CALORIMETRIC MEASUREMENTS OF FORMATION ENTHALPY OF ALLOYS FROM Ni-Al-Cr SYSTEM

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Abstract

Nickel-rich part of ternary system Ni-Al-Cr is crucial for currently used nickel superalloys and alloys based on intermetallic phase Ni_3Al. Those materials are dedicated to work at elevated temperature and consist, among others, of ordered phase γ′ and disordered phase γ in different proportions. Therefore, it is essential to learn high temperature course of phase boundaries γ′/γ′+γ and γ′+γ/γ in Ni-Al-Cr system. Series of alloys, which chemical composition from the Ni75Al25 ÷ Ni65Cr35 section of discussed system, were prepared and were tested using high-temperature solution calorimeter. The device allows for determination of formation enthalpy of alloys at temperatures up to 1273 K. Formation enthalpy of alloys from Ni75Al25 ÷ Ni65Cr35 section was determined for three temperatures: 873 K, 996 K and 1150 K. On the basis of changes in the enthalpy of formation value with increase of chromium content in alloys, presence of characteristic points was found. It was assigned to phase boundaries γ′/γ′+γ and γ′+γ/γ. Likewise, it was similar to previous ranges tested by author which are: Ni75Al25 ÷ Ni75Cr25 and Ni75Al25 ÷ Ni87Cr13.

Keywords: Solution calorimetry, enthalpy of formation, Ni-Al-Cr system, phase boundary

1. INTRODUCTION

Industrial alloys based on intermetallic phase Ni_3Al with chromium content are two-phase alloys and consist of predominant ordered phase γ' and disordered phase γ [1]. However, nickel superalloys have predominant disordered phase γ over ordered phase γ' [2]. Due to that, it is vital to precisely determine phase boundaries γ'/γ'+γ/γ in the Ni-Al-Cr system.

In the case of phase boundaries γ'/γ'+γ/γ from Ni-Al-Cr system, literature data base mainly on microscopic studies and phase analysis of samples submitted to rapid cooling [3]. It is connected with difficulties of the research of the changes occurring at elevated temperatures. Up-to-date shape of Ni-Al-Cr phase diagram was elaborated using CALPHAD method [4, 5]. Key matter in case of this method is providing reliable experimental data which is used in optimization models. One of the most important data is formation enthalpy of alloys.

Author of this paper took into account difficulties related to preserving proper structure during rapid cooling of alloys from Ni-rich part of Ni-Al-Cr system [6] and used "in situ" method for direct determination of phase boundaries γ'/γ'+γ/γ at elevated temperatures. Specially designed high-temperature solution calorimeter was used [7, 8]. The device allows for direct determination of enthalpy of formation of alloys at temperatures up to 1273 K, which is possible due to application of intermediate container allowing for heating of samples.

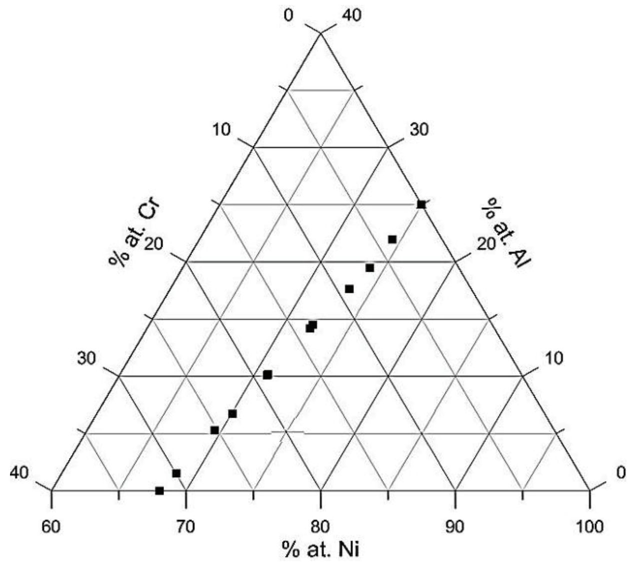
Alloys from Ni75Al25 ÷ Ni65Cr35 section of Ni-Al-Cr system were examined. Calorimetric measurements were conducted at three temperatures: 873 K, 996 K and 1150 K. Likewise in case of previously analyzed by author alloys from sections Ni75Al25 ÷ Ni75Cr25 and Ni75Al25 ÷ Ni87Cr13 [8, 9], areas of phase boundaries occurrence were determined based on characteristic points of break in course of formation enthalpy with increase of chromium content. In order to divide analyzed courses into sections referring to ranges of occurrence of corresponding phases and for precise determination of points referring to places of occurrence of phase boundaries γ'/γ'+γ and γ'+γ/γ, statistical model described in one of author's paper was used [9].

2. SAMPLES PREPARATION AND EXPERIMENT

Alloys with chemical composition from Ni75Al25 ÷ Ni65Cr35 section of ternary system Ni-Al-Cr were selected for study (**Table 1**). Samples were prepared from metals of purity: Al (99.99 %), Ni (99.95 %) and Cr (99.5 %) using casting method. Casting was performed in induction vacuum furnace VSG-02 Balzers, in alundum crucible in vacuum of order 1.3 Pa. Alloys were casted into bentonite form, rods of 3 mm diameter were obtained. Chemical composition of the samples was analyzed. Aluminum and chromium were analyzed with atomic absorption spectroscopy, rest of alloy was nickel. **Table 1** presents results of chemical compound analysis of tested samples. Subsequently alloys were subjected to heat treatment: alloys were placed in ceramic tubes that were put in quartz capsules in vacuum. Samples were kept at temperature 1173Kfor 72 h in order to homogenize. Afterwards rapid cooling was conducted in water with ice.

Table 1 Chemical composition of samples from the Ni75Al25 ÷ Ni65Cr35 section of Ni-Al-Cr system. Component content is given in atomic %

No.	Component content (at. %)		Alloy composition
	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	13.3	15.5	Ni71.2Al15.5Cr13.3
6	13.7	15.1	Ni71.2Al15.1Cr13.7
7	18.8	11.4	Ni69.8Al11.4Cr18.8
8	18.9	11.3	Ni69.8Al11.3Cr18.9
9	23.2	8.6	Ni68.2Al8.6Cr23.2
10	25.1	7.1	Ni67.8Al7.1Cr25.1
11	30.0	4.0	Ni66.0Al4.0Cr30.0
12	32.1	2.0	Ni65.9Al2.0Cr32.1



Research were conducted in high-temperature solution calorimeter, which detailed construction and operating principle were described in previous papers of author [7, 8]. Samples after reaching intermediate container in calorimeter were heated at temperature of the experiment for time between 24 up to 72 hours. Afterwards, it was dropped directly into metallic bath (as a material of the bath, aluminum was used) where it was dissolved with accompanying thermal effect registered by computer. Formation enthalpy was determined based on dependence:

$$\Delta_f H = x_A \Delta H_A^{ef.} + x_B \Delta H_B^{ef.} + x_C \Delta H_C^{ef.} - \Delta H^{ef.}_{A_{x_A} B_{x_B} C_{x_C}} \quad (1)$$

where:

$\Delta_f H$ - formation enthalpy of the alloy;

X_A, X_B, X_C - concentrations (mole fractions) of the alloy components,

$\Delta H_{A}^{ef.}, \Delta H_{B}^{ef.}, \Delta H_{C}^{ef.}, \Delta H_{A_{x_A}B_{x_B}C_{x_C}}^{ef.}$ - heat effects accompanying the dissolution of the components and the alloy in the bath. It is worth mentioning, that thermal effect consists of: heating, melting and solving of the sample in the bath.

3. RESULTS

Calorimetric experiments were conducted for three temperatures: 873 K, 996 K and 1150 K. **Tables 2** and **3** present obtained results of formation enthalpy of tested alloys in above temperatures. Results for alloy Ni75Al25 referring to stoichiometric phase Ni_3Al in case of temperature 873 K and 1150 K were taken from paper [10]. **Figure 1** presents absolute value of obtained formation enthalpy as a function of chromium concentration of analyzed alloys with indicated phase boundaries γ'/γ'+γ/γ using statistical elaboration proposed by author.

At all analyzed temperatures presented on **Figure 1** one can notice decrease of absolute value of formation enthalpy with increase of chromium concentration. It is related to increasing fraction of disordered phase γ, which occurs with alloy addition of chromium. It is important to mention that disordered phase γ is of higher energy than ordered phase γ'. Nature of changes of the formation enthalpy allows for division of tested area into sections referring to ranges of occurrence of phases which enables to directly determine phase boundaries γ'/γ'+γ/γ.

Table 4 presents results of statistical elaboration of points corresponding to places of occurrence of phase boundaries for alloys from Ni75Al25 ÷ Ni65Cr35 section of Ni-Al-Cr system.

The same statistical analysis was conducted for alloys from pseudo-binary section Ni75Al25 ÷ Ni75Cr25 and section Ni75Al25 ÷ Ni87Cr13, which solution calorimetric measurements are presented in papers [8, 9]. Contrary to mentioned above sections, in results presented in this paper, for temperature 873 K and 996 K, there is no distinct break point, proving presence of phase boundary γ'+γ/γ. Reason for this can be too low amount of samples with chemical composition from Ni75Al25 ÷ Ni65Cr35 section. It is possible however, that at temperatures 873 K and 996 K, analyzed range is two-phase or even three-phase. Appearance at temperature of 1150 K of distinct break point and decrease in the rate of change of formation enthalpy value indicates single phase disordered area of γ phase. It is consistent with tendency of increasing the range of existence of this phase in Ni-Al-Cr system together with temperature increase.

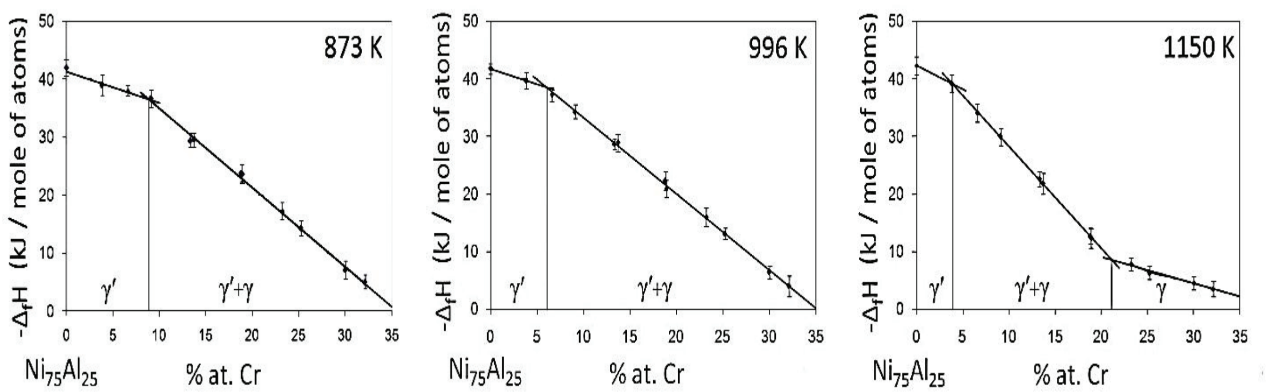


Figure 1 Course of formation enthalpy of alloys from section Ni75Al25÷Ni65Cr35 with indicated γ'/γ'+γ/γ phase boundaries at three temperatures

Table 2 Formation enthalpy at temperature 873 K, 996 K and 1150 K of alloys from Ni75Al25 ÷ Ni65Cr35 section of Ni-Al-Cr system obtained by calorimetric solution method

Temperature	**873 K**		**996 K**		**1150 K**	
Alloy	**Test no.**	**Formation enthalpy $\Delta_f H$, (kJ/mole) of atoms**	**Test no.**	**Formation enthalpy $\Delta_f H$, (kJ/mole) of atoms**	**Test no.**	**Formation enthalpy $\Delta_f H$, (kJ/mole) of atoms**
Ni75.0Al25.0			1	-41.5		
			2	-39.8		
			3	-41.0		
			4	-42.7		
	Average	-42.0 ± 1.4[1)]	Average	-41.8 ± 0.9	Average	-42.3 ± 1.6[1)]
Ni74.1Al22.1Cr3.8	1	-37.7	1	-38.4		
	2	-38.4	2	-40.8	1	-40.9
	3	-38.3	3	-38.3	2	-38.9
	4	-41.5	4	-41.1	3	-37.9
	Average	-39.0 ± 1.7	Average	-39.7 ± 1.5	Average	-39.2 ± 1.5
Ni73.1Al20.3Cr6.6	1	-38.1	1	-36.5	1	-34.8
	2	-38.9	2	-36.8	2	-32.3
	3	-37.1	3	-38.8	3	-35.2
	Average	-38.0 ± 0.9	Average	-37.3 ± 1.3	Average	-34.1 ± 1.6
Ni72.1Al18.8Cr9.1	1	-36.3	1	-34.8	1	-31.4
	2	-38.4	2	-32.9	2	-30.1
	3	-35.5	3	-35.2	3	-28.5
	Average	-36.7 ± 1.5	Average	-34.3 ± 1.2	Average	-30.0 ± 1.5
Ni71.2Al15.5Cr13.3	1	-27.6				
	2	-30.0	1	-29.4	1	-23.7
	3	-29.8	2	-27.6	2	-23.0
	4	-30.2	3	-29.3	3	-21.2
	Average	-29.4 ± 1.2	Average	-28.7 ± 1.0	Average	-22.6 ± 1.3
Ni71.2Al15.1Cr13.7	1	-31.0				
	2	-29.0	1	-27.3	1	-22.9
	3	-28.3	2	-30.1	2	-22.8
	4	-30.2	3	-29.3	3	-19.8
	Average	-29.6 ± 1.2	Average	-28.9 ± 1.5	Average	-21.8 ± 1.8
Ni69.8Al11.4Cr18.8	1	-23.1	1	-20.5	1	-11.2
	2	-25.5	2	-23.4	2	-13.9
	3	-22.9	3	-23.0	3	-12.9
	Average	-23.8 ± 1.5	Average	-22.3 ± 1.6	Average	-12.7 ± 1.4

[1)]Data from work [10]

Table 3 Formation enthalpy at temperature 873 K, 996 K and 1150 K of alloys from Ni75Al25 ÷ Ni65Cr35 section of Ni-Al-Cr system obtained by calorimetric solution method

Temperature	873 K		996 K		1150 K	
Alloy	Test no.	Formation enthalpy $\Delta_f H$, (kJ/mole) of atoms	Test no.	Formation enthalpy $\Delta_f H$, (kJ/mole) of atoms	Test no.	Formation enthalpy $\Delta_f H$, (kJ/mole) of atoms
Ni69.8Al11.3Cr18.9	1	-25.6	1	-19.3	1	-13.9
	2	-22.3	2	-22.3	2	-10.6
	3	-23.2	3	-21.0	3	-12.5
	Average	-23.7 ± 1.7	Average	-20.9 ± 1.5	Average	-12.3 ± 1.7
Ni68.2Al8.6Cr23.2	1	-15.7	1	-17.5	1	-8.1
	2	-13.1	2	-16.1	2	-8.7
	3	-14.2	3	-14.3	3	-6.6
	Average	-14.3 ± 1.3	Average	-16.0 ± 1.6	Average	-7.8 ± 1.1
Ni67.8Al7.1Cr25.1	1	-15.7	1	-13.7	1	-6.6
	2	-13.1	2	-13.8	2	-7.3
	3	-14.2	3	-11.9	3	-4.9
	Average	-14.3 ± 1.3	Average	-13.1 ± 1.0	Average	-6.3 ± 1.2
Ni66.0Al4.0Cr30.0	1	-5.8	1	-7.6	1	-4.8
	2	-6.7	2	-5.4	2	-3.3
	3	-8.9	3	-6.0	3	-5.4
	Average	-7.1 ± 1.6	Average	-6.4 ± 1.1	Average	-4.5 ± 1.1
Ni65.9Al2.0Cr32.1	1	-5.9	1	-5.4	1	-2.1
	2	-3.6	2	-4.6	2	-3.6
	3	-5.4	3	-2.0	3	-4.7
	Average	-5.0 ± 1.2	Average	-4.0 ± 1.8	Average	-3.5 ± 1.3

Table 4 Results of statistical analysis showing places of γ′/γ′+γ and γ′+γ/γ phase boundaries in alloys from Ni75Al25 ÷ Ni65Cr35 section of Ni-Al-Cr system - calorimetric solution method

Ni75Al25÷Ni65Cr35	873 K		996 K		1150 K	
	γ′/γ′+γ	γ′+γ/γ	γ′/γ′+γ	γ′+γ/γ	γ′/γ′+γ	γ′+γ/γ
Cr (at.%)	8.91	-	6.11	-	4.10	21.13
Standard error	0.59	-	0.95	-	1.04	0.82
-95% confidence level	7.70	-	4.32	-	2.12	19.93
+95% confidence level	10.12	-	8.02	-	5.91	23.86

4. CONCLUSION

1) Formation enthalpy was determined for alloys with chemical composition from Ni75Al25 ÷ Ni65Cr35 section of Ni-Al-Cr system. Measurements were conducted on particularly designed high-temperature solution calorimeter for temperatures: 873 K, 996 K and 1150 K.

2) Formation enthalpy values determined with calorimetrical measurements are vital thermodynamic data, which can be used for optimizing of Ni-Al-Cr phase diagram.

3) Decrease of absolute value of formation enthalpy for tested alloys together with increase of chromium content is visible. Moreover, characteristic break points in course of changes of formation enthalpy values in tested temperatures are present. On the basis of analogical research conducted on alloys with chemical composition from Ni75Al25 ÷ Ni75Cr25 and Ni75Al25 ÷ Ni87Cr13 sections from Ni-Al-Cr system, phase boundaries γ'/γ'+γandγ'+γ/γ were assigned.

4) In case of temperatures 873 K and 996 K, break point which could be assigned to phase boundary γ'+γ/γ was not stated. That can indicate presence of two- or more phased range.

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