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DETERMINATION OF γ'+γ / γ PHASE BOUNDARY IN Ni-Al-Cr SYSTEM USING DTA THERMAL ANALYSIS

Mechanical properties at elevated temperature, in modern alloys based on intermetallic phase Ni_3Al are connected with phase composition, especially with proportion of ordered phase γ' ($L1_2$) and disordered phase γ (A1). In this paper, analysis of one key systems for mentioned alloys – Ni-Al-Cr, is presented. A series of alloys with chemical composition originated from Ni-rich part of Ni-Al-Cr system was prepared. DTA thermal analysis was performed on all samples. Based on shape of obtained curves, characteristic for continuous order-disorder transition, places of course of phase boundaries γ'+γ / γ were determined. Moreover, temperature of melting and freezing of alloys were obtained. Results of DTA analysis concerning phase boundary γ'+γ / γ indicated agreement with results obtained by authors using calorimetric solution method.

Keywords: DTA thermal analysis, order-disorder transition, Ni_3Al, Ni-Al-Cr

1. Introduction

There are various phases in Ni-rich part of ternary system Ni-Al-Cr. Among others, single-phase regions denoted as γ' and γ separated by two-phase region γ'+γ can be found (Fig. 1). Phase γ' crystallises in ordered structure $L1_2$, γ phase, on contrary, in disordered structure A1 [1,2]. Both of them differ substantially in mechanical properties, and their content ratio determines strength properties of modern alloys based on intermetallic phase Ni_3Al with chromium addition, destined to work at elevated temperature [3÷5]. With temperature increase, in those alloys, next to ordered phase γ', disordered phase γ emerges until the moment of complete fading of phase γ'. In literature, such a continuous ordering reaction with occurring two-phase region is known as second-order order-disorder transition (2O-OD) [6,7].

This paper presents continuation of research which purpose was to determine high-temperature phase boundaries γ' / γ'+γ and γ'+γ / γ in Ni-Al-Cr system. Existing elaboration of this system, using common CALPHAD procedure raises doubts due to using experimental data obtained from samples cooled rapidly [8÷10]. In case of alloys based on intermetallic phase Ni_3Al, it is related with difficulties of keeping high-temperature structure after quenching [11,12].

Therefore, authors of this paper decided to rely on results obtained directly at elevated temperature. First experiments on alloys of chemical composition from range Ni75Al25÷Ni75Cr25 and Ni75Al25÷Ni87Cr13 of Ni-Al-Cr system were conducted using high-temperature calorimeter solution type, designed by themselves. Phase boundaries γ' / γ'+γ and γ'+γ / γ in Ni-Al-Cr system were determined based on change of formation enthalpy of alloys with different chromium content. Research was conducted for temperatures: 873K, 996K and 1150K [13,14].

Subsequently, thermal analysis was carried out. 2O-OD transition occurring in described alloys, according to literature shows a peak with a λ shape, as it is shown on Fig. 1 [6,7,15]. It allows for determination of transition temperature (TC) as the temperature corresponding to a minimum point of the endothermic peak on the heating curve. Transition temperature is usually very close to the temperature at the onset of a peak in the cooling curve, which means that the cooling curve is also viable for the determination of the transition temperature. Transition temperature in case of investigated alloys, based on intermetallic phase Ni_3Al with chromium addition, corresponds to high-temperature phase boundary γ'+γ / γ. Using thermal analysis methods such as DSC and DTA, for alloy research from Ni75Al25÷Ni75Cr25 section enabled identification of course of high-temperature phase boundary γ'+γ / γ. At the same time, agreement of results obtained with calorimetric solution method was met [16].

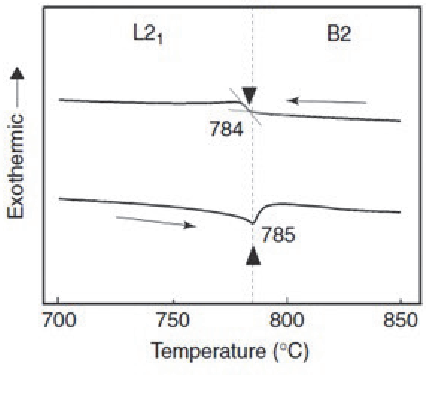

Fig. 1. Thermal analysis curves showing 2O-OD transition of Co50Cr26Ga24 alloy [7]

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In this work, DTA thermal analysis was used for alloys analysis from range Ni75Al25÷Ni87Cr13 in order to determine temperature of phase transitions. Apart from direct determination of phase boundary γ′+γ / γ at elevated temperature, melting and freezing temperature of alloys were determined.

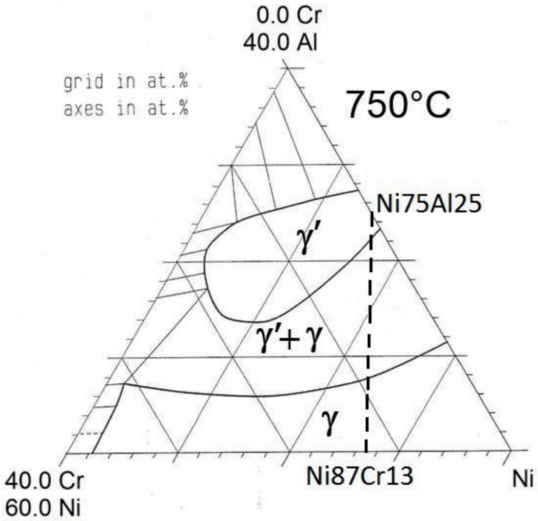

Fig. 2. Isothermal section of Ni-rich part of Ni-Al-Cr system at temperature 750°C proposed by Taylor and Floyd [10]. Broken line shows section with chemical composition representing alloys studied in this work

2. Experimental data

For research, the same alloys were used as in previous paper of authors [14]. Their chemical composition is from the range Ni75Al25÷Ni87Cr13 of Ni-Al-Cr system (Fig.2). In order to prepare alloys, metals of high purity: Al (99,99%), Ni (99,98%) and Cr (99,5%) were melted in alundum crucible, in Balzers vacuum induction furnace VSG-02, at temperature higher about 150°C from liquidus temperature. Subsequently, alloys were casted to ceramic moulds, as a consequence bars of 3mm diameter were obtained, which were cut into pieces of 12mm length. Chemical composition of alloys was obtained by aluminum and chromium determination, using atomic absorption spectrometry. Residual alloy content was nickel. Table 1 presents results of chemical analysis of twelve prepared alloys.

TABLE 1

Chemical composition of samples from Ni75Al25÷Ni87Cr13 section. Component content is given in atomic %

No.	Component content [at. %]		Alloy
	Cr	Al	
1	0,0	25,0	Ni75,0Al25,0
2	1,4	22,4	Ni76,2Al22,4Cr1,4
3	2,6	20,0	Ni77,4Al20,0Cr2,6
4	3,7	18,0	Ni78,3Al18,0Cr3,7
5	5,1	15,1	Ni79,8Al15,1Cr5,1
6	6,2	13,2	Ni80,6Al13,2Cr6,2
7	7,2	11,0	Ni81,8Al11,0Cr7,2
8	8,0	9,5	Ni82,5Al9,5Cr8,0
9	9,4	6,6	Ni84,0Al6,6Cr9,4
10	10,4	4,8	Ni84,8Al4,8Cr10,4
11	11,5	2,9	Ni85,6Al2,9Cr11,5
12	12,4	1,0	Ni86,6Al1,0Cr12,4

DTA analysis was conducted on thermal analyzer STA 449 F3 Jupiter from NETZSCH company. Using high-temperature graphite furnace and ceramic protective tube enables thermal analysis at temperature up to 1650°C. All experiments were carried out with protective atmosphere of high purity argon (Ar 6.0). Results were elaborated using Proteus program (version 6.0.0), NETZSCH.

In previous work, authors stated lack of clear influence of heating and cooling rate on transition temperature order-disorder in alloys from Ni75Al25÷Ni75Cr25 section [16]. Based on that and in order to compare results within the scope of the same Ni-Al-Cr system, in this work all measurements were determined with rate 20°C/min.

3. Results and discussion

Thermal analysis DTA was performed on all samples presented in Table 1. Only in case of alloys: Ni77,4Al20,0Cr2,6, Ni78,3Al18,0Cr3,7, Ni79,8Al15,1Cr5,1 and Ni80,6Al13,2Cr6,2, thermal effects were identified, which can be assigned to order-disorder transition (Fig. 3÷6). Endothermic peak is visible during heating and exothermic peak during cooling, as can be observed in Fig. 1. In studied alloys, endothermic effect is connected with completion of disordered phase γ precipitation and exothermic effect is connected with beginning of γ′ phase ordering. Therefore, transition temperature determined in Fig 3÷6 can be assigned to phase boundary γ′+γ / γ. Difficulty in determination of temperature of 2O-OD transition in residual alloys and during heating of alloys Ni79,8Al15,1Cr5,1 and Ni80,6Al13,2Cr6,2 is a result of low sensitivity of DTA method related to measuring apparatus design. Authors noted this problem during research of alloys from Ni75Al25÷Ni75Cr25 section, where using DSC method enabled to observe more distinct effects of 2O-OD transition [16].

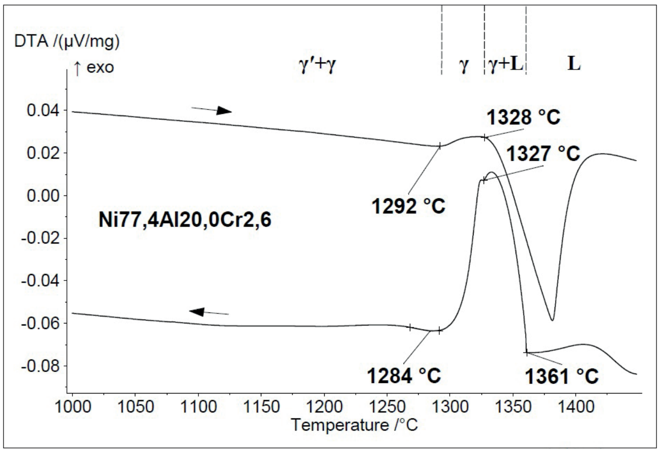

Fig. 3. DTA curves registered during heating and cooling of alloy Ni77,4Al20,0Cr2,6 (20°C/min). On top, stability range of particular phases is indicated

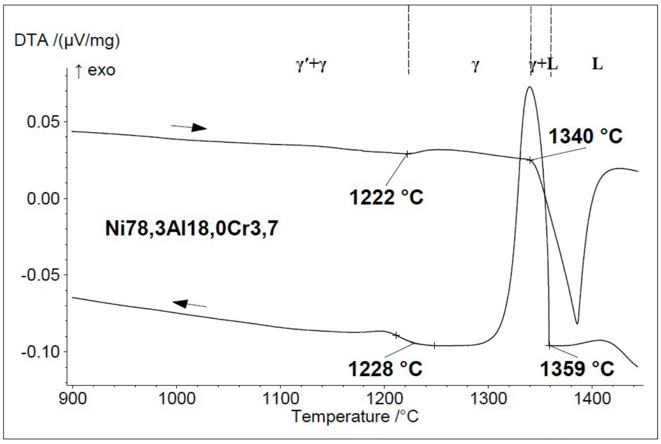

Fig. 4. DTA curves registered during heating and cooling of alloy Ni78,3Al18,0Cr3,7 (20°C/min). On top, stability range of particular phases is indicated

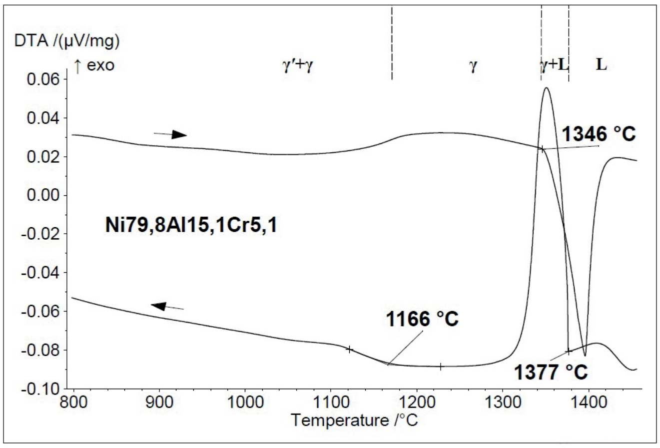

Fig. 5. DTA curves registered during heating and cooling of alloy Ni79,8Al15,1Cr5,1 (20°C/min). On top, stability range of particular phases is indicated

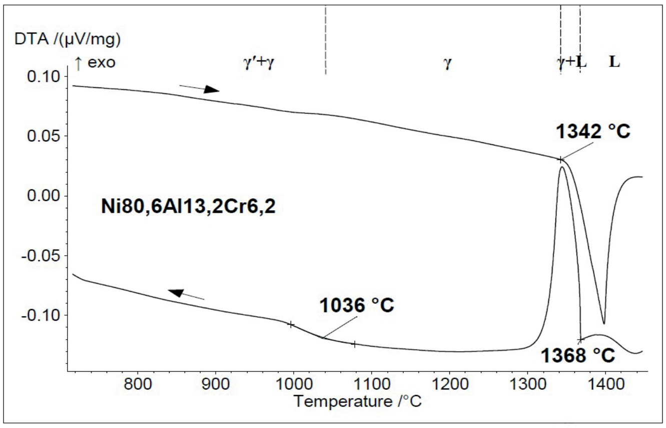

Fig. 6. DTA curves registered during heating and cooling of alloy Ni80,6Al13,2Cr6,2 (20°C/min). On top, stability range of particular phases is indicated

Substantial thermal effects visible in Fig 3÷6 are related to melting and freezing of studied alloys. Starting temperature of those transitions was determined by indication of first deviation of registered curve from baseline. Analogical approach was applied for other alloys from the Ni75Al25÷Ni87Cr13 section (Fig. 7).

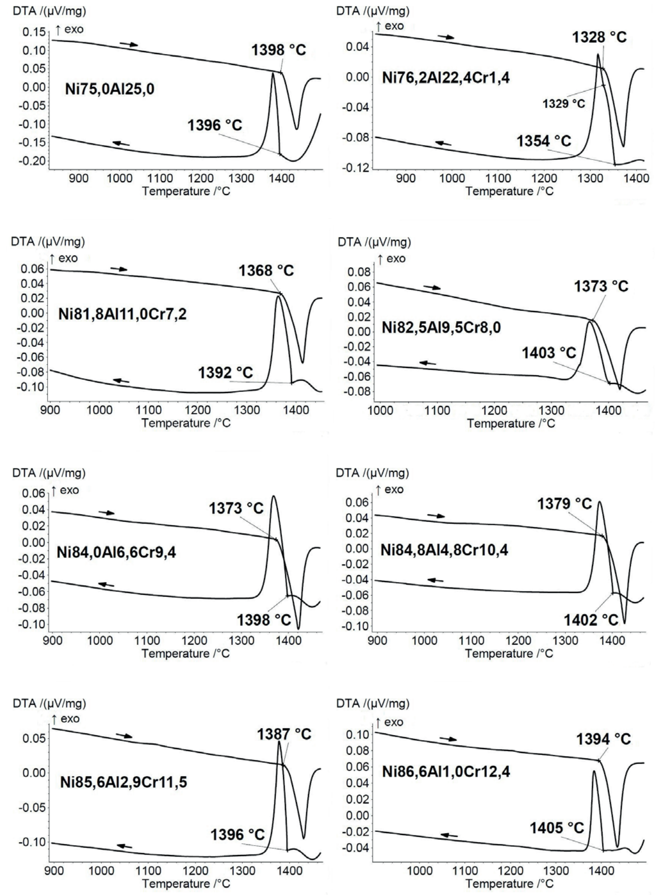

Fig. 7. DTA curves registered during heating and cooling of alloys from Ni75Al25÷Ni87Cr13 section (20°C/min)

In table 2, melting and freezing temperatures are presented for examined alloys, determined during heating and cooling with rate of 20°C/min. In case of alloys Ni76,2Al22,4Cr1,4 and Ni77,4Al20,0Cr2,6 apart from exothermic peak accompanying freezing, presence of slight exothermic effect at temperature 1329°C and 1327°C was noticed. In both cases, temperature is close to melting temperature of alloys (1328°C), determined with use of heating curve. It is worth to indicate, that melting temperature determined for alloy Ni75,0Al25,0 corresponding to stoichiometric intermetallic phase Ni_3Al is close to literature value – 1395°C [17÷19].

Transition temperatures determined during thermal analysis DTA of alloys from Ni75Al25÷Ni87Cr13 section were collected and compared with results obtained using calorimetric solution method (Fig. 8) [14]. Results referring to phase boundary γ′+γ / γ in both methods present agreement. In Fig. 8 it is visible, that at elevated temperature, with an increase of chromium concentration, participation of disordered phase γ increases at cost to ordered phase γ′. Schematic occurrence ranges of particular phases in studied alloys are indicated also in Fig 3÷6. It is worth mentioning that method used in this work allow for measurements at temperature range unavailable for calorimetric method. Melting and freezing temperature of alloys from Ni75Al25÷Ni87Cr13 section showed in this paper, may be used for determination of solidus and liquidus surface in ternary system Ni-Al-Cr.

TABLE 2

Melting and freezing temperature of alloys from Ni75Al25÷Ni87Cr13 section, determined from curves registered during thermal analysis DTA with rate of 20°C/min

No.	Alloy	Heating/Cooling rate of 20°C/min	
		Melting point, °C	Freezing point, °C
1	Ni75,0Al25,0	1398	1396
2	Ni76,2Al22,4Cr1,4	1328	1354
3	Ni77,4Al20,0Cr2,6	1328	1361
4	Ni78,3Al18,0Cr3,7	1340	1359
5	Ni79,8Al15,1Cr5,1	1346	1377
6	Ni80,6Al13,2Cr6,2	1342	1368
7	Ni81,8Al11,0Cr7,2	1368	1392
8	Ni82,5Al9,5Cr8,0	1373	1403
9	Ni84,0Al6,6Cr9,4	1373	1398
10	Ni84,8Al4,8Cr10,4	1379	1402
11	Ni85,6Al2,9Cr11,5	1387	1396
12	Ni86,6Al1,0Cr12,4	1394	1405

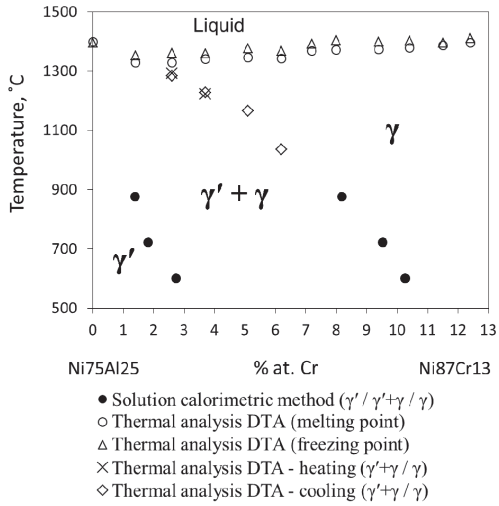

Fig. 8. Comparison of thermal analysis DTA results for alloys from Ni75Al25÷Ni87Cr13 section of Ni-Al-Cr system with results obtained from calorimetric solution method

4. Conclusions

Thermal analysis DTA was used to determine phase boundary $\gamma'+\gamma / \gamma$ in Ni-Al-Cr system. Order-disorder transition accompanying change of ordered phase γ' to disordered phase γ with temperature increase, exhibit characteristic thermal effect, which is possible to observe using thermal analysis methods.

1. Based on curves registered during heating and cooling of alloys from Ni-rich part of ternary system Ni-Al-Cr, in case of alloys: Ni77,4Al20,0Cr2,6, Ni78,3Al18,0Cr3,7, Ni79,8Al15,1Cr5,1 and Ni80,6Al13,2Cr6,2, thermal effects were noticed, which presence correspond to phase boundary $\gamma'+\gamma / \gamma$.
2. Temperature corresponding to phase boundary $\gamma'+\gamma / \gamma$ determined in this paper is in agreement with results obtained using calorimetric solution method.
3. In relation to calorimetric solution method, using thermal analysis DTA allowed for conducting research at temperature exceeding 1000°C and as a consequence, determination of melting and freezing temperature of alloys was possible. Disadvantage of used DTA method is relatively low sensitivity, resulting from construction of measuring apparatus.
4. Melting and freezing temperature of alloys from Ni75Al25÷Ni87Cr13 section determined in this paper can be used for determination of solidus and liquidus surface in ternary system Ni-Al-Cr.

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