

# Analysis of thermal-chemical interactions at the ceramic mould – molten nickel alloy interface

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Received 23.06.2010; accepted in revised form 25.06.2010

## Abstract

A model of thermal-chemical interactions at the ceramic mould – molten nickel alloy interface was described. Studies were carried out on mould coated with a layer of modifier based on zirconium silicate and cobalt aluminate. The thermodynamic calculations indicated the possibility of chemical reactions taking place between the chemically active nickel alloy constituents (Al, Ti, Hf, Ta and Nb) and components of the modifying coating. The result of such interactions is possible formation on the surface of mould and casting of “new compounds” which can be the source of casting defects, like burns-on, pitting, etc., the fact proved by extensive X-ray microanalysis. In addition, the possibility of crack formation on mould surface and of the molten metal penetration into thus formed crevices was observed.

**Keywords:** Nickel superalloys, Chemical reaction, Casting defects, Thermodynamic potential

## 1. Introduction

Creep-resistant nickel and cobalt alloys are the leading materials used for near-net-shape castings operating as parts of aircraft engines in both static and rotating steering systems exposed to the effect of high temperatures under mass forces. These castings are required to offer, among others, high fatigue resistance, high-temperature creep resistance and corrosion resistance in media containing products of fuel combustion. The main group of castings that should satisfy these quality requirements are parts responsible for the safety of flight, including turbine discs, compressor blades, high-pressure turbine blades and other similar elements [1-5].

Currently, the near-net-shape castings used as parts of aircraft engines are made by the investment casting process from modern

grades of nickel and cobalt alloys, such as IN-713C, IN-100, IN-738, RENE-77, MAR-M-247 and MAR M 509.

The required performance characteristics of castings of this type (e.g. turbine blades) can be satisfied only if high quality surface and total absence of internal defects, shrinkage and gaseous microporosities in particular, is ensured, since no additional machining is carried out on the surface of these elements. The manufacturing process used most often in this case is investment casting in ceramic moulds. 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 full casting solidification.

To reduce thermal-chemical effects at the metal-mould interface it is necessary to apply protective films and coatings. For example, in the case of metal moulds and/or traditional sand moulds these will be the coatings based on coal dust, chalk, etc.

In the case of moulds for cast parts of aircraft engines (blades, turbines, etc.) made by investment casting process, the application of such neutral coatings can pose some problems. Sometimes, to refine grains and produce equiaxial crystals, the surface of moulds should be coated with chemically active coatings which also act as modifiers. The composition of such coatings is usually based on corundum ( $\text{Al}_2\text{O}_3$ ), or zirconium silicate ( $\text{ZrSiO}_4$ ) and cobalt aluminate ( $\text{CoAl}_2\text{O}_4$ ) used in amounts of 5 to 10 wt.% [6-9].

## 2. Materials and methods of investigation

The tested materials were parts of a ceramic mould coated with modifying agent and metallic specimens cut out from castings in areas adjacent to the mould surface. Castings were made from IN713C, IN100 and MAR-247 alloys. The modifying coating contained zirconium silicate ( $\text{ZrSiO}_4$ ) and 5% cobalt aluminate ( $\text{CoAl}_2\text{O}_4$ ). 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 Hitachi S-3400N (SEM) scanning electron microscope at a magnification of 20x - 500x. Two different techniques of examinations were applied, i.e. SE (SEM) detector for metallic specimens and BSE (VP-SEM) detector operating in low vacuum for ceramic specimens.

The thermodynamic analysis of possible chemical reactions was based on HSC programme [10].

## 3. Research problem

Processes that occur at the ceramic mould material – molten nickel alloy interface can be of thermal character only or of thermal-chemical character when occurring close to the mould surface and when the liquid alloy contains some constituents of high chemical activity. In the former case, the consequence is usually loss of mechanical properties suffered by the moulding material, resulting in natural deformation of the casting shape. In the latter case, regions of „new material”, which is the product of chemical reactions going on between the active constituents, are formed on the surface of both mould and casting; they can stick permanently to the casting surface resulting in the burn-on and scab defects.

In both cases, due to thermal effects, macro- and microcracks can be formed on mould surface. This phenomenon is particularly dangerous when cracks are formed before the start of the solidification process. Under such conditions, the cracks are acting as capillaries and „suck in” the liquid metal, which subsequently solidifies inside the cracks forming scab defects.

The intensity of the phenomena which occur at the mould – molten metal interface depends mainly on the following factors:

1. Alloy melt temperature, especially overheating above the alloy liquidus temperature  $T_{lik}$ .
2. Foundry mould surface temperature at the instant of alloy pouring.
3. Thermophysical properties of moulding material, especially the heat conductivity, specific heat, density, and heat accumulation

coefficient. Additionally, it is worth noting that these coefficients have values depending on temperature changes!

4. Chemical composition of cast alloy, especially the presence of constituents characterised by high chemical activity, e.g. Al, Hf, Ta, Nb, etc.

5. Phase composition in the subsurface layer of foundry mould.

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 full solidification and start of linear shrinkage. An “air gap” appears then, breaking the direct casting – mould contact and changing the conditions of heat flow.

In the examined nickel alloys, the highest chemical activity have the following elements:

- 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 the course of events that take place at the mould [with modifying coating] – molten alloy interface.

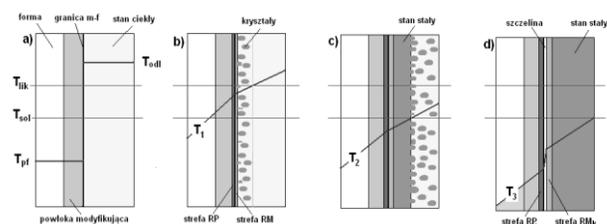


Fig. 1. Model of thermal-chemical interaction at the modifier-coated mould – molten nickel alloy interface

The first stage (a) corresponds to the situation which prevails immediately after filling of mould with molten metal. Of course, this is purely theoretical state, because filling of mould takes some time and since the very beginning the surface of mould is in contact with liquid alloy. At the mould – molten alloy interface, chemical reactions can occur between the constituents of modifying coating and molten alloy, as illustrated by stages (b) and (c). A result of these reactions is the formation of „zones of influence” on mould surface (RP) and in the subsurface region of molten alloy (RM). The zones are growing until the moment when temperature drops to the value of  $T_{sol}$ . Since that moment, the linear shrinkage of the casting starts and a consequence of this effect is the formation of gas gap. The gap breaks the contact that alloy has had so far with the mould surface and changes the heat transfer conditions. Now, the mould surface – cast alloy interaction area is growing no longer.

Considering the composition of the modifying coating, the thermodynamic possibility of the following chemical reactions was analysed:

- A.  $\text{ZrSiO}_4 = \text{ZrO}_2 + \text{SiO}_2$
  - B.  $\text{ZrO}_2 + \text{Hf} = \text{HfO}_2 + \text{Zr}$
  - C.  $1,5(\text{ZrO}_2) + 2\text{Al} = \text{Al}_2\text{O}_3 + 1,5\text{Zr}$
  - D.  $2,5(\text{ZrO}_2) + 2\text{Ta} = \text{Ta}_2\text{O}_5 + 2,5\text{Zr}$
  - E.  $\text{ZrO}_2 + \text{Nb} = \text{NbO}_2 + \text{Zr}$
  - F.  $\text{SiO}_2 + 2\text{Nb} = 2\text{NbO} + \text{Si}$
  - G.  $2,5(\text{SiO}_2) + 2\text{Ta} = \text{Ta}_2\text{O}_5 + 2,5\text{Si}$
  - H.  $\text{SiO}_2 + \text{Hf} = \text{HfO}_2 + \text{Si}$
  - I.  $1,5(\text{SiO}_2) + 2\text{Al} = \text{Al}_2\text{O}_3 + 1,5\text{Si}$
- and

- a.  $\text{CoO} \cdot \text{Al}_2\text{O}_3 = \text{Al}_2\text{O}_3 + \text{CoO}$
- b.  $3(\text{CoO} \cdot \text{Al}_2\text{O}_3) + 2\text{Cr} = 3\text{Co} + \text{Cr}_2\text{O}_3 + 3(\text{Al}_2\text{O}_3)$
- 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.  $\text{CoO} \cdot \text{Al}_2\text{O}_3 + 2/3\text{Al} = 4/3(\text{Al}_2\text{O}_3) + \text{Co}$
- e.  $2(\text{CoO} \cdot \text{Al}_2\text{O}_3) + \text{Nb} = 2\text{Co} + \text{NbO}_2 + 2(\text{Al}_2\text{O}_3)$
- f.  $5(\text{CoO} \cdot \text{Al}_2\text{O}_3) + 2\text{Ta} = 5\text{Co} + \text{Ta}_2\text{O}_5 + 5(\text{Al}_2\text{O}_3)$
- g.  $2(\text{CoO} \cdot \text{Al}_2\text{O}_3) + \text{Hf} = 2\text{Co} + \text{HfO}_2 + 2(\text{Al}_2\text{O}_3)$

## 4. The results of investigation and discussion of results

The evaluation focussed only on the determination of the thermodynamic potential of chemical reactions. This means that the probability of the occurrence of reaction was analysed, without going into the problem of its kinetics. The reaction can take place only with the negative value of  $\Delta G$ . The results of calculations are shown in Figs. 2, 3 and 4.

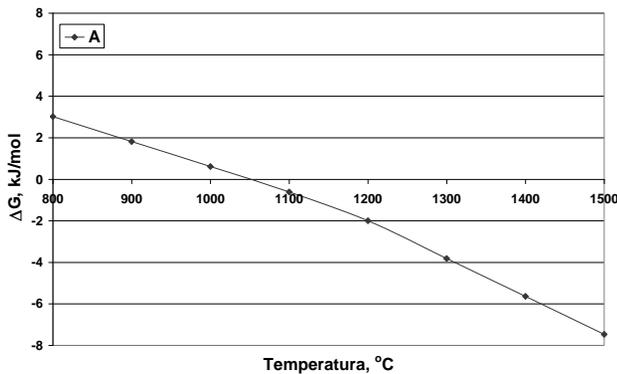


Fig. 2. Thermodynamic potential  $\Delta G$  changing in function of temperature for the reaction of zirconium silicate decomposition

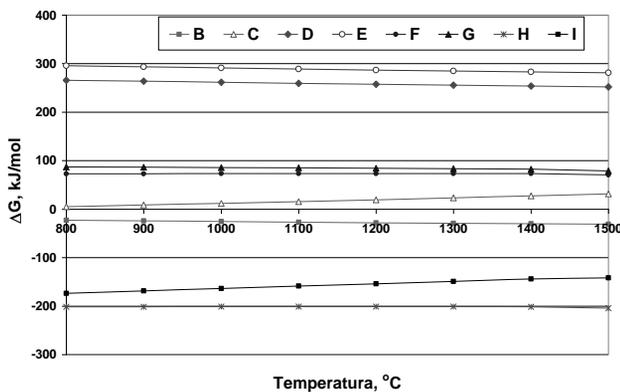


Fig. 3. Thermodynamic potential  $\Delta G$  changing in function of temperature for reactions B, C, D, E, F, G, H and I

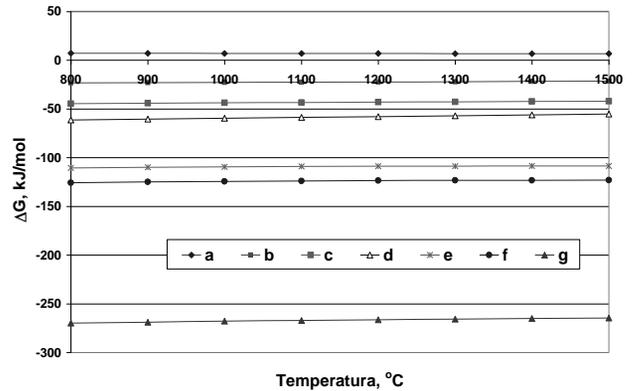


Fig. 4. Thermodynamic potential  $\Delta G$  changing in function of temperature for reactions a, b, c, d, e, f and g

Above 1050°C, zirconium silicate  $\text{ZrSiO}_4$  (Fig. 2) can undergo decomposition to  $\text{ZrO}_2$  and  $\text{SiO}_2$  oxides. The interface temperature at the moment of mould pouring is comprised in a range of 1420 to 1460°C, in which the thermodynamic potential assumes the lowest negative value. From Figure 3 it follows that the negative value of potential  $\Delta G$  indicates that only reactions B, I and H have the chance of occurring. So, in the fields of reaction, from the side of mould surface, the presence of hafnium oxides  $\text{HfO}_2$  (especially in MAR-247) and aluminium oxides  $\text{Al}_2\text{O}_3$  can be expected. On alloy surface, increased concentration of Zr and Si and of oxygen is possible in all alloys.

On the other hand, from Figure 4 it follows that, within the examined temperature range, only the reaction of the aluminate decomposition is impossible in terms of thermodynamics. Other reactions are characterised by a negative value of  $\Delta G$ . The most intense course should have the reactions between cobalt aluminate and hafnium (g), tantalum (f), niobium (e), aluminium (d) and titanium (c). So, in the fields of reaction, from the side of mould surface, one can expect the presence of oxides of hafnium  $\text{HfO}_2$ , tantalum  $\text{Ta}_2\text{O}_5$  (especially in MAR-247), aluminium  $\text{Al}_2\text{O}_3$ , titanium  $\text{TiO}$  and  $\text{TiO}_2$  and niobium  $\text{NbO}_2$ . On the external casting surface one can expect increased concentration of oxygen (in all alloys) and cobalt, while in the surface layer of MAR-247 casting, increased concentration of Zr and Si, as a consequence of the strongly reducing effect of Hf and Ta (both being active alloy constituents) is highly probable. The negative value of the thermodynamic potential of the chemical reactions is for these constituents the highest. Hence, in the surface layer of casting, the content of Hf and Ta can be much lower than in the regions lying deeper in the casting.

The results of thermodynamic calculations were confirmed by observations under microscope and X-ray microanalysis in selected regions of the mould and casting surface. Some results of this analysis are shown as an example in Table 1.

In the surface layer, besides the expected elements, i.e. Si, Zr, Al and Co, other constituents of the cast alloy appear as well. This mainly refers to Cr, Ni and Ti. High reactivity of hafnium and its presence in the surface layer of MAR-247 casting is confirmed.

The next stage of the investigations covered microanalysis of the chemical composition of metallic precipitates present in external mould layer and on the casting surface. Figure 5 shows example of the surface structure of a mould with modifying

coating after casting of MAR-247 and chemical composition of selected precipitates.

Table 1.

Chemical composition in selected mould surface area after alloy pouring

Cast alloy	Content, wt. %							
	Al	Si	Ti	Cr	Co	Ni	Hf	Zr
IN-100	4,2	24,6	2,1	0,3	3,8	0,8	-	64,2
IN-713C	3,5	23,9	-	1,0	5,3	-	-	66,3
MAR-247	3,5	20,8	0,1	0,5	4,3	2,8	3,3	64,7

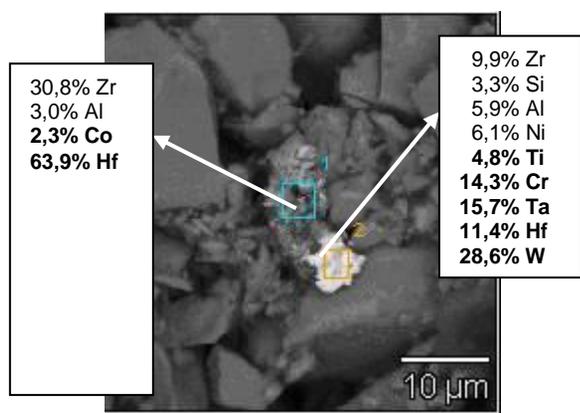


Fig. 5. Microstructure and chemical composition of precipitates in surface layer of mould poured with MAR-247

On the mould surface there are particles of „foreign” precipitates in which the presence of hafnium in amounts from 8,2 to 84,1 wt.% has been detected. In „bright” fine precipitates, tantalum was present in amounts of even up to 16 %. Probably these are the oxides of hafnium and tantalum. The presence of such alloying constituents as Ni, W, Ti and Cr proves alloy penetration into the microcracks on the mould surface (thermal and chemical effect).

On the casting surface there are particles of oxides of Si, Zr and Ti as well as Hf and Co (especially in MAR-247). In addition, „patches” with high content of the main alloying elements (Ni, Cr, etc.) „sticking” to the surface occur, proving intense thermal and chemical effects taking place at the mould surface – molten nickel alloy interface.

## 5. Conclusions

It has been proved that, at the mould surface – molten alloy interface, chemical reactions can take place between the mould components and molten alloy. The result of these reactions is the formation of "zones of influence" on the mould surface and in the subsurface area of molten alloy. Theoretical considerations and thermodynamic calculations were supported and verified by microanalysis of the chemical composition of „foreign” precipitates on the surface of the test moulds and castings.

In the regions of reaction, from the side of mould surface, one can expect the presence of oxides of hafnium  $\text{HfO}_2$ , tantalum  $\text{Ta}_2\text{O}_5$  (especially in MAR-247!), aluminium  $\text{Al}_2\text{O}_3$ , titanium  $\text{TiO}$  and  $\text{TiO}_2$  and niobium  $\text{NbO}_2$

On casting surface, the particles of oxides of Si, Zr and Ti, Hf and Co (especially in MAR-247) are observed, which proves intense thermal and chemical effects taking place at the mould surface – molten nickel alloy interface.

## Acknowledgements

Financial support of Structural Funds in the **Operational Programme - Innovative Economy (IE OP)** financed from the European Regional Development Fund - Project No POIG.0101.02-00-015/08 is gratefully acknowledged.

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Nickel-based superalloys have limitations at very high temperatures, and so components in the combustion chamber, where the temperature may reach as high as 1100 K, are usually made of cobalt-based alloys. The cobalt-based superalloys (Table 2) are not as strong as nickel-based superalloys, but they retain their strength up to higher temperatures. A somewhat lower coefficient of thermal expansion and better thermal conductivity than the nickel superalloys make cobalt alloys good candidates for applications where thermal fatigue is a critical design issue.

Figure 4: Ceramic investment casting mold with single-crystal starter at the bottom of the plate and single-crystal plate following directional solidification and removal of ceramic mold (courtesy of A. J. Elliott). The interfacial reaction between the ceramic substrates and alloys occurred at high temperature. Though the ceramics had different microstructures, similar continuous Y<sub>2</sub>O<sub>3</sub> reaction layer with thicknesses of about 25 μm at the alloy-ceramic interface in MgO, Al<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub> systems formed. The average area percentage of oxides in the alloy matrices were 0.59% (MgO), 0.11% (Al<sub>2</sub>O<sub>3</sub>), 0.09% (ZrO<sub>2</sub>), and 0.02% (Y<sub>2</sub>O<sub>3</sub>), respectively. The alloys, after reacting with MgO ceramic, had the highest inclusion content, while those with the lowest content were in the Y<sub>2</sub>O<sub>3</sub> system. Y<sub>2</sub>O<sub>3</sub> ceramic was the most beneficial for vacuum induction melting of high-purity Y-containing Ni-based alloys.

Future Activities. Conclusions. Advanced Thermal Storage System with Novel Molten Salt. December 8, 2011 – April 30, 2013. Matthieu Jonemann. Halotechnics has developed critical knowledge of the salt/ceramic interaction at elevated temperatures, and this knowledge is being applied to the design of a commercial size system. The technical design details and experimental results are presented and discussed. They include the design of the internally insulated 700 °C tank, the thermal-fluid properties of the molten salt, the pump performance, the corrosion testing results, and the lessons learned.

2 The shape and type of tetrahedral elements used in Finite Element Analysis (FEA) can influence the accuracy of results.

23. Acronyms and Abbreviations ACS American Ceramic Society. —Corresponding author. Tel: (+34) 947258907. But the same chemical system should be employed in both sides of HTX, so that compatibility of structural alloy with two different species is not required at the working temperature. [109]. The graphical analysis of the parameters given in the latter one shows an anomalous value for the 33 mol% ZrF<sub>4</sub> compositions (whose standard deviation is higher, as for the 60 and 80 mol%). But, if we interpolate between 40 and 45 % for the usual 42 mol% the curve fits with the others, which shows the accuracy in this molar concentration range. The measurement of thermal properties in molten salts has been pointed out by many authors as an arduous task, specially in the case of conductivity. Statistical analysis of the experimental results using techniques like fractional factorial test and Taguchi experimental design is presented. Spraying parameters such as plasma arc current, torch input power, arc voltage, surface roughness of the substrate are identified as the significant factors affecting the efficiency of coating deposition.

2.3.6 Thermal Spraying. It is the generic category of material processing technique that apply consumables in the form of a finely divided molten or semi molten droplets to produce a coating onto the substrate kept in front of the impinging jet. The nature of bonding at the coating-substrate interface is not completely understood. It is normally assumed that bonding occurs by the mechanical interlocking.