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Oxidation models of the growth of corrosion products on the intermetallic coatings strengthened by a fine dispersive Al_2O_3

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Abstract: In this paper the cyclic oxidation test of intermetallic coatings with iron and nickel aluminium is presented. The oxidation behavior of coatings strengthened by a fine dispersive Al_2O_3 was investigated in aggressive gases for exposure times of up to 500 hours. The surfaces of the composite coatings after the corrosion test in air were analyzed by light and scanning microscopy observation. An analysis of the corrosion products' phase composition was conducted by an X-ray diffraction method. The results obtained from the presented investigations enable the elaboration of the two models of the growth of corrosion products on the intermetallic coatings strengthened by a fine dispersive Al_2O_3, first- on the coating with FeAl phase and second on the coating with NiAl intermetallic phase. The results show that the composite, thermally sprayed coatings have very good high-temperature corrosion resistance.

Keywords: Intermetallic phases, Oxidation resistance, HVOF

1. INTRODUCTION

The intermetallic phases based on based on the high aluminium activity have very attractive properties such as low density, high melting temperature, high thermal conductivity very good oxidation and hot corrosion resistance and good mechanical properties [1,9]. The good properties of this materials have been playing an active role for the application in high temperature and corrosive environments. The publication about the HVOF coatings based on the intermetallic are not complete. It is effect of information protection concern new materials used in technology. The authors of this paper design new coating materials based on the intermetallic phases for the power plant and waste combustion. The proposed composite coatings have not commercially available counterparts. The complex investigation of there materials are presented in [10-16] and as the results of the high temperature exposure of intermetalic coatings they are elaborated two oxidtion models of this coatings. In this paper the models are presented.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

Composite powders obtained by SHS method with NiAl and FeAl intermetallic matrix are the base materials [10]. The composite powders were thermally sprayed on K10 steel by

HVOF method in Jet Kote II system. The coatings contain the NiAl phase were strengthened by a fine dispersive Al_2O_3 and modificated by Cr and the intermetallic coatings based on the FeAl phase were only strengthened by dispersive Al_2O_3 The coatings are designated as. NiAl (Cr)-Al_2O_3 and FeAl-Al_2O_3.

Kinetics tests of the coatings' mass change were carried out by periodic oxidation method. The procedure of corrosion resistance test in air and temperature 950^0 C and the scheme of the installation to examine gaseous corrosion are shown in [11]. Kinetics of corrosion processes was analyzed through an analysis of the weight of growing scale after 24, 48, 72…500 h exposure time. The reaction rate constant **(k_p)** was calculated from the parabolic law [10]:

$$\left[\frac{\mathbf{\Delta m}}{\mathbf{A}}\right]^2 = k_p \bullet \mathbf{t} + \mathbf{C} \tag{1}$$

where **Δm** is the mass increment after exposure time **(t)** and **C** is the free parameter (correlated with initial, non-parabolic run).

The coating surface after the corrosion test was observed by light microscopy (Richert 2) and is presented in [10-16]. The morphology and chemical composition of the corrosion products after the test was determined by Hitachi S-4200 scanning microscopy with a voyager system (Noran analysis system of the characteristic X-radiation of elements). The phase composition analysis of corrosion products was performed by an X-ray diffraction method. The diffraction patterns were collected using an X-Pert Philips diffractometer equipped with a graphite monochromator on diffracted beam and with the following slits (in the sequence from Cu tube to counter): Soller (2^o), divergence (1/2°), antiscatter (1/2°), Soller (2^o) and receiving (0.15 mm).

The morphology, chemical and phase composition of the corrosion products after the test obtained from the above procedures enable the elaboration of the presented corrosion models.

3. RESULTS AND DISCUSSION

The obtained values of k_p parameters are comparable for all studied materials and indicate excellent high temperature corrosion resistance. The corrosion rate of NiAl(Cr)-Al_2O_3 coatings is controlled by the diffusion of corrosion products in the channels. The composite coatings with NiAl intermetallic phase have higher oxidation resistant then once with FeAl matrix (table 1).

Table 1.
Parabolic reaction rate constant

Coatings	Parameter k_p [$g^3/(cm^6 \circ s)$]
FeAl- Fe_xAl_y	$3{,}4 \circ 10^{-10}$
NiAl(Cr)-Al_2O_3	$4{,}9 * 10^{-11}$

The parabolic rate law of the corrosion products on studied coatings is determined by a slow-growing, adherent, continuous oxide layer. On the Fe_xAl_y-Al_2O_3 coatings the corrosive layer contain the iron and aluminum oxides (table 2). The morphology structure, after 48 hours corrosion test, show, that the grow of aluminum oxides on the surface of HVOF coatings decreas the grow of iron oxides (fig. 1 a-b). As the results, we can observed the nodular structure of corrosion products on the surface of Fe_xAl_y-Al_2O_3 coatings (fig 1b)

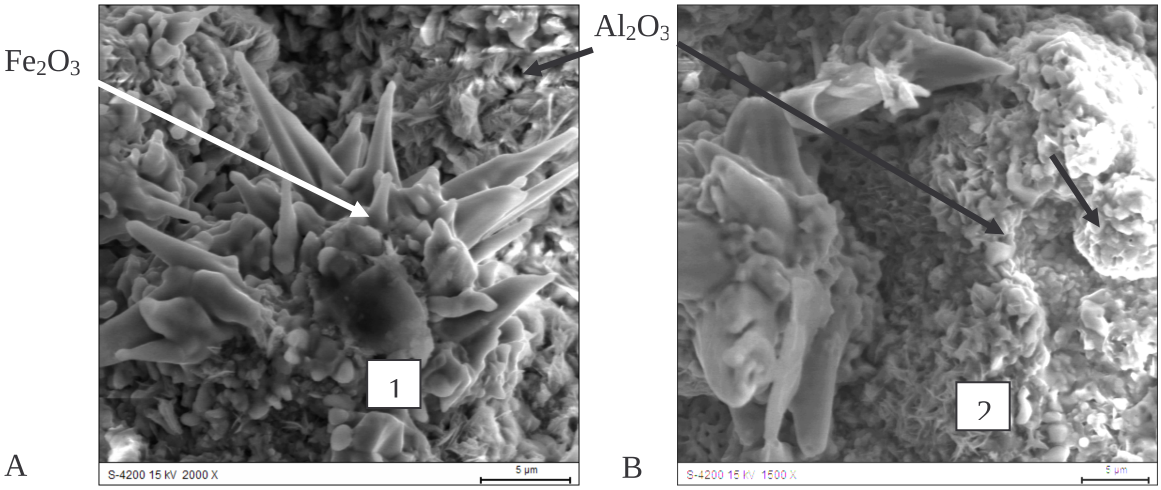
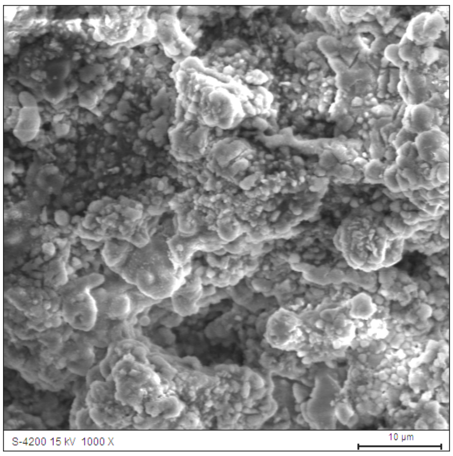


Figure 1. Morphology of corrosion products on the Fe_xAl_y-Al_2O_3 coating after A) 24 h; B) 48 hoxidation test

Table 2 .
Chemical composition of corrosion products presented in fig.1

A)	**point 1**	
symbols	**at [%]**	**wg [%].**
O	14,13	4,50
Fe	85,87	95,50

B)	**point 2**	
	at [%]	**wg [%]**
O	38,77	23,25
Al	45,43	45,94
Ca	3,43	5,15
Fe	12,37	25,66



symbol	**at [%]**	**wg [%].**
O	24.08	18.65
Al	45.90	42.35
Cr	2.93	5.21
Ni	17.08	33.79

Figure 2. Morphology and chemical composition of corrosion products on the NiAl(Cr)-Al_2O_3 coating after 24 h oxidation test.

The morphology structure of the corrosion products on the NiAl(Cr)-Al_2O_3 coatings is only nodular and wishers of oxides are not observed (fig.2.). The chemical composition show that the oxides of nickel, chromium and aluminum are occurred always together (table in fig.2)

The phase analysis of the corrosion products after 48 and 500 hours corrosion test are presented in table 3. The X-ray pattern indicates that the iron oxide on the surface of the Fe_xAl_y-Al_2O_3 coating is the Fe_2O_3 phase and the corrosive layer on the surface of NiAl(Cr)-Al_2O_3 contains such phases as: Al_2O_3, Cr_2O_3, NiO , NiAl $_4$, Ni_3Al (after 48 hours) and Al_2O_3, $NiCr_2O_4$, NiO , $NiAl_2O_4$(after 500 hours of corrosion test)

Table 3.
Phase composition of corrosion products after the oxidation test.

Coatings:	**Exposure time [hours]**	**Phase composition of corrosion products**				
NiAl(Cr)-Al_2O_3	**48**	**Al_2O_3**	**Cr_2O_3**	NiO	**NiAl $_4$**	**Ni_3Al**
	500	**Al_2O_3**	**$NiCr_2O_4$**	NiO	**$NiAl_2O_4$**	
FeAl-Al_2O_3	**48**	**Al_2O_3**	**FeAl**	**Fe_2O_3**		
	500	**Al_2O_3**	**FeAl**	**Fe_2O_3**		

The presented results enable the elaboration of the two models of the growth of corrosion products on the intermetallic coatings strengthened by a fine dispersive Al_2O_3.

4.OXIDATION MODELS OF THE GROWTH OF CORROSION PRODUCTS ON THE INTERMETALLIC COATINGS

The oxidation models of the growth of corrosion products on the intermetallic coatings are presented in Fig. 5 for Fe_xAl_y-Al_2O_3 coatings and in fig 6 for NiAl(Cr)-Al_2O_3 coatings. The models take into account the chemical composition of coatings and phase composition of the corrosion product.

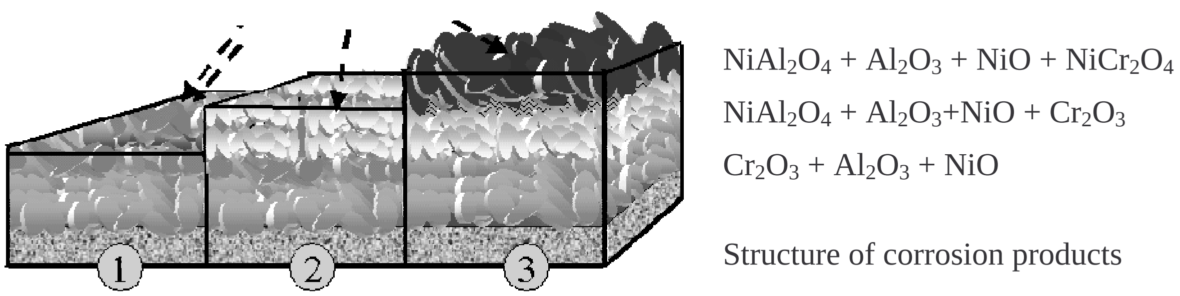


Figure 3. Oxidation model of the NiAl(Cr)-Al_2O_3 coating during 1) –24 h; 2) – 48h; 3) 500 h corrosion test.

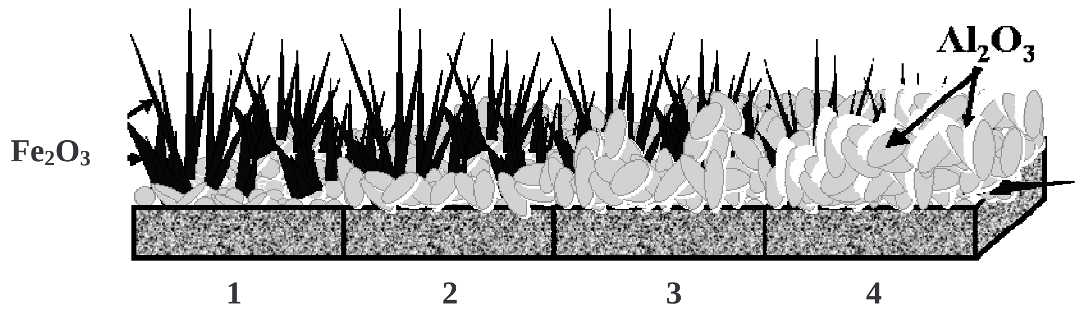


Figure 4. Oxidation model of the FeAl-Al_2O_3 coating during 1) 12h; 2) 24 h; 3)48 h; 4) 500h corrosion test

5. CONCLUSION

All investigations on corrosion resistance confirm good properties of composite coatings with intermetallic phases.

The results indicate that:

- during the corrosion test, adhesive oxide layers are formed
- the layers ensure high oxidation resistance,
- the layers contain stable alumina scale,
- the stable α-Al_2O_3 phase on the surface of Fe_xAl_y-Al_2O_3 coatings form a nodular structure of the corrosion products
- the nodular structure is more protective than the whiskers structure
- the coatings with an NiAl matrix are of higher oxidation resistance than those with FeAl.

The composite coatings are the perspective materials in applying at elevated temperature in oxidant environments. The coatings are preferred to application as protection of the water-walls and of boiler tubes for combustion of the waste.

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