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DTA THERMAL ANALYSIS OF ALLOYS FROM NICKEL-RICH PART OF Ni-Al-Cr SYSTEM

Thermal analysis allows for determination of temperature specific for the beginning and the end of phase transitions occurring in studied samples. In this paper results obtained from DTA (Differential Thermal Analysis) of alloys of chemical composition referring to nickel-rich part of Ni-Al-Cr system, specifically from section Ni75Al25÷Ni65Cr35 are presented. Those alloys are based on intermetallic phase Ni_3Al. Referring to measurements obtained during heating and cooling, characteristic peaks related to occurrence of phase transition of order-disorder type were noted as well as melting and solidification temperature of alloys was determined. Results of thermal analysis DTA of studied range were compared with results obtained for section Ni75Al25÷Ni75Cr25 and Ni75Al25÷Ni87Cr13, additionally results of measurements performed on high-temperature solution calorimeter were collated. Both methods presented good compatibility.

Keywords: Ni-Al-Cr system, order-disorder, DTA analysis

1. Introduction

Nickel-based super alloys are one of up to date materials dedicated to work at elevated temperature [1,2]. Despite of high complexity of chemical composition, their microstructure consists mostly of two phases indicated as γ and γ'. Phase γ is disordered nickel solid solution that crystallizes in structure A1 and γ' ordered intermetallic compound based on Ni_3Al, crystallizes in structure $L1_2$. In case of nickel-based superalloys, high-temperature mechanical properties are controlled by the dispersion of γ' phase in γ matrix. On the other hand, there are alloys based mostly on intermetallic phase Ni_3Al, where ordered phase γ' is a phase dominant over the disordered phase γ. In both mentioned group of materials, ternary Ni-Al-Cr system is crucial. Chromium as an addition improves anticorrosive properties of alloys as well as ductility [1-5]. It may substitute both: aluminum and nickel in lattice nodes of ordered phase. This reflects in occurrence of γ' in Ni-Al-Cr system (Fig. 1).

In alloys from Ni-rich part of Ni-Al-Cr system, with temperature increase 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 (in this case γ'+γ) is known as second-order order-disorder transition (2O-OD) [6,7]. As a result, high-temperature mechanical characteristics of alloys based on intermetallic phase Ni_3Al with chromium addition are correlated with ordered – disordered phase ratio.

One of methods used for identification of phase transition occurring in metal alloys is thermal analysis. In this paper DTA method (Differential Thermal Analysis) was used for studies of series of alloys from Ni75Al25÷Ni65Cr35 section of Ni-Al-Cr system (Fig. 1). A big advantage of this method is a possibility to conduct measurements directly at elevated temperature, also exceeding a range of thermal stability of studied alloys. That allowed for determination of melting and solidification temperature of studied alloys [8]. Results obtained in this paper, Author compared with results from previous papers, related to thermal analysis of alloys from Ni75Al25÷Ni75Cr25 and Ni75Al25÷Ni87Cr13 section of Ni-Al-Cr system and measurements performed on high-temperature solution calorimeter.

2. Samples preparation and experimental data

Series of alloys were prepared for measurements with chemical composition from Ni75Al25÷Ni65Cr35 section of Ni-Al-Cr system (Fig. 1). 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 150°C higher temperature from liquidus temperature. Alloys were casted to ceramic moulds, as a consequence bars of 3 mm diameter were obtained. 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 prepared alloys. The same alloys were used in previous work of Author for calorimetric measurements [10].

All alloys were submitted to preliminary heat treatment for homogenization. At first, alloys were placed in ceramic tubes,

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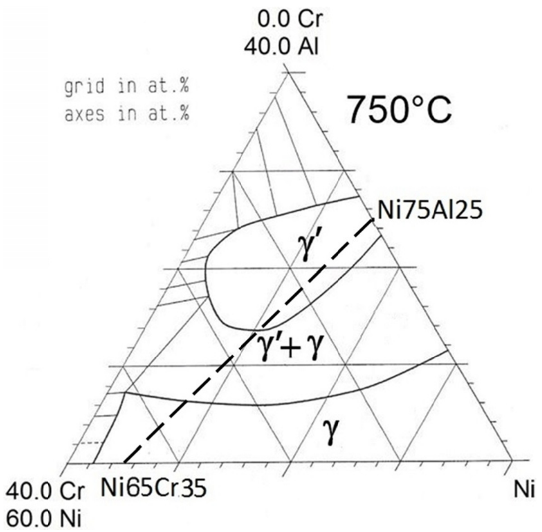

Fig. 1. Isothermal section of Ni-rich part of Ni-Al-Cr system at temperature 750°C proposed by Taylor and Floyd [9]. Broken line shows Ni75Al25÷Ni65Cr35 section with chemical composition representing alloys studied in this work

that were put in quartz capsules in vacuum, subsequently samples were heated at temperature 900°C for 48 hours. Afterwards cooling with furnace was conducted. Finally samples were cut into pieces of 12 mm length.

TABLE 1

Chemical composition of samples from the Ni75Al25÷Ni65Cr35 section of Ni-Al-Cr system

No.	Constituent content [% at.]		Alloy
	Cr	Al	
1	0.0	25.0	Ni75.0Al25.0
2	3.8	22.1	Ni74.1Al22.1Cr3.8
3	6.6	20.3	Ni73.1Al20.3Cr6.6
4	9.1	18.8	Ni72.1Al18.8Cr9.1
5	13.7	15.1	Ni71.2Al15.1Cr13.7
6	18.8	11.4	Ni69.8Al11.4Cr18.8
7	23.2	8.6	Ni68.2Al8.6Cr23.2
8	25.1	7.1	Ni67.8Al7.1Cr25.1
9	30.0	4.0	Ni66.0Al4.0Cr30.0
10	32.1	2.0	Ni65.9Al2.0Cr32.1

DTA analysis was conducted on thermal analyzer STA 449 F3 Jupiter from NETZSCH company. Each temperature cycle started with heating of the sample with 20°C/min rate from 40°C up to temperature of 1500°C, followed by cooling also with 20°C/min rate. Those parameters were based on previous work, in which Authors stated lack of clear influence of heating and cooling rate on transition temperature order-disorder in alloys from Ni75Al25÷Ni75Cr25 section [11]. 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. All experiments were carried out with protective atmosphere of high purity argon (Ar 6.0) and alundum crucible were used. Results were elaborated using NETZSCH Proteus program (version 6.0.0).

3. Results and discussion

Figures 2-10 present DTA curves recorded during heating and cooling of examined alloys from Ni75Al25÷Ni65Cr35 section of Ni-Al-Cr system. For all samples, melting and solidification temperature was determined based on first deviation from the baseline. Sample marked as Ni75.0Al25.0, that stoichiometric composition refer to phase Ni_3Al, was submitted to DTA analysis in one of previous work of Author. Results are given in Table 2.

TABLE 2

Melting and freezing temperatures of alloys from Ni75Al25÷Ni65Cr35 section of Ni-Al-Cr system determined during thermal analysis DTA with rate of 20°C/min

No.	Alloy	Temperatures, °C	
		Melting	Freezing
1	Ni75.0Al25.0	1398	1396
2	Ni74.1Al22.1Cr3.8	1349	1367
3	Ni73.1Al20.3Cr6.6	1332	1357
4	Ni72.1Al18.8Cr9.1	1336	1371
5	Ni71.2Al15.1Cr13.7	1336	1382
6	Ni69.8Al11.4Cr18.8	1358	1390
7	Ni68.2Al8.6Cr23.2	1357	1388
8	Ni67.8Al7.1Cr25.1	1365	1396
9	Ni66.0Al4.0Cr30.0	1367	1390
10	Ni65.9Al2.0Cr32.1	1362	1377

Samples marked as Ni65.9Al2.0Cr32.1, Ni66.0Al4.0Cr30.0 and Ni67.8Al7.1Cr25.1 don't indicate presence of other thermal effects than correlated to melting and solidification (Figs. 2-4).

In case of alloys marked as Ni68.2Al8.6Cr23.2, Ni69.8 Al11.4Cr18.8, Ni71.2Al15.1Cr13.7, Ni72.1Al18.8Cr9.1 and Ni73.1Al20.3Cr6.6 (Figs. 5-9), based on derivative and shape of curves, presence of additional thermal effects was stated during heating and cooling. It was assigned to 2O-OD transition, that for researched alloys indicated phase boundary $\gamma' + \gamma / \gamma$ (see Table 3). Above transition temperature, ordered phase γ' declines and only disordered phase γ occurs. Temperature of the transition was determined based on literature data, that describes that during thermal analysis of alloys in which 2O-OD transition occurs, on the heating curve appears characteristic peak with a λ shape. Critical temperature of transition is determined based on minimum point of endothermic peak accompanying heating of sample. Temperature determined in this way, is closest to temperature at the onset of an exothermic peak, noticed during cooling of the same sample. It means cooling curves can be also used for determination of temperature of 2O-OD transition [6,7].

Also in sample Ni74.1Al22.1Cr3.8 (Fig. 10), presence of order – disorder transition can be stated at temperature of approx. 1330-1340°C. It is indicated by deviation from curve visible before melting peak (endothermic effect) and solidification peak (exothermic.effect), confirmed by shape of second derivative. In order to distinguish both effects, measurement should be conducted with sample of substantially lower weight, using DSC method (Differential Scaning Calorimetry). Contrary to DTA

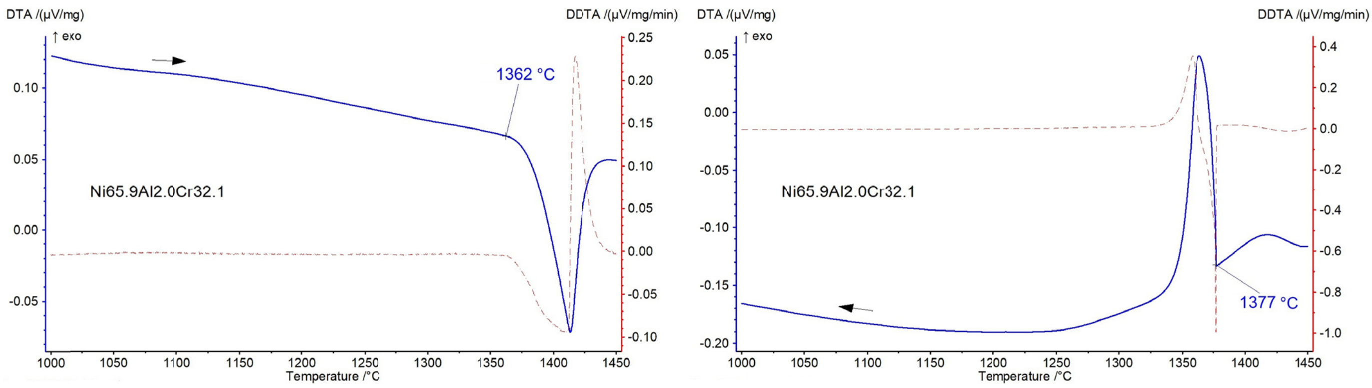

Fig. 2. DTA curves registered during heating (left) and cooling (right) of alloy Ni65.9Al2.0Cr32.1 (20°C/min)

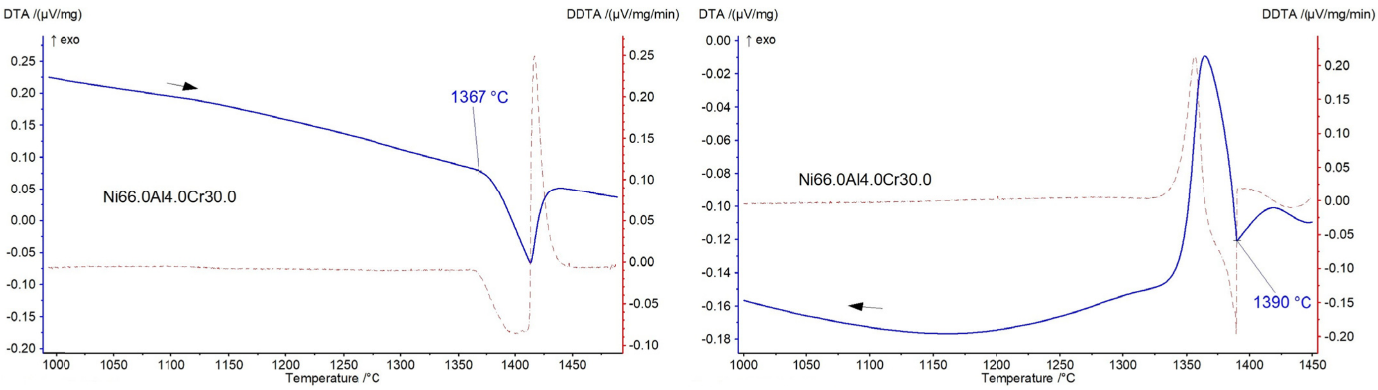

Fig. 3. DTA curves registered during heating (left) and cooling (right) of alloy Ni66.0Al4.0Cr30.0 (20°C/min)

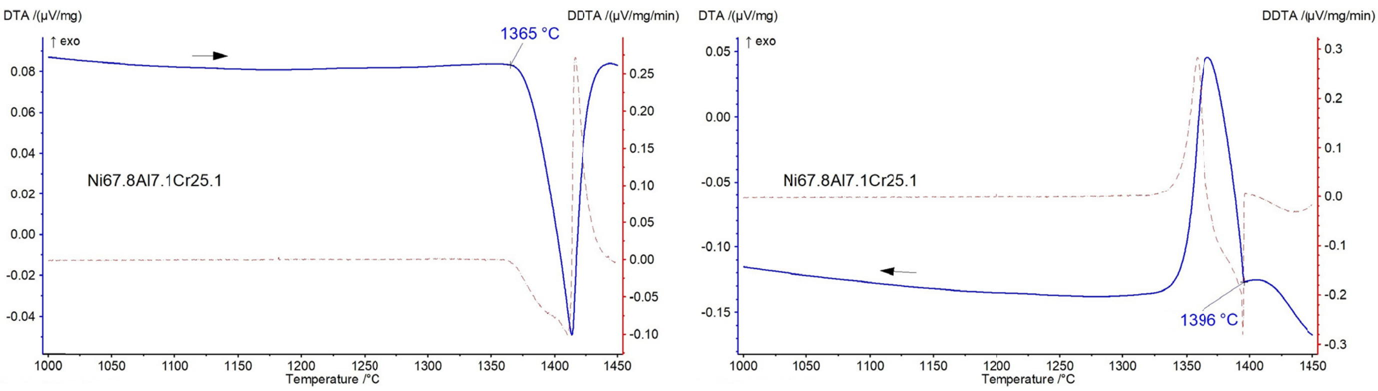

Fig. 4. DTA curves registered during heating (left) and cooling (right) of alloy Ni67.8Al7.1Cr25.1 (20°C/min)

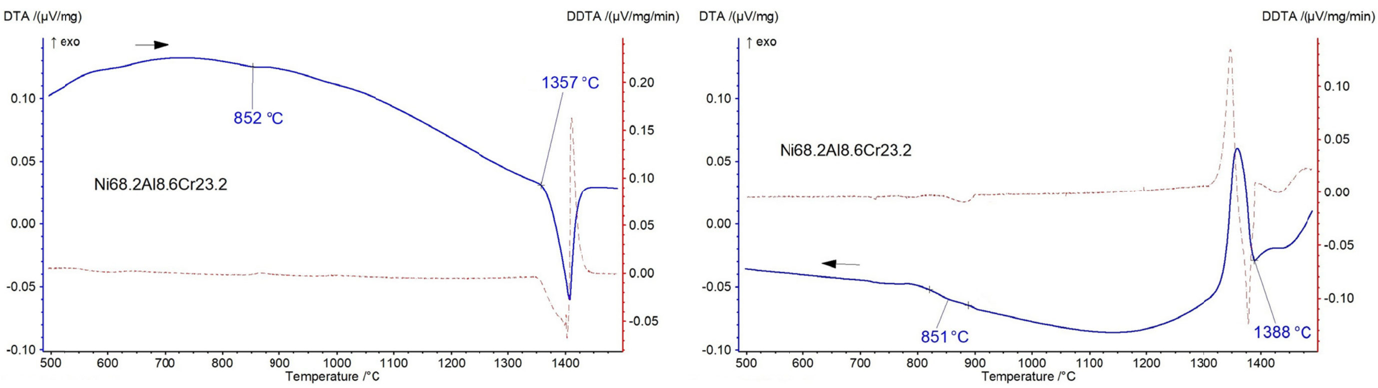

Fig. 5. DTA curves registered during heating (left) and cooling (right) of alloy Ni68.2Al8.6Cr23.2 (20°C/min)

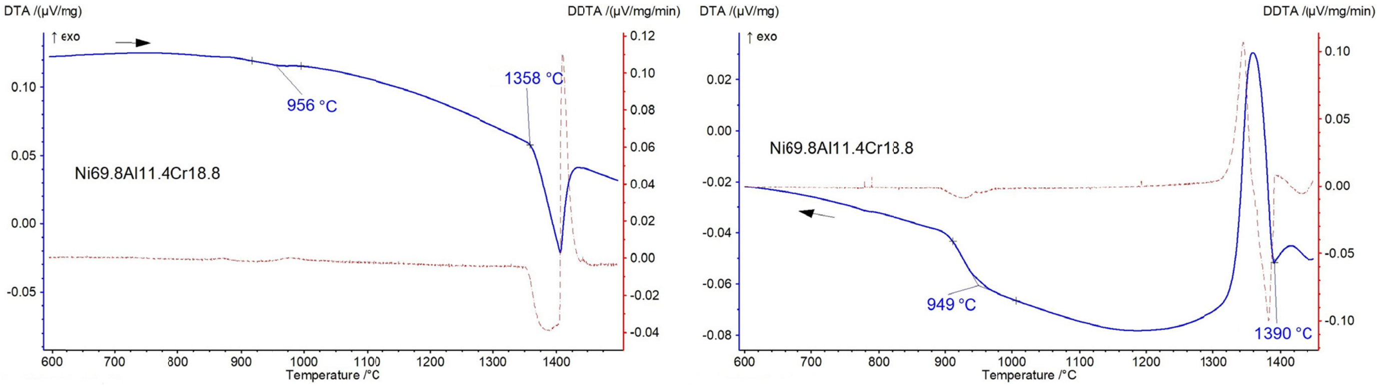

Fig. 6. DTA curves registered during heating (left) and cooling (right) of alloy Ni69.8Al11.4Cr18.8 (20°C/min)

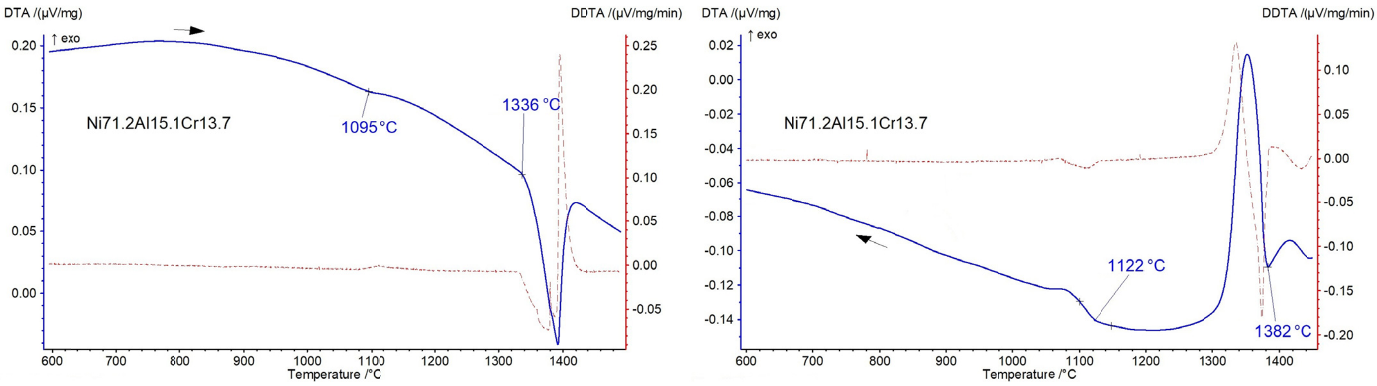

Fig. 7. DTA curves registered during heating (left) and cooling (right) of alloy Ni71.2Al15.1Cr13.7 (20°C/min)

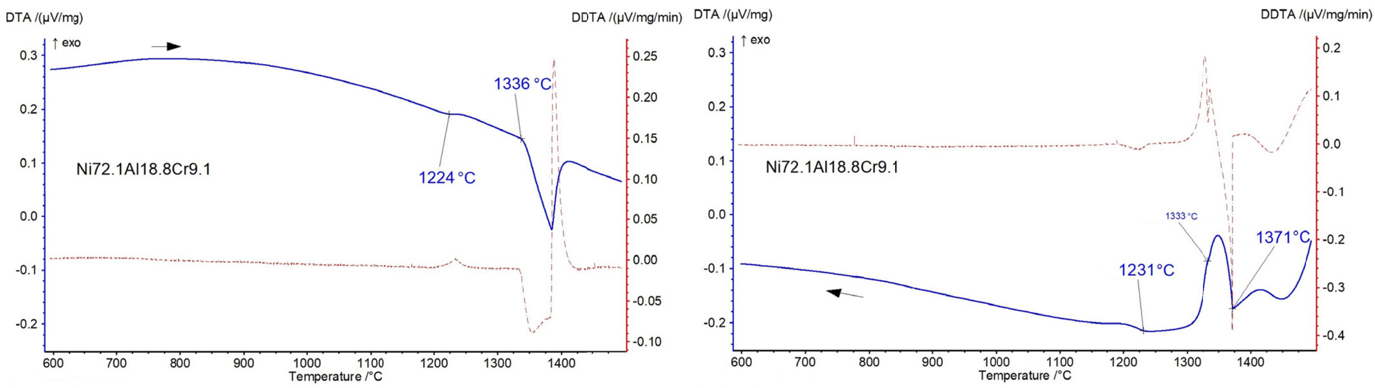

Fig. 8. DTA curves registered during heating (left) and cooling (right) of alloy Ni72.1Al18.8Cr9.1 (20°C/min)

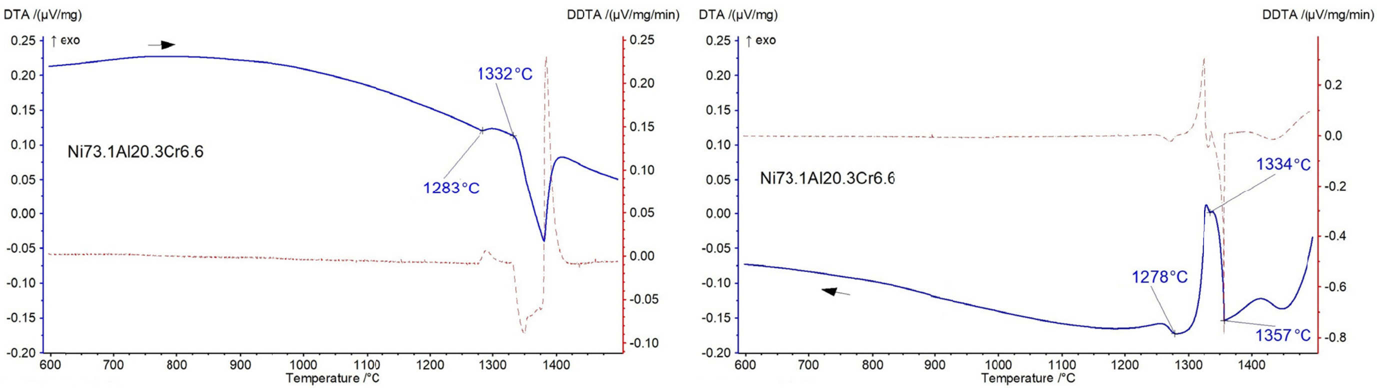

Fig. 9. DTA curves registered during heating (left) and cooling (right) of alloy Ni73.1Al20.3Cr6.6 (20°C/min)

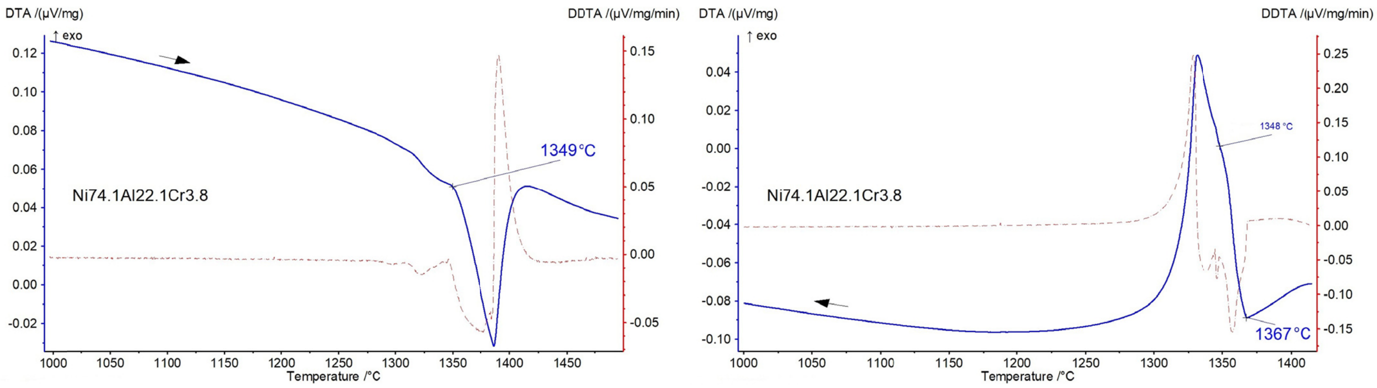

Fig. 10. DTA curves registered during heating (left) and cooling (right) of alloy Ni74.1Al22.1Cr3.8 (20°C/min)

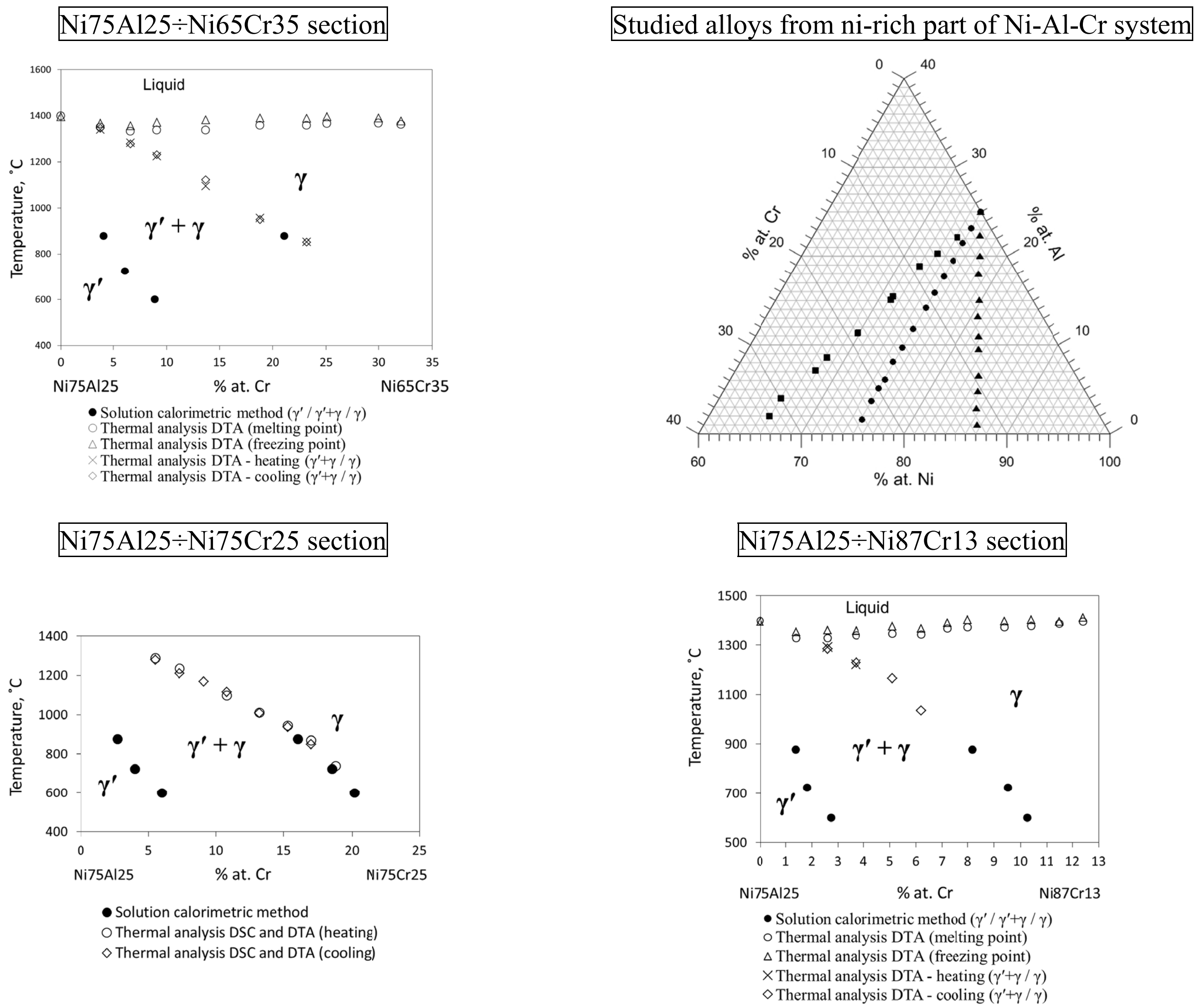

Fig. 11. Comparison of thermal analysis results obtained in this work for Ni75Al25÷Ni65Cr35 section of Ni-Al-Cr system with results obtained by Author for section Ni75Al25÷Ni65Cr35 and Ni75Al25÷Ni87Cr13, including results from calorimetric measurements

method, this method is more sensitive, that is confirmed by DSC measurements conducted by Author and co-workers on alloys from Ni75Al25÷Ni75Cr25 section of Ni-Al-Cr system [11].

However, it is worth to underline, that thermal analysis DTA or DSC does not allow for unequivocal determination of phase boundary $\gamma' / \gamma' + \gamma$ in alloys from Ni-rich part of Ni-Al-Cr system. With occurrence of disordered γ phase during temperature increase, minor thermal effect is visible, which has continuous course and lasts until end of disordering ($\gamma' + \gamma / \gamma'$ phase boundary).

TABLE 3

Temperatures of phase boundary $\gamma' + \gamma / \gamma$ in alloys from Ni75Al25÷Ni65Cr35 section of Ni-Al-Cr system determined during thermal analysis DTA with rate of 20°C/min

No.	Alloy	$\gamma' + \gamma / \gamma$ temperature, °C	
		Heating	Cooling
1	Ni75.0Al25.0	—	—
2	Ni74.1Al22.1Cr3.8	ca. 1330	ca. 1340
3	Ni73.1Al20.3Cr6.6	1283	1278
4	Ni72.1Al18.8Cr9.1	1224	1231
5	Ni71.2Al15.1Cr13.7	1095	1122
6	Ni69.8Al11.4Cr18.8	956	949
7	Ni68.2Al8.6Cr23.2	852	851
8	Ni67.8Al7.1Cr25.1	—	—
9	Ni66.0Al4.0Cr30.0	—	—
10	Ni65.9Al2.0Cr32.1	—	—

In research related to phase boundaries from Ni-Al-Cr system, authors commonly rely on samples submitted to rapid cooling [12-14]. Due to difficulty in obtaining by samples thermodynamic balance, in this paper it is suggested to conduct studies directly at elevated temperature. Apart from presented results of thermal analysis DTA, measurements using solution calorimeter were conducted [10,15]. In this method, huge differences in binding energy between ordered and disordered phase were used. Phase boundaries $\gamma' / \gamma' + \gamma$ and $\gamma' + \gamma / \gamma$ at temperature 600°C, 723°C and 877°C were determined based on enthalpy of formation of alloys from the range Ni75Al25÷Ni65Cr35 as a function of chromium concentration [10].

Figure 11 presents comparison of results obtained in this paper with results obtained for section Ni75Al25÷Ni75Cr25 and Ni75Al25÷Ni87Cr13 also with measurements using high temperature solution calorimeter. Lack of melting and solidification temperature in case of alloys from Ni75Al25÷Ni75Cr25 section results from the fact that the device used for DSC measurements does not allow for exceeding temperature of 1300°C. However, keeping on mind similarity in location of those points for two other sections similar results for Ni75Al25÷Ni75Cr25 can be expected. Additionally, good agreement of results obtained with different measurement methods in range of phase boundary determination $\gamma' + \gamma / \gamma$ was stated.

Simultaneously, difficulty in determination of phase boundary $\gamma' / \gamma' + \gamma$ using thermal analysis was confirmed. Sensitivity of DTA method also hinder registration of effects related to 2O-OD transition for alloys from Ni-rich part of Ni-Al-Cr system below temperature of 1000°C. However, taking into consideration difficulty and time required for calorimetric measurements, thermal analysis should be considered as valuable completion of research of alloys directly at elevated temperature.

4. Conclusions

1. Thermal analysis DTA was used for measurements of nine alloys in Ni-rich part of Ni-Al-Cr system with chemical composition from Ni75Al25÷Ni65Cr35 cross-section.
2. Melting and solidification temperature of alloys during heating and cooling with rate 20°C/min was determined.
3. In case of alloys marked as Ni68.2Al8.6Cr23.2, Ni69.8 Al11.4Cr18.8, Ni71.2Al15.1Cr13.7, Ni72.1 Al18.8Cr9.1 and Ni73.1Al20.3Cr6.6, presence of thermal effects characteristic for order-disorder transition was stated. It was assigned to presence of phase boundary $\gamma' + \gamma / \gamma$.
4. Temperatures corresponding to phase boundary $\gamma' + \gamma / \gamma$ obtained in this paper with DTA thermal analysis method were complied with results from solution calorimetry, showing good compatibility. Additionally, results from thermal analysis from two other cross-section: Ni75Al25÷Ni65Cr35 and Ni75Al25÷Ni87Cr13 from Ni-Al-Cr system were compared.
5. Limitation of DTA method with registration of thermal effects related to order-disorder transition in alloys from Ni-rich part of Ni-Al-Cr system was stated.

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REFERENCES

[1] R.C. Reed, The Superalloys Fundamentals and applications, 2006 Cambridge University Press.
[2] M.J. Donachie, S.J. Donachie, Superalloys A Technical Guide Second Edition, 2002 ASM International.
[3] V. Levitin, High Temperature Strain of Metals and Alloys: Physical Fundamentals, 2006 Wiley-Vch.
[4] J. Klöwer, U.Brill, Heubner, Intermetallics **7**, 1183-1194 (1999).
[5] W. Malec, K. Rzyman, M. Czepelak, A. Wala, Archives of Metallurgy and Materials 56, 1007-1014 (2011).
[6] K. Kobayashi, R. Kainuma, K. Fukamichi, K. Ishida, J. Alloy. Compd. **403**, 161 (2005).
[7] R. Kainuma, I. Ohnuma, K. Ishida, Determination of phase diagrams involving order-disorder transitions, in: J.-C. Zhao (Ed.), Methods for Phase Diagram Determination 2007, Elsevier Ltd. (2007).
[8] Y. Mishima, Y.M. Hong, T. Suzuki, Materials Science and Engineering A **146**, 123-130 (1991).
[9] A. Taylor, R.W. Floyd, J. Inst. Met. **81**, 451 (1952).
[10] T. Maciąg, in: METAL 2016 Conference proceedings, 1480-1485, Tanger, Brno 2016
[11] T. Maciąg, K. Rzyman, R. Przeliorz, Archives of Metallurgy and Materials. **60**, 1871-1876 (2015).
[12] W. Huang, Y.A. Chang, Intermetallics **7**, 863-874 (1999).
[13] N. Dupin, I. Ansara, B. Sundman, Calphad **25** 2, (2001).
[14] V. Raghavan, Journal of Phase Equilibria and Diffusion **27** 4, 381-388 (2006).
[15] T. Maciąg, K. Rzyman, J. Therm. Anal. Calorimetry **133**, 189-197 (2013).