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T. MACIĄG*,#, K. RZYMAN*, R. PRZELIORZ*

# DSC ANALYSIS OF ORDER–DISORDER TRANSITION IN $Ni_3Al$ BASED ALLOYS FROM Ni-Al-Cr SYSTEM

# ANALIZA DSC PRZEMIAN TYPU PORZĄDEK-NIEPORZĄDEK W STOPACH NA OSNOWIE $Ni_3Al$ Z UKŁADU Ni-Al-Cr

Ni-Al-Cr system is significant for industrial alloys based on intermetallic phase $Ni_3Al$, that crystallizes in crystal lattice $L1_2$. It is indicated as γ′, contrary to disordered phase γ which occurs with addition of chromium. DSC analysis was performed on alloys of chemical composition from Ni75Al25÷Ni75Cr25 range of Ni-rich part of Ni-Al-Cr system. In addition, few measurements were conducted using DTA method. Based on curves registered, it was possible to identify characteristic temperature during heating and cooling of the sample. It corresponds to existence of phase boundary γ′+γ / γ in examined alloys. Results of thermal analysis were compared with results obtained with other method performed by authors which is solution calorimetric method.

*Keywords:* Ni-Al-Cr system, intermetallic phase $Ni_3Al$ , order-disorder, DSC analysis

Układ Ni-Al-Cr jest ważnym układem dla przemysłowych stopów na osnowie fazy międzymetalicznej $Ni_3Al$, która krystalizuje w uporządkowanej sieci $L1_2$. Oznacza się ją jako γ′ w odróżnieniu od fazy nieuporządkowanej γ, która pojawia się wraz z dodatkiem stopowym chromu. Wykonano serię stopów, których skład chemiczny leży na linii Ni75Al25÷Ni75Cr25 w bogatej w nikiel części układu Ni-Al-Cr i poddano je analizie DSC. Dodatkowo wykonano kilka pomiarów metodą DTA. Na podstawie zarejestrowanych krzywych udało się zidentyfikować charakterystyczne temperatury podczas nagrzewania i studzenia próbki. Odpowiadają one miejscom występowania granicy międzyfazowej γ′+γ / γ w stopach. Wyniki analiz termicznych zestawiono z wynikami innej metody zastosowanej przez autorów tj. kalorymetrycznej metody typu rozpuszczania.

## 1. Introduction

Ni-Al-Cr system is crucial for commonly used Ni-based superalloys, which are used in aviation, military or chemical industry [1]. Ni-rich part of this system is also basis for modern used alloys based on intermetallic phase $Ni_3Al$ [2÷4]. It crystallizes in ordered lattice $L1_2$ and is marked as γ′, contrary to disordered phase γ crystallizing in A1 lattice. Disordered phase γ occurs with alloy addition of chromium content (Fig. 1). Cr as an addition improves anticorrosive properties of alloys as well as ductility [5÷6]. 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. 2). High-temperature mechanical characteristics of alloys based on intermetallic phase $Ni_3Al$ are correlated with ordered – disordered phase ratio. Order–disorder (OD) transition which occurs in discussed alloys represents discontinuous type which means that between phase γ′ and γ two-phase area γ′+γ exists (Fig. 2).

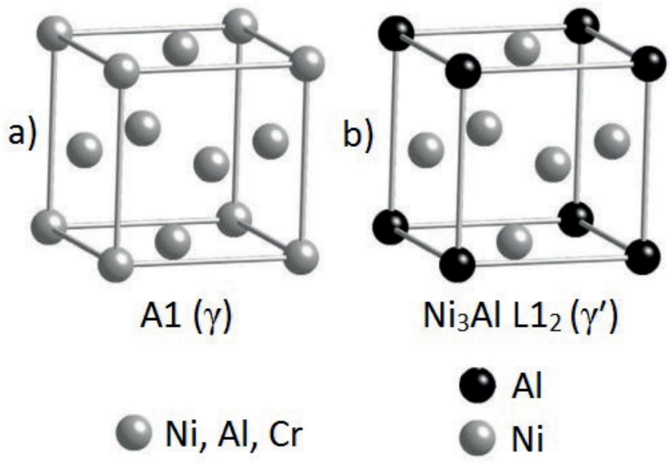


Fig. 1 Elementary cell a) disordered phase γ in Ni-Al-Cr system; b) ordered phase γ′ (intermetallic phase $Ni_3Al$)

* SILESIAN UNIVERSITY OF TECHNOLOGY, FACULTY OF MATERIALS ENGINEERING AND METALLURGY, 8 KRASINSKIEGO STR., 40-019 KATOWICE, POLAND
# Corresponding author: tomasz.maciag@polsl.pl

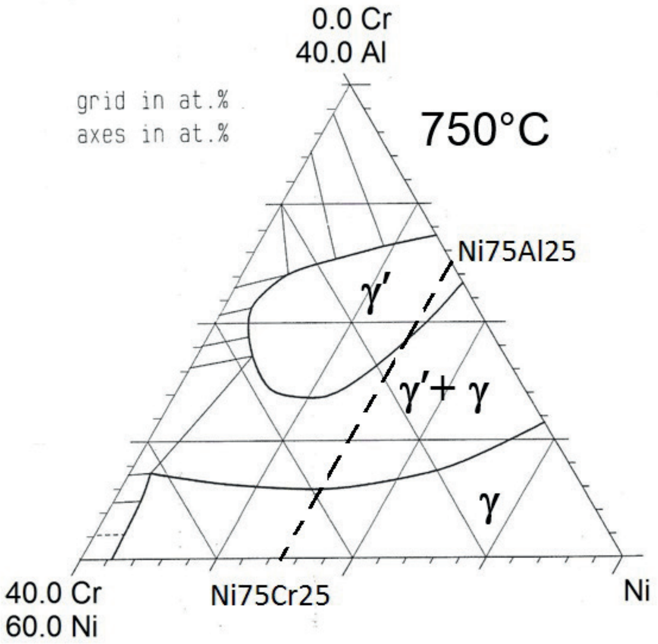


Fig. 2. Isothermal section of Ni-rich part of Ni-Al-Cr system at temperature 750°C proposed by Taylor and Floyd [7]. Broken line shows section with chemical composition representing alloys studied in this work

This work is an attempt of experimental determination of characteristic temperature: starting of disordered γ phase appearance and ending of ordered γ′ phase decomposition in alloys from Ni-rich part of Ni-Al-Cr system. Authors proposed usage of differential scanning calorimetry (DSC) completed with measurements from differential thermal analysis (DTA). It is worth to indicate that using thermal analysis in research of subtle transitions in alloys is often difficult and requires additional confirmation obtained with other testing methods [8÷11]. In this work alloys of chemical composition from section Ni75Al25÷Ni75Cr25 of Ni-Al-Cr system were examined (Fig.2). In the scope are alloys with meaningful industrial applications. This range was already examined by authors with innovative using of solution calorimetry [12]. Results represent valuable experimental data, which is missing in literature. Moreover it can be used for phase boundaries optimization of Ni-rich part of Ni-Al-Cr system, by using computational method e.g. Calphad [13÷14].

## 2. Experimental details

For alloy preparation metals of high purity were used: Al (99,99 %), Ni (99,98 %) and Cr (99,5%). Compounds were melted in vacuum induction furnace VSG-02 (Balzers) in alundum crucible, at temperature 150°C higher than liquidus temperature. Subsequently alloys were casted into ceramic mould. Chemical composition was determined using atomic absorption spectrometry (ASA). Aluminum and chromium were analyzed, assuming that rest of alloys is nickel. Table 1 shows results of chemical compound analysis.

TABLE 1

Chemical composition of examined alloys.

| No. | Constituent content [% at.] | | Alloy |
|---|---|---|---|
| | Cr | Al | |
| 1 | 18,8 | 6,1 | Ni75,1Al6,1Cr18,8 |
| 2 | 17,0 | 8,1 | Ni74,9Al8,1Cr17,0 |
| 3 | 15,3 | 9,7 | Ni75,0Al9,7Cr15,3 |
| 4 | 13,2 | 11,8 | Ni75,0Al11,8Cr13,2 |
| 5 | 10,8 | 14,2 | Ni75,0Al14,2Cr10,8 |
| 6 | 9,1 | 15,9 | Ni75,0Al15,9Cr9,1 |
| 7 | 7,3 | 17,7 | Ni75,0Al17,7Cr7,3 |
| 8 | 5,5 | 19,5 | Ni75,0Al19,5Cr5,5 |

All alloys were submitted to preliminary heat treatment for homogenization. First alloys were placed in ceramic tubes, that were put in quartz capsules in vacuum, next samples were heated at temperature 900°C for 48 hours. Afterwards cooling with furnace was conducted.

Differential calorimeter Setaram MultiHTC S60 was used for DSC analysis. Samples cylinder shaped had diameter of 3mm and 10mm length. They were placed in alundum crucibles, for reference $Al_2O_3$ was used. Measurements were conducted in protective atmosphere of argon. Heating and cooling rate was 5°C/min. Due to maximum range of DSC calorimeter, alloys of numbers 7 and 8 were performed on NETZSCH thermal analyzer STA 449 F3 Jupiter with DTA method. In this case alundum crucibles and protective argon atmosphere were used as well, however, length of sample was decreased to approx. 4 mm, and heating and cooling rate was increased up to 20°C/min.

## 3. Results and discussion

Figures 3÷8 show DSC curves, figure 9÷10 presents DTA curves recorded during heating and cooling of examined alloys. During thermal analysis of alloys in which second order OD (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 [15]. 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 [15÷16].

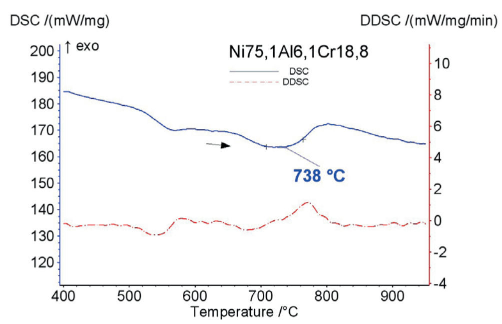


Fig 3. DSC curve registered during heating (5°C/min) of alloy Ni75,1Al6,1Cr18,8

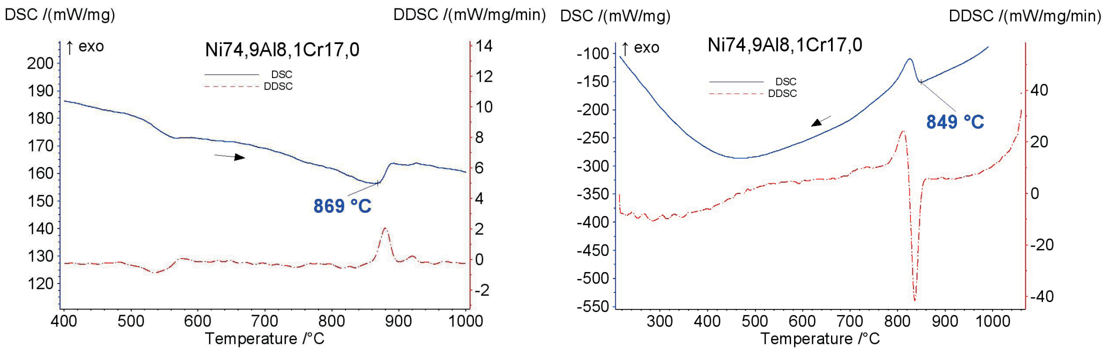


Fig. 4. DSC curves registered during heating and cooling (5°C/min) of alloy Ni74,9Al8,1Cr17,0

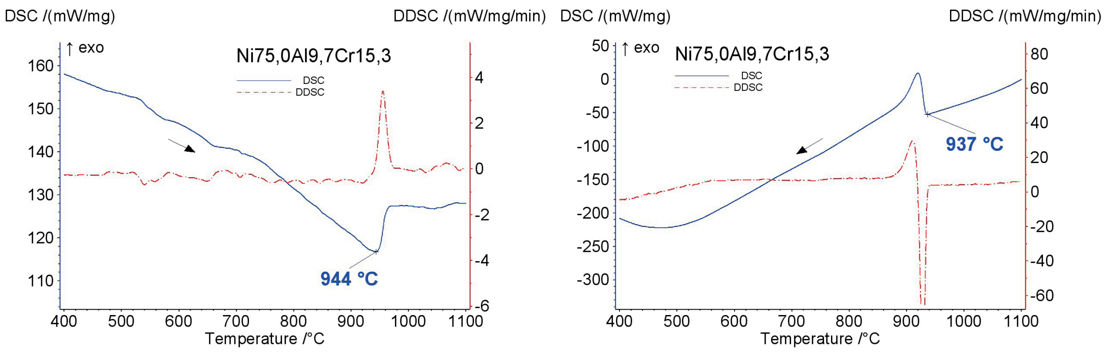


Fig. 5. DSC curves registered during heating and cooling (5°C/min) of alloy Ni75,0Al9,7Cr15,3

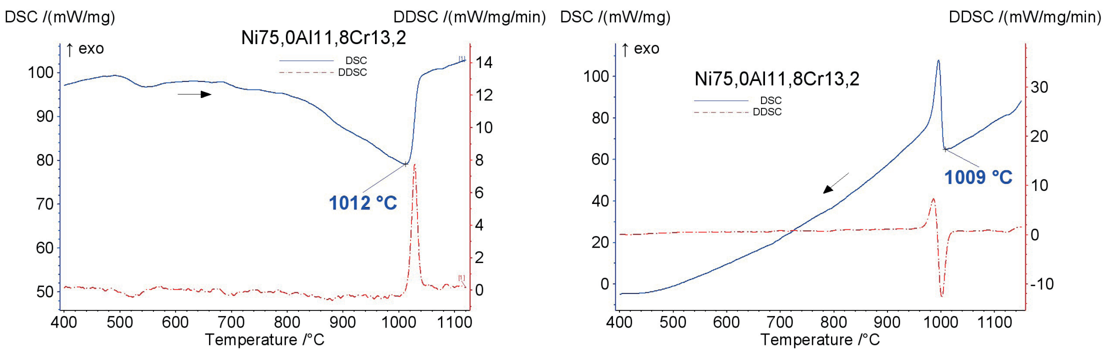


Fig. 6. DSC curves registered during heating and cooling (5°C/min) of alloy Ni75,0Al11,8Cr13,2

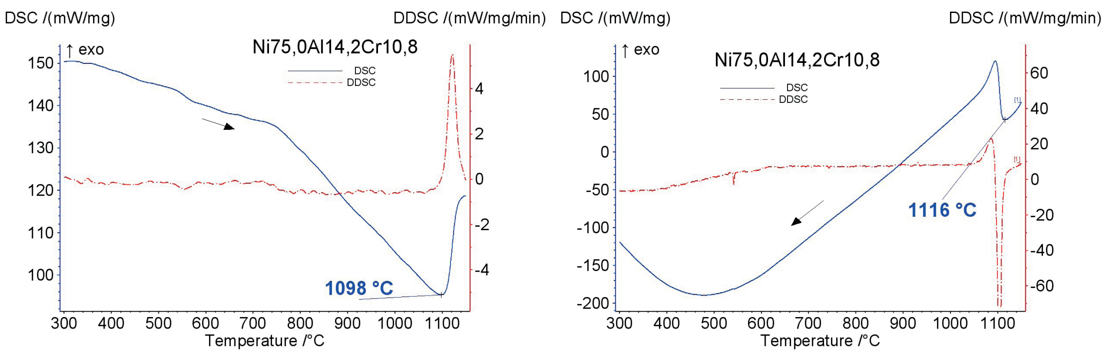


Fig. 7. DSC curves registered during heating and cooling (5°C/min) of alloy Ni75,0Al14,2Cr10,8

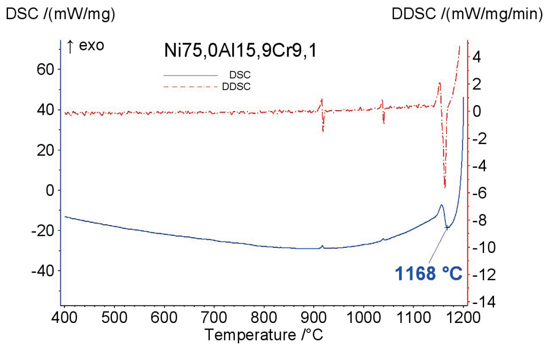


Fig. 8. DSC curve registered during cooling (5°C/min) of alloy Ni75,0Al15,9Cr9,1.

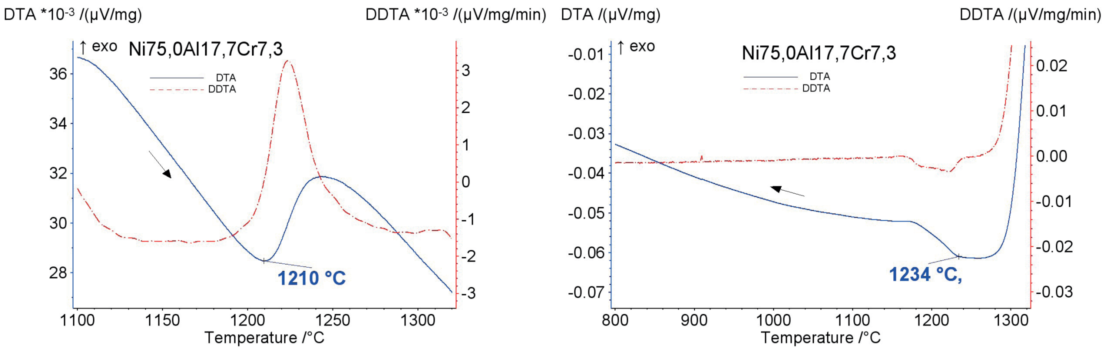


Fig. 9. DTA curves registered during heating and cooling(20°C/min) of alloy Ni75,0Al17,7Cr7,3

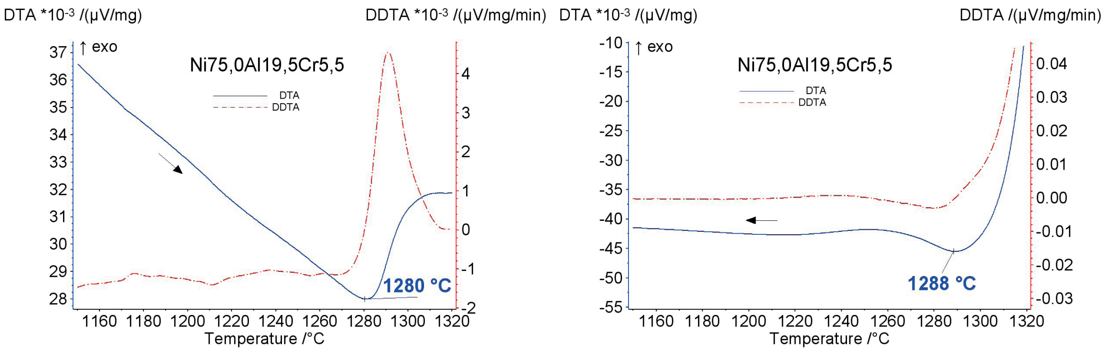


Fig. 10. DTA curves registered during heating and cooling (20°C/min) of alloy Ni75,0Al19,5Cr5,5

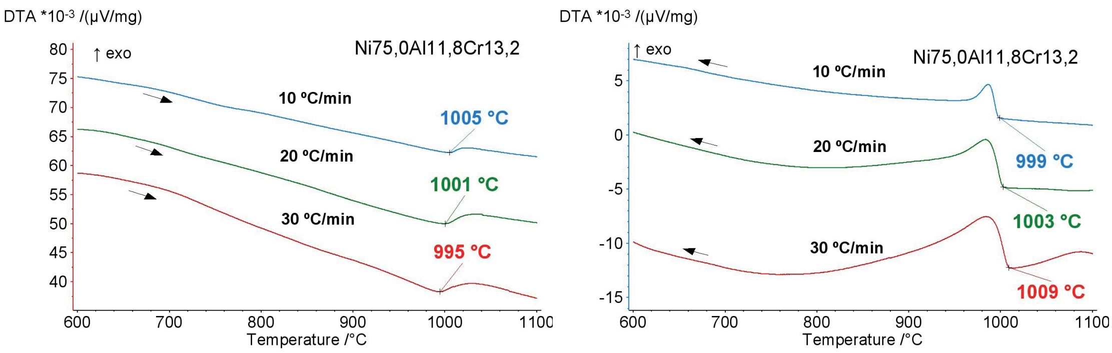


Fig. 11. DTA curves registered during heating and cooling with different rate of alloy Ni75,0Al11,8Cr13,2

Heating curves presented on figures 3÷10, clearly show a minimum of endothermic peak, shaped similar to the one described above. In case of studied alloys, it should be interpreted as an ending of precipitation of disordered phase γ at the expense of exhaustion of ordered phase γ′. Transition temperature determined this way refers to phase boundary γ′+γ / γ. Cooling curves are a confirmation of this reasoning. This curves indicates clear exothermic effect which reflects heat transfer by the sample as a result of gradual precipitation of ordered phase γ′. Temperature of beginning of exothermic effect refers also to phase boundary γ′+γ / γ. In case of Ni75,1Al6,1Cr18,8 (Fig. 3) no exothermic effect during cooling was observed, however for Ni75,0Al15,9Cr9,1 alloy (Fig. 8) no endothermic effect was observed during heating.

Measurements analogical to those presented in this paper were performed by Hong et al. In the experiment alloys from Ni-rich part of Ni-Al-Cr system were examined using DTA method [17÷19]. Authors obtained during heating and cooling curves similar to those presented on Fig 3÷10. Determination of phase boundary γ′+γ / γ was based on averaging characteristic temperature, defined during heating and cooling. Hong et al. stated also lack of influence of heating and cooling rate on average value of temperature in range 0,08÷0,33°C/min, it is also proven in experiment conducted by authors of this paper. Alloy Ni75,0Al11,8Cr13,2 was analyzed with use of DTA method with heating and cooling rate: 10, 20 and 30°C/min (Fig. 11). Average temperature of phase boundary γ′+γ / γ in all cases was 1002°C. Differences in obtained values for the same alloy during DSC analysis (Fig. 6) result from higher sensitivity of measuring device used in this method.

Differences between sensitivity in DSC and DTA measurements are shown specifically at temperature range lower than 700°C. Curves registered during heating using DTA are smooth, meanwhile DSC curves present more varied effects, which existence can be confirmed based on course of the first derivative. It does not occur however during cooling of samples. Taking into consideration difficulties related with delays in heat transfer resulting from design of measurement system also shape of used samples and problems with obtaining single-phase structure of samples in room temperature, an attempt to interpretation of those effects is much more complex and difficult. Hence, based on DSC and DTA curves it is not possible to determine clearly phase boundary γ′ / γ′+γ in Ni-Al-Cr system.

Temperatures referring to phase boundary γ′+γ / γ obtained in this paper using thermal analysis are presented on Fig. 12, together with results obtained also by authors using solution calorimetric method. In this method, huge differences in binding energy between ordered and disordered phase were used. Phase boundaries γ′ / γ′+γ and γ′+γ / γ at temperature 600°C, 723°C and 877°C were determined based on enthalpy of formation of alloys from the range Ni75Al25÷Ni75Cr25 as a function of chromium concentration [12].

It is visible that results obtained from two different methods are complementary and remain in good compatibility. Calorimetric measurement solution method presents more reliable data at lower temperature range (below 1000°C), during which long-lasting heating is used for reaching thermodynamic equilibrium. It also allows for determination of phase boundary γ′ / γ′+γ whereas thermal analysis DSC/DTA are relevant for investigation of OD transition occurring at temperatures beyond calorimetric solution method scale.

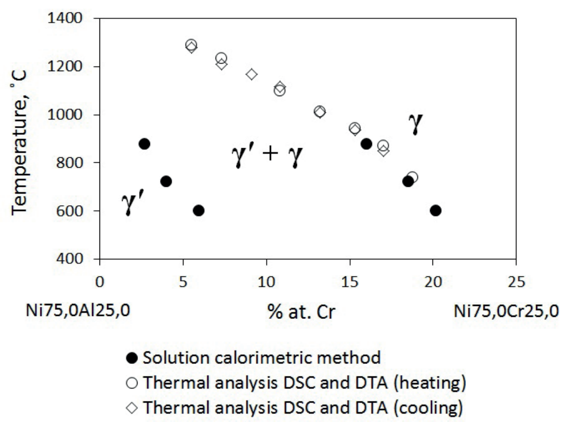


Fig. 12 Compilation of phase boundaries γ′ / γ′+γ and γ′+γ / γ obtained in this paper and with use of solution calorimetric method [12].

## 4. Conclusions

Thermal analysis DSC and DTA was used in order to determine temperature of OD transition occurring in alloys based on intermetallic phase $Ni_3Al$. 2O-OD transition takes place, in which, with the increase of temperature, gradual precipitation of disordered phase γ at the expense of disordered phase γ′. Temperature of beginning and ending of OD transition corresponds to phase boundaries γ′ / γ′+γ and γ′+γ / γ in Ni-Al-Cr system.

1. Based on DSC and DTA measurements, characteristic shape of curves registered during heating and cooling of alloys was determined, it refers to order-disorder transition. Minimum of endothermic peak during heating and onset temperature of exothermic effect during cooling was determined. Similar values were obtained, which refer to temperature of existence of phase boundary γ′+γ / γ.
2. Based on DTA experiment (10, 20 and 30°C/min), lack of influence of heating and cooling rate on average temperature of phase boundary γ′+γ / γ was confirmed, which was determined based on characteristic temperature defined during heating and temperature defined during cooling of alloy.
3. Temperatures corresponds to phase boundary γ′+γ / γ obtained in this paper with thermal analysis method were complied with results from solution calorimetry, showing good compatibility.

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