ARCHIVES
of
FOUNDRY ENGINEERING
Published quarterly as the organ of the Foundry Commission of the Polish Academy of Sciences
ISSN (1897-3310)
Volume 9
Issue 2/2009
97-100
22/2

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

Received 26.02.2009; accepted in revised form: 30.03.2009

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 $CoO*Co_2O_3$, 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 Zr SiO_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°C/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) $CoO{\cdot}Al_2O_3 = Al_2O_3 + CoO$

(B) $ZrSiO_4 = ZrO_2 + SiO_2$

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

(C) $2(CoO{\cdot}Al_2O_3) + 3Si = 2Al_2O_3 + 2CoSi + SiO_2$

(D) $2(CoO{\cdot}Al_2O_3) + 5Si = 2Al_2O_3 + 2CoSi_2 + SiO_2$

(E) $CoO{\cdot}Al_2O_3 + Mg = MgO + Co(l) + Al2O3$

(F) $2(CoO{\cdot}Al2O3) + B + C = Co_2B + 2Al_2O_3 + CO_2$

(G) $CoO{\cdot}Al_2O_3 + Fe = Al_2O_3 + Co + FeO$

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

(a) $CoO{\cdot}Al_2O_3 + 2/3Cr = 1/3Cr_2O_3 + Co + Al_2O_3$

(b) $CoO{\cdot}Al_2O_3 + 2/3Al = 4/3\ Al_2O_3 + Co$

(c) $CoO{\cdot}Al2O3 + 1/2Ti = Al_2O_3 + Co + 1/2TiO_2$

(d) $3(CoO{\cdot}Al_2O_3) + Ni + 5Al = NiAl_3 + 4Al_2O_3 + 3Co$

(e) $CoO{\cdot}Al_2O_3 + Ni = Al_2O_3 + Co + NiO$

(f) $3(CoO{\cdot}Al_2O_3) + 2Cr = 3Co + Cr_2O_3 + 3Al_2O_3$

(g) $CoO{\cdot}Al_2O_3 + Ni = NiO{\cdot}Al_2O_3 + Co$

(h) $3(CoO{\cdot}Al_2O_3) + Ni + 3Al = NiAl + 4Al_2O_3 + 3Co$

(i) 3(CoO·Al2O3) +3Ni + 3Al = Ni3Al+ 4Al2O3+3Co

(h) CoO·Al2O3+ 1/2Mo = Al2O3 + Co + 1/2Mo

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

1. Co3O4 + Ni + 3Al = 1/3Ni3Al + 4/3 Al2O3 + 3Co
2. Co3O4 + 8/3Al = 4/3Al2O3 + 3Co
3. Co3O4 + 17/3Al = 4/3Al2O3 + 3CoAl

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

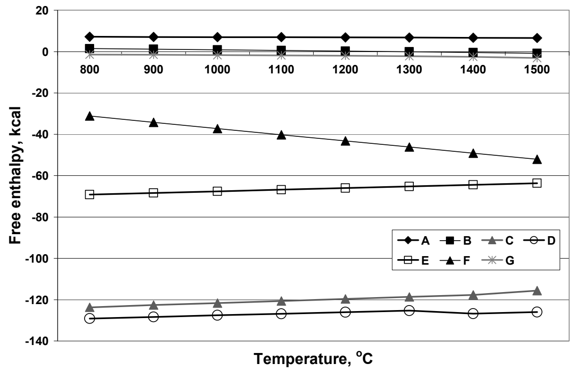


Fig.1. Free enthalpy in function of temperature for reactions included in groups 1 and 2

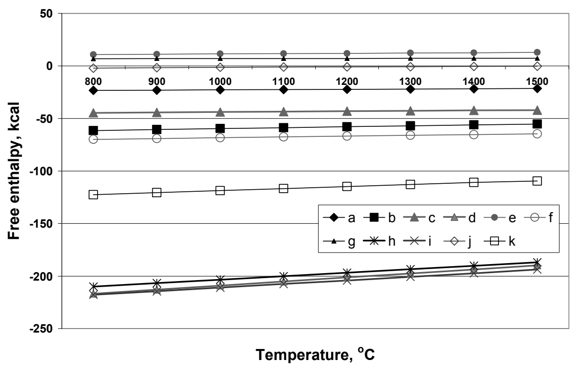


Fig. 2. Free enthalpy in function of temperature for reactions included in group 3

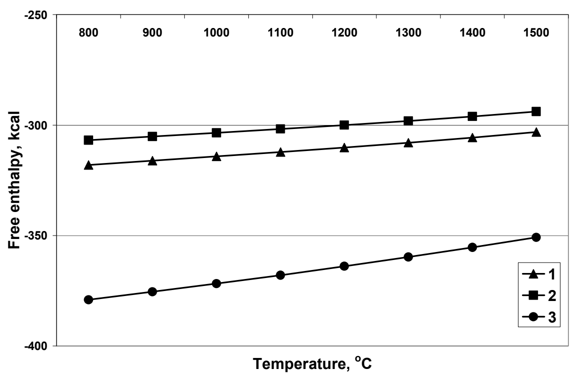


Fig. 3. Free enthalpy in function of temperature for reactions included in group 4

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 ZrSiO4 coating + 10% $CoAl_2O_4$ + colloidal silica on sample of aluminium and IN-713C alloy .

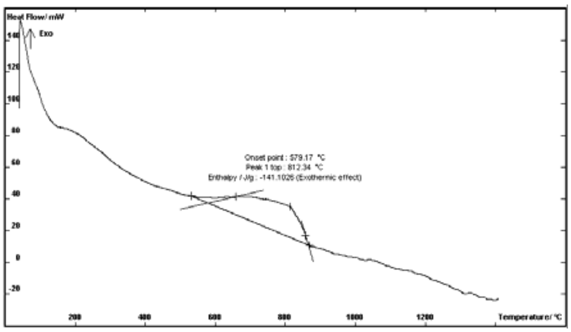


Fig. 4. DSC curve plotted for cobalt aluminate $CoAl_2O_4$

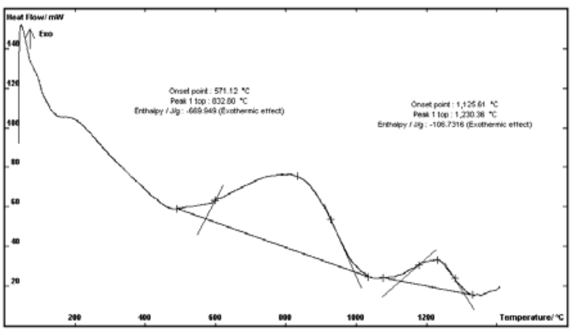


Fig. 5. DSC curve plotted for a mixture of $ZrSiO_4$ + 10% $CoAl_2O_4$

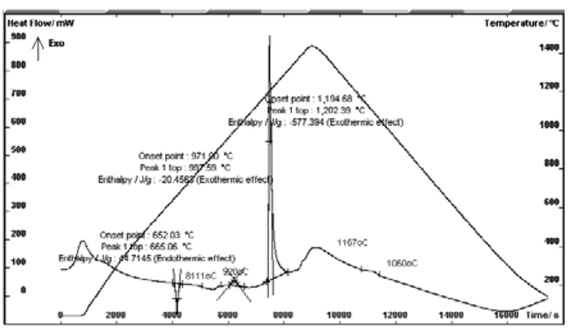


Fig. 6. DSC curve plotted for a mixture of $CoAl_2O_4$ + 10% Al powder + colloidal silica

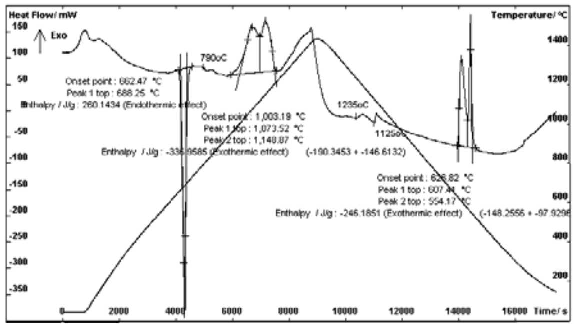


Fig. 7. DSC curve plotted for a system of ZrSiO4 coating+ 10% $CoAl_2O_4$ on Al sample

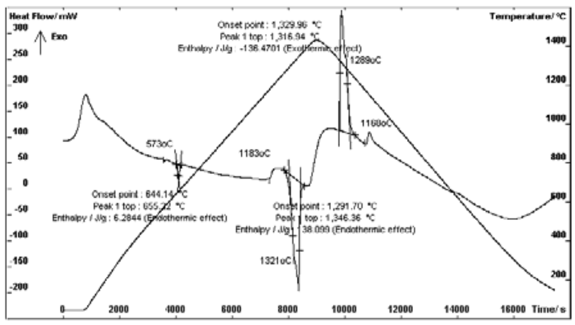


Fig. 8. DSC curve plotted for a system of ZrSiO4 coating + 10% $CoAl_2O_4$ on IN-713C alloy sample

4. Discussion of results

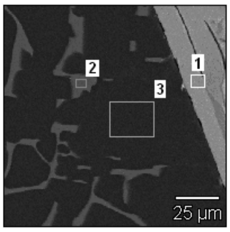
The conducted thermodynamic calculations indicate that cobalt aluminate (reaction A) is stable within the examined range of temperatures, as confirmed by a positive value of the free enthalpy. This statement has also been proved by the DSC curve (Fig. 4), which shows only a fuzzy exothermic effect within the temperature range from 600 to 800^{o}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^{o}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^{o}C. The exothermic effect observed on a DSC curve (Fig.5) is probably related with the formation of zironium 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 Ni_3Al. 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^{o}C, followed by exothermic effects within the temperature range from 1000 to 1200^{o}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 Co_2Al_9 and $ZrAl_3$ takes place. This fact is further confirmed by the results of X-ray microanalysis shown in Figure 9.



Area	Al	Si	Co	Zr	Faza
1	40.31	5.61	-	54.08	**$ZrAl_3$**
2	64.07	1.84	33.24	-	**Co_2Al_9**
3	100.00	-	-	-	-

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).

The studies were done under a Commissioned Research Project PBZ-MNiSW–03/I/2007 financed by the Ministry of Science and Higher Education.

References

[1]. F. Zupanic, T. Boncina, A. Krizman, F.D. Tichelaar: Structure of continuously cast Ni-based superalloy Inconel 713C, Journal of Alloys and Compounds, v. 329, issue 1-2, (2001), pp.290-297.

[2]. M.Tabuchi, K. Kubo, K. Yagi, A.T. Yokobori Jr, A. Fuji: Results of a Japanese round robin on creep crack growth evaluation methods for Ni-base superalloys , Engineering Fracture mechanics, volume 62, issue 1, (1999), pp. 47-60.

[3]. Superalloys, Metal Powder Report, v. 51, issue 9, (1996), p.39.

[4]. A. Smith, A. Mainwood, M. Watkins: The kinetics of the capture of nitrogen by nickel defects in diamond , Diamond and related materials, v. 11, issue 3-6, (2002), pp. 312-315.

[5]. M. Lachowicz: Characteristics of microstructural changes and crack formation mechanism detected during welding and heat treatment of Inconel 713C superalloy, Doctor's Thesis, Politechnika Wrocławska (2006).

[6]. Hartman D., Muerrle U., Reber G.: The effects electron beam refining on the cast ability of IN 713 C, Metal, (1992), issue 5, pp. 443-447.

[7]. L. Liu, T. Huang, Y. Xiong: Grain refinement of superalloy K4169 by addition of refineries cast structure and refinement mechanisms, Materials Science and Engineering A, 394, (2005), pp.1-8

[8]. Y. Xiong, J. Du, X. Wie, A. Yang, L. Liu: Grain refinement of Superalloy IN 718C by the addition of Inoculants, Metallurgical and Materials Transactions A, vol. 35A, July (2004), pp. 2111-2114.

[9]. Y. Xiong, A. Yang, Y. Guo, W. Liu, L. Liu: Grain refinement of superalloys K3 and K4169 by the addition of refineries, Science and Technology of Advanced Materials, issue 2, (2001), pp. 13-17.

[10]. W. Jin, F. Bai, T.Li, G. Yin,: Grain refinement of superalloy IN100 under the action of rotary magnetic fields and inoculants, Material Letters 62 (2008), pp.1585-1588.

[11]. W. Seok Cho, M. Kakihana: Crystallization of ceramic pigment $CoAl_2$ O_4 nanocrystals from Co–Al metal organic precursor, Journal of Alloys and Compounds, 287, 1999, pp. 87–90

[12]. A. Sirijaruphana, A. Horváth, J. G. Goodwin: Cobalt aluminate formation in alumina-supported cobalt catalysts: effects of cobalt reduction state and water vapor, Catalysis Letters Vol. 91, Nos. 1–2, November 2003

[13]. HSC Chemistry Ver.(4), Copyright (C), Outokumpu Research Oy, Pori, Finland, A. Roine

[14]. L.Liu, R. Zhang, L. Wang: A new method of fine grained casting for nickle-base superalloys, Journal of Materials Processing Technology, 77, 1998, pp. 300-304.