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EFFECT OF MODIFICATION ON MICROSTRUCTURE AND MECHANICAL PROPERTIES OF COBALT CASTING SUPERALLOY

WPŁYW MODYFIKACJI POWIERZCHNIOWEJ NA MIKROSTRUKTURĘ I WŁAŚCIWOŚCI MECHANICZNE ODLEWNICZEGO NADSTOPU KOBALTU

Cobalt based heat – resisting superalloys are widely used for turbine blades and stationary elements of gas turbines (combustion space and stator blades) in aero-engines. These elements are generally produced by the investment casting method. The use of cobalt aluminate ($CoAl_2O_4$) for reducing relative grain size of precision investment castings results in higher mechanical properties. The aim of the present work was settlement of basic physical and chemical properties of cobalt aluminate powder and its concentration in the interior surface of invested mould on the grain size and the microstructure, and in consequence, mechanical properties of high temperature creep resisting superalloy MAR M 509. For this purpose, the ceramic moulds were made with different kinds of cobalt aluminate (manufactured by two different companies: Mason Color and Permedia Lublin) and its concentration in the primary slurry was from 0 to 10% mass. in zirconium flour. Stepped and cylindrical samples were casted for microstructure and mechanical examinations. The average grain size of the matrix (γ phase), was determined on the stepped samples. The influence of surface modification on the grain size of up to section thickness was considered. The microstructure investigations with the use of light microscopy and scanning electron microscopy (SEM) enable to examine the influence of the surface modification on the morphology of carbides precipitations. Verification of the influence of $CoAl_2O_4$ on the mechanical properties of castings were investigated on the basis of results obtained form tensile and creep tests.

Żarowytrzymałe stopy na osnowie kobaltu stosowane są na łopatki oraz stacjonarne elementy turbin gazowych (komór spalania, łopatek kierowniczych) silników lotniczych. Odlewy tych elementów wykonywane są najczęściej metodą wytapianych modeli. W stosowanej obecnie technologii wytwarzania tych elementów poprawę właściwości mechanicznych uzyskuje się przez modyfikację mikrostruktury warstwy wierzchniej odlewu za pomocą glinianu kobaltu ($CoAl_2O_4$). Celem pracy było ustalenie wpływu właściwości fizycznych i chemicznych proszku glinianu kobaltu oraz stężeń modyfikatora w warstwie wierzchniej formy na rozmiar ziarn, mikrostrukturę a przez to właściwości mechaniczne żarowytrzymałego nadstopu kobaltu MAR M 509. W tym celu wykonano formy ceramiczne różniące się rodzajem modyfikatora (produkcji firm: Mason Color i Permedia Lublin) oraz jego zawartością (0-10%mass. w mączce cyrkonowej) w warstwie wierzchniej formy. Następnie do przygotowanych wcześniej form odlano próbki schodkowe i walcowe odpowiednio do badań mikrostruktury i właściwości mechanicznych. Na wykonanych odlewach schodkowych określono średnie pole powierzchni płaskiego przekroju ziarna. Zwrócono również uwagę na sposób oddziaływania modyfikatora na rozmiar ziarn w zależności od grubości przekroju odlewu. Obserwacje mikrostruktury za pomocą mikroskopu świetlnego i elektronowego mikroskopu skaningowego (SEM) umożliwiły przeprowadzenie analizy oddziaływania modyfikatora na rozmiary i morfologię wydzieleń fazy węglikowej. Sposób oddziaływania modyfikatora na właściwości mechaniczne odlewów próbek z nadstopu MAR-M 509 określono na podstawie statycznej próby rozciągania i przyspieszonego pełzania.

1. Introduction

Cobalt based superalloy MAR-M 509 belongs to the modern generation of creep and heat resisting superalloys which are used for turbine blades and stationary elements of gas turbines (combustion space and stator blades). These elements are mostly produced by the investment casting method. The major move to control the quality of investment cast blades and vanes was the incorporation of controlled grain size which influences the properties of finished castings [1 -3].These control of grains size in the casting operation was accomplished by the control of processing parameters such as casting temperature, mold preheating temperature, and the use of grain nucleates in the face of the mold. For nickel and cobalt based superalloys, it was found that

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cobalt aluminate ($CoAl_2O_4$) has the best nucleating effect [4-7]. Cobalt aluminate can be introduced into a face coat slurry by substitution of a certain percentage of the refractory flour. This percentage is highly variable ranging from 1 to 10% (or higher) and depends upon the specification requirements, the alloy being cast, the section thickness, and other factors. 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 occurres between cobalt oxide and aluminum hydroxide what results in a spinel structure of cobalt aluminate compound [8]. It has been found that increase of Co content in precursors causes that more phases with different Co content are formed with the same spinel structure. Subsequetnly, the final product is milled to a fine particle size, typically 99,9 passing through 44 microns [8-9]. The goal of the present work was to settle of basic physical and chemical properties of cobalt aluminate powder and its concentration in the interior surface of invested mould on the grain size and the microstructure, and in consequence, mechanical properties of high temperature creep resisting superalloy MAR-M 509.

2. Experimental procedure

The alloy used in this study is MAR-M 509. 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 [10]. 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 primary slurry of different cobalt aluminate content was prepared (0, 5, 10%mass. $CoAl_2O_4$ in zirconium flour). In additions, different kinds of modifier (manufactured by two different companies: Mason Color and Permedia Lublin) were used to prepare the first slurry. In previous investigations [11], it was found that the two inoculant powders characterize different average diameter of particle size (Mason Color d_{50}=6.49μm, Permedia Lublin d_{50}=0.683 μm) and its distribution (Mason Color d = 0.56÷27.56 μm, Permedia Lublin d=0.138-2.646 μm). The cobalt content of the two cobalt aluminate powders was also different: Mason Color C_{Co}=39,43% and Permedia Lublin C_{Co}=32,53%).

TABLE 1

Chemical composition of cobalt superalloy MAR-M 509 (%mass.)

C	Ni	Cr	W	Ta	Zr	Ti	Fe	Si	Co
0.55	9.82	22.88	6.89	3.79	0.35	0,18	0.16	0.05	55.33

Stepped samples were cut in order to make an observation of microstructure on the cross sections of separate step casting. Polished sections were etched in HCl/H_2O_2 mixture to reveal the grain microstructure. Macro- examination was performed by the means of the image analysis software APHELION 2.3. The surface area of grain cross-section (A), standard deviation s, and the average shape factor of grains $\bar{f}$ were calculated [10]. 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.

Samples of 6.25 mm diameter were rolled from cylindrical castings for mechanical properties investigations [11]. Tensile tests were carried on by the means of strength testing machine WPM ZWICK Mops-h according to ASTM E8 [12] standard. The offset yield strength $R_{0,2}$, tensile strength R_m, unit elongation A_4, and percentage reduction of area of the specimen Z were evaluated. Creep tests were made by the use of creep machine W+B Walter+bai+AG according to ASTM E139 [13] standard. The operating condition of creep tests were as follows: the temperature T= 1091°C, and the stress σ_p= 62 MPa. The total time duration of creeping t_z, unit elongation A_4, and percentage reduction of area of the specimen Z were evaluated.

3. Results and discussion

The macrostructure investigations showed that the grain size of γ matrix in the cross section of casting depends on the section thickness of casting, the concentration of $CoAl_2O_4$ in the first layer of ceramic mould and also the kind of inoculant (Tab. 2). The average surface area of grain cross section decreases with higher velocity of cooling (the cross section thickness). For example the average surface area of grain cross section of nonmodified superalloy MAR-M 509 on the cross section of casting was 5.03mm^2 – measured on the cross section with 49mm of height while for 5mm of step heigh it was 0.38 mm^2 (Tab.2). Grain sizes of superalloy reduce with the enlargement of cobalt aluminate concentration in the surface layer of the mould. However, as it is shown in Table 2, the difference is not so significant, as the inoculant content increases above 5%mass. The most effective nucleant is the one produced by Mason Color firm with a higher cobalt content of the cobalt aluminate. The average value of surface area of grain cross section measured on the cross section of the castings with thickness of 5mm was 0.095mm and 0.075mm respectively for 5 and 10%mass. of modifier content. Whereas, for the castings modified by Permedia Lublin powders, for the same thickness of casting the grain size was 0.16mm^2 and 0.15mm^2. The experiment showed that the cobalt content in cobalt aluminate is an important factor which influences the grains size of cobalt based superalloy MAR-M 509. This is in agreement with the results obtained by Guerra and Niles [8] who studied the influence of cobalt content of modifier ($CoAl_2O_4$) on grain refinement of high chrome-nickel base alloy Inconel -625.

TABLE 2

The stereological parameters of macrostructure of superalloy MAR-M 509 depending on the inoculant's content and the section thickness of the cast (height of stair))

The section thickness, mm	Cobalt aluminate concentration, %mas.														
	0%			Mason Color 5%			Permedia Lublin 5%			Mason Color 10%			Permedia Lublin 10%		
	$\bar{A}$, mm^2	s, mm^2	$\bar{f}$	$\bar{A}$, mm^2	s mm^2	$\bar{f}$	$\bar{A}$, mm$_2$	s mm^2	$\bar{f}$	$\bar{A}$, mm^2	s mm^2	$\bar{f}$	$\bar{A}$, mm^2	s mm^2	$\bar{f}$
49	5.03	5.834	2.37	1.5	1.98	2.19	2.59	3.89	2.19	0.84	0.73	2.42	2.03	2.43	1.95
29	2.66	4.938	2.32	1.98	2.11	2.64	3.12	2.96	2.27	1.09	1.39	3.10	1.27	1.54	2.46
23	3.56	3.86	1.71	0.97	1.99	2.83	2.23	3.68	2.43	0.66	0.69	2.39	0.91	1.10	2.52
17	1.71	2.62	2.68	0.66	1.18	2.71	0.80	1.14	2.47	0.4	0.97	2.57	0.52	0.73	3.10
11	0.73	0.86	1.83	0.27	0.37	3.51	0.22	0.41	2.7	0.19	0.23	2.59	0.28	0.338	2.96
5	0.38	0.61	2.85	0.095	0.11	1.97	0.16	0.14	1.93	0.076	0.13	3.19	0.15	0.16	4.17

The smallest value of the average shape factor of grains, which was evaluated on the small section thickness (5mm), was found for the 5% contamination of cobalt aluminate. Modification of larger thickness of castings (11-29mm) causes that grains formed during crystallization are more elongated in the direction of heat outflow from the casting. However, the grains formed in the modified castings with 49mm of thickness have more equiaxial shape.

The microstructure of modified and nonmodified castings is typical for that kind of alloys, Fig.1. It consists of γ matrix (point 1, Tab. 3) and precipitations of carbides MC and $M_{23}C_6$ type, as it shown in Fig. 1. The main element of MC type carbides is tantalum (point 3, Tab. 3) and they are mostly distributed in acicular shape (Fig. 1, 2). While the chromium and vanadium -rich $M_{23}C_6$ type carbides (point 2, Tab. 3) appear in eutectic mixture (λ+$M_{23}C_6$), as is shown in Fig. 1, 2. Modification of superalloy MAR-M 509 does not change the microstructural constituents of the invested alloy but effects on their shape. In the case of modified microstructure the primary carbide particles MC are thinner. Moreover, there was remarked the eutectic refinement (Fig. 2).

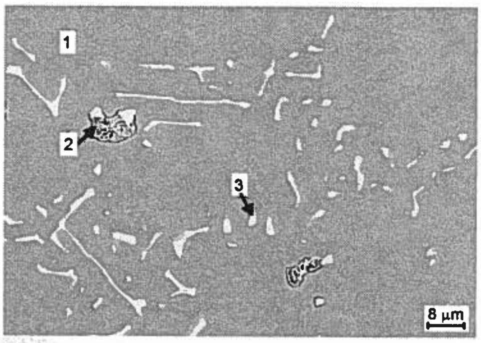

Fig. 1. The microstructure of modified superalloy MAR- M 509 on the cross section of casting with 11mm height

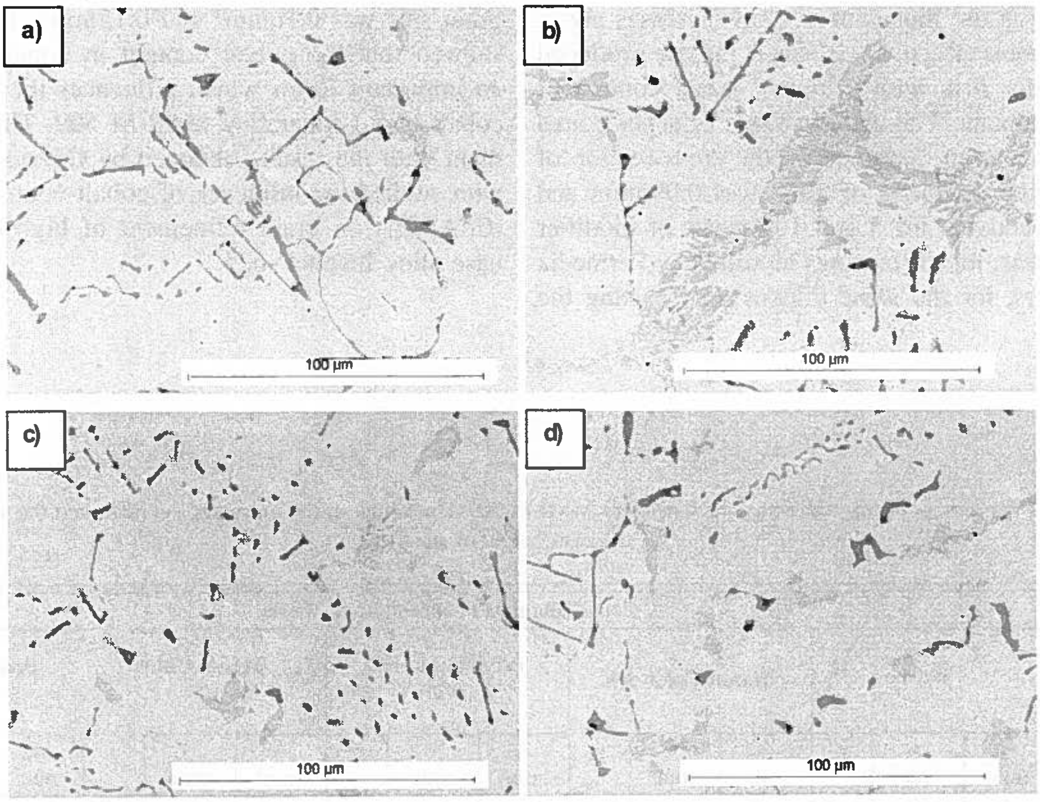

Fig. 2. The microstructure of superalloy MAR-M 509 in the cast state: (a), (b) the nonmodified sample, (c), (d) the modified sample with 5% of $CoAl_2O_4$

Table 4 presents mechanical properties obtained from the room temperature tensile tests. There is no significant difference between nonmodified and modified samples. Only, the yield and tensile strength slightly drops for the castings modified by the use of the Mason Color inoculant.

TABLE 3

Chemical composition of the matrix and carbides in areas 1, 2, 3 marked on Fig. 1))

Points	Ti, %		Cr, %		Co, %		Ni, %		Zr, %		Ta, %		W, %	
	at.	mas.	at.	mas.	at.	mas.	at.	mas.	at.	mas.	at.	mas.	at.	mas.
1			25.51	21,64	59,63	56,42	10,81	10,35					4,05	11,59
2			68.50	57.66	22.22	21.20	3.20	3.04					6,08	18,10
3	10,90	3.79	6.00	2.27					23.70	15.71	53.44	70.27	5.96	7.97

TABLE 4

Results of tensile test of superalloy MAR-M 509))

Kind of inoculant	Mechanical properties				
	$CoAl_2O_4$ concentration % mas.	$R_{0.2}$, MPa	R_m, MPa	A_4, %	Z, %
None	0	542	705	2,53	4,8
Mason Color	5	516	696	2,48	4,53
	10	482	674	2,68	5,52
Permedia Lublin	5	549	731	2,64	4,33
	10	545	718	3,76	7,45

Table 5 presents the results of the creep testing. The total time duration of creeping t_z at the temperature1091°C and stress 62MPa was longer. The use of more inoculant content in the surface layer of ceramic mould prolonged the total time duration of creeping. Among the modified samples of 5% of $CoAl_2O_4$ the longest duration time of creeping had the sample with Mason Color powder (the samples with finer grains). Just in opposite, for 10% of $CoAl_2O_4$ contamination as better inoculant appears the Permedia Lublin powder (the samples with coarser grains). Modification improves the plasticity (unit elongation and contraction in area) of the alloy in high temperature 1091°C (Tab.5).

TABLE 5

Results of the creep testing of superalloy MAR-M 509))

Kind of inoculant	$CoAl_2O_4$ concentration	The total time duration of creeping	Elongation	Contraction in area
	C %mas.	t_z, h	A_4, %	Z, %
None	0	25,7	14	10,66
Mason Color	5	30,8	18	13,5
	10	32	12	23
Permedia Lublin	5	29,1	14,3	17,92
	10	33	18,4	14

Analysis of microstructure of superalloy after creep testing revealed existence of numerous cracks which were mostly situated in multiphase regions; along the primary carbides and in eutectic regions (Fig.3). The nucleation of fractures initiated on the particle – matrix boundary. There were observed cracks in the primary carbides as well (Fig.3a) The refinement of carbides during the modification process could influence the decrease of velocity of crack nucleations and higher creep strength.

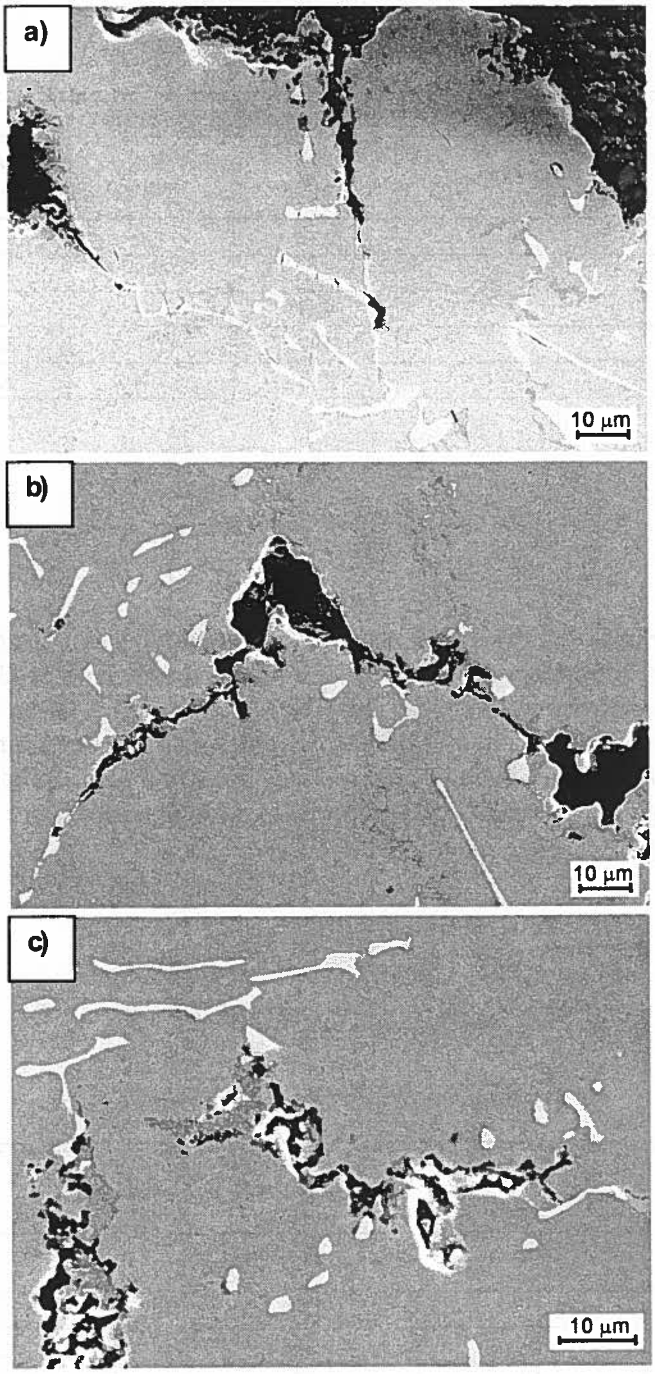

Fig. 3. The microstructure of superalloy MAR-M 509 after the creep test (a) nonmodified with visible cleavable cracks in primary carbides (b) nonmodified with visible cohesive failure in grain boundary (c) modified, cracks are situated in eutectic areas

4. Conclusions

The modification of the surface layer of superalloy MAR-M 509 results in grain refinement – γ matrix. The grains size of the superalloy can be controlled by the inoculant amount added to a slurry and kind of inoculant. Higher cobalt content of product (Mason Color) gave better grains size reduction than the lower cobalt content in the powder (Permedia Lublin). The difference in particle size in the two products can be a factor but it was not evaluated.

Cobalt aluminate effects on the carbides refinement. There were observed the reduction of relative volume of "chinese script" carbides and eutectic size reduction.

Modification of superalloy did not change the yield and tensile strength at room temperature. What is more, there was observed a little drop of them for the samples modified by Mason Color powder with more finer macrostructure.

The total time duration of creeping tz at the temperature 1091°C and stress 62MPa increases with enlargement of cobalt aluminate content in the surface layer of the mould. The rupture time was about 20% longer. Moreover, modified alloy posses better plasticity than nonmodifed one. The microstructure investigations revealed that mechanical properties at elevated temperature are better not only because of grain size reduction but also due to the refinement of carbide precipitations.

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