03		112 Fe_2Ti	2.036	4		
10.20		201 Fe_2Ti	2.003	4		
10.45		004 Fe_2Ti	1.955	1		
11.00		Ti	1.859	2		
11.15		202 Fe_2Ti	1.834	2		
11.55		104 Fe_2Ti	1.771	1		
12.12			1.689	1		
12.65		203 Fe_2Ti	1.619	1		
13.10		Fe_2Ti ?	1.565	1		
13.86	200		1.480	14	1.485	40
15.20		123 Fe_2Ti	1.353	1		
15.60		006 Fe_2Ti	1.319	2		
16.50		205 Fe_2Ti	1.249	1		
17.05	211		1.209	16	1.214	80
19.78	220		1.048	3	1.052	30
22.24	310		0.937	3	0.941	70
24.45	222		0.857	1	0.859	30
26.70	321		0.789	1	0.795	100

Microprobe analysis results (on FeTi only)
$\langle x_{Ti} \rangle = 50.9\%$, $\sigma = 0.7\%$
$\langle x_{Ti} + x_{Fe} \rangle = 99.5\%$, $\sigma = 1\%$
FeTi seems to be CsCl type as line 100 appears.

(b) $Fe_{0.67}Ti_{0.33}$ hexagonal

θ	Experiment: Mo anticathode			Ref. 10: Cr anticathode	
	hkl	d_{hkl}	I/I_0	d_{hkl}	I/I_0
4.96	100	4.102	10	4.133	10
5.25	002	3.876	7	3.889	10
5.61	101	3.628	8	3.649	10
8.56	110	2.383	21	2.388	30
9.32	103	2.190	55	2.199	100
9.95	200	2.052	7	2.068	10
10.05	112	2.032	100	2.038	100
10.25	201	1.993	87	1.998	100
10.53	004	1.941	21	1.947	30
11.22	202	1.823	29	1.828	30
11.63	104	1.759	11	1.760	10
12.7	203	1.613	9	1.620	10
14.95	300	1.375	4	1.382	10
15.37	123	1.338	17	1.341	60
15.86	006	1.298	21	1.302	60
16.6	205	1.241	25	1.247	60
16.95	124	1.216	9	1.223	10
17.33	220	1.191	26	1.196	60

Microprobe analysis results
$\langle x_{Ti} \rangle = 31.1\%$, $\sigma = 0.6\%$
$\langle x_{Ti} + x_{Fe} \rangle = 98.8\%$, $\sigma = 0.5\%$

TABLE 3
CoTi system
(a) CoTi cc(B_2)

θ	Experiment: Mo anticathode		
	hkl	d_{hkl}	I/I_0
6.85	100	2.973	3
9.73	110	2.098	100
13.80	200	1.487	18
16.99	211	1.214	29
19.70	220	1.052	7
22.20	310	0.939	8

$\langle a \rangle$ (Å) = 2.971, $\sigma = 0.003$
Microprobe analysis results
$\langle x_{Co} \rangle = 50.4\%$, $\sigma = 0.8\%$
$\langle x_{Co} + x_{Ti} \rangle = 99.3\%$, $\sigma = 1\%$
For the two other phases, $CoTi_2$ and Co_3Ti, RX and electron microprobe analysis show that reaction of mixing is not achieved. Calorimetric measurements on these two phases cannot, therefore, be considered.

(b) $Co_{0.67}Ti_{0.33}$

Hexagonal structure						Cubic structure		
θ	Experiment: Mo anticathode			Ref. 11: Co anticathode		Ref. 12: Cu anticathode		
	hkl	d_{hkl}	I/I_0	d_{hkl}	I/I_0	hkl	d_{hkl}	I/I_0
5.05		4.029	≈0	4.09	10			
5.22	101	3.889	5	3.94	10			
5.27	004	3.861	5	3.86	10			
5.66	102	3.596	2	3.64	10			
8.37	{105 (002 Ti_2O)}	2.436	1	2.41	10			
8.68	110	2.350	7	2.36	20	220	2.36	10
9.30		2.194	4					
9.42	106	2.167	8	2.17	50			
10.16	{201 114}	2.010	100	2.02	100	311	2.012	100
10.40	202	1.965	12	1.98	50			
10.60	{107 008}	1.928	20	1.93	50	222	1.925	50
10.82	203	1.889	5	1.90	20			
11.38	204	1.797	1	1.80	20			
11.78		1.737	2					
12.05	205	1.699	4	1.71	10			
12.30		1.665	≈0			400	1.667	5
12.86		1.593	2					
13.35	211	1.536	2	1.53	10	331	1.533	10
				1.42	10			
15.11	300	1.360	1	1.365	10	422	1.365	10
15.58	{1 0 11 216}	1.320	2	1.328 1.311	20 20			
16.05	{304 0 0 12}	1.283	33	1.283	20	{511 333}	1.288	50
16.27				1.266	10			
16.81	2 1 10	1.226	2	1.231	10			
17.46	220	1.182	5	1.183	50	440	1.182	50
17.93		(1.152)	(2)					
18.36		(1.126)	(1)					
20.05		1.034	1			620	1.053	5
20.40		1.017	2			533	1.019	10
20.52		1.012	7			622	1.010	20

Microprobe analysis results
$\langle x_{Ti} \rangle = 31.7\%$, $\sigma = 0.7\%$
$\langle x_{Co} + x_{Ti} \rangle = 99.2\%$, $\sigma = 1\%$

Product check

Products are checked after each experiment. Electron microprobe analyses are made with a Camebax driven by a computer which also corrects the mea-

TABLE 4

(a) $Ni_{0.33}Ti_{0.67}$ cubic (96 F)

θ	Experiment: Mo anticathode			Ref. 15: Co anticathode	
	hkl	d_{hkl}	I/I_0	d_{hkl}	I/I_0
3.11	111	6.537	9	6.51	10
			0	3.99	2
6.25	222	3.257	5	3.26	6
7.2	400	2.829	2	2.820	2
7.88	331	2.587	4	2.587	4
8.88	422	2.297	26	2.302	30
9.41	511—333	2.169	100	2.171	100
10.25	440	1.993	27	1.994	30
10.65	531	1.919	4	1.906	6
10.88	600—442	1.879	11	1.880	8
11.95	533	1.713	2	1.720	2
				1.700	2
12.60	444	1.626	4	1.628	4
13.00	711—551	1.576	5	1.579	4
13.60	642	1.507	3	1.507	2
14.00	731—533	1.466	6	1.468	6
				1.410	2
14.96	733	1.379	1	1.378	2
15.48	822—660	1.329	26	1.329	25
15.80	751—555	1.302	7	1.302	10
				1.294	2
16.66	911—753	1.237	3	1.238	6
16.75	842	1.231	8	1.231	8
17.50	931	1.179	2	1.182	2
18.24	933—771	1.133	14	1.133	25

Microprobe analysis results
$\langle x_{Ni} \rangle = 33\%, \sigma = 1\%$
$\langle x_{Ni} + x_{Ti} \rangle = 97\%, \sigma = 0.6\%$

(b) $Ni_{0.5}Ti_{0.5}$ cubic (B_2)

θ	Experiment: Mo anticathode				Ref. 13: Co anticathode		Ref. 14: Cu anticathode	
	hkl	*hkl* other phases	d_{hkl}	I/I_0	d_{hkl}	I/I_0	d_{hkl}	I/I_0
6.8	100		2.995	1	2.972	5		
8.95		422 $NiTi_2$	2.280	1				
9.55	110		2.137	100	2.102	100	2.111	100
10.32		440 $NiTi_2$	1.980	3				
10.50		202 Ni_3Ti	1.946	5				
11.88	111		1.723	2	1.716	5		
13.70	200		1.497	10	1.486	50	1.496	40
15.54		205 Ni_3Ti	1.324	1				
16.17		202 Ni_3Ti	1.273	2				
16.82	211		1.226	4			1.222	60

Microprobe analysis results
$\langle x_{Ni} \rangle = 52\%, \sigma = 2.7\%$
$\langle x_{Ni} + x_{Ti} \rangle = 97\%, \sigma = 1\%$

(c) $Ni_{0.75}Ti_{0.25}$ hexagonal

θ	Experiment: Mo anticathode			Ref. 16: Cu anticathode	
	hkl	d_{hkl}	I/I_0	d_{hkl}	I/I_0 computed
9.16	200	2.228	21	2.216	8
9.6	201	2.126	59	2.135	46
9.86	004	2.071	39	2.085	36
10.4	202	1.965	100	1.949	100
11.86	203	1.726	35	1.727	22
13.3	122	1.542	3	1.549	27
13.6	204	1.508	7	1.513	5
15.55	205	1.323	6	1.326	9
16.18	220	1.273	26	1.274	20
17.6	206	1.173	24	1.172	18
19.13	224	1.082	24	1.087	25
19.45	402	1.065	13	1.068	14

Microprobe analysis results
$\langle x_{Ni} \rangle = 76.8\%$, $\sigma = 0.3\%$
$\langle x_{Ni} + x_{Ti} \rangle = 98.5\%$, $\sigma = 1\%$

surements. X-Ray diffraction patterns of sample powders are made with a goniometer using MoK_α radiation ($\lambda = 0.7093$ Å). Tables 2–4 give the results of both tests and compare them with data available in literature.

RESULTS

Table 5 gives our results and compares them with those of Kaufman's [1,2] and Miedema et al.'s [3,4] calculations. Experimental results from Kubaschewski and Dench [17,18] are also given.

DISCUSSION AND CONCLUSION

FeTi system

There is a discrepancy, for the phase $Fe_{0.5}Ti_{0.5}$, between Miedema's calculation and Kubaschewski's experimental result (and then Kaufman's estimation) on the one hand and our own result on the other hand. Thirteen measurements have been made in three different experiments and all fall within the range −29700 to −33700 J mole^{-1}. Oxidization cannot be invoked as we do not find oxide lines in the X-ray diffraction patterns; only traces of Ti_2O [19] are detected. If we take into account the traces of Ti and $Fe_{0.67}Ti_{0.33}$ we find in the samples, we can consider that $Fe_{0.5}Ti_{0.5}$ would be stable only at high temperature. It can be noted that the systems FeZr [20] and FeHf [21] do not exhibit equiatomic compounds. In the same way, $Ni_{0.5}Ti_{0.5}$ is sometimes considered to decompose below 900 K [22,23]. In such a hypothesis, Kubaschewski's measurement at 298 K could not be

TABLE 5

Enthalpy of mixing of intermediate phases in the systems FeTi, CoTi, and NiTi

	System	Crystal structures		Temperature of reaction (K)	ΔH (J mole^{-1})	Kaufman's values [1,2] (J mole^{-1})	Miedema's values [3,4] (J mole^{-1})	Earlier experimental works [17,18] (J mole^{-1})
		Com-ponents	Compound					
FeTi	$Fe_{0.5}Ti_{0.5}$	Fe f.c.c.	b.c.c. (CsCl)	1450	−31 000 $\sigma = 1000$	−20 292 (Fe, Ti b.c.c.)	≈−19 000	−20 292 ± 2000 (298 K)
	$Fe_{0.67}Ti_{0.33}$	Ti b.c.c.	Laves	1514	−27 600 $\sigma = 1000$	−25 694 (Fe, Ti h.c.p.)		
CoTi	$Co_{0.33}Ti_{0.67}$		f.c.c.	1230	Incomplete reaction	−39 662 (Co, Ti f.c.c.)		
	$Co_{0.5}Ti_{0.5}$	Co f.c.c.	b.c.c. (CsCl)	1490	−44 300 $\sigma = 500$	−42 154 (Co, Ti b.c.c.)	≈−38 000	
	$Co_{0.67}Ti_{0.33}$	Ti b.c.c.	Laves	1432	−34 100 $\sigma = 600$	−36 410 (Co, Ti h.c.p.)		
	$Co_{0.75}Ti_{0.25}$		Hexagonal	1204	Incomplete reaction	−31 223 (Co, Ti h.c.p.)		
NiTi	$Ni_{0.33}Ti_{0.67}$	Ni f.c.c.	f.c.c. complex	1202	−29 300 $\sigma = 500$	−28 794 (Ni, Ti f.c.c.)		−26 800 ± 2000 (298 K)
	$Ni_{0.5}Ti_{0.5}$	Ti b.c.c.	b.c.c.	1460	−34 000 $\sigma = 2000$	−39 957 (Ni, Ti b.c.c.)	≈−49 000	−33 900 ± 2000 (298 K)
	$Ni_{0.75}Ti_{0.25}$		Hexagonal	1513	−42 900 $\sigma = 1000$	−37 028 (Ni, Ti h.c.p.)		−34 700 ± 2000 (298 K)

retained. But with this enthalpy of mixing, $Fe_{0.5}Ti_{0.5}$ would show a higher and congruent melting point.

CoTi system

Our results and Kaufman's assessment are in agreement for $Co_{0.5}Ti_{0.5}$ and $Co_{0.67}Ti_{0.33}$. For the other two phases ($Co_{0.33}Ti_{0.67}$ and $Co_{0.75}Ti_{0.25}$) alloying reactions occur very slowly and remain unfinished as both the X-ray and microprobe analysis show.

NiTi system

The agreement between our results and Kubaschewski's is satisfactory except for $Ni_{0.75}Ti_{0.25}$. For $Ni_{0.5}Ti_{0.5}$, all the samples we have checked by X-ray diffraction show small amounts of $Ni_{0.33}Ti_{0.67}$ and $Ni_{0.75}Ti_{0.25}$. This can be interpreted in two ways.

(a) $Ni_{0.5}Ti_{0.5}$ could decompose eutectoidally below 900 K as some diagrams show [22,23] and, in this case, our samples at room temperature would be slightly decomposed.

(b) Segregation of $Ni_{0.75}Ti_{0.25}$ can occur while the alloying reaction is starting. If this is the case, our value can be accounted for because we have simultaneous formation of $Ni_{0.75}Ti_{0.25}$, with a higher heat of mixing, and of liquid (close to the composition $Ni_{0.33}Ti_{0.67}$) with a lower heat of mixing than that of $Ni_{0.5}Ti_{0.5}$. The total deviation can only be small because the two perturbations counterbalance each other and the total amount of wrong phases is just a small part of the bulk.

This attempt, the first of a series devoted to transition metal alloys, shows that enthalpies of mixing of intermediate phases can be measured by direct reaction calorimetry at high temperatures. This helps to improve the work of diagram calculators and our own knowledge of transition metal alloys that are becoming more and more interesting in the industrial search for new materials for high-temperature uses.

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