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Franciszek Binczyk*, **Józef Śleziona, Paweł Gradoń**

Silesian University of Technology, Chair of Materials Technology, ul. Krasińskiego 8, 40-019 Katowice, Poland
** Corresponding author: E-mail: franciszek.binczyk@polsl.pl*

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MODIFICATION OF MACROSTRUCTURE OF NICKEL SUPERALLOYS WITH COBALT NANOPARTICLES

The paper presents the results of studies on the effect of combined surface and bulk modifications on the macrostructure of castings made from remelted, post-production IN-713C, IN-100 and MAR-247 waste alloys. Surface modification was carried out by applying onto the wax pattern surface, a coating containing zirconium silicate and cobalt aluminate. Bulk modification was carried out when the cast liquid alloy was passed through a special ceramic filter containing, among others, cobalt aluminate. The nanoparticles of cobalt, acting as crystallisation nuclei, are the product of a modifier reaction ($CoAl_2O_4$ inoculant) with the chemically active constituents of the nickel alloys and with the additional filter components in the form of Al and Ti powders. The filters were placed in the mould pouring basin. The beneficial effect of combined modification on the macrostructure (equiaxial crystals) and mechanical properties was stated. The effect of the active constituents present in the nickel alloys and in the filter material was confirmed. A particularly strong refining effect on the macrostructure of equiaxial crystals was obtained in the MAR-247 alloy, which contained the strongest chemically active additives of Hf, Ta and Nb. A hypothetical model of the surface and bulk modification was developed. A strong influence of the alloy pouring temperature on the modification effect was reported. Modification was most effective when the pouring temperature did not exceed 1440°C.

Keywords: nickel superalloys, macrostructure, modification, pouring temperature, nanoparticles, $CoAl_2O_4$ inoculant

MODYFIKOWANIE MAKROSTRUKTURY NADSTOPÓW NIKLU NANOCZĄSTKAMI KOBALTU

Zamieszczono wyniki badań wpływu łącznego modyfikowania powierzchniowego i objętościowego na makrostrukturę odlewów wykonanych po przetopie odpadów poprodukcyjnych ze stopów IN-713C, IN-100 i MAR-247. Modyfikację powierzchniową zrealizowano poprzez naniesienie na model woskowy powłoki zawierającej krzemian cyrkonu i glinian kobaltu. Modyfikację objętościową zrealizowano podczas odlewania ciekłego stopu przez specjalne filtry ceramiczne, zawierające między innymi glinian kobaltu. Nanocząstki kobaltu, pełniące rolę zarodków krystalizacji, są produktem reakcji modyfikatora (inoculant $CoAl_2O_4$) z aktywnymi chemicznie składnikami stopów niklu oraz dodatkowymi składnikami filtrów w postaci proszków Al i Ti. Filtry umieszczono w zbiorniku wlewowym formy. Stwierdzono korzystny wpływ łączonej modyfikacji na makrostrukturę (kryształy równoosiowe) i właściwości mechaniczne. Potwierdzono oddziaływanie aktywnych składników obecnych w stopach niklu i materiale filtrów. Szczególnie silny efekt rozdrobnienia makrostruktury kryształów równoosiowych uzyskano dla stopu MAR-247, który zawiera najbardziej aktywne chemicznie dodatki Hf, Ta i Nb. Opracowano hipotetyczny model modyfikacji powierzchniowej i objętościowej. Stwierdzono istotny wpływ temperatury odlewania stopu na efekt modyfikowania. Efekt modyfikowania jest szczególnie widoczny przy temperaturze odlewania poniżej 1440°C.

Słowa kluczowe: nadstopy niklu, makrostruktura, modyfikacja, temperatura, nanocząstki, inokulant $CoAl_2O_4$

INTRODUCTION

Currently, the near-net-shape castings of aircraft engine parts are made from modern grades of nickel and cobalt alloys such as RENE-77, IN-100 IN-713C, and MAR-247 [1, 2]. On solidification, these alloys develop a specific type of macrostructure, composed of frozen and columnar grains. Structures of this type are prone to crack formation and propagation, resulting in fatal failure of aircraft engines [3, 4]. Therefore, every attempt should be made to obtain a structure of equiaxial grains within the whole casting volume.

The fundamental problem in the casting technology of these alloys is how to control the type and size of the grains for the specific operating conditions of different parts of an aircraft engine. Along with an increase of grain size, high-temperature creep resistance improves, and therefore a structure of this type is most desirable in the case of rotating parts operating in a combustion chamber. Castings of a fine-grained structure offer higher mechanical properties at low temperatures and better resistance to thermal fatigue, and as such are successfully used for fixed elements operating at low temperatures. A schematic diagram is shown in Figure 1.

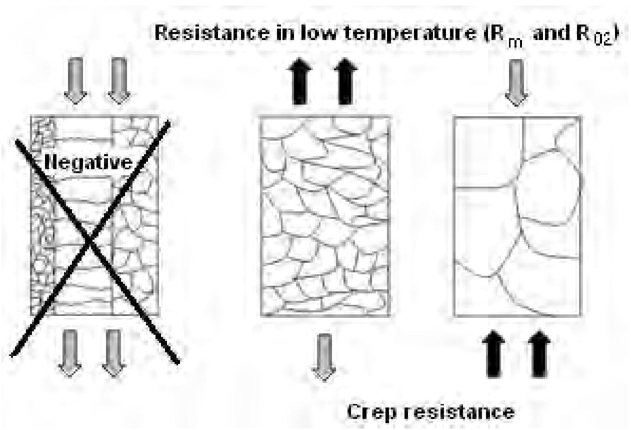


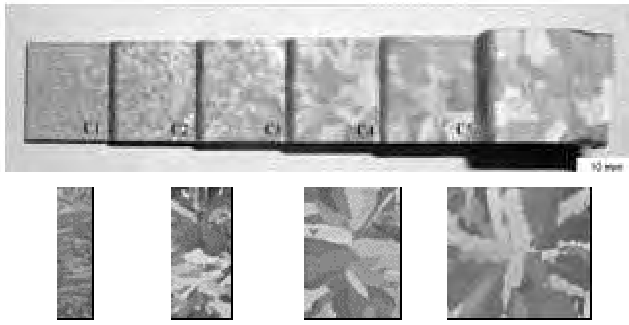
Fig. 1. Schematic representation of low- and high-temperature property effects on microstructure

Rys. 1. Schemat wpływu mikrostruktury na nisko- i wysokotemperaturowe właściwości

Literature data mention numerous studies looking for some means to improve the macro- and microstructure of nickel superalloys by using the techniques of refining [5, 6] and modification. A simple solution is surface modification with nanoparticle inoculants, which are included in the composition of a coating directly touching the casting surface [7-11]. In [12], the results of the modification of the Inconel 718 alloy with microadditions of cobalt oxide CoO were presented. A minor degree of structure refinement with slight improvement of mechanical properties was obtained. The authors of this study investigated the solidification process [13,14] and the effect of bulk modification taking place in an IN-713C nickel superalloy on the stereological parameters of its macrostructure [15-17]. In [18], the results of the studies on the effect of repeated remelting of IN-713C, IN-100 and MAR-247 alloys on the chemical composition and mechanical properties were presented. The results disclosed in these studies can serve as a good example of the beneficial effect that inoculating with a mixture of zirconium silicate, $CoAl_2O_4$ inoculant, Al and Ti powders, and colloidal silica is expected to have on the crystallisation and refinement of equiaxial grains.

RESEARCH PROBLEM

The surface modification applied so far (with a modifier placed in the internal layer of the mould), though enables making near-net-shape castings satisfying the predetermined requirements, does not guarantee obtaining a homogeneous structure of equiaxial crystals. The modifying effect occurs only in a thin surface layer of the casting and decreases strongly with a decreasing cooling rate, as seen in the elements of a stepped test piece with steps of 6 mm (C1), 11 mm (C2), 17 mm (C3), 23 mm (C4) thickness, shown in Figure 2. The surface modifying coating (applied on the wax pattern) consists of a mixture containing 10% $CoAl_2O_4$ and 90% zirconia powder and a binder in the form of colloidal silica. As demonstrated in Figure 2, the macrostructures in the specimen cross-sections show the effect of modification - superficial or penetrating to a very small depth only. Probably, after solidification of the first solid layer, the liquid alloy is cut off from the modifier-feeding source (the "source" of Co particles). Pointing towards the central areas, a zone of very fine columnar crystals is formed. As literature data suggest, the mechanism of the modifying effect of cobalt aluminate $CoAl_2O_4$ has not been fully explained yet.



C1 - 6 mm C2 - 11 mm C3 -17 mm C4 - 23 mm

Fig. 2. Macrostructure on surface and in cross-sections of cast stepped test piece after surface modification

Rys. 2. Makrostruktura powierzchni oraz przekrojów poprzecznych odlewu próby schodkowej modyfikowanego powierzchniowo

In [19] it has been observed that after pouring liquid metal into a mould coated with an inoculant, the cobalt particles present in the $CoAl_2O_4$ aluminate may undergo reduction due to the effect of the chemically active constituents of the nickel alloys, among others – aluminium:

$$CoAl_2O_4 + \frac{2}{3}Al = Co + \frac{4}{3}Al_2O_3$$

Owing to a strong agreement that exists between the crystal lattice of the nickel superalloy matrix (γ phase) and high-temperature Co particles, these particles can play the role of the crystallisation nuclei, provided they are not dissolved in the liquid alloy first. Therefore, the lower the temperature and the shorter the time of contact between the liquid alloy and mould surface, the stronger the modifying effect is, which is particularly well visible in the thin elements of the stepped test piece. Therefore, it has been decided to undertake research on bulk modification as a source of crystallisation nuclei formation before the liquid alloy enters the mould cavity (for example, in a gating system when the liquid alloy is flowing through the filtrating element).

THERMODYNAMIC CALCULATIONS

In [20], a model of the thermo-chemical phenomena taking place at the ceramic mould - liquid alloy interface (IN-713C, IN-100 and MAR-247 alloys) was described. The content of the main elements in the examined alloys is compared below:

- IN-713C (0,19% C, 13,25% Cr, 6,13% Al, 0,83% Ti, 4,21% Mo, 2,19% Nb, remainder Ni),
- MAR-247 (0,15% C, 8,56% Cr, 5,59% Al, 10,0% Co, 1,08% Ti, 0,65% Mo, 1,40% Hf, 9,98% W, 3,17% Ta, remainder Ni),
- IN-100 (0,16% C, 8,56% Cr, 5,66% Al, 13,41% Co, 4,66% Ti, 3,01% Mo, 0,8% V, remainder Ni).

Studies were carried out on a mould with a modifying coating based on zirconium silicate and cobalt aluminate. The results of an X-ray microanalysis of the precipitates on the mould and casting surface revealed the strongest chemical activity of **Al, Ti, Cr and Nb** in the IN-713C alloy, **Al, Ti, Cr and V** in the IN-100 alloy, and **Al, Ti, Cr, Hf and Ta** in the MAR-247 alloy.

Hence it follows that chemical reactions take place when the liquid nickel alloy is flowing through the filter and contacts the surface where the particles of cobalt aluminate $CoAl_2O_4$ are present. To check this point of view, the free enthalpy of possible chemical reactions was calculated. The results of the computations made by HSC software [21] are shown in Figure 3.

a. $CoO{\cdot}Al_2O_3 = Al_2O_3 + CoO$
b. $3(CoO{\cdot}Al_2O_3) + 2Cr = 3Co + Cr_2O_3 + 3(Al_2O_3)$
c. $CoO{\cdot}Al_2O_3 + 1/2Ti = Al_2O_3 + Co + 1/2(TiO_2)$
d. $CoO{\cdot}Al_2O_3 + 2/3Al = 4/3\ (Al_2O_3) + Co$
e. $2(CoO{\cdot}Al_2O_3) + Nb = 2Co + NbO_2 + 2(Al_2O_3)$
f. $5(CoO{\cdot}Al_2O_3) + 2Ta = 5Co + Ta_2O_5 + 5(Al_2O_3)$
g. $2(CoO{\cdot}Al_2O_3) + Hf = 2Co + HfO_2 + 2(Al_2O_3)$

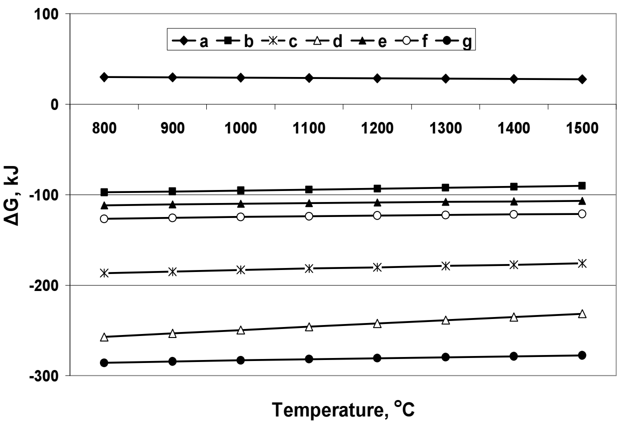


Fig. 3. Free enthalpy ΔG in regards to temperature for $CoAl_2O_4$ reaction with selected constituents of nickel alloys

Rys. 3. Wyniki obliczeń entalpii właściwej reakcji $CoAl_2O_4$ z wybranymi składnikami stopów niklu

The positive value of the specific enthalpy makes the decomposition of cobalt aluminate (a) within the examined range of temperatures impossible. Cobalt aluminate can enter into reaction with some specific constituents of nickel alloys. The most intense reactions will occur between the cobalt aluminate and hafnium (g), tantalum (f) and niobium (e). Less intense reactions may take place with aluminium (d), titanium (c) and chromium (b). Hence it can be concluded that the potential nuclei for "in situ" crystallisation can form according to the models shown in Figure 4.

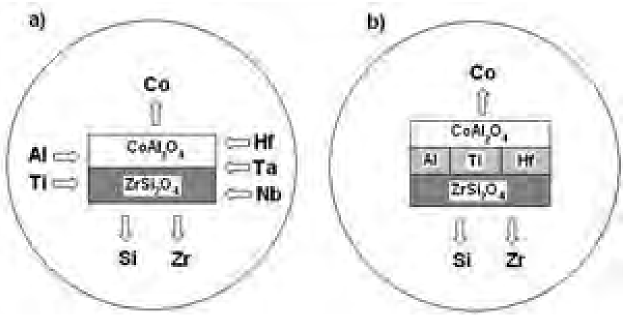


Fig. 4. Models of operation of components of modifying mixture with active alloying constituents (a) and active components of modifying mixture (b)

Rys. 4. Modele sposobu oddziaływania składników mieszanki modyfikującej z aktywnymi składnikami stopu (a) i aktywnymi składnikami mieszanki modyfikującej (b)

MATERIALS AND METHODS OF INVESTIGATION

The melting charge was composed of post-production waste IN-713C, MAR-247 and IN-100 alloys in the form of gating systems and defective castings. The ceramic moulds with modifying coating were made by the investment process. The modifying filter was placed in the pouring basin. To avoid rapid heat losses, the moulds were "wrapped" with wool insulation, as shown in Figure 5. The modifier-containing ceramic filters (made according to the author's genuine idea) are shown in Figure 6.

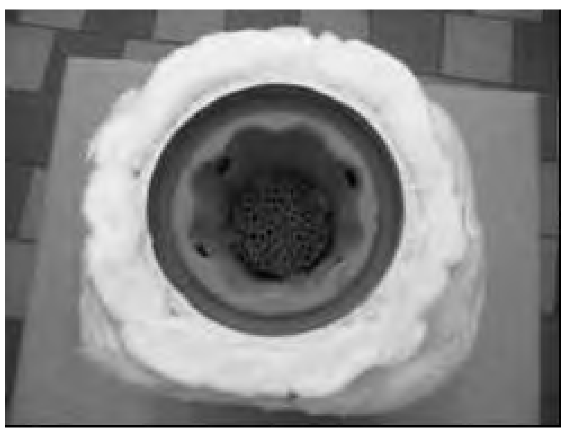


Fig. 5. Ceramic mould with thermal insulation and modifying filter placed in pouring basin

Rys. 5. Forma ceramiczna z izolacją cieplną i filtrem modyfikującym w zbiorniku wlewowym

Melting was carried out in a vacuum induction furnace, type IS 5/III, made by Leybold - Heraeus, in a crucible rammed from MPi refractory material based on MgO. The charge weight was 8,5 kg. Melting was conducted in a vacuum of 10÷2 hPa. Before pouring, argon at a pressure of 900 hPa was introduced to the furnace chamber. The temperature of the melt in the crucible was measured with a Pt-PtRh10 immersion thermocouple, and additionally with a laser pyrometer. The temperature of pouring was 1465°C. An example of a casting made from the IN-713C alloy is shown in Figure 6.

Fig. 6. Casting made from IN-713C alloy

Rys. 6. Odlew ze stopu IN-713C

RESULTS AND DISCUSSION

The effectiveness of the modification was evaluated from the results of the casting macro- and microstructural examinations. Figure 7 shows the macrostructure of the starting charge materials, while Figure 8 shows the same macrostructure after modification.

The macrostructure of the charge materials (unmodified castings) is in a prevailing part composed of columnar crystals. As might be expected, the combined treatment of surface and bulk modification resulted in the formation of equiaxial crystals within the whole casting volume. As follows from Figure 7, the highest degree of grain refinement was obtained in the casting made from the MAR-247 alloy. This is probably due to the very active influence of the additions of hafnium and tantalum present in this alloy. Thus, earlier findings following from the thermodynamic calculations have been confirmed. In the remaining castings made from the IN-713C and IN-100 alloys, the effect of modification is less intense due to the weaker reducing effect of aluminium and titanium.

Fig. 7. Macrostructure of charge materials (casting diameter 30 mm)

Rys. 7. Makrostruktura wsadu wyjściowego

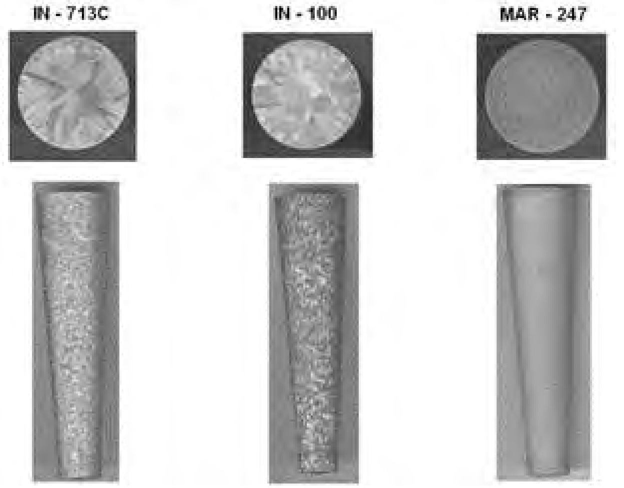


Fig. 8. Macrostructure of castings (13x25x100 mm) for investigated Ni alloys after surface and bulk modification

Rys. 8. Makrostruktura odlewów z badanych stopów po modyfikowaniu powierzchniowym i objętościowym

HYPOTHETICAL MODEL OF MODIFICATION WITH COBALT NANOPARTICLES

The nuclei-forming power of cobalt nanoparticles has been confirmed by the results of X-ray microanalysis of the distribution of this constituent in the outer layer of the IN-713C alloy casting. The microanalysis was made with an optical glow discharge GDS GD Profiler HR emission spectrometer. The results are shown in Figure 9.

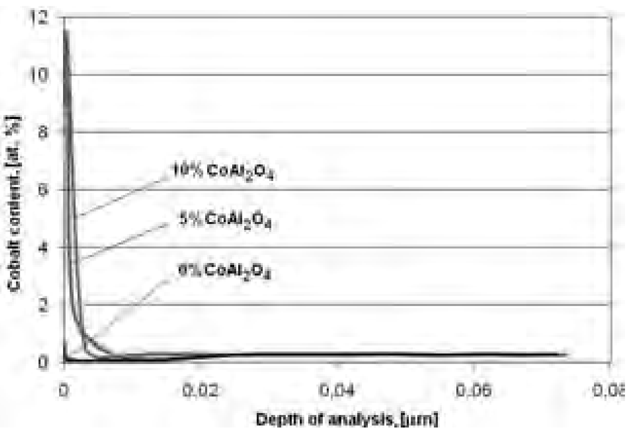


Fig. 9. Cobalt concentration in the surface layer of IN-713C alloy casting

Rys. 9. Stężenie kobaltu w warstwie powierzchniowej odlewu ze stopu IN-713C

A hypothetical model of the modifying effect of Co particles on the nuclei-forming process in regards to the cooling rate (the value of undercooling) is shown in Figure 10.

The modifying effect of cobalt particles can be discussed with a breakdown into the several successive stages of the process:

Stage 1 (in the range of T_{cast} to T_{rCo} - the temperature of the dissolution of cobalt particles in the alloy melt): The formation of Co particles as a result of the reduction process induced by the chemically active alloying elements, such as Al, Ti, Cr, Hf, present in the alloy and in the modifying mixture. Immediate dissolution of these particles in the melt at a temperature above T_{rCo}. When the alloy temperature at the time of pouring considerably exceeds the level of T_{rCo}, the modification does not occur, as confirmed by the results of experiments carried out for a casting pouring temperature above 1470°C. Only a weak surface modifying effect is possible, due to a sudden drop in the molten alloy temperature at the mould surface.

Stage 2 (in the range of T_{rCo} to T_{sol}):
The Co particles are stable and can unite into clusters of a size critical for the given undercooling, which depends on the cooling rate in, e.g. the subsequent elements of a stepped test piece.

Stage 3 (in the range of T_{liq} to T_{sol}):
On the thus formed nuclei, the grains grow and their size depends on the number of crystallisation nuclei formed by the high-temperature Co particles combination. The number and size of the nuclei depend on the degree of alloy undercooling in selected parts of the casting.

Stage 4 (after casting solidification):
Regular solidification of the casting with a well-defined macrostructure. Possible changes in microstructure are the result of structure ordering (γ to γ' transformation) with the formation of microporosities, stresses and other precipitation processes.

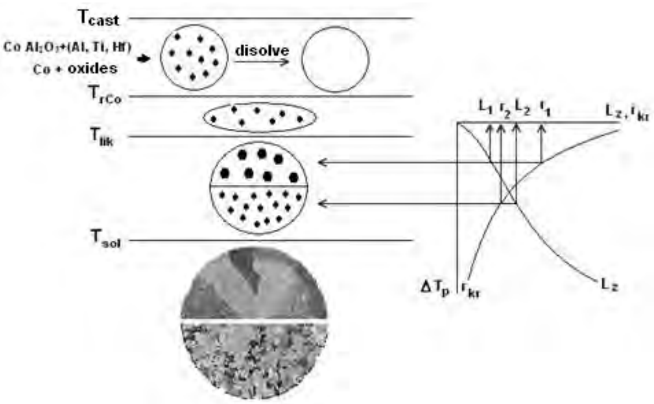


Fig. 10. Hypothetical model of nickel alloy modification due to nuclei-forming power of Co particles

Rys. 10. Hipotetyczny model modyfikowania stopów niklu w wyniku zarodkotwórczego działania cząstek Co

CONCLUSIONS

The study clearly shows that the combination of surface modification (modifying coating on the mould surface) with bulk modification (modifier as a component of the filter) is greatly responsible for the formation of equiaxial crystals within the entire volume of the casting.

The bulk modification alone leads to a mixed structure of equiaxial and columnar crystals. The consequence of modification is an obvious increase of the mechanical properties, yield strength and tensile strength in particular. Compared to an unmodified melt, after the combined modification, these properties grow by about 10 to 15%. Unfortunately, all this is at the cost of the decreasing high-temperature creep resistance [22].

To sum up, it can be concluded that:

1. The basic parameter determining the effect of modification (both surface and bulk) is the pouring temperature of nickel alloys.
2. The effect of modification is particularly well visible at a pouring temperature below 1440°C. Hence it can be concluded that the temperature T_{rCo} should be lower than 1440°C.
3. Surface modification (modifier in the first layer of the ceramic mould) occurs only on the surface, because the "source" of Co particles is cut off from the liquid alloy as soon as the first solid layer is formed on the mould surface. On the thus formed nuclei, only columnar crystals can grow.
4. The higher the cooling rate, the finer the columnar grains formed in surface modification and equiaxial grains formed in bulk modification are.

Acknowledgements

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