A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
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HEAT CAPACITIES OF SOME BINARY INTERMETALLIC COMPOUNDS IN Al-Fe-Ni-Ti SYSTEM

CIEPŁO WŁAŚCIWE NIEKTÓRYCH DWUSKŁADNIKOWYCH ZWIĄZKÓW MIĘDZYMETALICZNYCH Z UKŁADU Al-Fe-Ni-Ti

High- and low-temperature C_p measurements were carried out for binary: $AlNi_3$, FeTi and Ni_3Ti intermetallic compounds employing various DSC methods and equipment; two different sample preparation techniques were used as well. Low temperature interval ranged from 103 to 623 K, and high temperature range was spread from 313 to 873 K. Results were then fitted to Kelley equation: $Cp = a + b{\cdot}T + c{\cdot}T^{-0.5} + d{\cdot}T^{-1} + e{\cdot}T^{-3} + f{\cdot}T^{-2}$ and Cp vs T curves were presented as graphs.

Keywords: A. intermetallics, B. thermochemical properties

Przeprowadzono nisko- i wysokotemperaturowe pomiary ciepła właściwego dwuskładnikowych związków międzymetalicznych: $AlNi_3$, FeTi oraz Ni_3Ti za pomocą różnych metod i sprzętu różnicowej kalorymetrii skaningowej; zastosowano również dwie różne metody przy-gotowania próbek do badań. Pomiary niskotemperaturowe przeprowadzono w zakresie 103 do 623 K, natomiast zakres pomiarów wysokotemperaturowych leżał w granicach: 313 do 873 K. Wyniki badań opisano równaniem Kelley'a: $Cp = a + b{\cdot}T + c{\cdot}T^{-0.5} + d{\cdot}T^{-1} + e{\cdot}T^{-3} + f{\cdot}T^{-2}$ a krzywe Cp w funkcji temperatury przedstawiono na wykresach.

1. Introduction

Although applications of $AlNi_3$, FeTi and Ni_3Ti differ substantially: as construction material, hydrogen storage and shape memory, respectively, they belong to the same big family of Al-Fe-Ni-Ti system intermetallic phases, and this work is the part of the extensive study on thermochemical properties of the intermetallic compounds related to quaternary system mentioned before.

2. Sample preparation

Preparation, heat treatment and phase identification of Ni_3Ti phase was reported in our earlier work [1], and the method used for $AlNi_3$ differed only by the use of alumina crucibles instead of magnesia employed for titanium-containing alloy.

Samples of FeTi were prepared by levitation melting, and then homogenized at 1000°C for 1 month in the evacuated silica capsules filled with magnesia powder to avoid the contact of alloy with silica. SEM BSE pictures in Figure 1 show the microstructure of the sample in "as cast" form, a), and after homogenization, b). Results of EDS spot analysis of homogenized sample are listed in Table 1, and XRD diagram of the same sample is presented in Figure 2.

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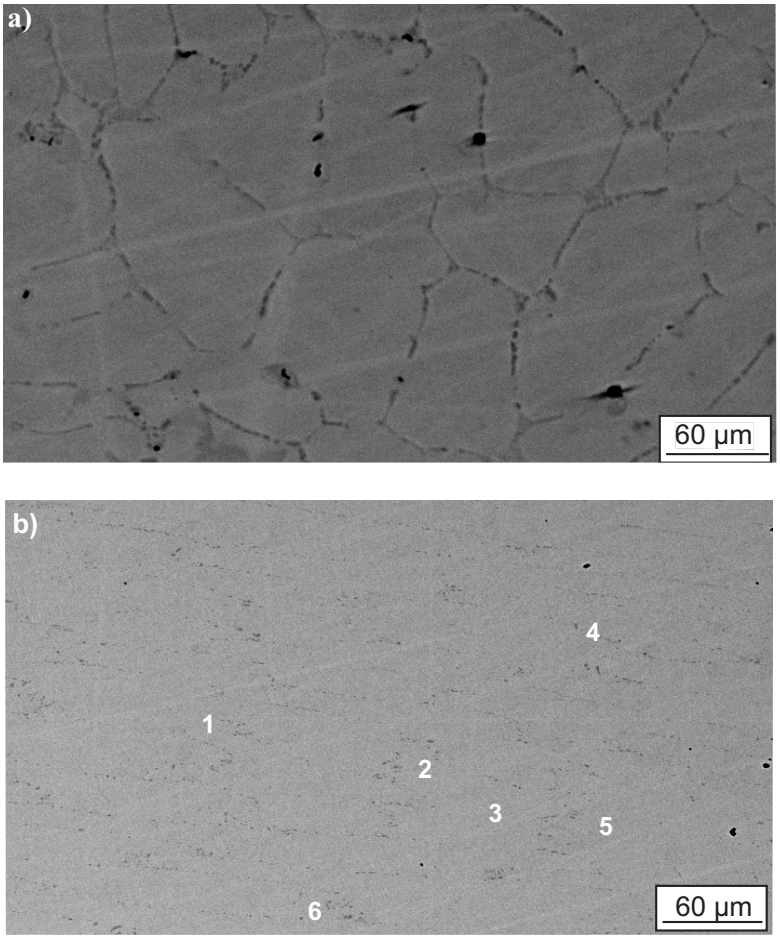

Fig. 1. SEM BSE pictures of FeTi sample: a) “as cast”, and b) after homogenization

TABLE 1

Results of spot analysis of FeTi sample after homogenization, Fig. 1 b)

Spot No.	at. % Ti	at. % Fe	Remarks
1	50.6	49.4	grey area
2	50.5	49.5	grey area
3	57.6	42.4	small dark spot
4	50.8	49.2	grey area
5	52.4	47.6	small dark spot
6	50.7	49.3	grey area

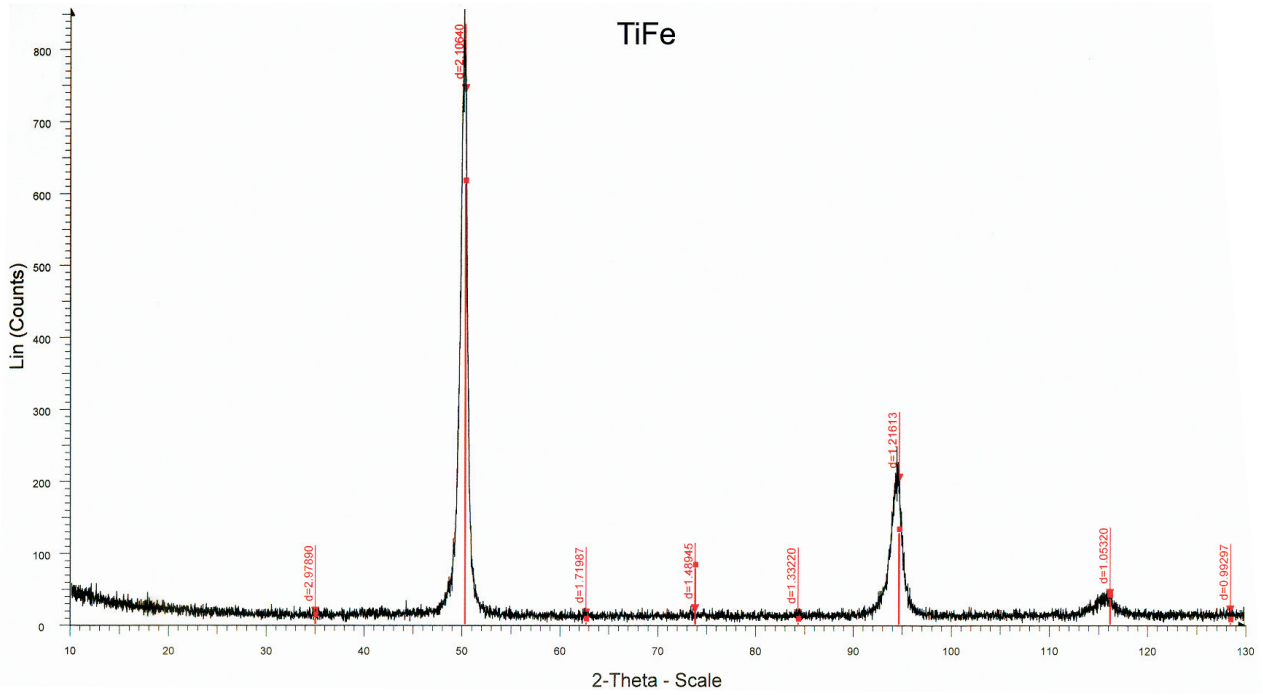

Fig. 2. XRD pattern of FeTi sample after homogenization

3. Experiment equipment and techniques

Low temperature measurements were carried out on differential scanning calorimeter TA Q 1000, while DSC Du Pont 910 was used for high temperature range.
Tzero^{TM} calibration method was employed to determine C_p of intermetallic phases using Q 1000 calorimeter within low temperature range, and three-run classical technique was used for high temperature measurements following ASTM E1269 [2] standards.
Samples of about 50 mg were placed in aluminum containers and experiments were run under inert atmosphere of argon or helium. The optimal heating rate of 20 degrees per minute was determined during preliminary runs, and the sapphire single crystal was used as the reference sample.

4. Results

Because of large amount of experimental points, results were presented in the form of point's fitted curves, as can be seen in the subsequent figures. Measurements were made for both temperature ranges for FeTi phase, whereas only low temperature experiments were performed for $AlNi_3$ and Ni_3Ti; high temperature data for last two compounds have already been pub-lished elsewhere ([3] and [1] respectively).

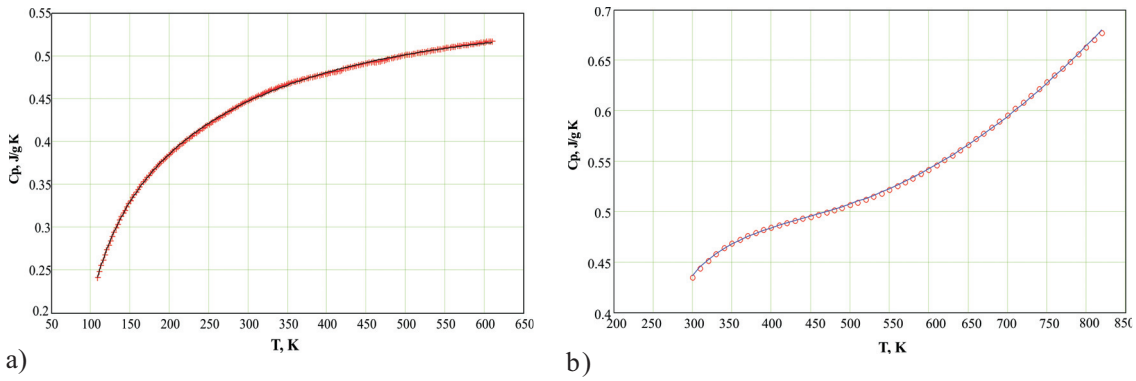

Fig. 3. Low- a) and high- b) temperature C_p vs T curve for FeTi intermetallic phase

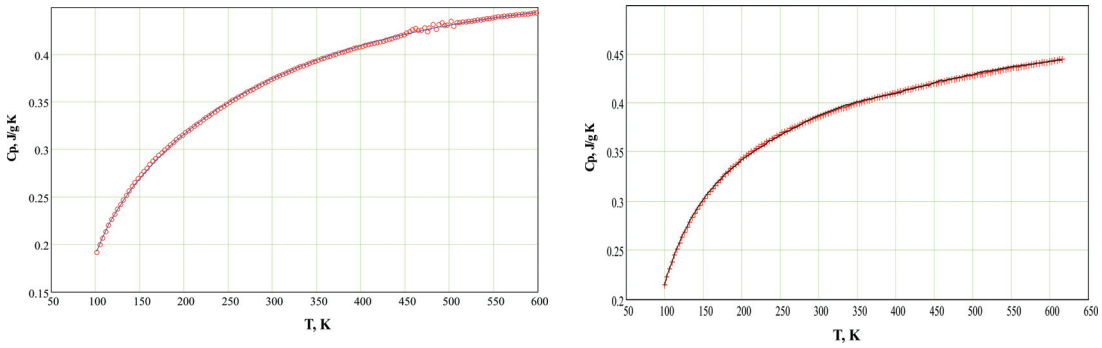

Fig. 4. Low-temperature C_p vs. T curves for $AlNi_3$ (left) and Ni_3Ti (right)

5. Analytical description of heat capacity data

Thermodynamic description of materials follows current Scientific Group Thermodata Europe (SGTE) standards [4], especially from the point of view of applications in CALPHAD method [5].

According to [4] Gibbs energy of substance α, $G(\alpha)$ is temperature dependent as given below:

$$G(\alpha) = A + B \cdot T + C \cdot T \cdot \ln(T) + D \cdot T^2 + E \cdot T^{-1} + F \cdot T^3 \quad (1)$$

and parameters A, B, C, D, E, F for most of substances in various crystal structures are listed in [4] and are known as SGTE Unary Database. Other thermodynamic functions of the substance α like entropy, $S(alpha)$, enthalpy, $H(\alpha)$, and heat capacity, C_p may be derived from (1) the last in the form:

$$C_p = -C - D \cdot T - 2E \cdot T^{-2} - 6F \cdot T^2 \quad (2)$$

or simpler as:

$$C_p = a + b \cdot T + c \cdot T^{-2} + d \cdot T^2. \quad (3)$$

Equations (2) and (3) are known as Kelley's equation, describing temperature dependence of heat capacity at temperatures above 0°C. Sometimes for the better fit to experimental data other powers of T like: $T^{-0.5}$, T^{-1} or T^{-3} are added. C_p curves shown in figures 3 and 4 represent in general fit of experimental values to Kelley equation in the form:

$$C_p = a + b \cdot T + c \cdot T^{-0.5} + d \cdot T^{-1} + e \cdot T^{-3} + f \cdot T^{-2} \quad (4)$$

although not all the coefficients were used for each case, as can be seen in Table 2:

TABLE 2

Kelley equation (4) parameters for all intermetallics investigated

Phase	$C_p = a + b \cdot T + c \cdot T^{-0.5} + d \cdot T^{-1} + e \cdot T^{-3} + f \cdot T^{-2}$					
	a	b	c	d	e	f
DuPont 910						
FeTi	-4.8777	$2.228 \cdot 10^{-3}$	147.175	-1155.3	–	–
Q1000						
Ni_3Ti	0.385	$9.016 \cdot 10^{-5}$	1.362	-31.44	$9.126 \cdot 10^{4}$	
$AlNi_3$	0.764	$-1.103 \cdot 10^{-4}$	-5.592	-20.67	$-1.822 \cdot 10^{5}$	$3.837 \cdot 10^{3}$
FeTi	0.0849	$2.74 \cdot 10^{-4}$	10.4541	-97.03	–	

There are no C_p data available in the literature for $AlNi_3$ phase in the temperature range investigated in this work. C_p value of Smith et al. [6] for Ni_3Ti at 200 K: 0.3808 J/g·K is higher than our data: 0.3532 J/g·K at the same temperature. Wang et al. [7] determined heat capacity of FeTi within wide temperature range; their data at 200 K: 0.4167 J/g·K is a bit higher than our value of 0.3938 J/g·K, and at 500 K Wang's result of 0.5058 J/g·K agrees excellently with our 0.5078 J/g·K.

Some slight discrepancies between low- and high-temperature C_p values for FeTi observed in Fig.3 in the region, where both measurements ranges overlap

each other (between 300 and 600 K) are caused by difference in sensitivity of DSC devices, and change of curvature in the high-temperature graph (Fig.3 b) is most probably the result of uncontrolled heat losses via gas of protective atmosphere.

6. Summary

Methods of sample preparation followed by appropriate heat treatment resulted in a homogeneous, single phase material.
Phase identification and chemical composition determination were made by XRD and SEM methods.
Heat capacity measurements were carried out in the wide temperature interval including sub-zero range using two different DSC devices.
Experimental results were fitted to Kelley equation, revealing excellent fit.
They were then presented as C_p versus T curves, and numerical values of equation parameters were listed in the table.
Reasonable agreement is observed between our results and available literature data.
Finally, heat capacities for all three intermetallic phases display substantial negative deviation from Kopp-Neuman rule.

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REFERENCES

[1] A. Sypien, A. Wierzbicka-Miernik, T. Czeppe, L. A. Zabdyr, Heat Capacity of Nickel Titanides, submitted to Intermetallics.
[2] ASTM E1269-05, Standard Test Method for Determining Specific Heat Capacity by Dif-ferential Scanning Calorimetry, ASTM International 14.02 (2005).
[3] A. I. Kovalev, M. B. Bronfin, Yu. V. Loshchinin, V. A. Vertogradskii, High Temp. High Press. **8**, 581-584 (1976).
[4] A. T. Dinsdale, CALPHAD **15(4)**, 317 (1991).
[5] L. A. Zabdyr, Strategia CALPHAD, IMIM PAN, Krakow, 2005.
[6] J. F. Smith, R. Luck, Q. Jiang, B. Predel, J. Phase Equilibria **14(4)**, 494-500 (1993).
[7] H. Wang, R. Lück, B. Predel, Z. Metallkd. **84(4)**, 230-6 (1993).