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Interactions at the mould – modifying coating – molten nickel alloy interface

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Abstract

The study describes thermal-chemical interactions that take place in the molten nickel alloy-ceramic mould system, where the mould is either coated with a modifying coating („blue" mould) or is not („white" mould). The ceramic mould based on zirconium silicate was made by investment process at the WSK Rzeszów Foundry. The main component of the modifying coating was cobalt aluminate $CoAl_2O_4$ added in an amount of 10%. Thermodynamic calculations indicated the possibility of chemical reactions taking place between the chemically active nickel alloy constituents (Al, Ti, Hf, Ta and Nb) and the components of a ceramic mould and modifying coating. The result of such interactions is the risk of the formation of cracks on the surface of mould and molten metal penetration into these cracks, combined with the formation of casting defects, like burns-on, pitting, etc., as proved by extensive X-ray microanalysis. Changes of chemical composition in the surface layer of castings were also reported.

Keywords: Nickel Superalloys, Modification, Chemical Reaction, Thermodynamic Potential, Oxides

1. Introduction

The near-net-shape castings for parts of aircraft engines, like turbine disks, compressor blades, and high-pressure turbine blades are required to offer stable mechanical properties, combined with resistance to both corrosion and high-temperature creep [1÷3].

The required performance characteristics of these elements can be satisfied only when high quality surface and total absence of internal defects, shrinkage and gaseous microporosities in particular, are ensured. Castings are usually made in ceramic moulds by investment process. The final surface quality of "precision castings" depends not only on foundry mould accuracy but also on interactions taking place at the mould-molten metal interface since the moment of mould pouring until the complete solidification of casting. These thermal-chemical effects are often enhanced by the use of modifying coatings applied on the ceramic mould surface, mainly to refine the casting macrostructure containing equiaxial grains. In the majority of cases, coatings of this type are based on zirconium silicate ($ZrSiO_4$) and cobalt aluminate ($CoAl_2O_4$), added in an amount of 5 do 10wt.% [4÷7].

The elements of aircraft engines are usually cast from nickel alloys, e.g. IN-713C, IN-100, MAR-247. Some of these alloys contain, besides Al and Cr, highly active chemical elements, like Hf, Ta and Nb. The said elements have a positive impact on the process of surface and bulk modification (intensive reduction of Co particles) and a negative impact on casting surface quality, changing the chemical composition in an external layer of casting. All these effects are likely to be caused by the high-rate chemical reactions taking place between the active chemical constituents of nickel alloys and cobalt aluminate [8, 9].

2. Test materials and methods

The tested materials were ceramic samples cut out from the foundry moulds with and without the modifying coating and metal specimens cut out from castings in areas adjacent to the examined mould surface. Castings were made from IN713C, IN100 and MAR-247 alloys. The modifying coating contained zirconium silicate $ZrSiO_4$ and 10% cobalt aluminate $CoAl_2O_4$. As regards ceramic materials, the investigations were carried out on moulds in initial state and after pouring with metal. Microstructural examinations were carried out under a Hitachi S-3400N (SEM) microscope at magnifications from 20x to 500x. Two different techniques of examinations were applied, i.e. SE (SEM) detector – for metal specimens and BSE (VP-SEM) detector operating in low vacuum for ceramic specimens. Chemical composition in surface layer of castings was analysed by a GDS GD PROFILER HR glow discharge optical emission spectrometer. The thermodynamic analysis of possible chemical reactions was based on a HSC programme [10].

3. The research problem

Processes occurring at the mould–molten nickel alloy interface are of a thermal-chemical character, mainly due to the presence in both these areas of the constituents characterised by very high chemical activity, especially when the system additionally includes a modifying coating based on cobalt aluminate.

The intensity of the interactions that occur at the mould–molten metal interface depends on the following factors:

1. Mould without modifying coating („white" mould) or with coating („blue" mould).
2. Pouring temperature.
3. Phase composition in the subsurface mould area.
4. Foundry mould surface temperature.
5. Chemical composition of the cast nickel alloy, especially the presence of constituents characterised by high chemical activity, like Al, Hf, Ta, Nb, etc.
6. Time of molten alloy–mould surface direct contact until the moment when first crystals appear in so called „frozen zone".
7. Time until the casting solidifies within its whole volume and the linear shrinkage starts. An "air gap" appears then breaking the direct contact between the casting and mould and changing the conditions of heat flow.

In the examined nickel alloys, the following elements are characterised by the highest chemical activity:

- Al, Ti, Cr and Nb in IN-713C alloy,
- Al, Ti, Cr and V in IN-100 alloy,
- Al, Ti, Cr, Hf and Ta in MAR-247 alloy.

Figure 1 shows schematically the „flow" of constituents in liquid alloy-mould and mould-liquid alloy systems.

At the mould–molten alloy interface, chemical reactions can occur between the components of ceramic mould, modifying coating and some constituents of molten alloy. As a result of these reactions, „zones of influence" are formed on the mould surface (zone I) and in the near-surface region of molten alloy (zone II).

The result of these interactions is the formation of new chemical compounds on the surface of both mould and casting as well as changes of the chemical composition in the casting surface layer. The "zones of influence" are growing until the moment when temperature drops to the value T_{sol}.

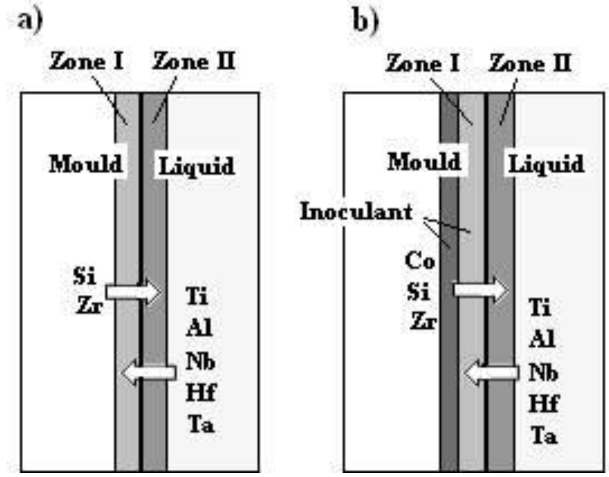


Fig. 1. Schematic representation of chemical interactions at the interface of: a) mould material-molten alloy, b) modifying coating-molten alloy

Since that moment, the linear shrinkage of the casting starts and an immediate consequence of this effect is the formation of gas gap. The gap breaks the contact that the alloy has had so far with the mould surface and changes the heat transfer conditions. Now the mould surface–cast alloy interaction areas stop growing.

An analysis was made of the possible thermodynamic course of chemical reactions taking place between the material of „white" mould (zirconium silicate) and active constituents of the nickel alloy:

A. $ZrSiO_4 = ZrO_2 + SiO_2$
B. $ZrO_2 + Hf = HfO_2 + Zr$
C. $1{,}5(ZrO_2) + 2Al = Al_2O_3 + 1{,}5Zr$
D. $2{,}5(ZrO_2) + 2Ta = Ta_2O_5 + 2{,}5Zr$
E. $ZrO_2 + Nb = NbO_2 + Zr$
F. $SiO_2 + 2Nb = 2NbO + Si$
G. $2{,}5(SiO_2) + 2Ta = Ta_2O_5 + 2{,}5Si$
H. $SiO_2 + Hf = HfO_2 + Si$
I. $1{,}5(SiO_2) + 2Al = Al_2O_3 + 1{,}5Si$

and of the course of chemical reactions taking place between the modifying compound („blue" mould) and active constituents of the nickel alloy:

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

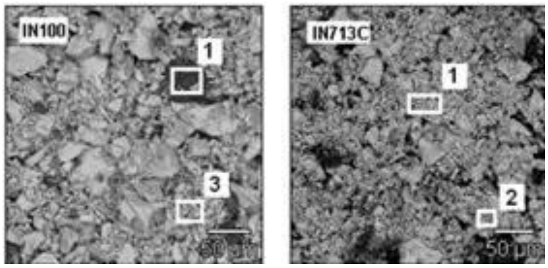
4. The results and discussion

The results of calculations and the evaluation of a thermodynamic potential of reactions in both groups are compared in [11]. It was observed that at a temperature above 1050^{o}C, zirconium silicate ZrSiO4 can decompose and form ZrO_2 and SiO_2 oxides. The temperature of interface at the moment of mould pouring is comprised in a range of 1420 to 1460^{o}C. So, only reactions B, I and H have the chance of occurring (the highest negative value of thermodynamic potential). This means that in zone I (Fig. 1a) the presence of hafnium oxide HfO_2 (especially in MAR-247 alloy) and aluminium oxide AL_2O_3 should be expected. In zone II (casting surface) increased concentration of Zr and Si and of oxygen is possible (in all alloys).

The decomposition of cobalt aluminate (within the examined range of temperatures) is impossible (positive values of thermodynamic potential). Other reactions in group II are characterised by a negative value of the thermodynamic potential. The most intense reactions are those taking place between cobalt aluminate and hafnium (g), tantalum (f), niobium (e), aluminium (d) and titanium (c). Therefore, in zone I (Fig. 1b), besides the components of a modifying coating, one can expect the presence of oxides, like HfO_2, Ta_2O_5 (especially in MAR-247 alloy), and Al_2O_3, TiO_2 and NbO_2. On the external surface of castings made from the IN-713C and IN-100 alloys (zone II), one can expect increased concentrations of oxygen (in all alloys) and cobalt. On the other hand, in the surface layer of MAR-247 casting, an increased concentration of Zr and Si, as a consequence of the strongly reducing effect of Hf and Ta, is highly probable. Hence, in the surface layer of casting, the content of Hf and Ta can be much lower than in the zones lying deeper in the casting. These suggestions were confirmed by microanalysis of the chemical composition in zones of mould reaction (I) and molten metal reaction after solidification (II). In the case of Inconel alloys, the precipitates formed in an external mould layer were observed to contain Cr and Ti, as shown in Fig. 2.

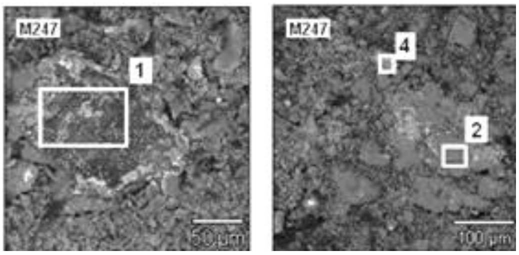
Particularly strong thermal and chemical reactions were observed in MAR-247 alloy. The external mould surface after pouring was strongly oxidised and had well visible local "coloured" spots. The analysis of chemical composition of the individual precipitates has indicated that the strongest were the reactions with Hf. The composition of the precipitates also included other alloying constituents, Cr, Ni and W in particular. The presence of these elements in precipitates can suggest the penetration of liquid alloy into the microcracks on a mould surface resulting from the intense thermal effects. Examples of chemical analysis of the precipitates formed on the surface of a "white" mould after casting of MAR-247 alloy are shown in Figure 3.

Intense reactions with Hf were also observed in zone II on the raw surface of castings made from MAR-247 alloy. The results of analysis of an average chemical composition on the surface of castings raw and after sand blasting, poured in "white" and "blue" moulds, are compared in Tables 1 and 2. In MAR-247 alloy, the concentration of Hf on the metal surface after knocking out of casting from mould exceeded 50wt.%. So high concentration of Hf and elevated content of Si and Zr on the raw casting surface, compared with the surface after sand blasting, prove strong oxidation of the MAR-247 alloy casting surface due to thermal and chemical interactions taking place with the "white" mould material. As an example, Figure 4 shows the results of chemical analysis of the precipitates „sticking" to the casting surface.



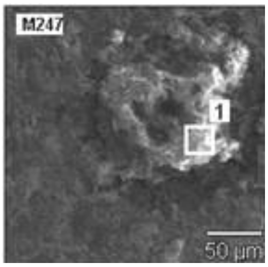
Alloys	Area	Content, wt. %				
		Zr	Al	Si	Ti	Cr
IN-100	1	38,4	0,6	60,4	0,6	-
	3	71,7	1,1	22,7	3,5	-
IN-713C	1	74,3	1,2	23,5	-	1,0
	2	63,5	8,5	23,5	2,7	1,8

Fig. 2. Microstructure and chemical composition (EDS) of precipitates in zone I of the „white" mould poured with Inconel alloys



Area	Content, wt.%							
	Zr	Al	Si	Cr	Ni	W	Hf	Co	Ti
1	9,8	20,2	7,5	27,5	16,1	8,9	5,2	3,8	1,0
2	76,3	0,4	21,4	-	2,0	-	-	-	-
4	9,8	4,7	5,4	26,6	39,0	13,9	7,0	3,6	0,5

Fig. 3. Microstructure and chemical composition (EDS) of precipitates in zone I of the „white" mould poured with MAR-247 alloy



Content, wt %			
Zr	Al	Si	Ti
41,4	2,3	13,2	0,6

Content, wt %			
Cr	Co	Ni	Hf
1,0	3,6	10,2	27,6

Fig. 4. Microstructure and chemical composition of precipitates present on the raw surface of MAR-247 casting ("white" mould)

On casting surface, the particles of oxides of Si, Zr and Ti as well as Hf and Co were observed (especially in MAR-247 alloy). Moreover, zones rich in main alloying elements „sticking” to the casting surface were also detected. Their presence proves very intense thermal and chemical interactions taking place at the mould-molten nickel alloy interface.

Table 1.
Chemical composition (EDS) of the casting surface – mould without modifying coating („white” mould)

Cast alloy*		Content, wt. % *												
		Al	Si	Zr	Ti	Cr	Co	Ni	Mo	Nb	Hf	Ta	W	V
IN-100	1	27,0	10,6	16,6	10,9	4,7	5,4	24,2	0,9	-	-	-	-	0,6
	2	21,2	1,1	-	3,4	7,7	11,9	52,8	1,8	-	-	-	-	0,1
IN-713C	1	21,1	3,8	10,0	2,4	10,8	-	45,8	3,9	2,2	-	-	-	-
	2	14,1	0,9	-	1,5	12,4	-	61,2	3,3	6,6	-	-	-	-
MAR-247	1	11,7	1,5	8,0	0,7	3,6	3,0	14,2	-	-	52,9	0,6	3,8	-
	2	15,9	0,2	0,5	0,7	6,9	8,0	47,8	-	-	5,6	4,2	10,2	-

Table 2.
Chemical composition (EDS) of the casting surface – mould with modifying coating („blue” mould)

Cast alloy*		Content, wt. %												
		Al	Si	Zr	Ti	Cr	Co	Ni	Mo	Nb	Hf	Ta	W	V
IN-100	1	21,2	12,0	17,3	12,9	4,5	8,8	22,7	0,2	-	-	-	-	0,4
	2	16,8	-	-	3,3	8,0	12,8	56,0	2,2	-	-	-	-	0,9
IN-713C	1	19,0	10,0	15,9	1,2	7,5	1,8	36,9	1,9	5,8	-	-	-	-
	2	17,9	-	-	0,7	12,0	-	64,4	3,1	1,9	-	-	-	-
MAR-247	1	15,0	5,8	3,2	1,2	14,9	6,2	28,2	0,2	-	11,9	1,9	11,5	-
	2	12,5	-	-	0,4	5,6	9,0	57,5	0,6	-	0,9	2,3	11,2	-

* 1 – as-cast, 2 – after sandblasting

The presence of modifying coating on the surface of the $ZrSiO_4$-based mould, containing the chemically active $CoAl_2O_4$ introduces a few major changes to the process taking place at the molten alloy-mould interface. The leading role is played by reactions taking place between the active nickel alloy constituents and cobalt aluminate. It has been confirmed that the most violent are the reactions of this compound with Hf (g), Ta (f), Nb (e), Al (d) and Ti (c) [11].

The microanalysis of chemical composition of numerous precipitates found on the mould surface after casting of Inconel alloys revealed the high content of Ti, Cr and Ni, which might have resulted from the penetration of molten alloy into the mould microcracks (thermal and chemical interactions). This has been confirmed by analysis of zone 1 done for the IN-100 alloy (7,8% Zr, 22,9% Al, 5,7% Si, 17,5% Ti, 11,2% Cr, 13,8% Co and 21,1% Ni). Similar results of the analysis were obtained for zone 1 in the IN-713C alloy. In zone 2, the content of about 12,5% Nb was stated. The results of these measurements are shown in Fig. 5.

On the surface of „blue” mould (zone 1) after casting of MAR-247 alloy, numerous “foreign” precipitates were noted. Examples of the results of analysis for MAR-247 alloy are shown in Fig. 6. The precipitates were characterised by high content of Hf, i.e. from 8,2 to 84,1wt.%. Additionally, the oxidised precipitates contained Ta in an amount of up to 16wt. %. Those were probably the oxides of hafnium and tantalum (zones 1 and 2) . The precipitates present in zone 4 contained mainly Zr and Si, while in zone 3 the alloying constituents were present (Cr, Ni, W, and Ti).

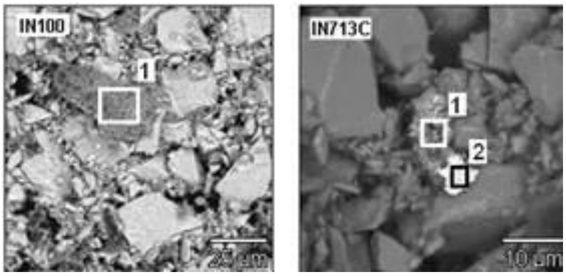


Fig. 5. Microstructure and chemical composition (EDS) of precipitates present in zone 1 of „blue” mould poured with Inconel alloys

Their presence proves intense thermal and chemical reactions, which give rise to alloy penetration into the microcracks on mould surface.

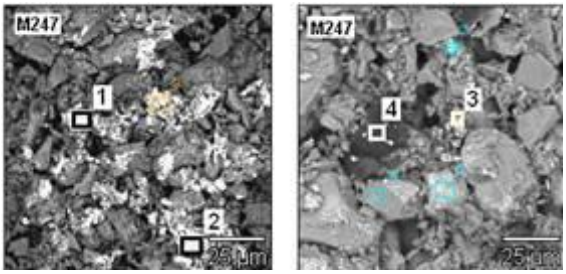


Fig. 6. Microstructure and chemical composition of precipitates present in zone I of „blue” mould poured with MAR-247 alloy

The interactions occurring on mould surface are reflected in zone II, from the side of liquid alloy. The evaluation of chemical composition on the raw surface of castings poured in "blue" moulds confirms the chemical activity of Hf and strong thermo-chemical interactions leading to high concentrations of Si, Zr and Al on the surface of castings. The results of chemical analysis carried out on the examined nickel alloys are shown as examples in Table 2.

The surface of MAR-247 casting had a high content of Hf, Ta and W, while on the surface of IN-713C casting, a high content of Nb was observed. Probably, these elements occur in the form of oxides. The presence of oxides on the casting surface proves the occurrence of strong chemical reactions taking place at the mould–molten alloy interface. Chemical analysis of precipitates present on the casting surface shown in Fig. 7 confirms the strong reactivity of Hf - a constituent of MAR-247 alloy (in zone 1) and of Nb - a constituent of IN-713C alloy (zone 2). Moreover, both these zones are characterised by high Co concentrations.

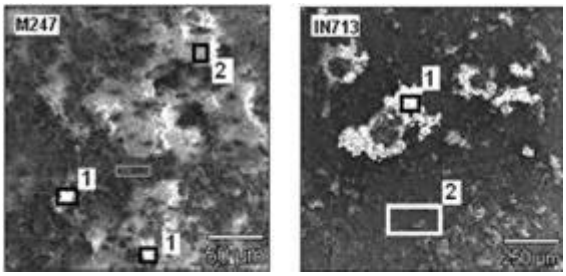


Fig. 7. Microstructure and chemical composition of precipitates present on the raw surface of castings made from MAR-247 and IN-713C alloys („blue" mould)

As follows from Table 2, after sand blasting, i.e. after the removal of the casting surface layer, the content of oxide-forming constituents decreases at the cost of an increasing content of the main alloying elements. So, a strong thermal-chemical interaction at the ceramic mould–molten nickel alloy interface can change the chemical composition in a surface layer of casting. This is particularly true in the case of Hf and Ta, which are the constituents of MAR-247 alloy. The content of these elements in a sub-surface layer of casting can be considerably lower, compared to zones lying deeper in the casting.

These conclusions were supported by the GD-OES depth profile analysis. The maximum profile depth obtained in tests was 50 μm. Clear differences in the concentration profiles of elements occurred in the subsurface layer - hence the presented graphs refer to a depth of 0.16 μm. The results of analysis obtained for MAR-247 alloy are shown as examples in Fig. 8.

Generally, the concentration of main alloying elements across the casting depth is independent of the mould surface condition („white" or „blue"). In each case, the concentration (proportional to the intensity of counts) was considerably lower directly at the surface and down to a depth of about 0,02 μm. This was caused by the high content of oxides of the alloying elements and mould constituents taking part in the chemical reactions. The immediate effect of intense reactions taking place between the cobalt aluminate and chemically active constituents, like Al, Ti, Ta and Hf is high near-surface content of Si, Zr and Co (up to 0,02 μm). The profile of Hf concentrations in casting from the „blue" mould clearly indicates an impoverishment of the subsurface layer in this element.

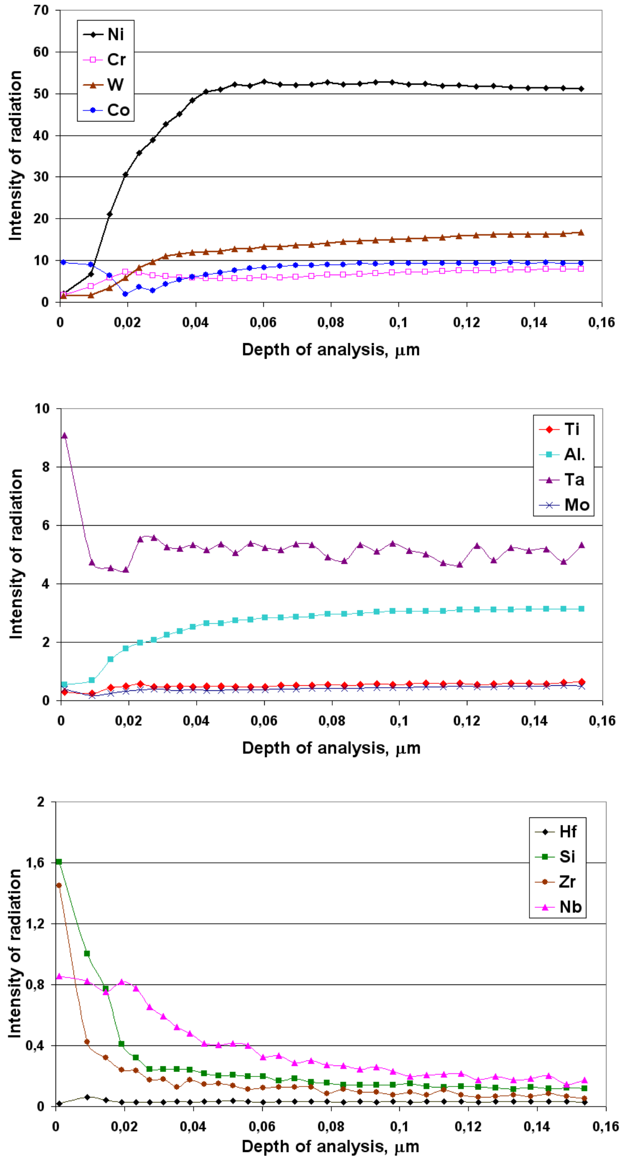


Fig. 8. Concentration of constituents in surface layer of MAR-247 alloy casting („blue" mould)

Particularly high intensity of reactions between cobalt aluminate and active alloying elements was confirmed by the examinations of MAR-247 alloy macrostructure, in which the obtained grain sizes were the smallest ones of all the examined nickel alloys.

5. Conclusions

Various chemical reactions were found to take place between mould components and liquid metal at the ceramic mould-molten nickel alloy interface. The result of these reactions was the formation of "zones of influence" on the mould surface and in the subsurface layer of molten nickel alloy. The intensity of reactions was definitely higher in the presence of cobalt aluminate particles. Calculations of the thermodynamically possible chemical reactions which might occur between the components of "white" mould (without modifying coating) and between the components of "blue" mould (with modifying coating) were confirmed by microanalysis of the chemical composition of "foreign" precipitates found on the surface of the examined moulds and by examinations of chemical composition across the casting depth profile. In zones of reaction, from the side of the „white" mould surface, hafnium oxides HfO_2 (especially in MAR-247 alloy) and aluminium oxides Al_2O_3 were traced. Moreover, on alloy surface, an increased concentration of Zr and Si was observed, due to the decomposition of zirconium silicate $ZrSiO_4$. In the case of "blue" mould, in zones of reaction from the side of mould surface, the presence of oxides of hafnium HfO_2, tantalum Ta_2O_5 (especially in MAR-247 alloy), aluminium Al_2O_3, titanium TiO and TiO_2, and niobium NbO_2 was stated.

On the raw casting surface, the particles of Si, Zr and Ti oxides were detected in the case of „white" mould, and of Hf and Co in the case of „blue" mould. In addition, zones rich in the main alloying elements (Ni, Cr, etc.) were "sticking" to the surface, thus proving the occurrence of intense thermal and chemical interactions taking place at the mould–molten nickel alloy interface.

The strongest thermal-chemical interactions were observed in MAR-M247 alloy. Raw castings made of this alloy were characterised by high concentration of Zr, Si and oxygen in the surface layer, which resulted from the high chemical activity of Hf and Ta. The negative thermodynamic potential in chemical reactions with the participation of these constituents assumed its highest values. These reactions were even more intense in the presence of cobalt aluminate. Therefore, the content of Hf and Ta in the surface layer of MAR-M247 castings was much lower than in the zones lying deeper in the casting, as indicated by the GD-OES depth profile analysis. The cobalt aluminate-supported grain refinement mechanism in nickel alloys is of a very complex character. Moreover, studies of this effect by traditional methods of chemical analysis are very difficult.

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