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Surface modification, microstructure and mechanical properties of investment cast superalloy

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Properties

ABSTRACT

Purpose: The aim of this work is 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, the microstructure and mechanical properties of high temperature creep resisting superalloy René 77.
Design/methodology/approach: 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 of the powder particles, phase composition, cobalt contamination. 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 and cylindrical shape were poured in the ceramic moulds prepared earlier. The average grain size of the γ phase, was determined on the stepped samples. The microstructure investigations let to examine the influence of the surface modification on the morphology of γ ' - phase and carbides precipitations. Samples were turned from cylindrical castings for mechanical properties investigations: creep tests.
Findings: Modification of the face coat of ceramic mould results in the reduction of the grains size of γ matrix and disintegration of carbide precipitates. It results in the improvement of mechanical properties of the alloy. On the grounds of the obtained results, it was found that the type of used modifier influenced the grain size of the alloy and its mechanical properties.
Research limitations/implications: The established physical and chemical properties of modifier let to get better control of grain size of the castings and their quality what will result in decrease of defective products.
Originality/value: It was proved that the effectiveness of cobalt aluminate modifier as an inoculant depends not only on its concentration in ceramic slurry but on its chemical composition. The researches allowed to find the optimal concentration of Co in $CoAl_2O_4$ to produce casting elements made from superalloy René 77.
Keywords: Nickel superalloys; Surface modification; Cobalt aluminate; Grain refinement; Mechanical properties

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1. Introduction

The nickel based superalloy René 77 is used for critical elements of aircraft engines such as turbine blades or turbine discs. These elements are usually produced by the investment casting method, which is used in production of parts of turbine engines of a high quality [1-5].

In the investment casting process an expendable pattern is made, usually by injecting a special wax- based material into a metal mould (Fig. 1). Then this pattern is dipped in a ceramic slurry, covered with ceramic stucco and left for drying. The dipping and stuccoing are repeated until a mould of necessary thickness is obtained. Having completely removed the wax by a steam autoclave the mould is fired. The mould is preheated to a specific temperature and filled with superalloy melt. When a casting is accomplished by the conventional method the shell, (mould) is discarded [6].

a) b)

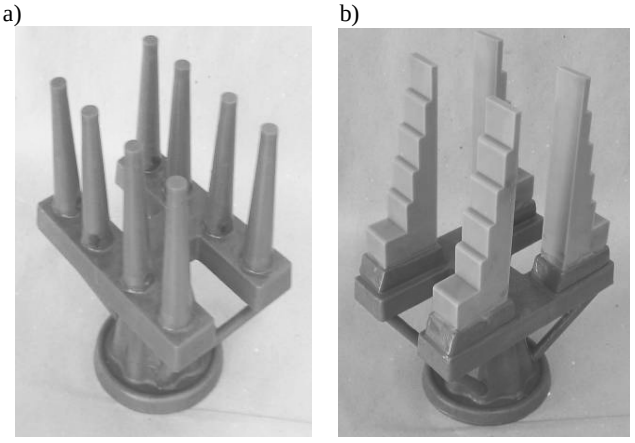


Fig. 1. Assembled wax tree of cylindrical (a) and stepped (b) wax pattern

Turbine blades produced by conventional precision casting method have coarse and inhomogeneous grain structure. Such a material does not fulfil basic requirements, which concern mechanical properties for the stuff used in aeronautical engineering [7-10]. As to obtain the optimum creep resistance, the incorporation of controlled grain morphology is indispensable. This control of grain size in the casting operation was achieved by the control of process parameters such as casting temperature, mould preheating temperature and by the chemical method of refinement of cast structure. The chemical method of grain refinement of superalloys during casting process is realized by the addition of inoculants (modifiers) into the interior surface of investment mould. Important factors that influence the grain size and the quality of the casting are: the type of modifier and the amount of modifier introduced into the mould. In the investment casting process usually the cobalt compounds has been used as nucleation catalysts. These have been cobalt and cobalt base compounds such as: cobaltous oxide, cobaltous hydroxide, cobaltosic oxide, cobalt silicate and cobalt aluminate. It was found that the use of pure cobalt or not very stable cobalt oxides can lead to dipcoats stability problems, spalling and variability of nucleation results because of chemical reaction which occurs during the mould preparing, dewaxing and annealing [11,12].

For nickel and cobalt based superalloys it was found that a stable phase with spinel structure – cobalt aluminate ($CoAl_2O_4$) has the best nucleating effect. 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 [1, 12-14]. 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 superalloy René 77 is about 5-6%mass [13]. 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 characterize cobalt aluminate in order to achieve the best nucleating effect.

Cobalt aluminate is produced by firing cobalt oxide (Co_3O_4) and aluminum hydroxide ($Al(OH)_3$) together at high temperature (1200-1300°C). During annealing the solid state reaction occurres between cobalt oxide and aluminum hydroxide what results in a spinel structure of cobalt aluminate compound [12]. It was found that increase of Co content in precursors causes that more phases with different Co content is formed with the same spinel structure [15,16]. The final product is than milled to a fine particle size, 99.9 passing through 44 microns [12].

The goal of present work was the settlement of basic physical and chemical properties of cobalt aluminate powder produced by different companies and its influence on the grain size and the microstructure, and in consequence, mechanical properties of high temperature creep resisting superalloy René 77.

2. Materials and methodology

The alloy used in this study is René 77. Chemical composition of the used melt is given in Table 1.

Stepped and cylindrical samples were casted by precision casting method respectively for microstructure and mechanical properties investigations [13,14]. 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. However, different kinds of modifier (manufactured by three different companies: Mason Color, Remet and Permedia Lublin) were used to prepare the first slurry.

Table 1.
Chemical composition of nickel superalloy René 77 (%mass)

Ni	Cr	Co	Mo	Ta	Al	Ti	C	B	Zr	Fe	S	Si
57	14.61	15.32	4.52	0.05	4.73	3.49	0.07	0.015	0.01	0.08	0.001	0.017

To find the difference between the nucleants produced by different companies physical and chemical properties were investigated. 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 phase structure of cobalt aluminate was identified by X-ray diffractometer ARL X'TRA. Observations of the cobalt aluminate powders with the use of transmission electron microscope Tesla BS 540 let to determine the morphology of cobalt aluminate particles. 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.

Cobalt content in modifiers was determined 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.

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 Marble's reagent ($10gCuSO_4$ $+50cm^3HCl$ $+50cm^3H_2O$). 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 - Ā, 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. Microstructure investigations were performed by the use of light microscope Nikon Epiphot 300 and scanning electron microscope (SEM) HITACHI S-3400N equipped with EDS spectrometer.

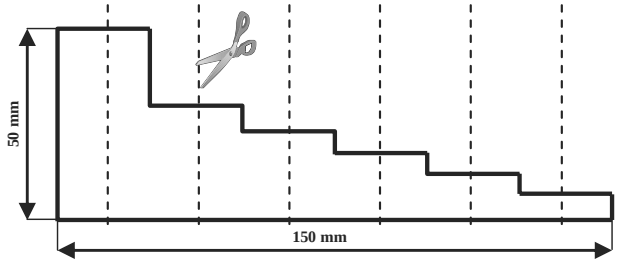


Fig. 2. Dimensions of stepped castings

Samples of 6.25 mm diameter were turned from cylindrical castings for mechanical properties investigations [13]. Creep tests were made by the use of creep machine W+B Walter+BaiAG according to ASTM E139 standard [18]. The operating condition of creep tests were as follows: the temperature T= 982ºC and the stress σ_p= 152 MPa. The total duration of creep test t_z, unit elongation A_4, percentage reduction of area of the specimen Z and steady state creep rate $\dot{\varepsilon}_s$, were evaluated.

3. Results and discussion

On the basis of results obtained from particle size investigations it was found that the particle size of the nucleate from Permedia Lublin firm is the finest particles and the exhibits the least scatter from 0.138-2.646 μm – Figs. 3, 4. The average diameter (median) of particles was determined from the plot (Fig. 3): Mason Color d_{50}=6.49 μm, Remet d_{50}=7.37 μm, Permedia Lublin d_{50}=0.683 μm

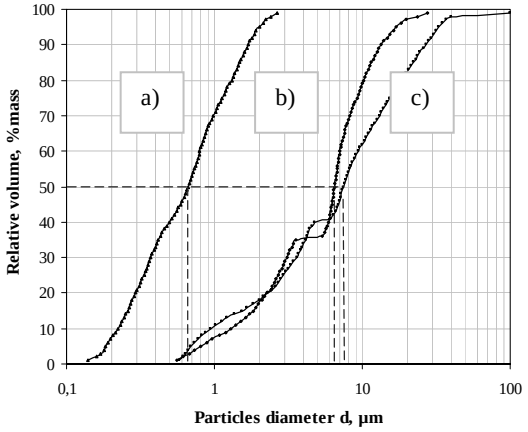


Fig. 3. Integral distribution plot of particle size of cobalt aluminate powder: a) Permedia, b) Mason Color, c) Remet

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 (Figs. 3, 4).

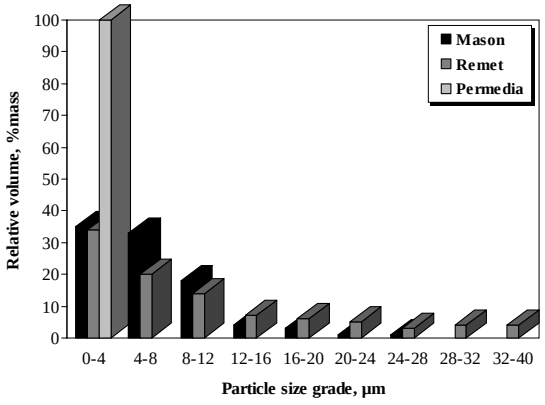
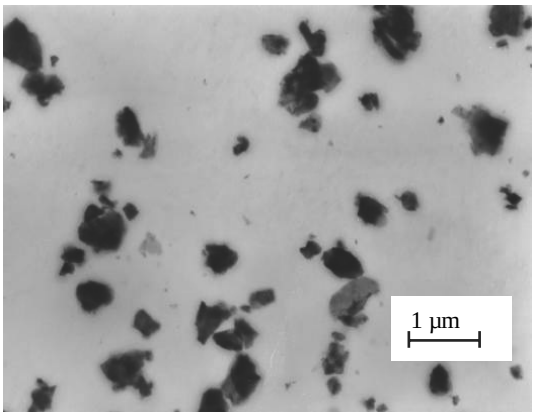


Fig. 4. Particle size distribution of cobalt aluminate powder from different companies

The observations of cobalt aluminate powders by the use of transmission electron microscopy confirmed that all of them posses fine particles (Fig. 5). It was not observed the difference in morphology of cobalt aluminate particles.

a)



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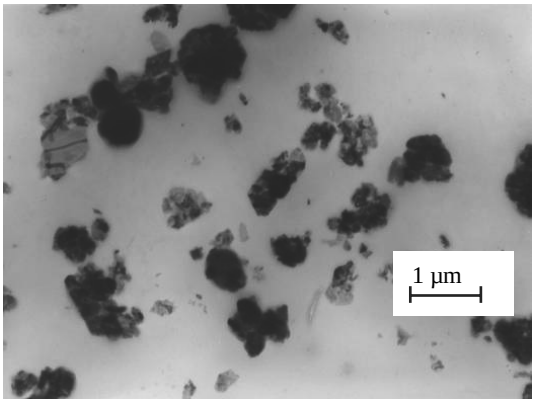

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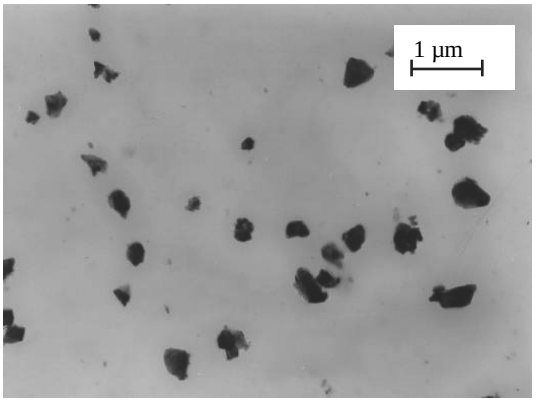
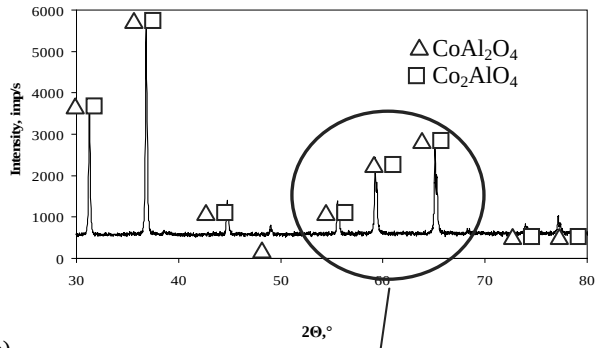


Fig. 5. Cobalt aluminate powders manufactured by companies: a) Mason Color, b) Remet, c) Permedia Lublin

Figure 6 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 sligthtly in the size of lattice: $CoAl_2O_4$ - a=0.810664 nm and Co_2AlO_4 – $Co^{2+}(Al^{3+}Co^{3+})O_4$ - a=0.8086 nm.

a)



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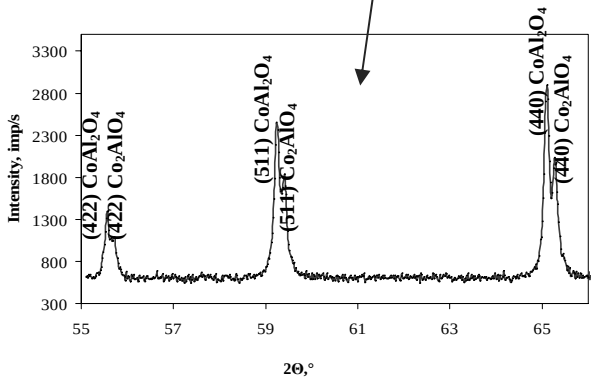


Fig. 6. Diffraction pattern of cobalt aluminate (Mason Color) powder

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=0.354 nm what is similar to the matrix structure of superalloy (FCC with lattice parameter a= 0.356-0.359 nm). Agglomerates of Co particles absorbs the atoms from the liquid phase and they are incorporated in the structure. Therefore it's possibile 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).

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 macrostructure of cross section of samples with thickness of 23 mm is shown in Figs. 7a), 7b). It is visible that inoculant acts most intensively close to the sample's surface. The macrostructure is not a homogeneous one in all of the samples. The reduction of grain size of invested alloy after investigated surface modification was obtained independently from the kind of used cobalt aluminate.

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

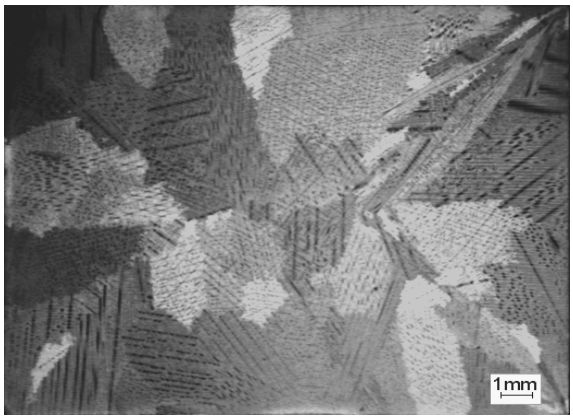
Kind of modifier/ series	Co content C_{Co}, %	Average content of Co, $\bar{C}_{Co}$, %
Mason Color/1	39.45	39.43
Mason Color/2	39.29	
Mason Color/3	39.55	
Remet/1	34.90	34.79
Remet/2	34.72	
Remet/3	34.75	
Permedia Lublin/1	32.64	32.53
Permedia Lublin/2	32.21	
Permedia Lublin/3	32.73	

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 (Table 3). From Figure 8 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.

On the basis of the results one can say that not only the amount of modifier added to a slurry influences the grain size of γ matrix of superalloy René 77 but also the cobalt content of cobalt aluminate. 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. It have been proved that higher cobalt content of cobalt aluminate causes better grain refinement of cobalt base superalloy MAR-M 509 [13,14].

It is difficult to decide how the size of $CoAl_2O_4$ particles influences grain refinement. It's possible that small differences between the size of grains of the powders will not influence the grain size. However the average diameter of grains and the characteristic of particle size distribution should be precisely determined. Different manufacturers offer different products so it is best to determine what differences exist and what impact they might have on modification process.

a)



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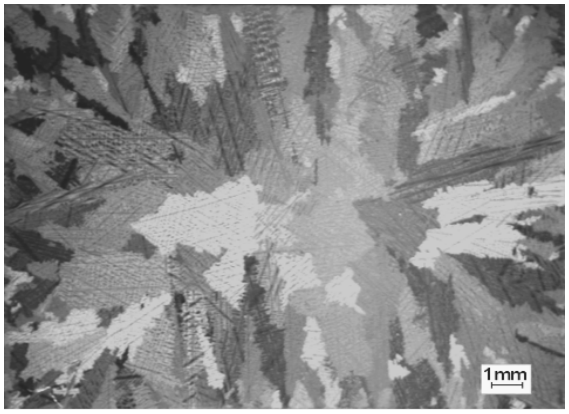


Fig. 7. The macrostructure of the superalloy René 77 on the cross section of casting with 23mm height: a) nonmodified, b) modified with 5%mass of $CoAl_2O_4$

Table 3.
The average surface area of grain cross section Ā depending on the section thickness of the cast (height of stair) and corresponding standard deviation s

The section thickness, mm	Cobalt aluminate concentration, %mass Type of modifier							
	None		5%, Mason Color		5%, Remet		5%, Permedia Lublin	
	Ā, mm^2	s, mm^2	Ā, mm^2	s, mm^2	Ā mm^2	s, mm^2	Ā mm^2	s, mm^2
50	6.4	6.0	2.6	3.1	1.9	2.0	3.8	4.7
29	6.8	7.5	2.5	3.3	2.6	4.3	4.4	5.8
23	13.3	11.7	1.3	2.3	1.0	2.2	4.5	5.8
17	6.6	7.2	0.7	1.1	0.7	0.8	1.5	2.3
11	3.5	3.9	0.3	0.5	0.5	0.8	1.1	1.5
5	1.1	1.3	0.1	0.1	0.3	0.3	0.4	0.7

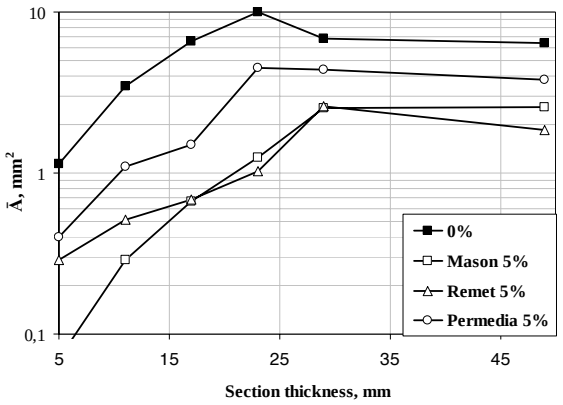
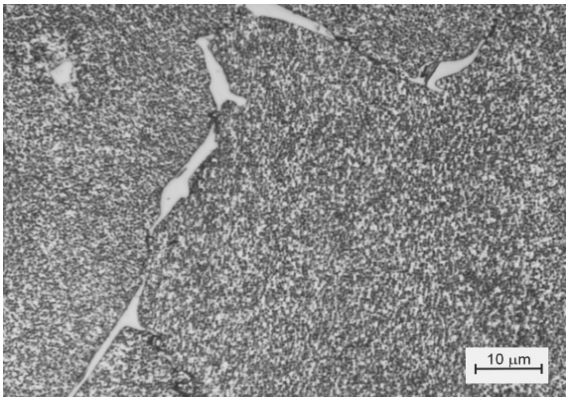


Fig. 8. The effect of varying the casting section thickness and modifier content on the variation of the average surface area of grain cross section

a)



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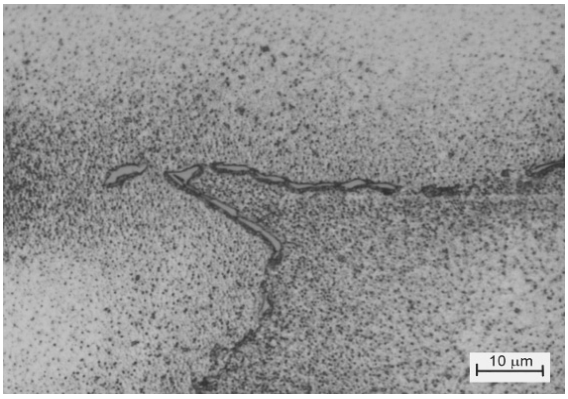


Fig. 9. The microstructure of the superalloy René 77 on the cross section of casting with 49mm height: a) nonmodified, b) modified with 5%mass of $CoAl_2O_4$

The microstructure investigations with the use of light microscopy revealed dendritic structure of modified and nonmodified castings, which is typical for that kind of alloys [19]. The carbides precipitations was observed on the boundaries and inside the grains. Fig. 9 presents carbides on grain boundaries. It was established, that modification effects the shape and size of the carbides. In the case of modified microstructure the carbide particles are thinner in comparison to nonmodified ones.

The observation of microstructure of superalloy René 77 under the higher magnification with the use of scanning electron microscopy revealed that it consists of super fine cubic particles of γ' phase (Fig. 10) and austenitic matrix. The influence of the surface inoculation on the morphology and size of γ' phase was not affirmed.

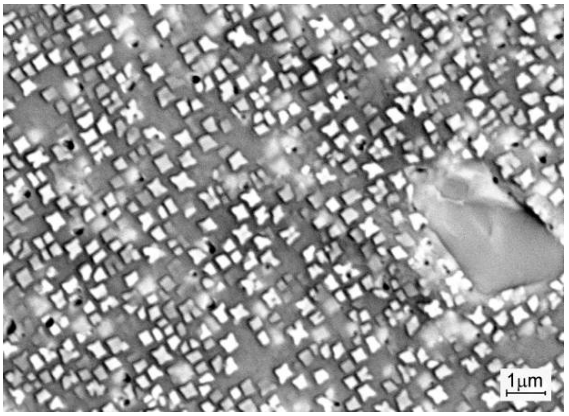


Fig. 10. The microstructure of the nonmodified superalloy René 77 on the cross section of casting with 11 mm height

Table 4.
Results of creep test of superalloy René 7

Type of modifier and its concentration, %	High temperature mechanical properties			
	t_z, h	A_4, %	Z, %	$\dot{\varepsilon}_s$, s
None 0%	33.2	16	16.2	$1.02 \cdot 10^{-7}$
Mason Color 5%	39.9	12.1	12.2	$2.13 \cdot 10^{-8}$
Remet 5%	40.6	12.7	11.41	$5.27 \cdot 10^{-8}$
Permedia Lublin 5%	38.5	13.2	15.4	$6.39 \cdot 10^{-8}$

Table 4 presents the results of the short term creep tests. The total time of creep test t_z at the temperature 982°C and stress 152 MPa improved from 33.5 to 40.6 h. Castings with inoculated surface layer of the mould have a better high temperature creep resistance independently on the type of used cobalt aluminate. However one may notice that the shortest time of creep was obtained for the Permedia Lublin modified samples. The steady

state creep rate was evaluated from the creep curves $\dot{\varepsilon}_s$, (Fig. 11, Table 4). Among the modified samples the higher value of steady state creep rate was found for the samples modified by Permedia Lublin powder and the lowest for the samples modified by Mason Color inoculant. The plasticity of superalloy slightly droped with 5%mass of $CoAl_2O_4$.

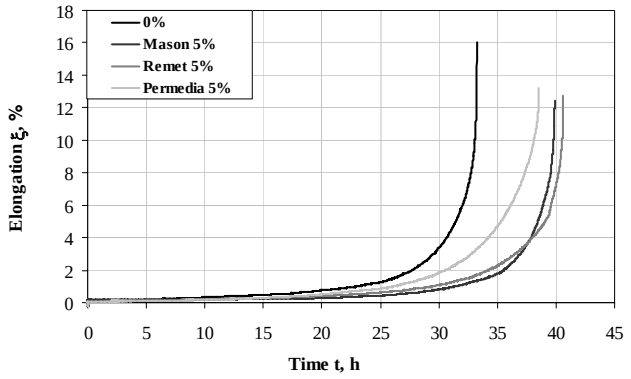


Fig. 11. Creep curves of superalloy René 77

The results of fracture surface analysis after creep test of René 77 are presented in Fig. 12. One may notice that they are ductile. The occurrence of many dimples with different sizes on their surface means that first small microvoids formed as consequence of plastic deformation and they enlarged to form a crack [20].

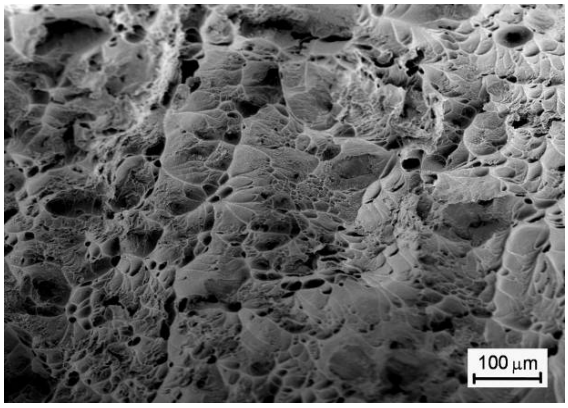
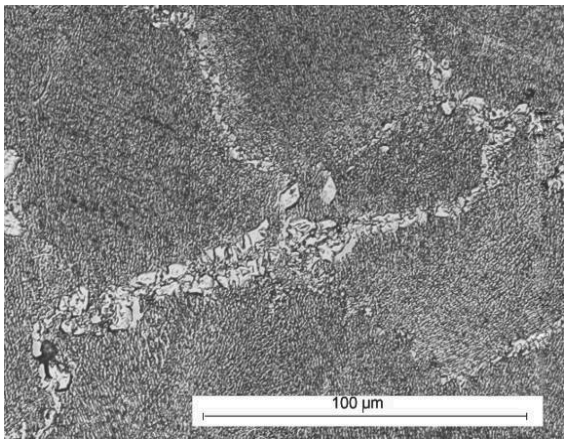


Fig. 12. Fracture surface of modified superalloy René 77 after the creep test

Cracking of superalloys had intercrystalline character and it occured along grain or dendritic crystals boundaries, as shown in Figure. During creep, nonmodified samples have more propensity to carbide coarsening and joining together in the grain boundaries (Fig. 13a) It could influenced the rate of crack nucleation and lower creep strength. The growth and directional elongation of γ' phase grains was observed in all investigated samples (Fig 14).

a)



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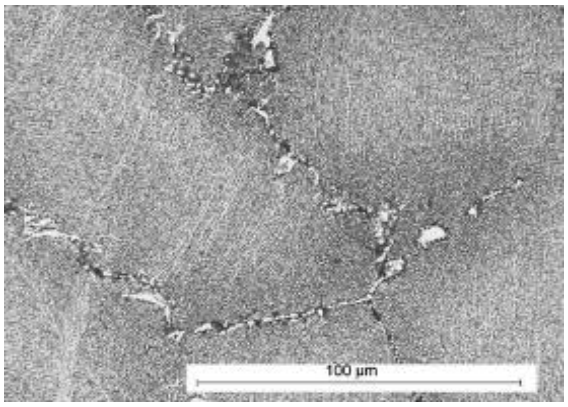

Fig. 13. The microstructure of superalloy René 77 after the creep test: a) nonmodified b) modified with 5%mass of $CoAl_2O_4$

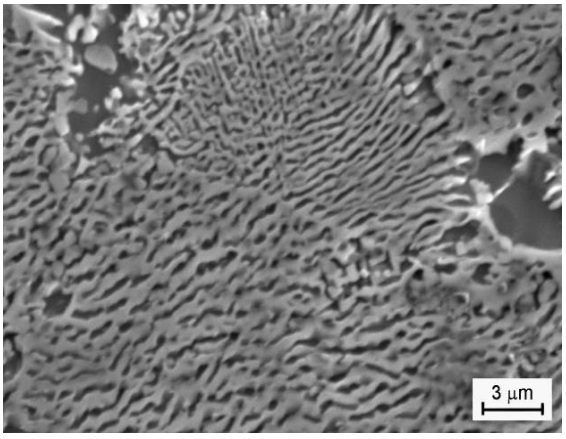

Fig. 14. The microstructure of superalloy René 77 after the creep test with visible γ' phas

4. Conclusions

Physical and chemical properties of cobalt aluminate modifier are different up to the manufacturer. The modifiers have different cobalt contamination and different grain size distribution. The modification of the surface layer of superalloy René 77 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 was proved, that modification of surface layer of ceramic mould has a positive effect on the mechanical properties at high temperature of the investigated superalloy. Castings with inoculated interior surface of the mould have a higher temperature creep resistance; the rupture time is about 12% longer. The longest time of creep exhibited samples with higher cobalt contamination and they had the smallest value of steady state creep rate.

On the grounds of the obtained results it was found that the optimal contamination of cobalt in cobalt aluminate modifier to produce casting elements made from superalloy René 77 is about 35-40% with 5-6%mass of its concentration in ceramic slurry. The lower concentration of cobalt in modifier yields the larger grain size and lower mechanical properties.

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References

[1] C.T. Sims, Superalloys II, Wiley&Sons, New York, 1987.
[2] J. Sieniawski, The criterion and estimation methods of the microstructure and properties of structural materials used for aeronautical engineering, Silesian University of Technology Publishing House, Katowice, 2002 (in Polish).
[3] J. Sieniawski, Nickel and titanium alloys in aircraft turbine engines, Advances in Manufacturing Science and Technology 27 (2003) 23-34.
[4] A. Hernas, High temperature creep resistance of steel and alloys, Silesian University of Technology Publishing House, Gliwice, 2000 (in Polish).
[5] M. Hetmańczyk, L. Swadźba, B. Mendla, Advances materials and protective coating in aeroengines application, Journal of Achievement in Materials and Manufacturing Engineering 24/1 (2007) 372-381.
[6] P.R. Beeley, R.F. Smart, Investment Casting, University Press, Cambridge, UK, 1995.
[7] A. Maciejny, Development of high temperature creep resisting alloys, Proceedings of the 1st Scientific International Conference „Achievements in Mechanical and Materials Engineering" AMME'92, Gliwice, 1992, 32-36.
[8] P. Jonsta, Z Jonsta, J. Sojka, L. Cizek, A. Hernas, Structural characteristics of nickel superalloy INCONEL 713LC after heat treatment, Journal of Achievements in Materials and Manufacturing Engineering 21/2 (2007) 29-32.
[9] G. Pucka, Production engineering of gas turbine blades castings made form ŻS6K alloy with regulated grain size Materials Engineering 4-5 (1984) 115-119 (in Polish).
[10] M. Błotnicki, K. Borla, Z. Adamonis, Influence of research-development works and new technological solutions on the stability of casting's quality assurance, Solidification of Metals and Alloys 26 (1996) 79-86 (in Polish).
[11] J. Hockins, Investment casting of superalloys, Proceedings of the 2nd International Symposium "Superalloys", Seven Spring, Pennsylvania, 1972, 263-270.
[12] R.C. Feagin, Dipcoat nucleation, Proceedings of the 12th Conference of the European Investment Caster's Federation, Eindhoven, 1967.
[13] M. Zielińska, J. Sieniawski, M. Poręba, Microstructure and mechanical properties of high temperature creep resisting superalloy René 77, Archives of Materials Science and Engineering 28/10 (2007) 629-632.
[14] M. Zielińska, J. Sieniawski, M. Wierzbińska, Effect of modification on microstructure and mechanical properties of cobalt casting superalloy, Archives of Metallurgy and Materials 53/3 (2008) 629-632.
[15] C. Wang., S. Liu, L. Liu, Synthesis of cobalt- aluminate spinels via glycine chelated precursors, Materials Chemistry and Physics 96 (2006) 361-370.
[16] M. Guerra, J. Niles, Cobalt aluminate levels in primary slurries, Proceedings of the 9th World Conference "Investment Casting", San Francisco, 1996, 1-9.
[17] J. Minczewski, Z. Marzenko, Analitycal chemistry 2, PWN, Warsaw, 1998 (in Polish).
[18] ASTME 139 Standard Test Methods for conducting Creep, Creep Rupture, and Stress-Rupture Tests of Metallic Materials.
[19] Metals Handbook vol. 9: Metallography of Heat Resisting Alloys, American Society for Metals.
[20] S.A. Sajjadi, S.M. Zebarjad, Effect of temperature on tensile fracture mechanisms of Ni-base superalloy, Archives of Materials Science and Engineering 28/1 (2007) 34-40.