

Calorimetric studies of the enthalpies of formation of alloys from $\text{Ni}_{75}\text{Al}_{25}$ - $\text{Ni}_{75}\text{Cr}_{25}$ and $\text{Ni}_{75}\text{Al}_{25}$ - $\text{Ni}_{85}\text{Cr}_{15}$ sections at 873 K

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Materials

ABSTRACT

Purpose: The main purpose of the study was to determine value of formation enthalpy ΔH of Ni₃Al-based alloys with chromium additions at temperature 873 K. Experiment was carried in order to determine the course of phase boundaries $\gamma' / \gamma' + \gamma / \gamma$ for Ni-Al-Cr system.

Design/methodology/approach: Experiment was performed with use of high temperature solution calorimeter. This “in situ” method allows to determine formation enthalpy in a wide range of temperature thanks to intermediate multi socket container which was applied in the device. It is fundamental because keeping the structure of examined alloys during quenching is extremely difficult, often impossible in this type of alloys.

Findings: Distinct breaks in the course of enthalpy of formation ΔH as a function of chromium concentration were discovered, that are assigned to courses of $\gamma' / \gamma' + \gamma / \gamma$ phase boundaries.

Research limitations/implications: Experiment will be proceeded at higher temperatures and completed with resistometric measurements. All results will be used in CAPLHAD procedure in order to optimize course of phase boundaries.

Originality/value: The results are valuable thermodynamic data and method proposed can become a new way of direct determination of phase boundaries in metallic systems.

Keywords: Metallic alloys; Intermetallic phases; Solution calorimetry; Formation enthalpy

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1. Introduction

Ni₃Al-based alloys are object of interest as construction materials designed for work at high temperature. Macroaddition used most often in industrial alloys based on Ni₃Al is chromium [1,2,3]. Alloys which are the object of interest of industry consist of two phases: ordered phase γ' and disordered phase γ . That is

why it is crucial to know precise course of phase boundaries of alloys based on Ni₃Al from Ni-Al-Cr system. Literature data raise concerns because samples rapidly cooled were used for studies [4,5], while, as mentioned in [6,7], freezing of structure of these alloys by quenching is very difficult, often impossible. Calorimetric “in situ” solution method allows to determine enthalpy of formation of alloys also in elevated temperatures [8]. Alloys based on Ni₃Al with chromium addition from two ranges

were examined: $\text{Ni}_{75}\text{Al}_{25}$ - $\text{Ni}_{75}\text{Cr}_{25}$ and $\text{Ni}_{75}\text{Al}_{25}$ - $\text{Ni}_{85}\text{Cr}_{15}$. Obtained results of $\Delta_f H$ are valuable data that allow to determine phase boundaries $\gamma' / \gamma^{*} + \gamma / \gamma$ twofold: directly and i.a. using CALPHAD procedure [9,10,11].

2. Measurement method

Experiment was carried with use of high temperature solution calorimeter [12,13].

2.1. Alloys preparation

Alloys were prepared using casting method. Casting was performed in induction vacuum furnace VSG-02 Balzers, in alundum crucible in vacuum of order 10^{-2} torr. Alloys were casted into graphite form, rods of 3 mm diameter were obtained. The shape of samples is adequate to sample injection system in calorimeter. 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 1173 K for 24 h in order to homogenize. Afterwards rapid cooling was conducted in water with ice. Chemical composition of the samples was analyzed. Dominant element in alloys, that is nickel was analyzed using gravimetric method, aluminum and chromium were analyzed with atomic absorption spectroscopy.

2.2. The measurement principle and experimental procedure

Determination of formation enthalpy with use of high temperature solution calorimeter relies on comparison of heat effects accompanying dissolving of alloys and its components in metallic bath [4]. For ternary alloys it can be presented as:

$$\Delta_f H = x_A \Delta_f H_A^{ef} + x_B \Delta_f H_B^{ef} + x_C \Delta_f H_C^{ef} - \Delta_f H_{A_x B_y C_z}^{ef} \quad (1)$$

where: $\Delta_f H$ - formation enthalpy of the alloy; x_A , x_B , x_C - concentrations (mole fractions) of the alloy components, $\Delta_f H_A^{ef}$, $\Delta_f H_B^{ef}$, $\Delta_f H_C^{ef}$, $\Delta_f H_{A_x B_y C_z}^{ef}$ - heat effects accompanying the dissolution of the components and the alloy in the bath.

Enthalpy of formation is determined for temperature, from which sample is dropped into the bath. Therefore intermediate multi socket container where samples were placed, was introduced into calorimeter. This allows a long term heating of samples and determining of enthalpy of formation $\Delta_f H$ in a wide range of temperature. In the research aluminum bath was used.

Preparation of the experiment began with triple gas pumping out from the interior of calorimeter with use of turbomolecular pump, alternately argon of high purity (99.9999%) was introduced. Finally experiments were conducted in argon atmosphere. Samples were placed in intermediate container and heated at temperature 873 K. After heating bath up to 1123 K,

device was left for 24 hours in order to stabilize base line and to achieve the equilibrium state of samples. Next, stirrer was installed, and device was ready for experiment. During first measurements, the device was calibrated by dissolving of aluminum samples; in this manner, amount of energy per conventional unit was determined [12]. After calibration, experimental samples were dropped into aluminum bath from intermediate container. Heat effect was registered by computer, a special software allowed to determine value of enthalpy accompanying dissolving samples in bath as well as enthalpy of formation of alloys.

3. Results

During experiment several series of measurements were conducted including two series that were performed to determine the heat of solution of Ni and Cr in aluminum. These lately mentioned data, necessary in computing of formation enthalpy (Eq.1) are presented in Table 1.

Table 1. Enthalpy of solution of nickel ΔH_{Ni}^0 and chromium ΔH_{Cr}^0 in liquid aluminum at 1123 K

Element	Measurement No.	ΔH_i^0 [kJ/g×atoms]
Ni	1	-149.8
	2	-150.4
	3	-149.9
	Average	-150.0
	Standard Dev.	0.3
Cr	1	-71.8
	2	-71.5
	3	-69.3
	Average	-70.8
	Standard Dev.	1.4

Very similar results at the same temperature were obtained by one of the authors (K.R.) with use of previously constructed calorimeter ($\Delta H_{\text{Ni}}^0 = -149.2 \pm 0.6$ [kJ/g×atoms] and $\Delta H_{\text{Cr}}^0 = -71.5 \pm 1.0$ [kJ/g×atoms] respectively) [13].

Formation enthalpy values of alloys from section $\text{Ni}_{75}\text{Al}_{25}$ - $\text{Ni}_{75}\text{Cr}_{25}$ obtained at 873 K with use of solution calorimeter are presented in Table 2.

Part of presented results, referring to $\text{Ni}_{75}\text{Al}_{25}$ - $\text{Ni}_{75}\text{Cr}_{25}$ pseudo-binary was examined at 873 K by one of the authors (K.R.) on previously designed calorimeter [4]. In studies mentioned above chromium concentration varied from 0 to 14 at.%. Fig 1 presents course of formation enthalpy of alloys from $\text{Ni}_{75}\text{Al}_{25}$ - $\text{Ni}_{75}\text{Cr}_{25}$ section as a function of chromium concentration. It is worth mentioning, that obtained results from [4] and from this work are very consistent.

Table 3 presents values of enthalpy of formation of alloys from $\text{Ni}_{75}\text{Al}_{25}$ - $\text{Ni}_{85}\text{Cr}_{15}$ section, and Fig. 2 shows enthalpy values as a function of Cr concentration for alloys from this range.

Table 2.
Enthalpy of formation for alloys from Ni₇₅Al₂₅ - Ni₇₅Cr₂₅ section at 873 K

Alloy	Temperature [K]	Measurement No.	Enthalpy of formation $\Delta_f H$ [kJ/mole of atoms]
Ni _{75.0} Al _{25.0} ¹⁾	873	Average	-42.0
		Standard Dev.	1.4
Ni _{75.0} Al _{23.0} Cr _{2.0} ¹⁾	873	Average	-39.0
		Standard Dev.	1.6
Ni _{75.0} Al _{21.0} Cr _{4.0} ¹⁾	873	Average	-39.8
		Standard Dev.	1.7
Ni _{75.0} Al _{18.5} Cr _{6.5} ¹⁾	873	Average	-37.3
		Standard Dev.	2.4
Ni _{75.0} Al _{16.0} Cr _{9.0} ¹⁾	873	Average	-32.0
		Standard Dev.	2.4
Ni _{75.0} Al _{13.5} Cr _{11.5} ¹⁾	873	Average	-24.2
		Standard Dev.	2.5
Ni _{75.0} Al _{11.0} Cr _{14.0} ¹⁾	873	Average	-20.1
		Standard Dev.	2.3
Ni _{74.0} Al _{9.0} Cr _{17.0}	873	1	-17.7
		2	-13.8
		3	-14.6
		Average	-15.4
		Standard Dev.	2.1
Ni _{75.1} Al _{6.1} Cr _{18.8}	873	1	-13.3
		2	-10.5
		3	-11.9
		Average	-11.9
		Standard Dev.	1.4
Ni _{75.0} Al _{5.1} Cr _{19.9}	873	1	-6.7
		2	-8.2
		3	-7.4
		Average	-7.4
		Standard Dev.	0.8
Ni _{75.0} Al _{3.7} Cr _{21.3}	873	1	-8.9
		2	-9.8
		3	-5.8
		Average	-8.2
		Standard Dev.	2.1
Ni _{75.1} Al _{1.6} Cr _{23.3}	873	1	-7.1
		2	-7.4
		3	-6.9
		Average	-7.1
		Standard Dev.	0.6

¹⁾ Data from [13]

Table 3.
Enthalpy of formation of alloys from Ni₇₅Al₂₅ - Ni₈₅Cr₁₅ section at 873 K

Alloy	Temperature [K]	Measurement No.	Enthalpy of formation $\Delta_f H$ [kJ/mole of atoms]
Ni _{75.0} Al _{25.0} ¹⁾	873	Average	-42.0
		Standard Dev.	1.4
Ni _{75.6} Al _{23.0} Cr _{1.4}	873	1	-39.9
		2	-40.8
		3	-37.9
		Average	-39.5
		Standard Dev.	1.5
Ni _{76.9} Al _{20.5} Cr _{2.6}	873	1	-35.9
		2	-37.5
		3	-33.9
		Average	-35.8
		Standard Dev.	1.8
Ni _{77.0} Al _{19.3} Cr _{3.7}	873	1	-31.7
		2	-28.8
		3	-31.2
		Average	-30.6
		Standard Dev.	1.5
Ni _{78.8} Al _{16.1} Cr _{5.1}	873	1	-28.0
		2	-25.5
		3	-24.5
		Average	-26.0
		Standard Dev.	1.8
Ni _{79.7} Al _{14.1} Cr _{6.2}	873	1	-21.4
		2	-22.8
		3	-18.9
		Average	-21.0
		Standard Dev.	2.0
Ni _{79.8} Al _{13.0} Cr _{7.2}	873	1	-16.5
		2	-16.8
		3	-19.4
		Average	-17.6
		Standard Dev.	1.6
Ni _{80.6} Al _{11.4} Cr _{8.0}	873	1	-12.1
		2	-14.5
		3	-14.4
		Average	-13.7
		Standard Dev.	1.4
Ni _{81.3} Al _{9.3} Cr _{9.4}	873	1	-10.6
		2	-7.3
		3	-9.4
		Average	-9.1
		Standard Dev.	1.7
Ni _{82.4} Al _{7.2} Cr _{10.4}	873	1	-6.3
		2	-5.6
		3	-4.0
		Average	-5.3
		Standard Dev.	1.2

Continuation of Table 3			
Ni _{82.5} Al _{6.0} Cr _{11.5}	873	1	-5.8
		2	-4.6
		3	-4.1
		Average	-4.8
		Standard Dev.	0.9
Ni _{83.6} Al _{4.0} Cr _{12.4}	873	1	-3.8
		2	-3.9
		3	-5.9
		Average	-4.5
		Standard Dev.	1.2

¹⁾ Data from [13]

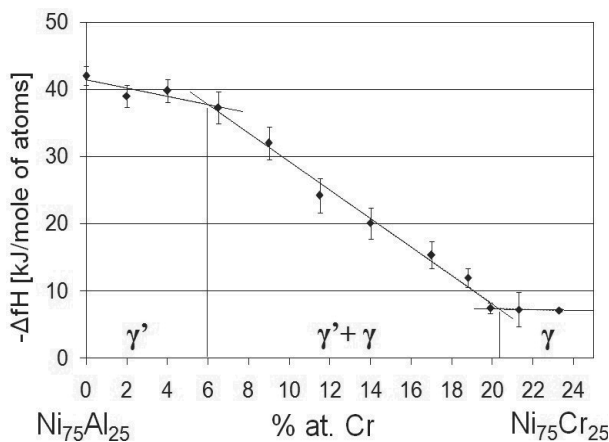


Fig. 1. Course of formation enthalpy of alloys from Ni₇₅Al₂₅ - Ni₇₅Cr₂₅ section as a function of chromium concentration at 873 K

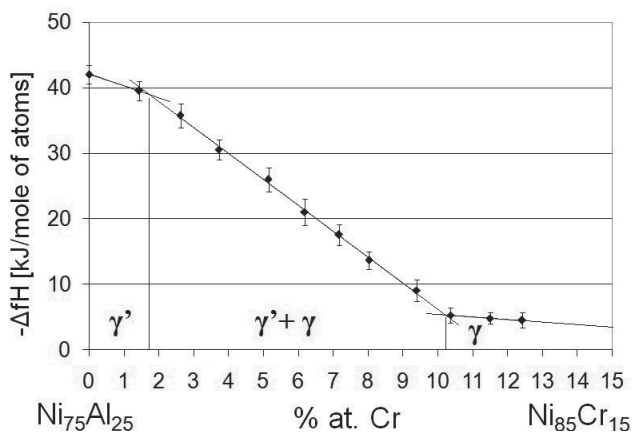


Fig. 2. Course of formation enthalpy of alloys from Ni₇₅Al₂₅ - Ni₈₅Cr₁₅ section as a function of chromium concentration at 873 K

4. Discussion

In every range examined: Ni₇₅Al₂₅ - Ni₇₅Cr₂₅ and Ni₇₅Al₂₅ - Ni₈₅Cr₁₅, decrease of absolute values of enthalpy of formation

$\Delta_f H$ is substantial with increase of chromium content in alloy. All figures show characteristic points of break of $\Delta_f H$ course. They are attributed to location of phase boundaries $\gamma' / \gamma' + \gamma$ and $\gamma' + \gamma / \gamma$. Above conclusion is due to the fact that ordered γ' phase is a phase of higher enthalpy than disordered γ phase. The highest negative value of formation enthalpy was noted for Ni₃Al – it equals $-42,0 \pm 1,4$ [kJ/mole of atoms]. This is because the intermetallic compound Ni₃Al crystallizes in high-ordered structure L1₂ with high density packing of atoms which is accompanied by a strong bonding between them [14]. Ellner [15] noted 8% reduction of aluminum atom radius in Ni₃Al as compared with atom radius in pure metal which also proves the tightly spacing of atoms in Ni₃Al. The appearance of disordered γ phase with increase of chromium concentration causes more rapid decrease of absolute values of formation enthalpy. In the case of calorimetric solution method it is connected with lower energy input necessary for bond breaking in dissolution process in the case of γ than γ' phase and is reflected by lower absolute values of formation enthalpy. Completion of the appearance of disordered phase γ accompanied stabilize formation enthalpy values which can be clearly seen in the all three figures.

Compositions of phase boundaries found in this work corresponds to the lower chromium concentrations than these from literature data [4]. This divergence is due to the fact that literature data are based on experimental studies where quenched samples were applied while results obtained in this work are based on *in situ* calorimetric method. As it was mentioned in [5,7] it is extremely difficult, often impossible to retain the structure of studied alloys by quenching, what means that it is extremely difficult to keep disordered γ phase by quenching to ambient temperature. Method proposed in this work can be used for direct determination of phase boundaries. In order to confirm the position of mentioned phase boundaries, authors are planning to continue calorimetric research and support it with another *in situ* method as resistometric measurements. Results will be applied also in CALPHAD procedure in order to optimize course of phase boundaries $\gamma' / \gamma' + \gamma$ and $\gamma' + \gamma / \gamma$ in Ni-Al-Cr system.

5. Conclusions

1. Values of formation enthalpy of alloys from Ni-Al-Cr system's sections: Ni₇₅Al₂₅ - Ni₇₅Cr₂₅ and Ni₇₅Al₂₅ - Ni₈₅Cr₁₅ were determined in this work with use of calorimetric solution method.
2. Introducing of intermediate container into calorimeter allowed to determine enthalpy of formation in elevated temperature 873 K.
3. During experiment a new, 10-socket intermediate container was used, that allows to performed a series of experiment of the same amount (10) of samples. This innovation increases accuracy of results and shortens time of experiment. A series contained samples of different composition.
4. Substantial decrease of absolute values of formation enthalpies with the increase of chromium concentration in alloys was noted.
5. Significant breaks of the course of values of enthalpy as a function of Cr concentration are attributed to phase boundaries $\gamma' / \gamma' + \gamma$ and $\gamma' + \gamma / \gamma$. For verification of position

of phase boundaries determined in this work another method *in situ* should be applied. Presently the authors will undertake resistometric studies as the method which fulfils this requirement.

6. Obtained values of enthalpy of formation can be used twofold: a) for direct determination of phase boundaries, and b) with other thermodynamic data, for elaboration of Ni-Al-Cr system with use of CALPHAD procedure.

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