Growth of corrosion products on thermally sprayed coatings with FeAl intermetallic phases in aggressive environments

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Abstract: The cyclic corrosion behavior of coatings with FeAl intermetallic matrix was investigated in agressive gases for exposure times of up to 500 hours. The composite coatings strengthened by a fine dispersive Al_2O_3 were thermally sprayed by HVOF method in Jet Kote 2 system. One portion of intermetallic coatings was sealed with an inorganic phosphate seal. The surfaces of HVOF sprayed coatings after a corrosion test were subjected to observation. A kinetics test was carried out by periodic method. Mass changes of the studied coatings during the corrosion test are presented. The surfaces of the composite coatings after the corrosion test in aggressive environments were analyzed by scanning microscopy observation. The results show that an adherent alumina scale and iron oxide layers were formed on all studied coatings. A stable α-Al_2O_3 phase on the surface of the studied coatings ensure high oxidation resistance. The corrosion rate is controlled by diffusion of corrosion products in the channels of oxide layer. An analysis of the corrosion products' phase composition was conducted by an X-ray diffraction method. The growth of corrosion products on the thermally sprayed coatings during the corrosion test and the chemical reactions between the corrosion products and aggressive environments are presented. All the results confirm good heat proofness of HVOF sprayed coatings with an intermetallic FeAl matrix.

Keywords: Intermetallic phases, Corrosion resistance

1. INTRODUCTION

The intermetallic materials from the FeAl system have very good corrosion resistance as well as in the air both in sulfur and chlorine mixed gas. The excellent properties of this materials are determined by their stable ordered crystal B2 structure (CsCl-type) in the composition range of 37-49 at.-% Al. The structure is stable to the melting point (1340^0C) and protective for the diffusion processes, due to its strong, stable chemical bonding, it creates the equi-atomic system [1-7]. Moreover, intermetallic based on high activity aluminum have good high temperature oxidation and hot corrosion resistance due to their ability to form protective Al_2O_3 scales [8-14]. The aim of this paper is to present new composite coatings for the water wall in a power plant or for the boiler in waste combustion. The composite coatings with FeAl matrix are strengthened by a fine dispersive Al_2O_3 and have no commercially available counterparts. Moreover, the present paper presents a proposed high temperature corrosion

mechanism for coatings with a FeAl intermetallic matrix in aggressive environments containing oxygen/sulfur and chlorine mixed gas at 973 K.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

The materials for the research are thermally sprayed fine-dispersion composite coatings. The coatings were obtained in accordance with Fig. 1.
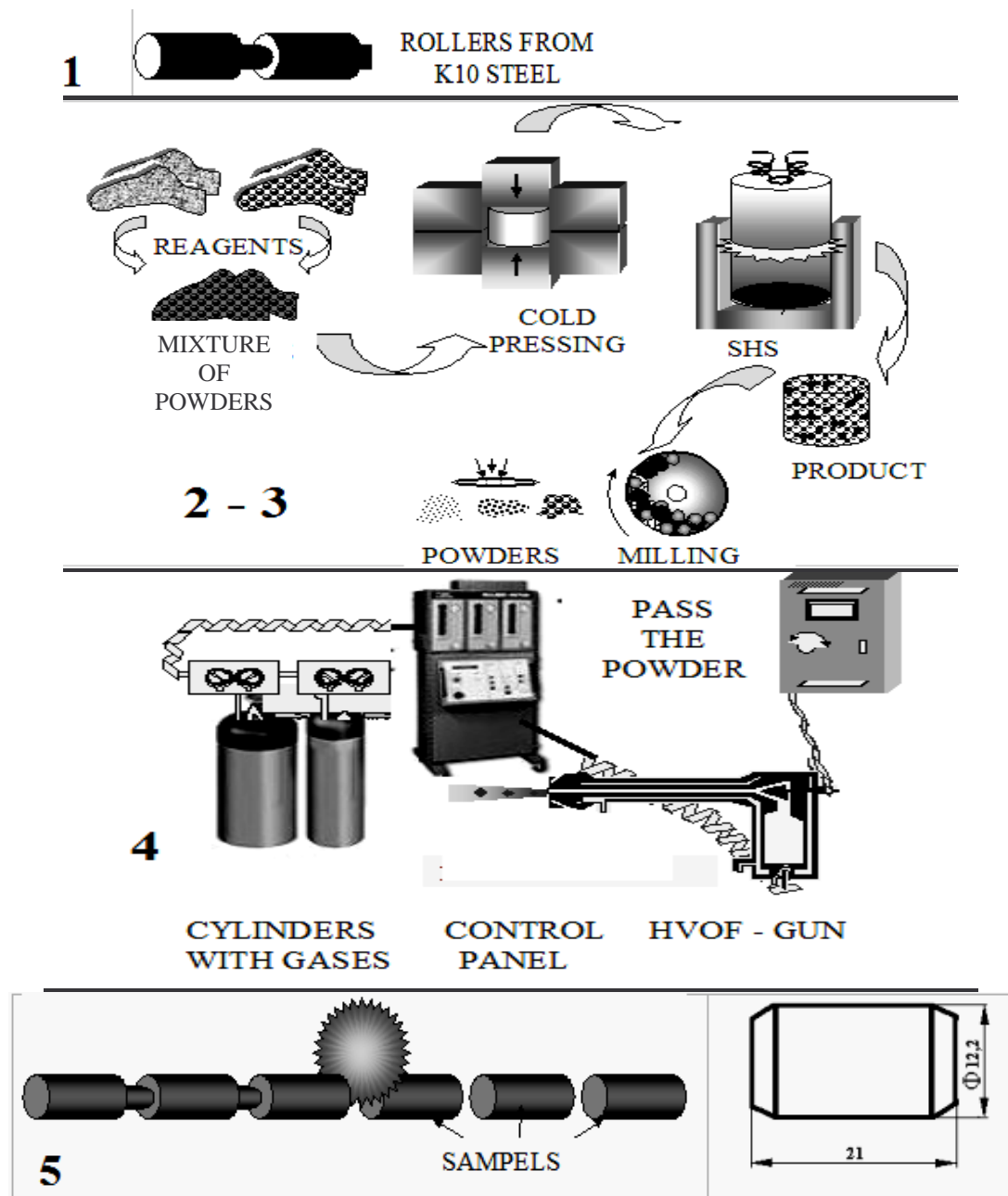

Figure 1. Five preparation stages of materials for corrosion test.

The five preparation stages of materials for a corrosion test are presented in Fig. 1. They encompass:

1. formation of substrate for coatings; 2. SHS-synthesis of material for coatings; 3. powder preparation for thermal spraying; 4. high velocity oxy-fuel method; 5. cutting the samples for the corrosion test. One portion of the thermally sprayed coatings was sealed with an inorganic phosphate seal [15-16]. Kinetics tests of the coatings' mass change were carried out by periodic oxidation method. The procedure of corrosion resistance test in an aggressive gas: N_2 + 9% O_2 + 0,2% HCl +0,08% SO_2 and **t**he scheme of the installation to examine gaseous corrosion are shown in paper 18. Kinetics of corrosion processes was analyzed through an analysis of the weight of growing scale after 24, 48, 72…500 h exposition time. The reaction rate constant **(k_c)** was calculated from the cubic law [17]:

$$\left[\frac{\Delta m}{A}\right]^3 = k_c \bullet t + C$$

(1)

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

The morphology, chemical and phase composition of the corrosion products after the test were presented in [18-20]. The thermodynamic conditions of the formation of corrosion products were analyzed on the base of the presented results and the diagrams of phase stability for studied materials. The phases' stability diagrams were obtained by an HSC analysis program. The results obtained from the above procedures enable the elaboration of the corrosion mechanism.

3. RESULTS AND DISCUSSION

The obtained values of k_c parameters are comparable for all studied materials and indicate excellent high temperature corrosion resistance. The cubic rate law of the corrosion products is determined by a slow-growing, adherent, continuous oxide layer.

Table 1.
Cubic reaction rate constant

Coatings	Parameter k_c [g^3/($cm^6 \circ s$)]
FeAl- Fe_xAl_y	$2.2 \circ 10^{-15}$
FeAl- Fe_xAl_y with seal	$2.8 \circ 10^{-16}$

The superimposed stability diagrams of Fe-S-O and Al-S-O at 600^0C are presented in Fig.3. The thermodynamics conditions indicate the formation of stable aluminum and iron oxide layers with the following parameters of partial pressure:

- for oxide p_{O2}=0,09 atm. = $9*10^3$ [Pa] and for sulfur p_s=1,7710^{-40}[atm.]=1, 77*10^{-35} [Pa]. However, the phase analysis of corrosion products on the surface of the coatings revealed that phases from the Fe-S system are also present in the scale (Fig. 4). The formation of those phases is possible, when partial pressure of the reactive elements in

the gas mixture can be changed during the corrosion process. The observed changes of partial pressure and the difference between the thermodynamic and phase analyses of corrosion products are caused:

- firstly, by the growth of corrosion products on the thermally sprayed coatings during the corrosion test and secondly, by the chemical reactions between corrosion products and aggressive environments.

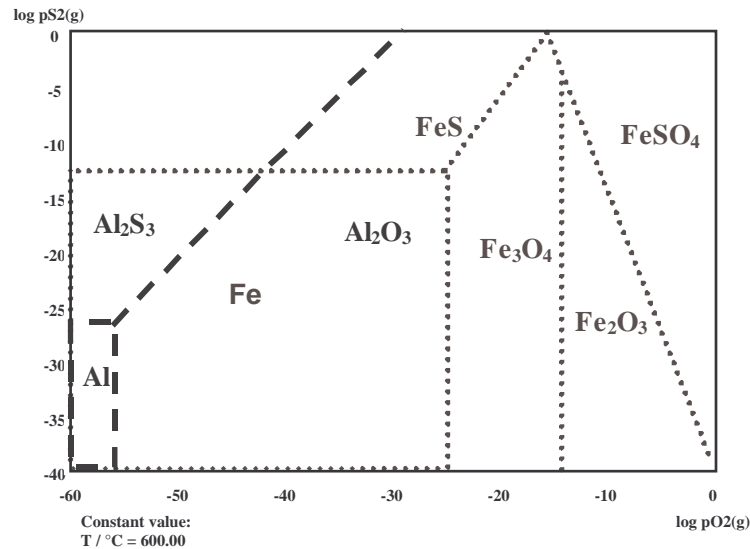The processes coverage is presented in paper [20].

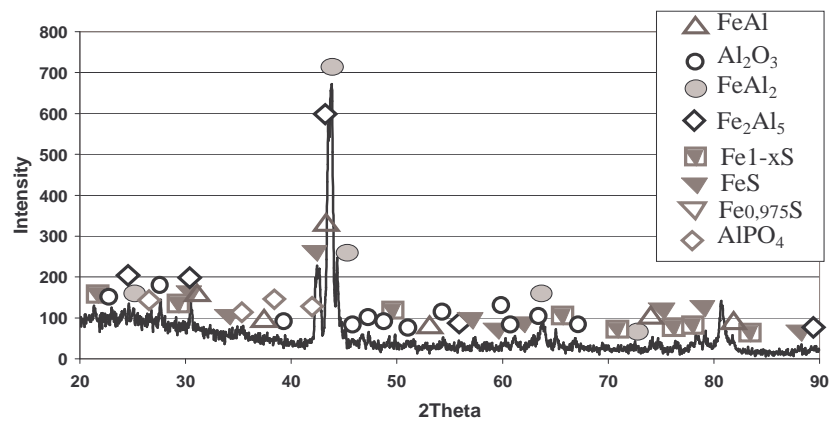Figure 2. Superimposed stability diagrams of Fe-S-O, Al-S-O at 600^0C.

Figure 3. Corrosion products on composite coatings with a seal after 48 h.

3. MECHANISM OF THE CORROSION PROCESS

The proposed mechanism of the corrosion process presented in Fig. 4 takes into account the chemical composition of coatings and phase composition of the corrosion product.
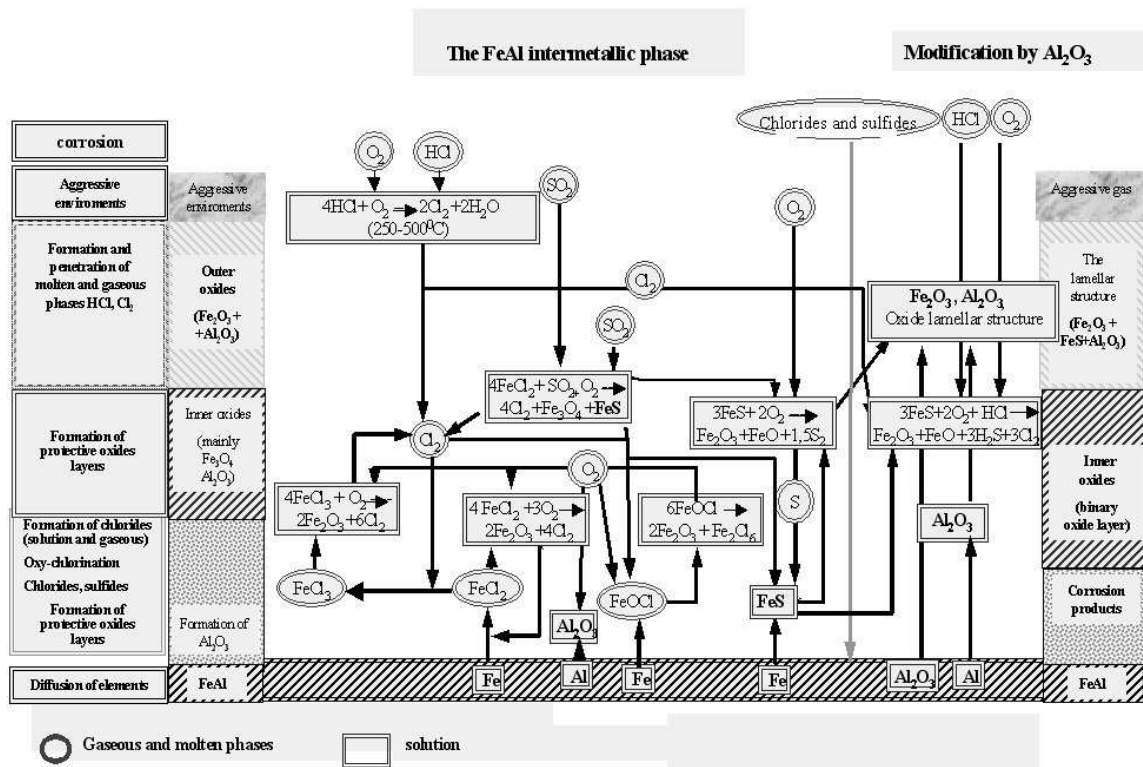
Figure 4.rrosion mechanism of intermetallic coatings in aggressive: N_2 + 9 vol.% O_2 + 0.2 vol.% HCl + 0.08 vol.% SO_2 gas mixture
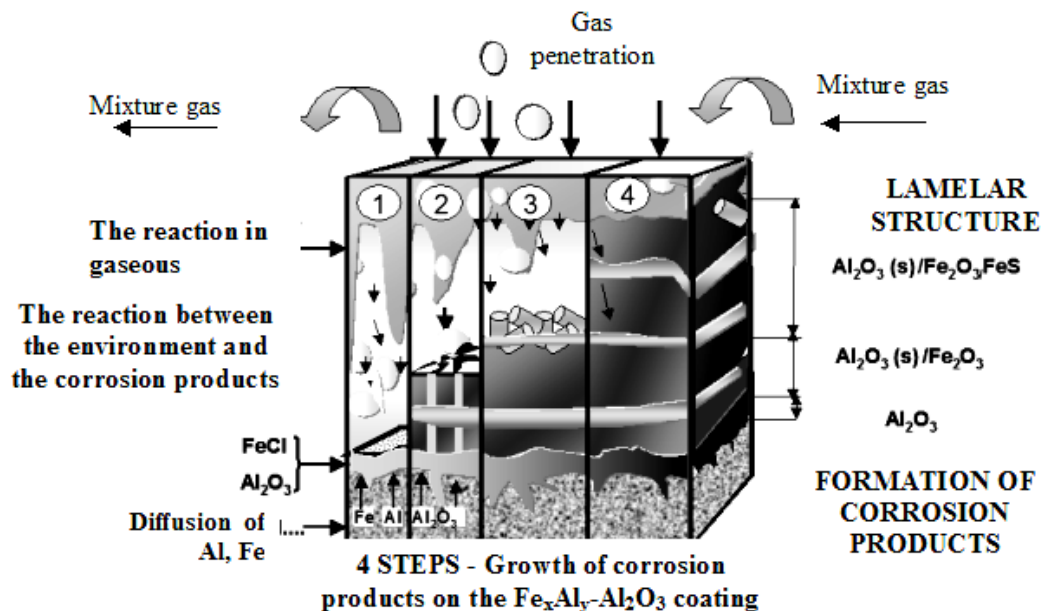

Figure 5. Model of the corrosion mechanism of intermetallic coatings in aggressive gas mixture: N_2 + 9 vol.% O_2 + 0.2 vol.% HCl + 0.08 vol.% SO_2.

To summarize, the proposed corrosion mechanism of intermetallic coatings in aggressive environments covers two ranges: at first – the linear rate law of initial corrosion products and next - stable, cubic rate low of the protective layers.

The initial stage included: ① formation of gaseous and solution chlorides ②slow growth of alumina layers③-④ the chemical reaction in gases and formation of sulfides and protective oxide layers (lamellar oxide structure with alumina and iron oxides) (the symbols are consistent with the designations in Fig.5.).

The proposed mechanism explains the changes in the kinetics corrosion process (at the beginning - initial range and next, a stable range). Moveover, it is consistent with Wagner's theory of sulfidation process [16]. The presented mechanism explains the difference between thermodynamic and phase analysis of corrosion products, it shows the complexity of the corrosion processes and of the chemical reactions between the corrosion products and aggressive environments, as well as the formation and penetration of molten and gaseous phases.

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