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Carbon Diffusion Protective Al-Si Coatings on High Temperature Creep Resistant Cast Steel

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This paper presents results of research of multilayer carbon diffusion protective aluminium-silicon coatings. Aluminium-silicon coatings created on high-temperature creep resist cast iron GX30NiCrSi30-18 were manufactured by immersion in active mixture containing aluminium and silicon powders, flux and binder. The samples prepared in this way were annealed at temperature about 900 °C. The samples differed in surface conditions (machined and as-cast conditions). The structure of these coatings is compact and triple zonal.

Keywords: hot corrosion, diffusion coatings, slurry cementation method.

INTRODUCTION

The equipment of carburizing furnaces is predominantly made of high-temperature creep resistant cast steel, especially Fe-Cr-Ni based alloys. These materials must exhibit high mechanical strength at elevated temperatures and resistance under thermal shock conditions. Extending of the equipment life is primary problem. Under such severe working conditions, however, it is difficult to maintain an acceptable compromise between mechanical strength and surface degradation resistance. On the surface of these materials a protective chromium oxide layer (Cr_2O_3) is formed. However, chromia surface layer only provides carburization resistance at temperatures below 1050 °C. Above this temperature the chromium oxide is converted to unprotective carbides (Cr_3C_2, Cr_7C_3). Only silica and alumina forming alloys are effective against carburization at temperatures above 1050 °C. Another defect of chromia forming alloys is that the chromium oxide layer is susceptible to cracking and spalling during creep and thermal shocks. One of the common solutions, therefore, is to develop alloys with optimum mechanical properties, then to confer resistance to carburizing using appropriate coatings. Coatings are generally protecting the high-temperature creep resistant cast steel against high-temperature corrosion. They reduce the activity of the surface in carbonizing atmosphere and extend life of the equipment. The main types of protective coatings used for these applications can be described as diffusion coatings. They are formed by the surface enrichment of an alloy with either aluminium, chromium or silicon. Diffusion are applied using a range of techniques, including pack cementation [1], slurry cementation, pack and gas-phase chemical vapour deposition (CVD) [2] and metallizing [3]. In these coatings most often intermetallic materials are formed. There are FeAl, Fe_3Al, NiAl, Ni_3Al. Intermetallic materials exhibit good wear and erosion resistance due to their high hardness, rapid work hardenability and corrosion resistance. Under industrial conditions the carbonized resistance of coatings is insufficient due to thermal shocks. The shocks cause accelerated destruction of protective coatings. There is a good case when coating has carbonizing atmosphere barrier and it is thermal shock resistant.

In this paper the results of Al-Si coating structure research have been described. These coatings on high temperature creep resistant cast steel were drawn up by the authors using a single step slurry cementation method.

EXPERIMENTAL

The samples were made of the high-temperature creep resistant cast steel containing approximately: 0.2 %wt. C, 18 % Cr, 30 % Ni, 0.7 % Mn, 1.5 % Si [4]. Machined and as-cast surface samples were used in the experiment. The substrates for the working suspension are: Al and Si powders, water solution of soluble glass as the binder and fused mixture of salts as the flux [5 – 10]. The chemical composition of the mixture was determined experimentally. The aluminium-silicon mixture was put (by immersion) on the cast steel. The samples were several times immersed and dried till the mixture mass density value 0.3 g(Al+Si)/cm^2. The samples covered with the mixture were annealed at the temperature of 900 ºC for 7 hours.

Coatings were examined using the following techniques:

- light and scanning electron microscopy – JOEL JSM-6100;
- XRD analysis (X-ray diffraction) – DRON-3 diffractometer, CoKα radiation, filter Fe (λ = 1,79021Å), X-ray tube voltage amounts to 40 kV, identification of phases was performed using Phillips X'Pert;
- microhardness tests – Buehler 2000, 50 G, 15 s;
- EDS (Energy Dispersive Spectrometry) – LINK ISIS of Oxford;
- WDS (Wavelength Dispersive Spectrometry) – IBEX of Noran Instruments.

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EXPERIMENTAL RESULTS AND DISCUSSIONS

The microscopic observations proved that there are no essential differences in the obtained coatings. The typical coating consists of three zones: the internal zone (1), the middle zone (2) and the external zone (3). The coating microstructure is shown in Fig. 1. This figure presents Al-Si coatings obtained on machined surface and rough cast surface. The thickness of the obtained coatings on the whole surface of samples is moderately uniform and the thickness of individual zones is comparable. The results of thickness measurements are shown in Table 1.

Table 1. Average thickness of Al-Si coatings obtained on rough cast and machined surfaces

Thickness [μm]	Zone 1	Zone 2	Zone 3	Total thickness
Rough surface	21.8	62	65.3	149.1
Machined surface	16.1	47.8	34.5	98.4

The Vickers hardness tests were performed on specimens with coatings in the 1st and the 2nd zones and the base material and without coating. Machined and as-cast surfaces specimens were used there. Tests results are shown in Fig. 2. It was found that the 3rd zone is brittle and it cracks during hardness tests. Therefore it was assumed, that the 3rd zone would not have protective properties [9].

The grinding of samples does not exert an evident influence on the coatings morphology. Both coatings have continuous and compact triple zone structure. There are noticeable differences in thickness of these coatings (Table 1).

XRD phase analysis was performed on sections parallel to the coating surface. Consecutive layers of the coating material were removed. Owing to such preparation of specimens, identification of most phases in each zone was possible.

Elemental mappings on coatings cross-sections, line and point quantitative analysis were performed by means of EDS X–ray microanalysis.

Results of the quantitative X-ray microanalysis are presented in Figs 3 and 4. There are no distinguishable differences between coatings with the machined and the as-cast surface in these figures. On the basis of XRD and point quantitative EDS analysis, the phase composition of coating were defined. Photographs of particular zones and their phase components in the zones are presented in Table 2.

This table does not contain external zone phase description because of the huge number of phase components. There are mainly: $Fe_3Al_2(SiO_4)_3$, Fe_2SiO_4, $FeAl_2O_4$, Na_2FeO_3, Na_3CrO_4, Fe_2O_3, $NiAl_2O_4$, Na_2O_2, AlF_3, Al_8Cr_5, NiSi, $CrSi_2$, β'Al(Ni,Fe), α(Fe,Cr,Ni), $Al(Ni,Fe)_3$.

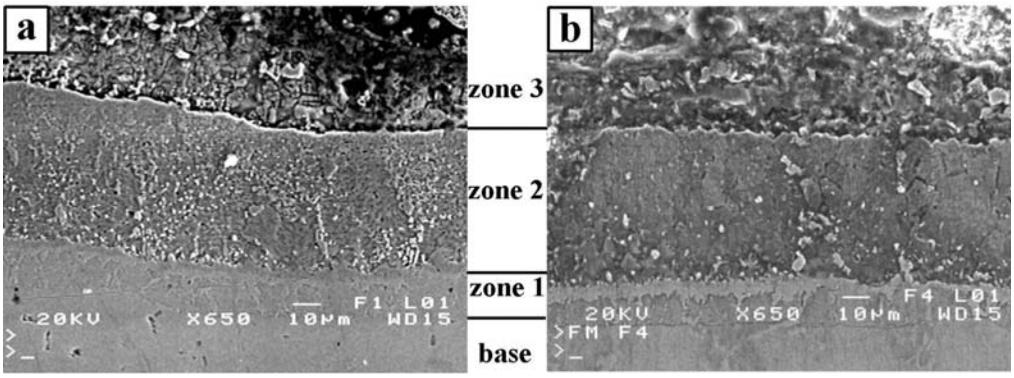
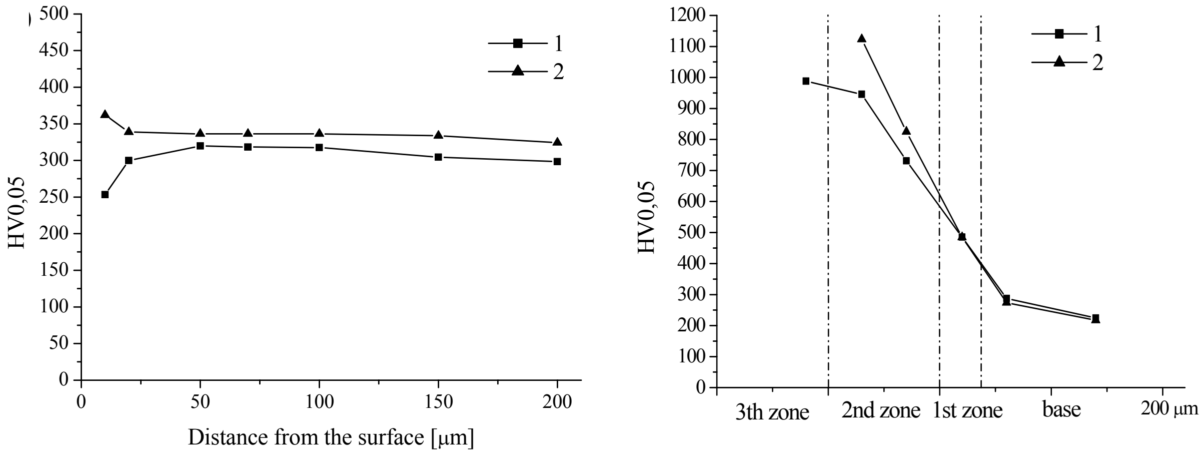


Fig. 1. Microstructure of Al-Si coating on: a – rough cast surface, b – machined surface



a b

Fig. 2. Microhardness: a – rough cast (1) machined cast (2); b – coatings Al-Si obtained on rough cast surface (1) and machined cast surface (2)

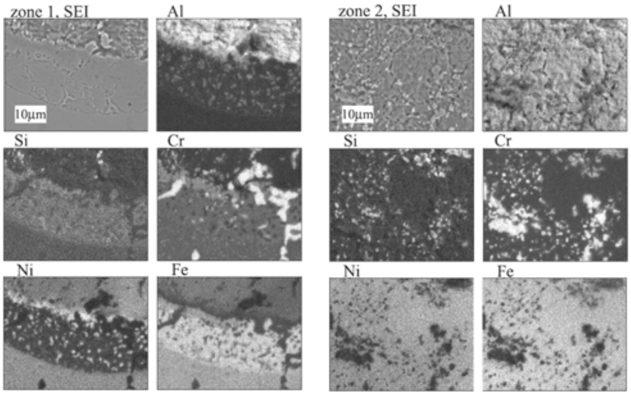


Fig. 3. Distribution of Al, Si, Cr, Fe, Ni of Al–Si coating on rough cast surface, mag. 2500×

The average contents of oxygen (WDS method) and other elements are shown in Table 3.

The method of coatings manufacturing described in this paper appeared to be more comfortable, less harmful than classic powder methods [5] and it is also easier than the cast method [6, 7].

Another advantage of this method is low consumption of substrate materials, possibility of the manufacturing uniform and good quality coatings on the complicated-shape elements. Moreover, there is a possibility to manufacturing coatings on not machined surfaces.

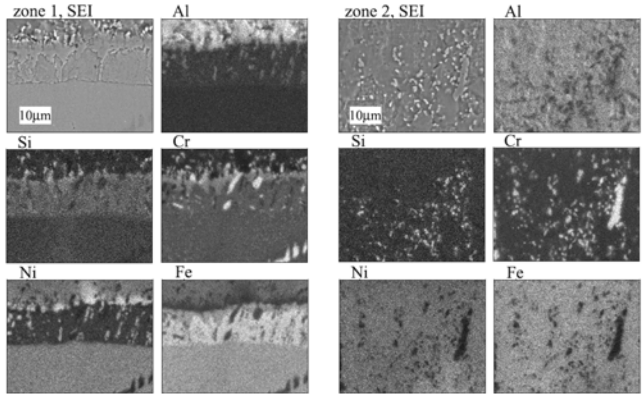
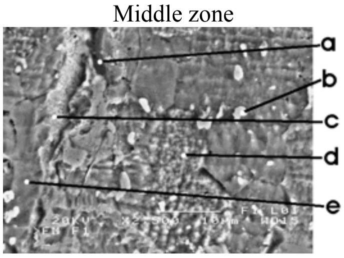
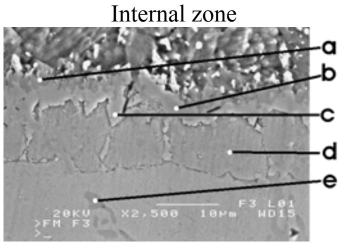


Fig. 4. Distribution of Al, Si, Cr, Fe, Ni of Al–Si coating on machined surface, mag. 2500×

Table 2. Structure of Al-Si coatings

Zone pictures	Symbol of component	Chemical composition [%wt.]					Phase composition
		Al	Si	Cr	Fe	Ni	
Middle zone 	a	11.4	0.2	11.8	41.8	33.9	γ(Fe,Ni,Cr)
	b	4.4	0.7	68.1	20.2	6.6	$Cr_{23}C_6$
	c	34.3	1.7	8,1	30.5	26.7	βAl(Fe,Ni)
	d	25.7	1.1	13.0	34.2	27.3	$Al(Fe,Ni)_3$, βAl(Fe,Ni), α(Fe,Cr,Ni)
	e	28.6	0.9	9.1	33.9	28.7	α(Fe,Cr,Ni), βAl(Fe,Ni)
Internal zone 	a	25.6	0.4	10.2	17.3	46.4	$AlNi_3$
	b	0.1	0.2	76.6	18.0	2.25	$Cr_{23}C_6$
	c	0.3	5.7	33.3	51.7	6.4	α(Fe,Ni,Cr),
	d	0.7	4.5	20.4	63.7	10.3	α(Fe,Cr,Ni), α(Fe,Si)*
	e	0.1	0.5	69.2	20.7	6.1	$Cr_{23}C_6$

* Probable phase.

Table 3. Chemical composition at individual zones of Al–Si coatings on rough cast surface and machined surface [% by weight]

	Coating on rough cast surface						Coating on machined surface					
	Al	Si	Fe	Ni	Cr	O	Al	Si	Fe	Ni	Cr	O
Zone 1	3.89	3.71	51.37	16.98	23.9	0.4	4.32	4.08	51.62	18.04	21.92	0.3
Zone 2	30.12	1.7	26.80	25.83	15.3	1.5	29.62	1.39	30.47	25.61	12.92	1.0
Zone 3	59.85	1.34	14.07	17.4	3.78	18.9	52.80	1.69	21.94	16.84	5.73	16.3

Both coatings created on the machined and as-cast surface have similar microstructure. Only minor differences in thickness of these coatings were observed (Table 1). Coatings on the rough cast surface are thicker. In these coatings diffusion of elements from the active mixture into the base material is easier, because the material surface have more defects in macro and microscopy meaning. Microhardness tests (Table 2, a)) speak for it.

In the 1st zone of coatings on the rough cast surface (Fig. 3) are more fine precipitations rich in Ni and Al against the background of solution. Also in these coatings the consist of oxygen is greater (Table 3), especially in the 3rd zone. This zone is rich in various oxides and spinels, because the surface of cast steels is covered with more oxides quantity than the machined surface.

It can be expected that the 3rd (external) zone phase composition will not cause the increase protective properties, while phases such as Al(Fe, Ni), $Al(Fe, Ni)_3$ in the 2nd (middle) zone ensure good protective properties [1].

The occurrence of the 1st (internal) zone rich in Fe ad Si in these coatings is advantageous for the sake of the arrangement of the microhardness in coatings (Fig. 2, b). This zone is expected to decrease the stresses gradient during change of temperature between the harder 2nd zone and the softer base [10 – 13].

CONCLUSIONS

1. The method of coating manufacturing by immersion has many advantages in comparison with methods used earlier.
2. The aluminium–silicon coatings on the high–temperature creep resist cast iron have compact and three zonal structures.
3. There are noticeable differences between coatings on the machined and not machined surface, so the coatings can be made on cast, without mechanical working of surface.
4. The coatings are characterized by comparable value of thickness. The structure of these coatings is continuous.
5. The external zone of coatings is rich in aluminium, hard and brittle. The middle zone is hard and rich in aluminium, nickel and iron. This zone contains intermetallic phases, which have protective properties against carburizing atmosphere.
6. The internal zone is rich in iron, chromium and silicon. The hardness value of this zone is between the hardness of middle zone and the base material. It is favorable in context of thermal shock resistance.

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