

Calorimetric examination of mixtures for modification of nickel and cobalt superalloys

F. Binczyk*, J. Śleziona, R. Przeliorz

Chair of Metal Alloys and Composites Engineering

Silesian University of Technology, Krasińskiego Str. 8, 40-019 Katowice, Poland

*Contact for correspondence: e-mail: franciszek.binczyk@polsl.pl

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Abstract

The study presents the results of thermodynamic calculations and calorimetric examination of thermal reactions taking place at high temperatures between the nanoparticle inoculants and metallic constituents of nickel and cobalt superalloys. The calculations and measurements were made for different compositions, containing cobalt aluminate CoAl_2O_4 , cobalt oxide $\text{CoO} \cdot \text{Co}_2\text{O}_3$, zircon flour ZrSi_2O_4 , powdered and metallic Al, powdered Ti, and IN-713C alloy. The obtained results have indicated the possibility of using certain mixtures as potential inoculating additives for the volume modification of nickel and cobalt superalloys. A characteristic feature of these alloys is the formation of a detrimental structure containing very large columnar crystal, present even in castings of a very high solidification rate. It has been proved that the inoculant most effective in the formation of the structure of equiaxial grains is the inoculant based on cobalt aluminate, colloidal silica and powdered aluminium.

Keywords: nickel superalloys, DSC analysis, temperature, modification, macrostructure, inoculant

1. Introduction

Creep-resistant nickel and cobalt superalloys are the base material for the cast „hot parts” of aircraft engines [1-3]. At present, the near-net-shape castings for parts of aircraft engines, poured in investment moulds, are made from the modern grades of nickel and cobalt alloys, including the IN-713C alloy. Irrespective of the solidification conditions, castings made from the alloys without modification have the structure composed of large, columnar and fringe crystals with only very small amount of the equiaxial crystals, distributed in central parts of casting. A structure of this type is prone to crack formation, which can result in fatal failure of aircraft engines [4, 5]. Investigations on how to refine the structure of these alloys mainly aim at producing, within the whole casting volume, the, so called, monocrystalline structure and the structure composed entirely of the homogeneous, in respect of shape and dimensions, equiaxial crystals. The so far applied surface modification (with inoculant

placed in the face layer of ceramic mould) has not been satisfactory from the point of view of the casting design.

World's technical literature provides abundant information on the methods of refining the macro- and microstructure of nickel superalloys by the technique of refining and inoculation with nanoparticle inoculants. Yet, to be able to choose the best inoculant, it is necessary to know first how the mechanism of the volume inoculation operates, and to explain the phenomena that take place during alloy casting between the constituents of the inoculant and the constituents of the cast alloy.

It has been observed that after casting the liquid metal into a mould coated with inoculant, the reaction of exchange takes place between CoAl_2O_4 and some active elements present in the examined superalloys (Al, Cr and Ti), resulting in the formation of cobalt particles [6-10]. Owing to a good compatibility between the crystal lattice present in the matrix of nickel superalloys and the high-temperature cobalt particles, before dissolving in liquid alloy, the latter can act as nuclei of crystallisation. The so far obtained

results of the investigations aiming at an explanation of the modifying effect of various additives indicate a favourable effect of the low temperature pouring on the refinement of equiaxial crystals. This is very important, considering the strong effect of the pouring temperature on the alloy castability and the ability to reproduce complex shapes of elements operating as parts of aircraft engines, e.g. blades.

2. Materials and methods of investigation

The thermodynamic calculations were made to investigate the possibility of decomposition of the main modifying constituents (CoAl_2O_4 and ZrSiO_4). As stated in the reference literature, cobalt aluminate melts at a temperature of about 850°C [11, 12]. As a next step, possible chemical reactions between these constituents and selected elements included in the composition of the IN-713C alloy and kept outside this composition were examined. The calculations were made according to a HSC program [13].

Next, for selected reactions, the verifying measurements were taken using a Multi HTC S60 scanning calorimeter. The measurements were carried out for the primary composition of inoculating mixtures, i.e. for cobalt aluminate and zircon flour, and for the mixtures containing additionally powdered Al and Ti. Some measurements were also taken for a system of inoculant - Al_{metal} and inoculant - IN-713C alloy.

The weight of the samples was similar and comprised in a range from 310 to 340 mg. The investigations were made under argon protective atmosphere, applying the heating and cooling rate of $10^\circ\text{C}/\text{min}$. The samples were preheated to a temperature of 1450°C .

3. The results of investigations

The thermodynamic calculations were carried out for the four groups of reactions:

1. Group 1 - Reactions of decomposition of the main inoculant constituents.

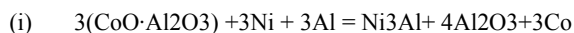
- (A) $\text{CoO}\cdot\text{Al}_2\text{O}_3 = \text{Al}_2\text{O}_3 + \text{CoO}$
 (B) $\text{ZrSiO}_4 = \text{ZrO}_2 + \text{SiO}_2$

2. Group 2 - Reactions between cobalt aluminate and metals from outside the IN-713C alloy composition.

- (C) $2(\text{CoO}\cdot\text{Al}_2\text{O}_3) + 3\text{Si} = 2\text{Al}_2\text{O}_3 + 2\text{CoSi} + \text{SiO}_2$
 (D) $2(\text{CoO}\cdot\text{Al}_2\text{O}_3) + 5\text{Si} = 2\text{Al}_2\text{O}_3 + 2\text{CoSi}_2 + \text{SiO}_2$
 (E) $\text{CoO}\cdot\text{Al}_2\text{O}_3 + \text{Mg} = \text{MgO} + \text{Co(l)} + \text{Al}_2\text{O}_3$
 (F) $2(\text{CoO}\cdot\text{Al}_2\text{O}_3) + \text{B} + \text{C} = \text{Co}_2\text{B} + 2\text{Al}_2\text{O}_3 + \text{CO}_2$
 (G) $\text{CoO}\cdot\text{Al}_2\text{O}_3 + \text{Fe} = \text{Al}_2\text{O}_3 + \text{Co} + \text{FeO}$

3. Group 3 - Reactions between cobalt aluminate and metals included in the IN-713C alloy composition.

- (a) $\text{CoO}\cdot\text{Al}_2\text{O}_3 + 2/3\text{Cr} = 1/3\text{Cr}_2\text{O}_3 + \text{Co} + \text{Al}_2\text{O}_3$
 (b) $\text{CoO}\cdot\text{Al}_2\text{O}_3 + 2/3\text{Al} = 4/3\text{Al}_2\text{O}_3 + \text{Co}$
 (c) $\text{CoO}\cdot\text{Al}_2\text{O}_3 + 1/2\text{Ti} = \text{Al}_2\text{O}_3 + \text{Co} + 1/2\text{TiO}_2$
 (d) $3(\text{CoO}\cdot\text{Al}_2\text{O}_3) + \text{Ni} + 5\text{Al} = \text{NiAl}_3 + 4\text{Al}_2\text{O}_3 + 3\text{Co}$
 (e) $\text{CoO}\cdot\text{Al}_2\text{O}_3 + \text{Ni} = \text{Al}_2\text{O}_3 + \text{Co} + \text{NiO}$
 (f) $3(\text{CoO}\cdot\text{Al}_2\text{O}_3) + 2\text{Cr} = 3\text{Co} + \text{Cr}_2\text{O}_3 + 3\text{Al}_2\text{O}_3$
 (g) $\text{CoO}\cdot\text{Al}_2\text{O}_3 + \text{Ni} = \text{NiO}\cdot\text{Al}_2\text{O}_3 + \text{Co}$
 (h) $3(\text{CoO}\cdot\text{Al}_2\text{O}_3) + \text{Ni} + 3\text{Al} = \text{NiAl} + 4\text{Al}_2\text{O}_3 + 3\text{Co}$



4. Group 4 - Reactions between cobalt oxide and metals included in the IN-713C alloy composition.

1. $\text{Co}_3\text{O}_4 + \text{Ni} + 3\text{Al} = 1/3\text{Ni}_3\text{Al} + 4/3\text{Al}_2\text{O}_3 + 3\text{Co}$
 2. $\text{Co}_3\text{O}_4 + 8/3\text{Al} = 4/3\text{Al}_2\text{O}_3 + 3\text{Co}$
 3. $\text{Co}_3\text{O}_4 + 17/3\text{Al} = 4/3\text{Al}_2\text{O}_3 + 3\text{CoAl}$

The results of the calculations are plotted in Figures 1 to 3.

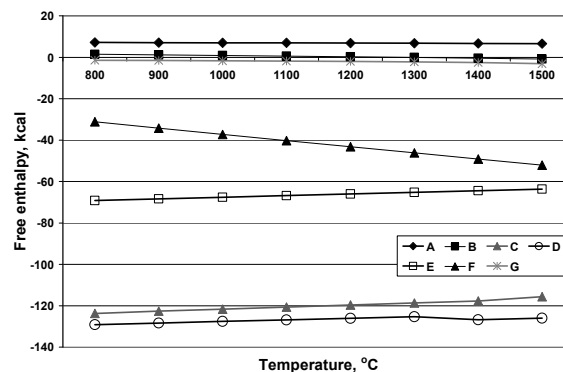


Fig.1. Free enthalpy in function of temperature for reactions included in groups 1 and 2

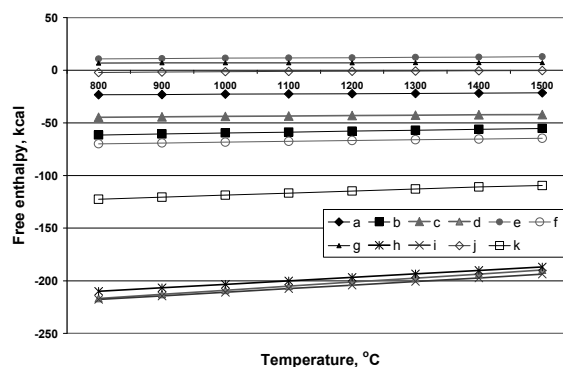


Fig. 2. Free enthalpy in function of temperature for reactions included in group 3

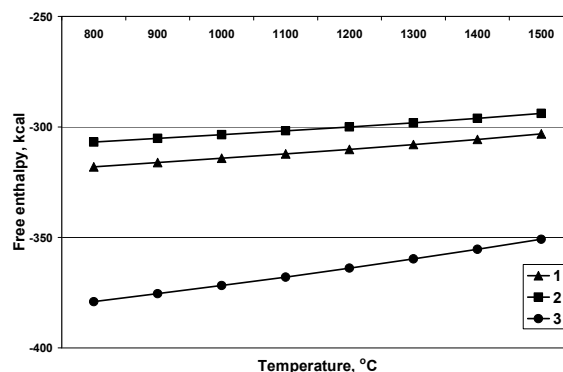


Fig. 3. Free enthalpy in function of temperature for reactions included in group 4

The criterion used in the evaluation of the possible course of reaction was the value of free enthalpy. The higher was the negative value of this enthalpy, the greater was the probability of the occurrence of reaction. The kinetics of the examined chemical reactions was disregarded.

Examples of the results of calorimetric analysis in the form of DSC graphs are shown in Figures 4 to 8 for the following compositions: cobalt aluminate CoAl_2O_4 , ZrSiO_4 + 10% CoAl_2O_4 mixtures, CoAl_2O_4 + 10% Al powder mixtures, Al powder and systems of ZrSiO_4 coating + 10% CoAl_2O_4 + colloidal silica on sample of aluminium and IN-713C alloy .

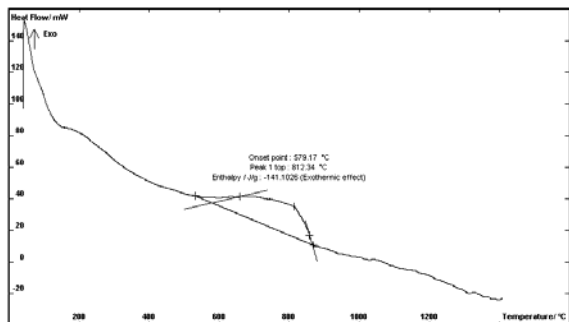


Fig. 4. DSC curve plotted for cobalt aluminate CoAl_2O_4

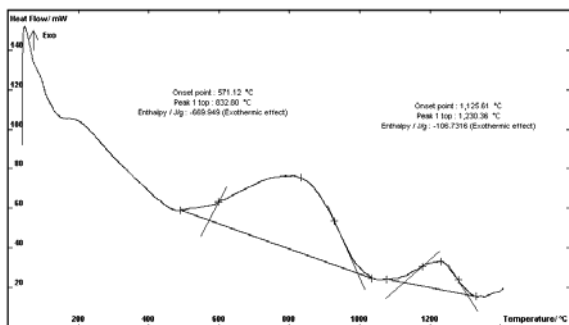


Fig. 5. DSC curve plotted for a mixture of ZrSiO_4 + 10% CoAl_2O_4

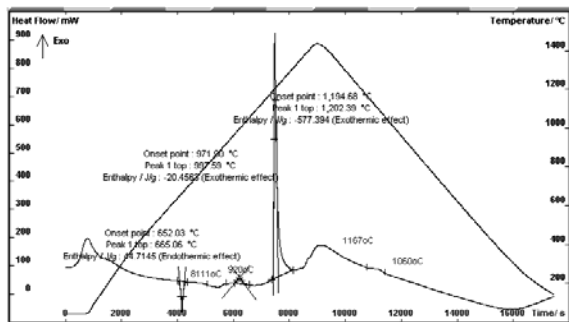


Fig. 6. DSC curve plotted for a mixture of CoAl_2O_4 + 10% Al powder + colloidal silica

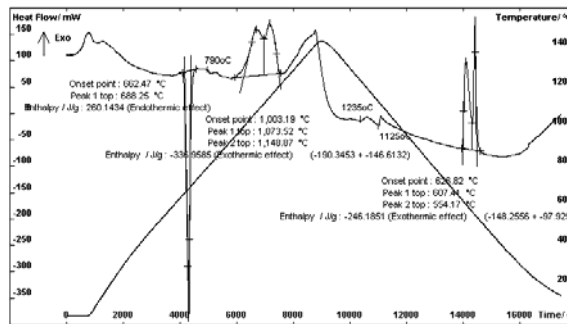


Fig. 7. DSC curve plotted for a system of ZrSiO_4 coating+ 10% CoAl_2O_4 on Al sample

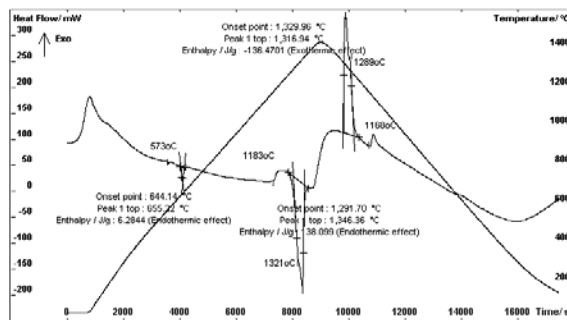


Fig. 8. DSC curve plotted for a system of ZrSiO_4 coating + 10% CoAl_2O_4 on IN-713C alloy sample

4. Discussion of results

The conducted thermodynamic calculations indicate that cobalt aluminate (reaction A) is stable within the examined range of temperatures, as confirmed by a positive value of the free enthalpy. This statement has also been proved by the DSC curve (Fig. 4), which shows only a fuzzy exothermic effect within the temperature range from 600 to 800°C. Probably, this is due to the effect of elastic recovery of the powdered material ground in the manufacturing process. Hence follows the conclusion that cobalt aluminate alone has no inoculating power. Moreover, the obtained results do not confirm the effect of this compound melting at a temperature of about 850°C. Similar results were obtained for a mixture of zircon flour and cobalt aluminate. The free enthalpy of reaction B reveals a small negative value only at a temperature above 1200°C. The exothermic effect observed on a DSC curve (Fig.5) is probably related with the formation of zirconium and silicon dioxides.

Among the examined reactions in Group 2, the most effective is cobalt aluminate with silicon and magnesium (reactions D, C and E). Yet, because these elements are not included in the composition of nickel superalloys, they cannot be used as components of an inoculating mixture, reducing cobalt atoms.

Among the examined reactions in Group 2, very effective is also cobalt aluminate with (Al + Ni), Al and Cr (reactions i, d, h, d, k, f and b), and these elements are present in all nickel and cobalt superalloys. The effect of a reaction between cobalt

aluminate and joint content of Al. and Ni is the formation of intermetallic phases of NiAl and Ni₃Al. Because of high melting point, the formed particles of these phases may also play the role of the nuclei of crystallisation [14].

Attention deserve the calculations of the free enthalpy made for reactions included in Group 4. The highest, negative value of the enthalpy points out to a high effectiveness of the formation of cobalt particles and intermetallic phases of CoAl, which act as inoculants.

The calculations are confirmed by the DSC curves shown in Figures 6 and 7. The endothermic effects of aluminium melting are observed at a temperature of about 660°C, followed by exothermic effects within the temperature range from 1000 to 1200°C. The said effects are the result of a reaction taking place between aluminium and cobalt aluminate. In the presence of zircon dioxide, the formation of the intermetallic phases of Co₂Al₉ and ZrAl₃ takes place. This fact is further confirmed by the results of X-ray microanalysis shown in Figure 9.

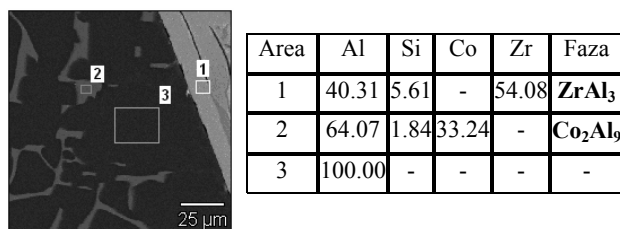


Fig. 9. The results of chemical microanalysis of the matrix and precipitates in Al sample after the calorimetric examinations

For a coating – IN-713C alloy system (Fig. 8), the DSC curve reveals an endothermic effect of Al melting, while the exothermic effect of Co reduction is not visible. Most probably, it takes place in contact with the liquid phase and is somehow overlapped by the stronger endothermic effect.

Summing up it can be observed that the inoculating mixtures for nickel alloys should satisfy the following conditions:

1. Contain the elements (or compounds of the elements) included in the composition of superalloys (Al., Cr, Ni, Co, Mo and W).
2. The melting point of the „in situ” formed particles should not be lower than the alloy casting temperature.
3. The difference between the densities of the inoculant and the alloy should not be too large to avoid flotations or the effect of sedimentation. When the density is too low, the inoculant has to be “forced” inside the alloy.
4. A good compatibility should be provided between the crystal lattice parameters of the refining agent and alloy, as it enables reducing the interfacial energy between these two systems. Generally, the difference between the parameters of the crystal lattice of the refiner and the alloy should not go below 10%.
5. The inoculant should be brittle and easy to disintegrate (in the case of intermetallic phases).

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