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Microstructure and kinetic growth of aluminide coatings deposited by the CVD method on Re 80 superalloy

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ABSTRACT

Purpose: The preliminary results of research on forming the aluminide coatings using CVD method were presented in the article.

Design/methodology/approach: The coatings were obtained in low activity process on the surface of Rene 80 superalloy. The microstructure analysis and chemical composition analysis were performed applying different values of aluminizing process parameters.

Findings: The authors present in the article the results of oxidation resistance analysis of aluminide coatings which were obtained on the surface of Rene 80 superalloy using various techniques.

Research limitations/implications: The research results revealed the possibility of obtaining coatings by low activity aluminizing.

Practical implications: This process can be used in aerospace industry to form oxidation resistant coatings.

Originality/value: It was shown that the coating created during the CVD process was characterized by a good oxidation resistance at the temperature of 1100°C.

Keywords: Metallic alloys; Corrosion; Technological design; Thin and thick coatings; Surface treatment

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MATERIALS

1. Introduction

The diffusion aluminizing process is one of the basic methods of surface protection for gas turbine blades against oxidizing influence of exhaust gases. The pack cementation-, out-of-pack-, slurry- and CVD method are most commonly used techniques of aluminizing [1,2]. Independently from the used aluminizing method, the coating formation mechanism consist in the reaction between the base material and the halide which contains aluminium. The β-NiAl is created as a result of aluminium diffusion. The reaction diagram is presented on Fig. 1.

Goward and Boone [3] used the pack cementation method and showed two possible courses of growth mechanism of aluminide layers. The authors used pack containing 15% of Al, 3% of amonium chloride and 82% of granular Al_2O_3 and observed that the Ni_2Al_3 phase is created in the first instance on the surface of nickel superalloy. During this process, called the high activity process, the inward diffusion of aluminium is the dominant growth mechanism. It has been proven by using the 15% of Ni_2Al_3, 3% NH_4Cl and 82% of aluminium oxide (Al_2O_3) that β-NiAl is the basic phase constituent. During this process, called the low activity process, the outward diffusion of nickel is the dominant growth mechanism. In the case of the high activity process it is necessary to perform the additional thermal treatment in order to obtain the transformation of Ni_2Al_3 phase into β-NiAl. The out-of-pack technique and vapour phase aluminizing are the extension of the pack cementation method. The Al powder and the Cr-Al granules are 100 mm distant from the surface of coated elements and are used as the source of aluminium in those methods. The process is conducted in the argon- or hydrogen atmosphere in the retort furnaces. Aluminium fluoride or ammonium fluoride is usually used as an activating agent [3,4]. It has been proven, that it is possible to perform aluminizing of internal cooling channels of blades using out-of-pack method.

It should be also considered that there is a limitation of parameters control during the out-of-pack aluminizing process. It is a result of using the solid-state activating agent introduced before the process. The largest possibilities of parameters control has the chemical vapour deposition process. Sun et al. [5] conducted the CVD aluminizing process with application $AlCl_3$- and hydrogen flow, which were produced inside the external generator over the aluminium- and aluminium oxide powder. Pure nickel was used as a base material. It has been proven, that the temperature growth in the $AlCl_3$ generator results in the growth Al concentration in the aluminide coating to above 60 at. %. The authors confirmed also that the temperature growth from 850 to 1050°C has a significant influence on the coating thickness. The amount of introduced aluminium during the CVD aluminizing process was insufficient for maintaining the thermodynamic equilibrium of the coating/gas phase interface. It is explained by high diffusion coefficient of aluminides in nickel. As long as the mentioned equilibrium is not present, there is an equilibrium state on the interface. If the concentration on the surface is known, the growth speed of the coating could be forecasted using the diffusion analysis in solid state.

The CVD aluminizing process has been developed for many years by the Howmet company [6]. The technological process is conducted - like in the case of described pack cementation method - as high- or low activity process. During the MDC-150L low activity process the aluminium chloride is generated inside the external generator through transferring the hydrogen chloride through the pure aluminium granules introduced to the retort in the pit furnace. During the MDC-150 high activity process, the Cr-Al granules were the additional source of aluminium. The granules were placed in the baskets around the central pipe distributing the reactive gas from the external aluminium generator. The conducted research on obtaining platinum-modified coating combined with the CVD aluminizing process showed that the coatings obtained during the low activity process were characterized by the best oxidation resistance. It was a result of hydrogen influence, which caused sulphur removal from the base material. It has been proven that during the high activity processes, it is necessary to utilize granules with very low impurities content. The reason of it was the presence of sulphur in aluminide layers obtained during the high activity process. The further work done by Howmet company was focused on introducing new elements to the aluminide layers. Warnes [8] proved the possibility of modifying the aluminide layers containing silicon and hafnium while using three external generators. The atmosphere containing (vol. %) 3.5% $AlCl_3$, 0.5% $SiCl_4$, 1.5% $HfCl_3$+$ZrCl_4$, 15% Ar and hydrogen (bal.) was used. The platinum-modified aluminide coatings obtained by this method had better oxidation resistance properties than the simple aluminized layers. Over the recent years, the Howmet company developed the technology which ensures the modification of aluminide layers by Si, Zr, Hf, Y with a use of only two external generators in the CVD system and one internal generator. It has been also proven, that there is a possibility of applying the low activity CVD aluminizing process of the CoCrAlY bondcoats [10]. The authors observed a growth of oxidation resistance of layers, which were submitted to overaluminizing process by using CVD method compared to the aluminized ones obtained with a use of the pack cementation method. The lower concentration of chromium and aluminium in the coating obtained by using the CVD method was a result of evaporation of those elements after formation of $CrCl_3$ and outward growth mechanism limited by the presence of impurities [11].

The simultaneously conducted research on determining the new aluminizing conditions makes possible to obtain thicker aluminide layers in shorter time. In the Howmet company [12] the CVD process with application of the low aluminium content and larger total gas flow through the retort is developed. The temperature of 1080°C, pressure value of 200 Torr and 1 vol. % of $AlCl_3$ with the gas flow of 300 scfh are considered to be optimal parameters for the Rene N5 alloy. The optimal parameters determined during the measurements allowed to shorten the time of CVD process from 16 to about 10 hours. Araki and Motojima [13] proposed the application of the preheating gases ($AlCl_3$, H_2) before the direct introduction to the chamber. The designed labyrinth system made of graphite provided the thickness growth from 13 to 19 μm for the formed coating, during the four-hour aluminizing process.

The different concept of aluminizing process with a use of CVD method was proposed by Kohlscheen and Storck [14]. The authors used the internal generator in which the Al-Cl granules were the source of aluminium. The $AlCl_3$ was obtained by transferring the granules through HCl. The performed calculations showed, that the increase of hydrogen chloride amount didn't ensure the larger thickness of the aluminium coating. It was explained by not sufficient surface of the granules, which reacted with hydrogen chloride. Those conditions didn't ensured creation of $AlCl_3$. The experimental verification confirmed, that the increase of hydrogen participation caused the growth of the aluminide coating. In the course of further research the method of silicon-aluminizing during one process was developed [15]. The granules mixture containing 90% wt. Si and 10% wt. Cr-Al were used for this purpose. The application of two-stage process caused the decay of aluminide coating deposited before the aluminizing process.

The recent work is focused on the influence assessment of the basic CVD aluminizing parameters on the microstructure of aluminide coating deposited on the high temperature creep resisting nickel alloys. The application of new BPXPro 325S device, available in the Research and Development Laboratory for Aerospace Materials at Rzeszów University of Technology, required correlating the analysed literature data with the technological capabilities of the device. During the first investigation, the focus was put on the higher flow values for hydrogen chloride used by i.a. the Howmet company [16].

The literature analysis showed, that during the low activity aluminizing process, it is necessary to decrease the amount of used hydrogen chloride. The recent work focuses on the assessment of influence of the basic aluminizing parameters using CVD method on the microstructure of aluminide coating deposited on the high temperature creep resisting nickel alloys. Application of new BPXPro 325S device, which is available in the Research and Development Laboratory for Aerospace Materials at the Rzeszow University of Technology required the correlation of available literature data with the device capabilities.

2. Experimental

The The authors analysed the high temperature creep resisting Rene 80 nickel superalloy. It's chemical composition was presented in the Table 1. Samples were made form bar; they had thickness of 4 mm and diameter of 14 mm. The samples were polished with water-resistant abrasive paper with gradation of 500, degreased in isopropyl alcohol with a use of ultrasonic cleaner and dried before the process.

Table 1.
The nominal chemical composition of Rene 80 alloy [wt.%]

Material	Ni	Co	Cr	W	Mo	Al	Ti	Zr	C
Rene 80	Bal.	9.5	14	4	4	3	5	0.06	0.17

Table 2.
The list of parameters used for aluminizing process implemented by CVD method

Run no.	Temp [°C]	P [mbar]	HCl flow [lNLPM]	H_2 flow [lNLPM]	Time [h]
1	1000	150	1.2	10.5	4
2	1000	150	1.4	10.5	4
3	1000	150	2.0	10.5	4
4	1000	100	1.4	10.5	4
5	1000	350	1.4	10.5	4
6	1000	150	1.4	10.5	2
7	1000	150	1.4	10.5	8

The aluminizing process using CVD method was conducted in the Research and Development Laboratory for Aerospace Materials at Rzeszow University of Technology. The Bernex BPX Pro 325S device was used. It is a conventional hot-wall CVD device. The aluminizing process was performed during the HTLA process (high temperature low activity). The aluminizing processes were conducted for different parameters values to analyse the growth kinetics of aluminide coating. Parameters used till now were used as a base values: HCl flow of 1.4 NLPM, hydrogen flow of 10.5 NLPM, temperature of 1000°C and pressure of 150 mbar. For the purposes of further tests the pressure value from 100 mbar to 359 mbar and the time from 2 h to 8h were chosen. The HCl flow of 1.2-2.0 NLPM and the hydrogen flow of 10.5 NLPM was applied. The parameters concerning particular processes are presented in Table 2. After finishing the analysis of the sample, the microstructure was investigated with a use of S-3400 Scanning Electron Microscope (Hitachi) equipped with electron probe microanalysis (Thermo).

3. Results and discussion

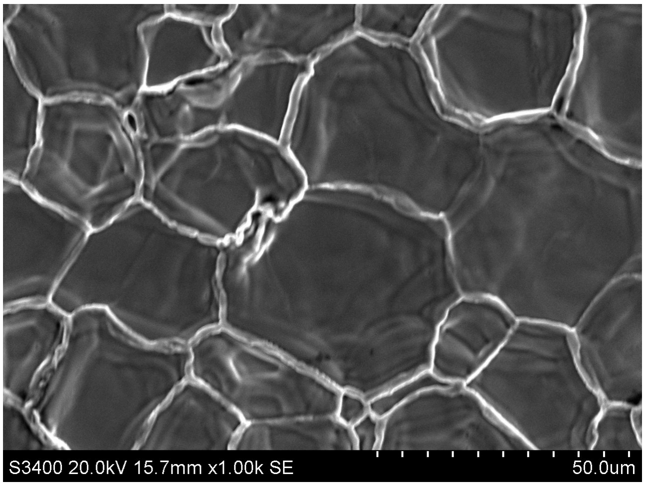
3.1. Microstructure and kinetic growth

The conducted aluminizing processes implemented with CVD method resulted in total coverage of the surface of all samples made of Re 80 alloy by the diffusion coating (Fig. 1). The microstructure of all deposited aluminide coatings were presented on Fig. 2.

For the base parameters of aluminizing process (1.4 NLPM HCl, 10.5 NLPM H_2, 150 mbar, 4 h, 1000°C) the aluminum content on the alloy surface was of 44.5 at. %. Two characteristic zones could be observed in the coating microstructure for the base parameters. Their structure was typical for coatings obtained in low activity process. The average aluminium content in the outer zone (area 1 on Fig. 3) was approx. 39 at.%. In the area near surface, the aluminium content was higher and was at the level of 45 at. % (point 3 on Fig. 3). In the lower part of the outer zone (point 4 on Fig. 3) the aluminium content was of 35 at.%. Chromium and cobalt were present, except the aluminium and nickel, in the outer area of the coating. In the outer diffusion zone the average aluminium content was of 23 at. %. The separations in components of Re-80 alloy - Cr, Co, W, Ti were present (area 2 on Fig. 3). The white-coloured separations contained 10-11 at.% of Cr, Co and W for aluminium content of 23 at.%. The aluminium content was higher in the base of diffusion zone and was at the level of 27 at.% (point 6 on Fig. 3).

The performed microstructure analysis of aluminide coatings created during CVD process conducted with different parameters values didn't prove that there is a significant difference in their chemical composition. It proved however that there is a difference as far as coating thickness is concerned. The influence of pressure value in the retort, HCl flow and time on the thickness of the coatings obtained during different processes is presented on Figs. 4-6. The thickness of coatings was in the range of 16-18 μm. It has been showed, that decrease of pressure in the retort during aluminizing process causes a small increase of thickness of the aluminide coating by approx. 1 μm (Fig. 4). It applied to the whole coating as well as to particular zones (external and the diffusion one). The authors noticed also a slight influence of hydrogen chloride flow on the coating thickness.

A small decrease of the coating thickness (by aprrox. 1 μm) was observed in case of HCl flow of 1.4 NLPM (Fig. 5). The duration of aluminizing process had the largest influence on the thickness of obtained coatings (Fig. 6). During the two-hour process, the thickness of obtained coating was of 9 μm. Increase of aluminizing time to 8 hours caused growth of thickness to 19 μm.



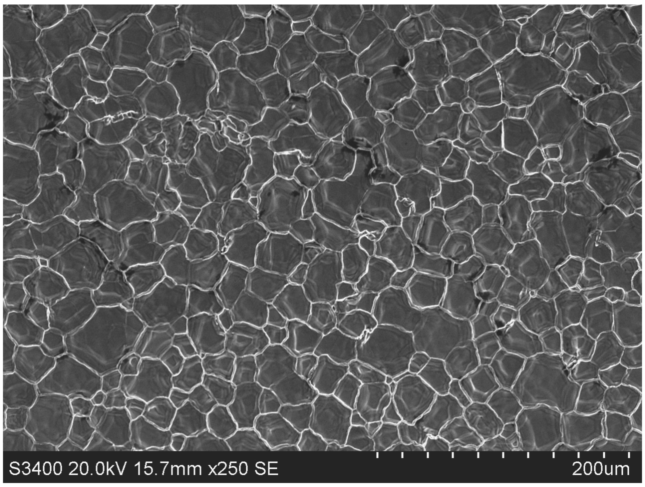


Fig. 1. Surface morphology of aluminide coatings deposited on Rene 80 superalloy by low-activity aluminizing. Process parameters: 1.4 NLPM HCl, 10.5 NLPM H_2, 150 mbar, 4 h, 1000°C

Table 3
The results of EDS microanalysis of areas presented on Fig. 2

Area/ point	Chemical composition (at.%)						
	Al	Ti	Cr	Fe	Co	Ni	W
1	39.29	0.63	2.84	1.09	6.67	49.48	-
2	23.09	1.84	10.64	-	10.18	43.42	10.83
3	45.14	-	0.81	1.15	4.21	48.51	0.18
4	35.18	1.42	4.16	0.87	7.02	50.59	0.76
5	23.10	1.45	11.76	-	11.93	40.95	10.82
6	27.71	1.92	8.51	0.86	9.52	46.27	5.21

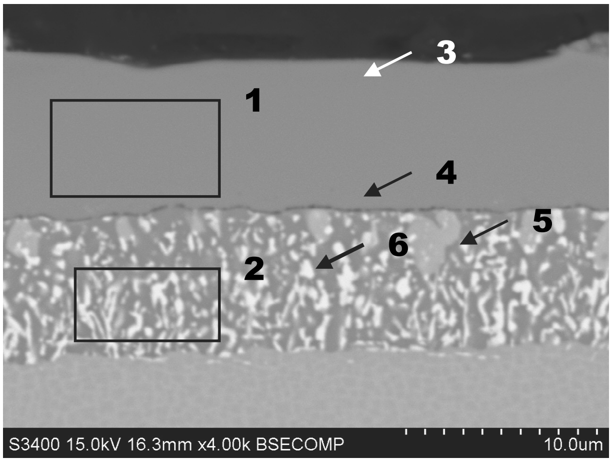


Fig. 2. The microstruture of aluminide coatings deposited on Rene 80 superalloy by low-activity aluminizing. Process parameters: 1.4 NLPM HCl, 10.5 NLPM H_2, 150 mbar, 4 h, 1000°C

4. Summary

The CVD method is one of most modern techniques of aluminizing of turbine blades in aircraft engines. The conducted technological trials made with BPX Pro 325S device showed a possibility of creating the aluminide coatings with a structure typical for low activity process. The coating consisted of the outer layer (β-NiAl phase) containing approx. 45 at.% of aluminium and the transition diffusion zone. The coating structure indicates the growth resulting from outward nickel diffusion. The analysis of coating growth kinetics didn't show the significant influence of pressure in the retort and the HCl flow on the thickness of formed coating. It is necessary to change a value of hydrogen chloride flow in order to increase the coating thickness.

The conducted research proved that the aluminizing using CVD method is an efficient way of surface protection against oxidation for Rene 80 alloy. It was confirmed by the result of cyclic oxidation test. High heat resistance of the coating obtained with CVD method can be a result of application of the hydrogen atmosphere. The method provides high quality of obtained coating [7].

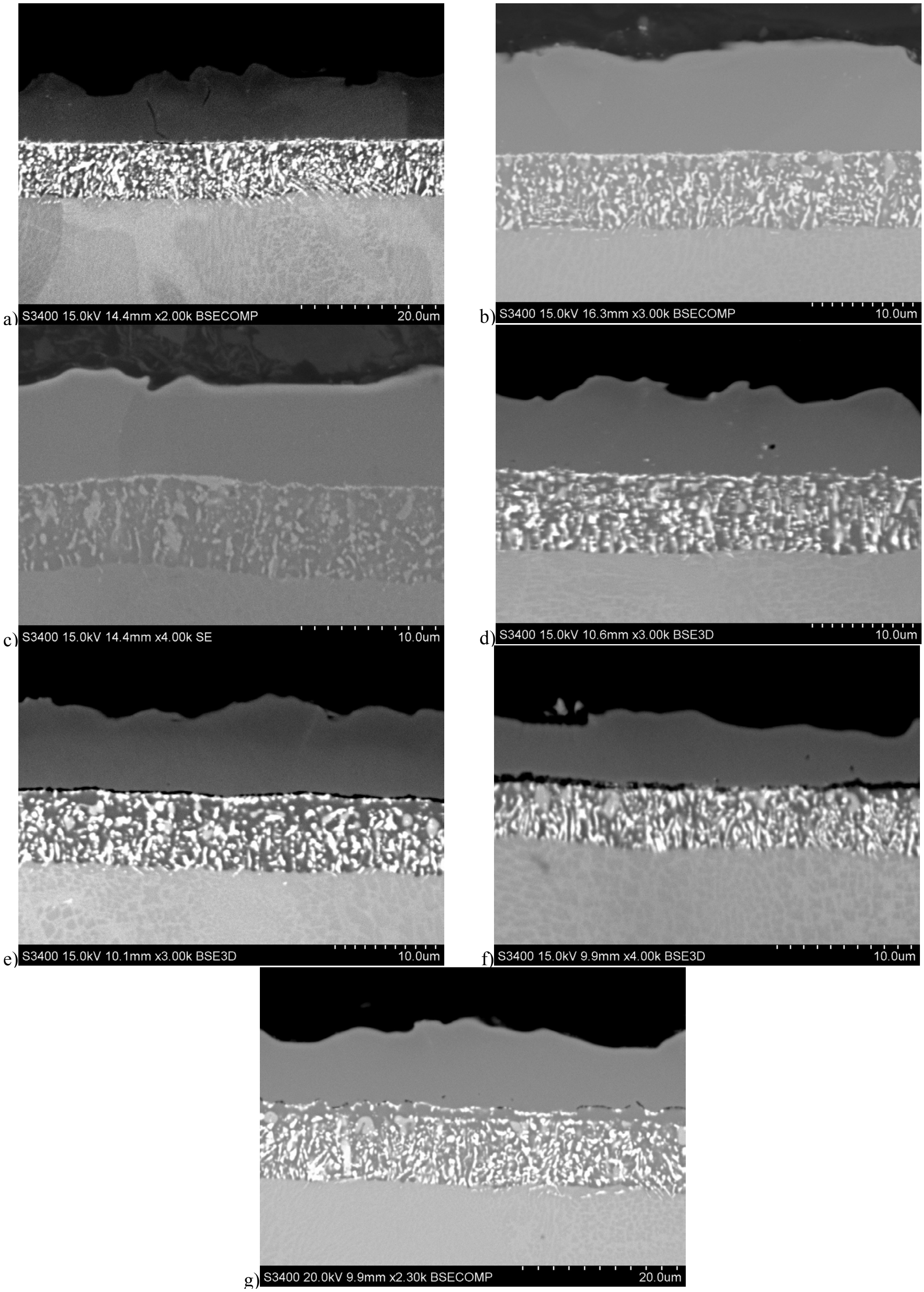


Fig. 3. Microstructure of aluminide coatings obtained during CVD aluminizing processes (see details of process parameters in Table 3) a) run 1 b) run 2, c) run 3, d) run 4, e) run 5, f) run 6, g) run 7

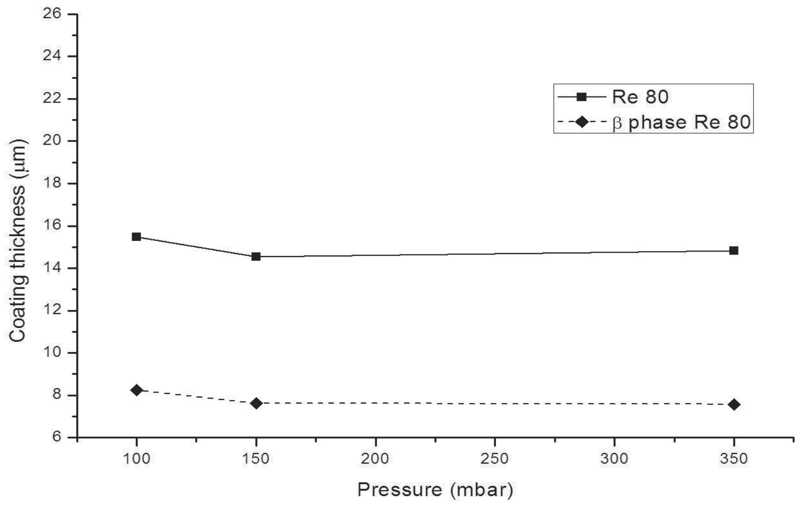


Fig. 4. The influence of pressure in retort on thickness of aluminide coating obtained on Re 80 superalloy by CVD method

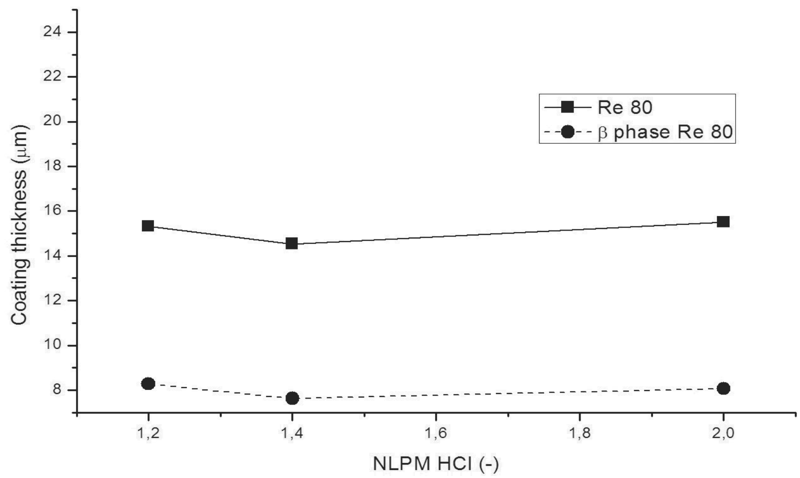


Fig. 5. The influence of HCl flow on thickness of aluminide coating obtained on Re 80 superalloy by CVD method

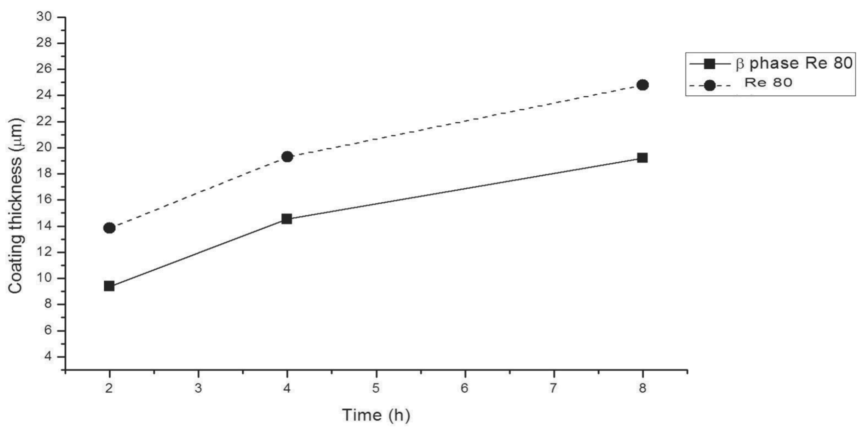


Fig. 6. The influence of process time duration on thickness of aluminide coating obtained on Re 80 superalloy by CVD method

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