Specific Heat Capacities of Some Ternary Aluminides

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Two different methods were employed to prepare samples of the ternary intermetallic phase: AlNi_2Ti , and of $\text{Al}_{0.4}\text{Fe}_{0.5}\text{Ni}_{0.1}$, $\text{Al}_{0.4}\text{Fe}_{0.3}\text{Ni}_{0.3}$, $\text{Al}_{0.4}\text{Fe}_{0.1}\text{Ni}_{0.5}$ solid solutions, respectively. Alloys were then subjected to heat treatment for homogenization. Phase identification was made by XRD phase analysis and by the SEM BSE technique, and chemical composition was determined using the EDS method. Heat capacity measurements were made within a temperature range from 100 to 600 K using the DSC technique. Results were listed in tables and then fitted to a Kelley equation; an example of C_p vs. T curve is given.

Keywords heat capacity, intermetallics, thermochemical properties

1. Introduction

Various combinations of alloying elements from Al-Fe-Ni-Ti system are used among others in “heavy duty” construction material applications. The properties of the material depend on several factors like chemical composition, phase constitution, stability, and transitions. On the other hand, various material properties may be considerably improved by proper heat treatment, but to do that, information is needed about phase equilibria of the material of interest in a certain temperature range. The information mentioned above are available from a reliable phase diagram. Phase diagrams are currently constructed by the CALPHAD method,^[1,2] and are based on the various kinds of thermodynamic and constitutional data of a material under consideration. Accuracy of the phase diagram calculated by CALPHAD approach depends in turn on the quality and amount of data used, therefore all the experimental works on thermodynamics and constitution of various alloy systems are of great interest for materials scientists and engineers.

Heat capacities of solid ternary alloys are relatively easy to measure, provided single-phase, homogeneous material is available, therefore special attention was paid to the proper sample preparation. Composition of alloys were chosen on the basis of phase diagrams presented in ternary alloys^[3] for Al-Fe-Ni and Ding et al.^[4] for Al-Ni-Ti systems.

2. Sample Preparation

Alloys were prepared from metals of at least 99.5% purity supplied by Alfa Aesar.

Samples corresponding to formulae: $\text{Al}_{0.4}\text{Fe}_{0.5}\text{Ni}_{0.1}$, $\text{Al}_{0.4}\text{Fe}_{0.3}\text{Ni}_{0.3}$, $\text{Al}_{0.4}\text{Fe}_{0.1}\text{Ni}_{0.5}$ were obtained by induction melting of the appropriate amounts of metals in alumina crucibles at about 1500 °C for 30–50 s, and then cooled quickly. It was found from EDS analysis, that $\text{Al}_{0.4}\text{Fe}_{0.5}\text{Ni}_{0.1}$ is homogeneous, while other alloys were subjected to homogenization in the evacuated quartz

Fig. 1 SEM BSE pictures of $\text{Al}_{0.4}\text{Fe}_{0.3}\text{Ni}_{0.3}$ (a) as cast alloy sample and after homogenization (b)

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capsules at 1000 °C for 24 h. Examples of microstructure of an “as cast” $\text{Al}_{0.4}\text{Fe}_{0.3}\text{Ni}_{0.3}$ alloy sample (a) and after homogenization (b) are shown in Fig. 1.

Alloy of composition AlNi_2Ti was prepared by melting components in a magnesia crucible in a resistance furnace under argon of high purity (glove box): oxygen <0.1 ppm, moisture <1 ppm, nitrogen <2 ppm. Homogenization was carried out directly after melting: temperature was lowered 100° below phase melting point, to 1,100 °C, and kept for 8 h, then temperature was lowered again during 12 h until 750 °C was reached, and sample was heated back to temperature ~1100 °C. This procedure was repeated 15 times, and then samples were subjected once again to EDS analysis, to confirm homogeneity.

Table 1 Results of C_p measurements of Al-Fe-Ni phases

$\text{Al}_{0.4}\text{Fe}_{0.1}\text{Ni}_{0.5}$		$\text{Al}_{0.4}\text{Fe}_{0.3}\text{Ni}_{0.3}$		$\text{Al}_{0.4}\text{Fe}_{0.5}\text{Ni}_{0.1}$	
<i>T</i> , K	C_p , J/g/K	<i>T</i> , K	C_p , J/g/K	<i>T</i> , K	C_p , J/g/K
102.4	0.2773	101.6	0.2590	101.1	0.2491
117.3	0.3205	116.4	0.3059	115.9	0.2968
132.2	0.3532	131.3	0.3428	130.8	0.3355
147.1	0.3789	146.3	0.3720	145.8	0.3659
162.1	0.4001	161.2	0.3963	160.8	0.3911
177.1	0.4171	176.2	0.4164	175.7	0.4113
192.1	0.4318	191.2	0.4336	190.7	0.4288
207.1	0.4443	206.2	0.4486	205.7	0.4437
222.1	0.4557	221.2	0.4622	220.7	0.4572
237.1	0.4661	236.2	0.4746	235.7	0.4696
252.1	0.4765	251.2	0.4868	250.8	0.4819
267.1	0.4854	266.2	0.4979	265.8	0.4925
282.2	0.4956	281.2	0.5102	280.8	0.5054
297.2	0.5036	296.2	0.5202	295.8	0.5158
312.2	0.5104	311.2	0.5286	310.8	0.5246
327.2	0.5156	326.3	0.5354	325.8	0.5330
342.3	0.5196	341.3	0.5410	340.9	0.5402
357.3	0.5227	356.3	0.5455	355.9	0.5462
372.3	0.5250	371.4	0.5492	370.9	0.5515
387.3	0.5267	386.4	0.5523	385.9	0.5557
402.4	0.5279	401.4	0.5548	401.0	0.5592
417.4	0.5285	416.4	0.5570	416.0	0.5620
432.4	0.5288	431.5	0.5584	431.0	0.5644
447.5	0.5312	446.5	0.5623	446.0	0.5690
462.5	0.5348	461.5	0.5670	461.1	0.5753
477.5	0.5386	476.5	0.5721	476.1	0.5817
492.5	0.5436	491.5	0.5791	491.1	0.5872
507.5	0.5462	506.6	0.5837	506.1	0.5909
522.5	0.5480	521.6	0.5872	521.1	0.5940
537.6	0.5494	536.6	0.5895	536.1	0.5973
552.6	0.5507	551.6	0.5923	551.1	0.6004
567.6	0.5514	566.6	0.5944	566.1	0.6032
582.6	0.5518	581.7	0.5966	581.1	0.6052
597.6	0.5517	596.7	0.5981	596.2	0.6072
612.7	0.5515	611.7	0.5995	611.2	0.6090

3. Measurement Procedures

Measurements were carried out within the relatively low-temperature range from 100 to 600 K using a differential scanning calorimeter, TA Instruments Q1000; $T_{\text{zero}}^{\text{TM}}$ technology and calibration for a sapphire single crystal were employed. $T_{\text{zero}}^{\text{TM}}$ technology introduces a new sensor for Q series 100 and 1000 of TA Instruments enabling an

Table 2 Results of C_p measurements for AlNi_2Ti phase

AlNi_2Ti	
<i>T</i> , K	C_p , J/g/K
102.0	0.2751
113.9	0.3093
125.8	0.3396
137.8	0.3621
149.7	0.3815
161.7	0.3979
173.7	0.4128
185.7	0.4263
197.7	0.4393
209.7	0.4512
221.7	0.4622
233.7	0.4724
245.7	0.4820
257.8	0.4911
269.8	0.4995
281.8	0.5082
293.8	0.5164
305.8	0.5240
317.8	0.5307
329.8	0.5366
341.9	0.5415
353.9	0.5457
365.9	0.5492
377.9	0.5520
389.9	0.5544
401.9	0.5563
414.0	0.5579
426.0	0.5587
438.0	0.5616
450.0	0.5674
462.0	0.5747
474.0	0.5814
486.0	0.5864
498.0	0.5895
510.0	0.5883
522.1	0.5884
534.1	0.5890
546.1	0.5903
558.1	0.5912
570.1	0.5920
582.1	0.5923
594.1	0.5926
606.1	0.5927

Table 3 Coefficients of Kelley equation of intermetallic phases investigated

Phase	$C_p = a + bT + cT^{-0.5} + dT^{-1} + eT^{-3} + fT^{-2}$, J/g/K					
	a	b	c	d	e	f
$\text{Al}_{0.4}\text{Fe}_{0.5}\text{Ni}_{0.1}$	0.805	1.055×10^{-5}	-4.548	-10.4	-6.39×10^4	596.3
$\text{Al}_{0.4}\text{Fe}_{0.3}\text{Ni}_{0.3}$	0.789	-3.811×10^{-5}	-3.239	-22.7	-2.444×10^3	233.7
$\text{Al}_{0.4}\text{Fe}_{0.1}\text{Ni}_{0.5}$	0.817	-1.178×10^{-4}	-4.396	-9.154	-4.931×10^4	433.2
AlNi_2Ti	1.659	-4.148×10^{-4}	-26.619	168.5	-297.5	-3.711×10^3

Fig. 2 C_p vs. T curve for AlNi_2Ti phase

improvement in the reproducibility of the baseline of the DSC instrument.

Samples of about 50 mg were placed in aluminum crucibles and protected by an atmosphere of pure argon or helium. Heating rate of 20°/min, although high, was found optimal after preliminary runs; for lower rates the reproducibility of results was worse. Specific heat capacity values were directly derived by the use of standard software of the instrument.

4. Results

A Kelley equation is usually used to describe temperature dependence of specific heat capacity on temperature in its original form:

$$C_p = a + bT + cT^{-2} + dT^2.$$

Sometimes, for a better fit to experimental data, additional terms are used like $T^{-0.5}$, T^{-1} , or T^{-3} . Analysis of our experimental data resulted in the introduction of additional terms, as below:

$$C_p = a + b \cdot T + c \cdot T^{-0.5} + d \cdot T^{-1} + e \cdot T^{-3} + f \cdot T^{-2}$$

Measurement results are listed in Tables 1 and 2, and fitted to a Kelley equation in the above form; equation coefficients are given in Table 3. An example of C_p versus

T curve for the AlNi_2Ti intermetallic phase is shown in Fig. 2.

5. Conclusions

Unique methods of preparation and heat treatment were employed to obtain single-phase, homogeneous alloy samples.

Specific heat capacities of ternary Al-Fe-Ni and Al-Ni-Ti alloys were measured for the first time ever.

Negative deviation from Neumann-Kopp rule was observed in all cases investigated.

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