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Criterion for selection the optimal physical and chemical properties of cobalt aluminate powder used in investment casting process

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Abstract

The aim of this work was to determine physical and chemical properties of cobalt aluminate ($CoAl_2O_4$) modifiers produced by different companies and the influence of different types of modifiers on the grain size of high temperature creep resisting superalloys: Inconel 713C, René 77 and MAR-M 509.
The first stage of the research work took over the investigations of physical and chemical properties of cobalt aluminate manufactured by three different companies: Remet, Mason Color and Permedia Lublin. There were determined the grain size distribution of cobalt aluminate powder, the average diameter and morphology of powder particles, phase composition, as well as sodium and cobalt content, pH value of water suspension and the bulk density. In the next step, the ceramic moulds were made with different kind of cobalt aluminate (Mason Color, Remet, Permedia Lublin) and its concentration (0, 5%) in the primary slurry. The samples of stepped shape were poured in the ceramic moulds prepared earlier. The average grain size of the γ phase was determined on the stepped samples.
It was established that physical and chemical properties of cobalt aluminate modifier are different up to the manufacturer. For example the modifiers manufactured by Permedia; Mason Color and Remet companies have different the average diameter of particles- $d_{50} =$),68; 6,49 i 7,36 μm, and also cobalt content $\bar{C}_{Co}$ =32,53%; 39,43% i 34,79%mass, respectively. The grain size of γ matrix of superalloys depends on the kind of used inoculant. The best grain refinement of the matrix of superalloys: Inconel 713C, René 77 and MAR-M 509 was observed in the castings modified with the use of Mason Color modifier. On the grounds of literature data and obtained results it was established that the cobalt content of cobalt aluminate influences the intensity of nucleation process during the crystallization of superalloys: Inconel 713C, René 77 i MAR-M 509.

Keywords: Investment casting, Nickel and cobalt based superalloys, Macrostructure, Modification, Cobalt aluminate

1. Introduction

Nickel and cobalt based superalloys castings are produced by investment casting methods which are being improved constantly. They are used for critical elements of aircraft engines; so called „Flight safety parts" (FSP). They are subject of exceptional requirements in the production and control respects. These elements have to fulfill a lot of requirements of the consumer's standards dealing with chemical composition, microstructure – and first of all the grain size, the microstructure of matrix, the type and relative volume of carbides, microporosity, and the structure roughness. This requirements apply to mechanical properties at the room temperature and creep strength with measurements of strain after breach[1-3].

Properties of casted blades of nickel and cobalt based superalloys are determined by grain size and orientation, morphology and spacing of γ', carbide phases, and the matrix microstructure [1, 3-5]. Turbine blades produced by conventional precision casting methods have coarse and inhomogeneous grain structure [6, 7]. Such a material often does not fulfill basic requirements, which concern mechanical properties for the stuff used in aeronautical engineering. The incorporation of controlled grain size improved mechanical properties [8, 12]. This control of grain size in the casting operations was accomplished by the control of processing parameters such as casting temperature, mould preheating temperature, and the use of grain nucleates in the face of the mould. For nickel and cobalt based superalloys it was found that cobalt aluminate ($CoAl_2O_4$) has the best nucleating effect [9]. The important factor, which influences the grain size and the quality of the casting is the amount of modifier introduced into the mould. The amount of cobalt aluminate in the primary slurry is highly variable, (ranging from 1 to 10% or higher) and depends on the specification requirements, the alloy being casted, the section thickness, and other factors [9-11]. On the grounds of the obtained results it was found that the optimal concentration of cobalt aluminate powder in ceramic mould to produce casting elements made from Inconel 713C superalloy is about 5-6%mass, however in case of ŻS6K - 2%mass. The higher concentration of modifier does not change the grain size significantly and does not improve mechanical properties of castings. So the next step in the study is to define what chemical and physical properties should cobalt aluminate characterize in order to archive the best nucleating effect.

Cobalt aluminate ($CoAl_2O_4$) belongs to the group of complex oxides with general formulas AB_2O_4 in which A ions are divalent cations occupying tetrahedral sites and B ions are trivalent cations in octahedral sites. Cobalt aluminate is typically produced by firing cobalt oxide (Co_3O_4) and aluminum hydroxide ($Al(OH)_3$) together at high temperatures (1200÷1300°C). During annealing the solid state reaction occurred between cobalt oxide and aluminum hydroxide what results in a spinel structure of cobalt aluminate compound [8]. It was found [14] that when a molar ratio of Co and Al is not stoichiometric, inversion between Co and Al may take place and as a result not only Al but also Co cations will occupy the octahedral sites: $Co^{2+}(Al^{3+}Co^{3+})O_4 – Co_2AlO_4$. So the increase of Co content in precursors cause that more phases with different Co content is formed with the same spinel structure.

The next stage of production of cobalt aluminate powder is milling the product to a fine particle size, typically 99,9 passing through 44 microns [8-9].

The goal of present work was the settlement of basic physical and chemical properties of cobalt aluminate powder produced by different companies (Remet, Mason Color and Permedia Lublin) and theirs influence on the grain size of the castings made from nickel (Inconel 713C, René 77) and cobalt (MAR-M 509) based superalloys.

2. Materials and methodology

To find the difference between the nucleates produced by different companies, physical and chemical properties were investigated. There were determined the grain size distribution of cobalt aluminate powder, the average diameter and morphology of powder particles, as well as sodium contamination and cobalt content, pH value of water suspension and the bulk density.

The particle size distribution and the average diameter of cobalt aluminate powder were measured by the use of X-ray disc centrifuge BI-XDC. The suspensions of cobalt aluminate powder (1.4g) and 0.01% water solution of sodium pyrophosphate (60÷70cm^3) were prepared. The agglomerates of cobalt aluminate particles were divided in ultrasonic washer.

The phase structure of cobalt aluminate was identified by X-ray diffractometer ARL X'TRA. The identification of phase components was made by the comparison of obtained results with PDF data [16].

The morphology of cobalt aluminate particles were determined with the use of transmission electron microscope Tesla BS 540. The microscopy samples were prepared by dispersing the cobalt aluminate in ethanol and shaking in ultrasonic washer. Such a suspension was applied on a copper grid with a carbon film.

There were investigated other properties of cobalt aluminate powder in the laboratory of Permedia Lublin company, such as: pH value of aqueous suspension in accordance with PN-EN ISO 787-9 standard, and bulk density in accordance with PN-86 C-04404/03 standard.

The sodium content in modifiers was determined by AAS (Atomic Absorption Spectrometry) method whereas the cobalt concentration - by classic complexometric method with 0.1M EDTA solution in the presence of murexide [17]. Before complexometric titration samples ($CoAl_2O_4$) had been melted with acid flux (potassium pyrosulfate - $K_2S_2O_7$) at the temperature of 250÷300°C. As a result of melting it had been received soluble in water, aluminum and cobalt sulfates: $CoAl_2O_4 + 4K_2S_2O_7 \rightarrow CoSO_4 + Al_2(SO_4)_3 + 4K_2SO_4$. After melting samples were dissolved in sulfuric acid and diluted in water.

The alloys used in this study were Inconel 713C, René 77 and MAR-M 509. Chemical compositions of the used melt is given in Table 1. Modified and no modified stepped samples were casted by precision casting method (Fig. 1). In order to achieve the modification effect on the surface layer of the casting the composition of the first layer of ceramic mould undergone changes – reacting directly with the liquid metal. The 5% of cobalt aluminate powder in zirconium flour was added into the primary slurry during preparation of ceramic face mould.

Table 1.
Chemical composition of nickel superalloys: Inconel 713C, René 77 and MAR-M 509 (%mass)

Alloy	Elements content, % mass													
	Ni	Cr	Co	Mo	W	Ta	Al	Ti	C	B	Zr	Fe	S	Si
Inconel 713C	73.88	13.9	0.04	4.49	-	0.015	6.51	0.92	0.092	-	0.07	0.05	0.007	0.003
René 77	57.087	14.61	15.32	4.52	-	0.05	4.73	3.49	0.07	0.015	0.01	0.08	0.001	0.017
MAR-M 509	9.82	22.88	54.6	-	6.89	3.79	-	0.18	0.55	0.003	0.35	0.16-	-	0.05

However, different kinds of modifier (manufactured by three different companies: Mason Color, Remet and Permedia Lublin) were used to prepare the first slurry.
Apart from the cobalt aluminate powder, the first layer of ceramic mould consisted of: the binder – colloidal silica: product from Dupont called Ludox SK: SiO_2=25% and pH=4÷7; refractory flour - zircon flour 325; additions – wetting agent: Vicawet 12, antifoam: Burst RSD–10.

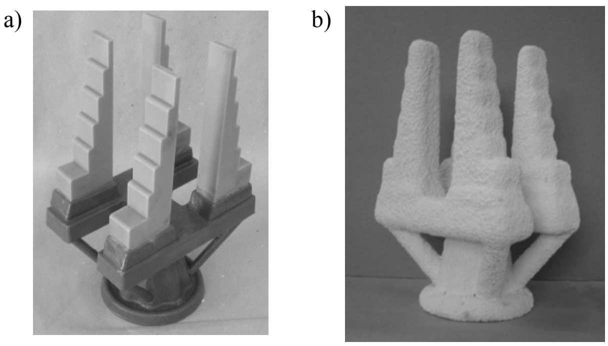

Fig. 1. Stepped wax pattern assembled in a wax tree a) and ceramic mould for casting of stepped samples b)

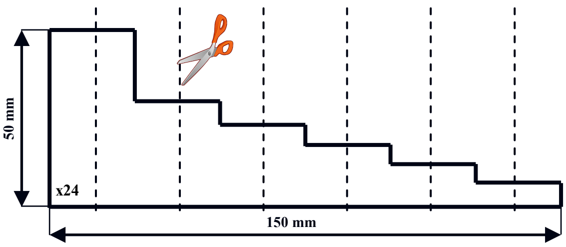

Fig. 2. Dimensions of stepped castings

Stepped samples were cut in order to make an observation of microstructure on the cross sections of separate step casting (Fig. 2). Polished sections were etched with reagents: 10g $CuSO_4$ + 50cm^{3}HCl + 50cm^3 H_2O and 100cm^3 HCl + 5cm^3 H_2O_2. Stereological parameters of microstructure were determined for cross sections of steps. Macro- examination was performed by the means of the image analysis software APHELION 2.3. The average surface area of grain cross section - $\bar{A}$, standard deviation - s were calculated. Images of grains of γ matrix were obtained by the means of stereoscope microscope Zeiss Stem 2000-C equipped with the digital camera.

3. Results and discussions

On the basis of results obtained from particle size investigations it was found that the particle size of the nucleate from Permedia Lublin firm has the finest particles and exhibits the least scatter from 0.138÷2.646μm – Fig. 3. The average diameter (median) of particles was determined from the plot (Fig. 3): Mason Color d_{50}=6.49μm, Remet d_{50}=7.37μm, Permedia Lublin d_{50}=0.683μm. Powders fabricated by Mason Color and Remet are characterized by similar average diameter of particles but the $CoAl_2O_4$ from Remet is characterized by great degree of particle coarseness (d = 0.54÷40,24μm) (Fig. 3c).

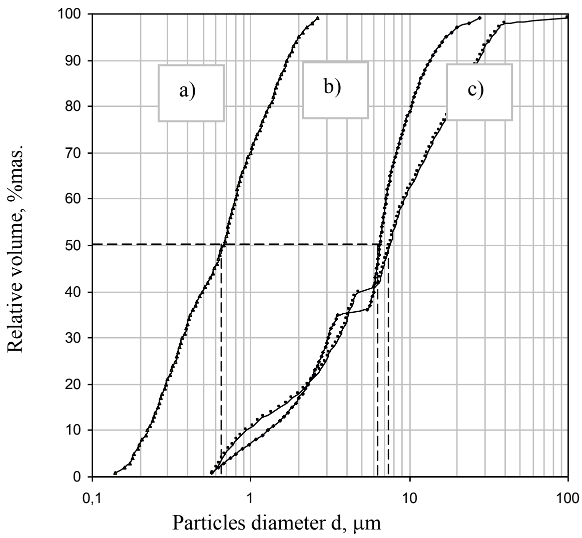

Fig. 3. Integral distribution plot of particle size of cobalt aluminate powder: a) Permedia, b) Mason Color, c) Remet

The observations of cobalt aluminate powders by the use of transmission electron microscopy confirmed that all of them posses fine particles (Fig. 4). It was not observed the difference in morphology of cobalt aluminate particles. However, cobalt aluminate from Permedia Lublin company has the fineness particles.

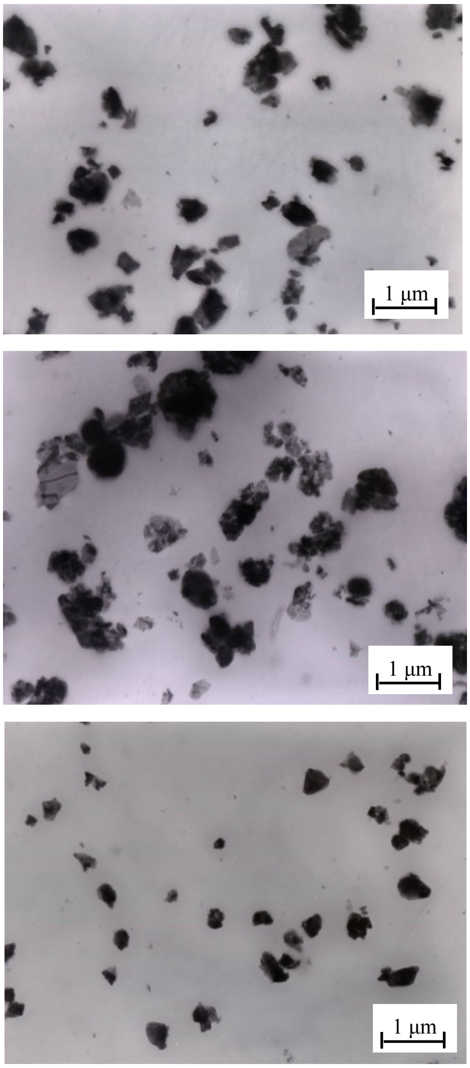

Fig. 5. Cobalt aluminate powders manufactured by companies: a) Mason Color, b) Remet, c) Permedia Lublin

Figure 5 shows the X-ray diffraction patterns of one exemplary cobalt aluminate powder. The results of X-ray diffraction analysis for all investigated powders were similar. A more detailed analysis of the XRD patterns under higher magnification let to affirm the existence of two phases $CoAl_2O_4$ and Co_2AlO_4. Both of them have the same spinel cubic (Fd3m) structure differing only slightly in the size of lattice parameter: $CoAl_2O_4$ - a=0.810664nm and Co_2AlO_4 – $Co^{2+}(Al^{3+}Co^{3+})O_4$ - a=0.8086nm.

It was proved [12] that surface grain refinement of the superalloy castings is mainly due to the nucleation effect of the cobalt particles produced during casting. Cobalt aluminate reacts at high temperature in vacuum with the elements such as Al, Cr, etc. contained in superalloy melt and Co in $CoAl_2O_4$ is displaced by this elements to form nearly pure Co fine particles. These particles have FCC structure with lattice parameter a=0.354nm what is similar to the matrix structure of superalloy (FCC with lattice parameter a = 0.356÷0.359nm). Agglomerates of Co particles absorbs the atoms from the liquid phase and they are incorporated in the structure. Therefore it's possible that higher concentration of cobalt in cobalt aluminate causes the possibility of formation greater quantity of pure cobalt and so more nucleates in the liquid alloy. That is why the cobalt content in the cobalt aluminate was evaluated (Table 2).

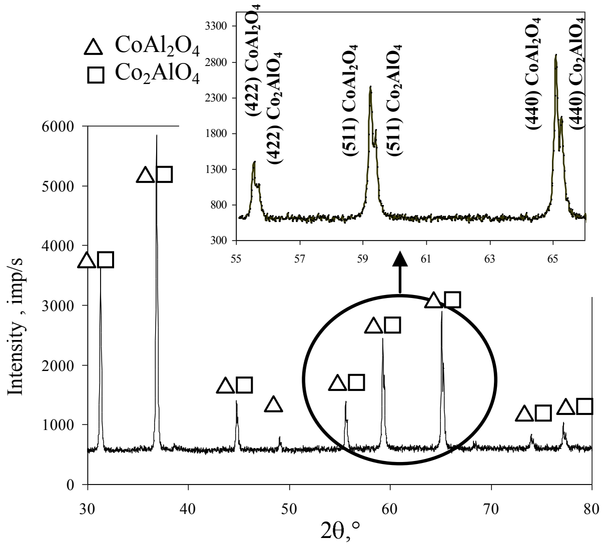

Fig. 5. Diffraction pattern of cobalt aluminate (Mason Color) powder

Table 2.
Cobalt content in the modifier powder of Mason Color, Remet and Permedia Lublin

Kind of modifier/ series	**Co content C_{Co}, %mass**	**Average content of Co, $\bar{C}_{Co}$, %mass**
Mason Color/1	39.45	
Mason Color/2	39.29	**39.43**
Mason Color/3	39.55	
Remet/1	34.90	
Remet/2	34.72	**34.79**
Remet/3	34.75	
Permedia Lublin/1	32.64	
Permedia Lublin/2	32.21	**32.53**
Permedia Lublin/3	32.73	

The results of cobalt content investigations are the mean values received from three separately conducted measurements. The higher concentration of Co is in Mason Color powder 39,43% and the lowest in Permedia Lublin one 32,53%. Intermediately it is possible to affirm that Mason Color powder has the greater amount of Co_2AlO_4 phase (with higher contamination of Co) than Remet and Permedia Lublin ones.

The quality of ceramic moulds and in consequence the quality of the castings depends on the thickness of the ceramic layer applied on the wax pattern. In turn, the thickness of the ceramic layer is a function of viscosity of the ceramic slurry. The decrease of pH value of ceramic slurry with colloidal silica results in higher viscosity and thickness of ceramic layer. It was established that pH value of cobalt aluminate should range from 8.5 to 10 [15]. Therefore, the measurements of pH value of cobalt aluminate water suspension and an alkaline elements contamination (sodium contamination) were performed. It was proved that modifiers manufactured by companies: Mason Color, Remet and Permedia Lublin have different pH value of aqueous suspension. The higher alkalinity characterizes the powders Mason Color - pH=9.93 and Remet – pH=9.42 companies (Table 3). The alkalinity of Permedia Lublin powder is lower and pH is 7.95 (Tab. 3). The results of sodium content investigations indicate that pH value of cobalt aluminate of aqueous suspension mostly depends on the sodium contamination C_{Na} (Tab. 3).

In the next stage of investigations it was determined the bulk density of the powders which characterizes the degree of surface area development of the particles. The value of surface area of particles influence on the mould compaction. The mould compaction influence on the mould strength and permeability. The first layer of the mould should have lower permeability in compare to the other layers. It was established that the higher degree of surface area development of particles has the cobalt aluminate manufactured by Permedia Lublin. The bulk density of this powder is two times lower in comparison to the powders from Remet and Mason Color company (Tab 3). It's possible that premeability of the mould modified by Mason Color and Remet powders is lower than permability of mould modified by the use of Permedia Lublin powder.

Table 3.
Physical and chemical properties of cobalt aluminate powders

Properties	Kind of the powder		
	Mason Color	Remet	Permedia Lublin
PH of aqueous suspension	9,93	9,42	7,95
Na content	545ppm 0,05%	209 ppm 0.02%	17 ppm 0.001%
Bulk density	1,242kg/dm^3	1,216kg/dm^3	0,607kg/dm^3

The effect of modification of the surface layer of the castings made from superalloys: Inconel 713C, René 77 and MAR-M 509 was investigated on the cross sections of the castings. The reduction of grain size of invested alloys after modification was obtained independently from the kind of used cobalt aluminate (Fig. 6.). The measurements of the average surface area of grain cross section of γ matrix in the cross section of casting revealed the differences in the size of grains up to the type of modifier. From Figure 6 one can see that the most coarse grain structure characterize the nonmodified castings. The finest macrostructure characterizes the samples which were modified by 5% of Mason Color and Remet powders with higher contamination of cobalt: 39.43%, 34.79 respectively. At the lowest cobalt contents 32.53% in $CoAl_2O_4$ (Permedia Lulin) the overall grain size is much larger.

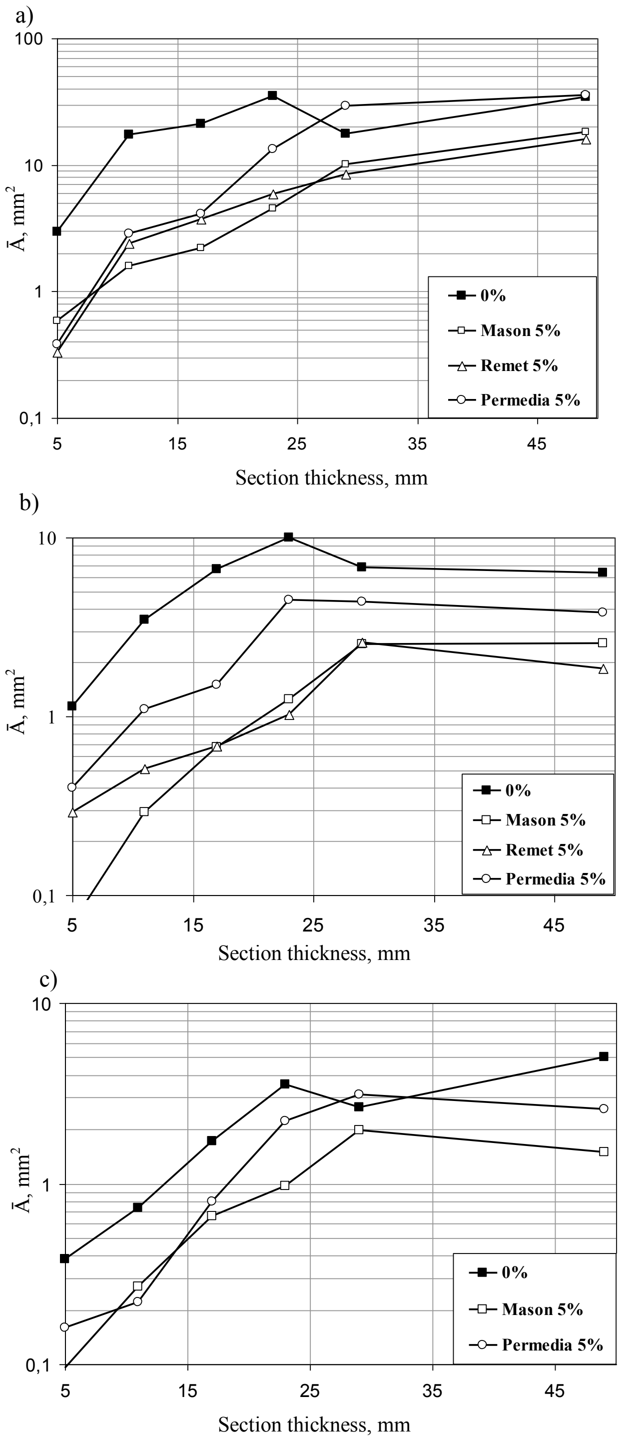

Fig. 6. The effect of varying the casting section thickness and modifier content on the variation of the average surface area of grain cross section Ā - measured on superalloy; a) Inconel 713C, b) René 77, c) MAR-M 509

Analysis of performed investigations revealed that cobalt content of cobalt aluminate - C_{Co} influences the grain size of γ matrix of superalloys: Inconel 713C, René 77 and MAR-M 509, especially in case of large sections. This results are in agreement with the effects obtained by Guerra and Niles [16] who studied the influence of cobalt content of modifier ($CoAl_2O_4$) on grain refinement of high chrome - nickel base alloy Inconel 625. They affirmed that 40% cobalt content yields equivalent results to a 44% cobalt product, with both giving better grain size reduction then the lower cobalt content samples. The 36% cobalt content product produced results which were close to the 40 or 44% cobalt products, but just slightly larger. At lowest cobalt contents (28 and 32%), the grain size was much larger than for higher levels [15].

4. Conclusions

Physical and chemical properties of cobalt aluminate modifier are different up to the manufacturer. The modifiers have different grain size distribution. The cobalt aluminate powder from Permedia Lublin company has the finesses particles (d_{50} = 0.68μm) whereas the modifiers from Mason Color and Remet companies have similar the average diameter of particles (d_{50} = 6,49μm; d_{50} = 7,36μm, respectively).

All investigated modifiers consist of two phases $CoAl_2O_4$ and Co_2AlO_4 with the same spinel structure. However, Mason Color powder has the greater relative volume of Co_2AlO_4, than Remet and Permedia Lublin ones. The powders have different pH value of aqueous suspensions which is relate with a sodium content. The Mason Color and Remet powders have the pH value in the range from 8.5 to 10 but the alkalinity of Permedia Lublin powder is too low – 7,95.

The modification of the surface layer of superalloys Inconel 713C, René 77 and MAR-M 509 with the use of all inoculants results in grain refinement of γ matrix . However the grain size of the superalloy depends on the kind of used inoculant. Higher cobalt level of product (Mason Color and Remet) gave better grain size reduction than the lower cobalt content in the powder (Permedia Lublin). From this test, a 35% cobalt content yielded very close results to a 40% cobalt product. The 32% cobalt content products results in smaller grain size reduction.

It has to be added that it was not determined what impact might have the particle size of inoculant - $CoAl_2O_4$ on the grain refinement of superalloys. It might be supposed that small difference in the particle size of the products did not affect on the performance. That is why the criterion for selection of particles size of the modifier is related with the grains size distribution of refractory flour.

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