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High-temperature corrosion resistance of NiAl(Cr)-Al_2O_3 coating in N_2+9%O_2+0.2% HCl+0.08%SO_2 atmosphere

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Properties

ABSTRACT

Purpose: The aim of this study was to determine the resistance of nickel and aluminium intermetallic phase-based coatings, modified with chromium and aluminum oxides, and to determine the hypothetical mechanism of these materials' corrosion.

Design/methodology/approach: The selected results of high temperature corrosion resistance of HVOF sprayed coatings with NiAl intermetallic phases are presented. The aggressive corrosion gas included: N_2+9%O_2+0.2% HCl+0.08%SO_2. The temperature of cyclic corrosion test was 927 K and the exposure time was 500 h. The macro and microstructure of coatings after and before corrosion test were analyzed by optics and scanning microscopy. The thermodynamically diagrams and phase diagrams of corrosion products after the test are presented. The phase composition of corrosion products was determined by X-ray analysys.

Findings: The proposed mechanism and growth of corrosion products on the NiAl(Cr)-Al_2O_3coatings are shown. The carried out tests allow the characterisation of the properties of coatings with NiAl phase, and supplement the state of knowledge in the scope of their high temperature corrosion resistance.

Practical implications: The new elaborated coating can be applied in elevated temperature and aggressive environments for protection of water walls boilers or waste combustors.

Originality/value: The elaboration of proposed mechanism of growth corrosion products on the NiAl(Cr)-Al_2O_3coating and the presentation of reaction during the corrosion process and degradation of coating.

Keywords: Intermetallic; Ni-Al phases; HVOF coating; Corrosion resistance; Corrosion mechanism

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1. Introduction

A significant number of publications and research thesis prepared and published within the last thirty years have dealt with the structure, mechanical properties and corrosion resistance of solid materials containing intermetallic phases. Alloys of intermetallic phases of nickel with aluminium are characterized by properties comparative to iron alloys: low density and high mechanical properties, as well as resistance to oxidation and to carburizing atmospheres, or those containing oxygen and sulphur [1-19]. Due to their high resistance to high-temperature corrosion in complex atmospheres, NiAl and Ni_3Al solid materials and coatings of intermetallic phases are designed for the protection of elements of boilers working as waste combustors. In the research, it was assumed that composite coatings with NiAl phase sprayed with the supersonic HVOF method may be characterised by high corrosion resistance in complex atmospheres containing oxygen, sulphur and chlorine [11-19]. The aim of this study was to determine the resistance of nickel and aluminium intermetallic phase-based coatings, modified with chromium and aluminum oxides, and to determine the hypothetical mechanism of these materials' corrosion.

2. Base materials

In order to create coatings in the process of HVOF supersonic thermal spraying, a composite powder, obtained in the process of activated self-propagating high-temperature syntheses (SHS), was used [11-14]. The produced nickel and aluminium intermetallic phase-based composite powder was homogenous throughout its volume (Fig. 1). The grains were characterised by a dispersive structure with a fraction of oxides.

The obtained composite material of the assumed phase composition: NiAl, Al_2O_3, Cr_2O_3, (Fig. 2) was thermally sprayed in the Jet Kote 2 supersonic system on rolls of K10 steel, in accordance with the diagram shown in Fig. 3.

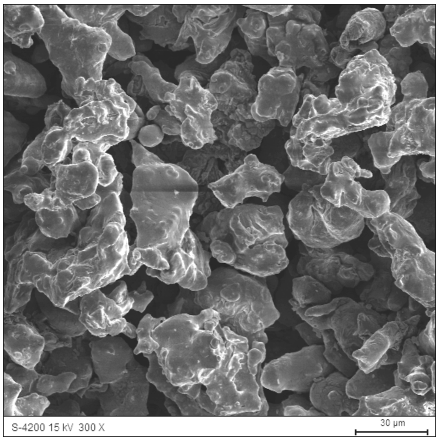

Fig. 1. The structure of composite powder

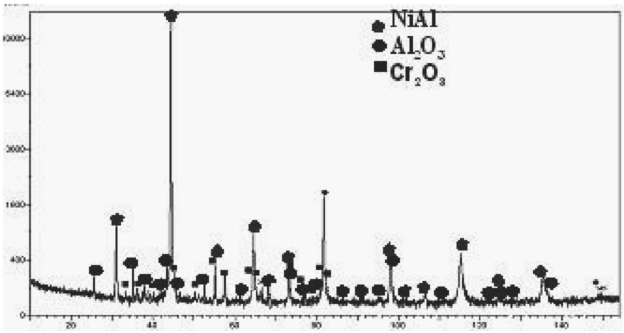

Fig. 2. Composition of NiAl(Cr) – Al_2O_3 powder after SHS synthesis

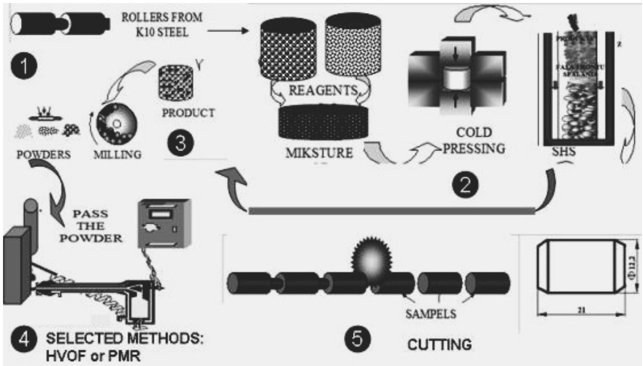

Fig. 3. Five stages of preparing the samples for the corrosion test

In the coatings spray system, a mixture of propan-butane gases was used and the powders were fed from a powder feeder (Miller Thermal). The selection of the parameters of thermal coating spraying was one of the tasks of the research project [11]. The coatings produced were examined paying special attention to corrosion.

3. Experimental procedure

The made samples were subjected to cyclic corrosion tests in an atmosphere of: $N_2 + 9\ \%\ O_2 + 0.2\ \%\ HCl + 0.08\ \%\ SO_2$ at a temperature of 600^0C. The stand for the corrosion tests is shown in diagram (Fig. 4).

Kinetics of corrosion processes was analyzed through an analysis of the weight of growing scale after 24, 48, 72…500 h exposed time. The change in mass after 24, 48…500 hours of test duration were defined, and the increase constants of k mass were determined from the formula (1).

$$\left(\frac{\Delta m}{A}\right)^3 = k_k \bullet t + C \qquad (1)$$

where:

Δm – mass increase in t time

C - free parameter, taking into consideration the initial non-cubic mass increase.

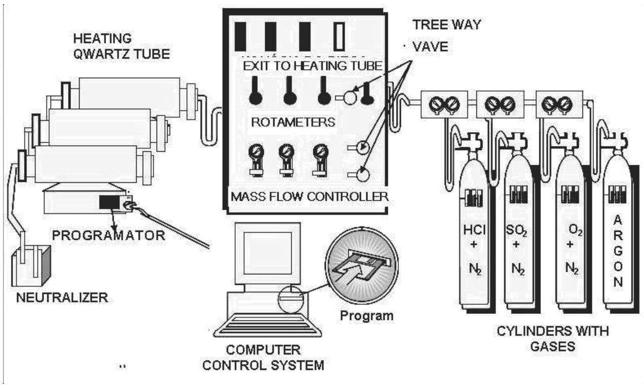

Fig. 4. Diagram of the stand for the corrosion test at an increased temperature in an amtosphere of aggressive gases

After subsequent process stages, tests of the coating surfaces' macrostructure were performed. A detailed analysis of corrosion products formed at the individual stages of the process was performed, specifying their morphology as well as chemical and phase composition. The observations were performed with the use of a Hitachi S-4200 scanning electron microscope. The test was to determine the changes of morphology of the coatings' surface, the way of corrosion products' growth, and to specify how the coating sealing process influences the surface development and the ways of corrosion products' growth. This was carried out using a Hitachi S-4200 scanning microscope with a Noran EDX attachment for the analysis of characteristic X-ray radiation. The chemical composition of the corrosion products located on the surface of the coating materials being tested was determined.

Qualitative phase analysis was carried out with the use of X-ray diffraction on policrystals. The tests were performed on a Philips's X'Pert model diffractometer with the use of a lamp with a copper anode and radiation length of $\lambda = 1.54178$ Å, powered by 30 mA current and 40 kV voltage. The registration was performed with the "step scanning" method with a 0.050 step and 4 seconds counting time. Qualitative phase analysis was performed based on the diffractograms obtained. The analysis was carried out based on reference diffractograms of the ICDD (International Center for Diffraction Data) index and an ASTM (American Society for Testing and Materials) card. The X-ray microanalysis tests and X-ray phase analysis tests were performed on flat samples. The results obtained were compared with thermodynamic data, and, with the use of the HRS programme, relative phase stability diagrams for the temperature of 600C (923 K) were determined. In order to make data interpretation easier, the diagrams obtained for Ni-O-S, Cr-O-S and Al-O-S were placed so that they would overlap.

An analogous procedure was performed with Ni-O-Cl, Cr-O-Cl and Al-O-Cl. The changes in samples' mass in time were measured and the curve of the corrosion processes' course was specified. The k_k mass increase constants were calculated. Analysis of the obtained results of the structural and thermodynamic tests was the basis for presenting an opinion on the coating corrosion mechanism with selected intermetallic phases in the atmosphere of N_2 + 9 % O_2 + 0.2 % HCl+ 0.08 % SO_2 and at a temperature of 600^0C (procedure – Fig. 5).

DETERMINING THE INPUT DATA

- test material
- tests results (mass measurements, morphology, chemical and phase composition of the corrosion products)
- analysis of literature on the issue of corrosion [1-26]

↓

INPUT DATA ANALYSIS

- compliance of the results with the literature data
- deviations of the results obtained from the phases stability diagrams for given temperature and pressure
- possible analogies of high-temperature corrosion in an environment with chlorine and sulphur content for heat resisting steels in relation to the corrosion process of the tested intermetallic phases
- possible analogies of high-temperature corrosion in chlorine and sulphur environment to the course of high-temperature corrosion in oxygen and sulphur environment concerning phases of Fe-Al system
- of reaction course possibilities of components diffusion

↓

PRESENTATION OF THE CORROSION MECHANISM

based on analysis of the literature and the results of tests

Fig. 5. The procedure of corrosion mechanism determination

The morphology, chemical and phase composition of the corrosion products after the test obtained from the above procedures and the data of literature [1-26] enable the elaboration of the presented corrosion models.

4. Results and discussion - corrosion resistance and suggested mechanism of NiAl(Cr)-Al_2O_3 coatings corrosion

The coatings produced were characterised by a homogenous structure, with no exfoliations or cracks, relatively low porosity and uniform overlapping (Figs. 6-7). Coatings marked with: NiAl(Cr) – Al_2O_3 were characterised by good adhesion to the substrate, and they met the assumed criteria so they could be tested paying special attention to their corrosion resistance.

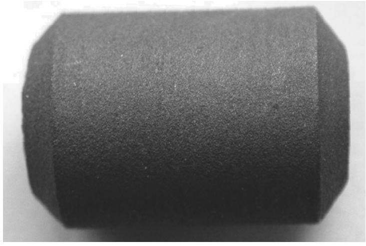

Fig. 6. A view of the NiAl(Cr) – Al_2O_3 coating surface, magn. 2x

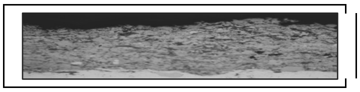

Fig. 7. Light microscope image of NiAl(Cr)-Al_2O_3 HVOF sprayed coating, magn. 25 0 x

4.1. Suggested mechanism of NiAl(Cr)-Al_2O_3 coatings corrosion

Due to the high corrosion aggressiveness of the atmosphere in which the coatings resistance tests were conducted, and the complexity of corrosion phenomena taking place in that environment, before determining and suggesting the corrosion mechanism, the obtained phase compositions were analysed and compared with Ni-O-S, Al-O-S and Cr-O-S and Ni-O-Cl, Al-O-Cl and Cr-O-Cl phase stability diagrams for the temperature of 600^0C (923 K), obtained with the help of the HSC programme (designed for determining and analysing stability diagrams) (Figs. 8-9).

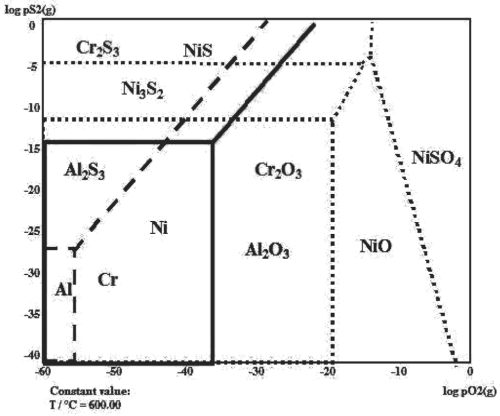

Fig. 8. Overlapped Ni-O-S, Cr-O-S and Al-O-S phases stability diagrams for temperature of 927 K

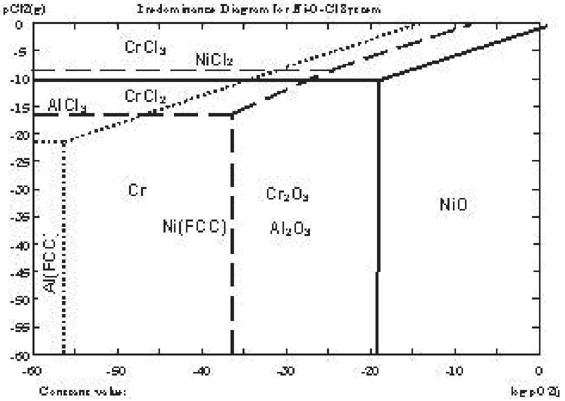

Fig. 9. Overlapped Ni-O-Cl, Cr-O-Cl and Al-O-Cl phases stability diagrams for temperature of 927 K

Analysis of phase composition of corrosion products formed on the surface of materials being tested enabled the identification of the following phases: after 48 h of test: aluminium oxide, chromium oxide, nickel chloride and nickel sulphide, and after completion of the test, only oxide phases (Al_2O_3 and Cr_2O_3). A nickel oxide phase, stable in the discussed conditions, was not identified (Fig. 10, Table 1).

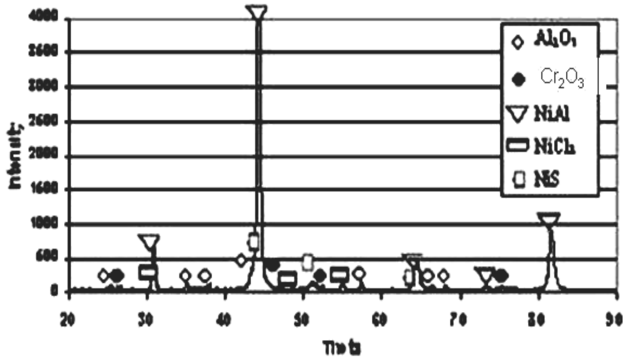

Fig. 10. X-ray diffraction of corrosion products after tests at a temperature of 600°C and in the period of 48 hours

Table 1.
Corrosion resistance of NiAl(Cr)-Al_2O_3 coatings, sprayed with the (HVOF) supersonic method

Test type:	Corrosion test		
Environment:	Mixture of aggresive gases: N_2+9%O_2+0.2%HCl+0.08%SO_2		
Temperature	600 ^0C (927 K)		
Test time:	500 hours		
	Mass increase [g/cm^2]		k_k mass increase constant [g^3/cm^{6}s]
Coating type:	Compliant with:		For the stabilization period
	linear law	cubic law	
NiAl(Cr)-Al_2O_3	7.4964	2.965	7.8 * 10^{-16}
Phase composition of corrosion products formed on the coatings' surface			
	After 48 h of test:		After 500 h of test
NiAl(Cr)-Al_2O_3	Ni, Al_2O_3, $NiCl_2$, NiS, Cr_2O_3		Cr_2O_3, Al_2O_3

However, in accordance with the phase stability diagrams for the Ni-O-S, Al-O-S, Cr-O-S and Ni-O-Cl, Al-O-Cl, Cr-O-Cl systems at a temperature of 600°C, it was found that the stable phases in the conditions of conducting the test, that is at partial pressure of: p_{o2}=0.09 atm. = 9•10^3 [Pa]; p_s=1.77•10^{-40}[atm.]=1, 77*10^{-35} [Pa]; p_{Cl}= 0.9•10^{-30}[atm]= 0.9•10^{-25}[Pa] are only oxide phases NiO, Cr_2O_3 i Al_2O_3. The additional formation of phases of NiS and NiCl type is possible only when the partial pressure of the corrosion component affecting the material is changed.

The formation of the abovementioned phases with simultaneous failure to identify nickel oxide was explained by the corrosion mechanism.

In the first stage, the analysis of the macrostructure (of surfaces) of coatings was performed and the registered mass change curves were interpreted, depending on the operation time of the materials being tested. The coatings, after the corrosion process, were characterised by a structure without any significant macroscopic changes, such as: exfoliation, cracks, peeling off or colour modification (Fig. 11). Continuous mass increase of the samples confirms that the corrosion products forming on the coatings' surface did not have a tendency to fall off. Moreover, in accordance with the obtained results of the tests of corrosion process kinetics of the NiAl(Cr)-Al_2O_3 coating, it was found that the mass change curves are characterized by two periods, depending on time. The first one – unstable, for which a linear approximation was applied, and a subsequent stabilization period, for which the mass increase constant was determined following the formula (1) for the cubic law (Fig. 12). This means making an assumption that the diffusion of the reacting substances in the scale being formed is a process which determines the rate of its growth [19-20].

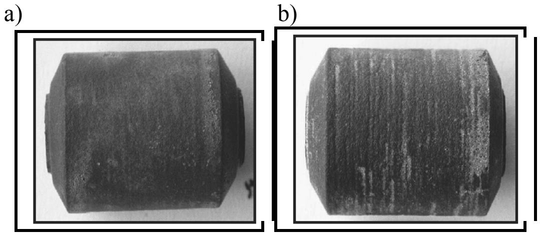

Fig. 11. View of the samples' surfaces, which were sprayed with the HVOF method after 500 hours of exposure at a temperature of 600^0C; a) NiAl(Cr) – Al_2O_3; b) NiAl(Cr) – Al_2O_3 U (sealed), magn. 1.5 x

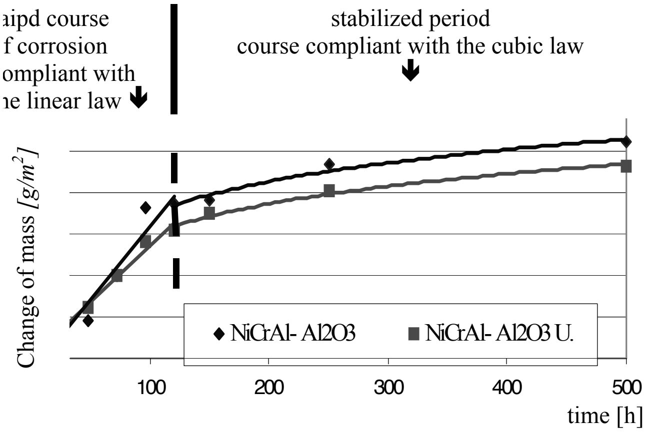

Fig. 12. Changes of the samples' mass in time function at a temperature of 600°C with marked periods which are characterized by the linear and cubic corrosion law

Therefore, during the scale's growth on the NiAl(Cr)-Al_2O_3 coating surface, it is possible to notice some analogies to the process of the chlorosulphonation of intermetallic phase-based coatings of Fe_xAl_y-Al_2O_3 type [15-16]. In both cases, the unstable initial mass increase can be explained by a series of corrosion phenomena, where the dominant role is played by a chlorination process which leads to the formation of usually volatile (possibly molten) corrosion products. The occurrence of new, unstable phases causes not only local disturbance of contact of the scale being created with the substrate, but also the formation of adventitious products of reaction, changing the partial pressures of the reactive gases. Therefore, there is a possibility of the formation of phases other than would result from a simple stability diagram analysis. Apart from oxide phases, the following phases can be formed: volatile $CrCl_2$ phase, and at higher partial pressures of chlorine – a stable $NiCl_2$ phase (Fig. 10).

Analysis of the literature on metal alloy corrosion in environments containing chlorine and sulphur compounds confirms that in the initial stage of the corrosion process both volatile and stable corrosion products are created in the form of chlorides, sulphides and oxides [15-16]. Whereas, both the chlorides formation and oxide and sulphide phases growth proceeds in accordance with the concentration of a given element, that is, in compliance with Fick's law. In consequence, the growing oxides may lead to the formation of a lamellar oxide structure inhibiting the corrosion processes.

In the case being discussed, the primary growth of oxides of Al_2O_3 and Cr_2O_3 type is connected with an excess of these elements in the coating. It should be noted that both aluminium and chromium were modifiers of the NiAl intermetallic phase-based coating. Moreover, it is supposed that the modification of the discussed coating with chromium causes, in the period of process initiation, the creation of a volatile chlorine phase of closer affinity to sulphur than aluminium. In the initial stage of the corrosion reaction, no aluminum sulphides are created, which could in consequence cause an increase of the chemical potential of sulphur above the equilibrium value, and the formation of an internal sulphuration zone, as happens in the case of non-modified intermetallic phases. The following facts support this:

1. Creation of aluminium sulphide on the substrate/scale interface would cause falling off and exfoliation of the layer of the growing scale. During the measurement of samples' mass changes, its growth was unambiguously identified (no losses were noted); macroscopic observation of the coatings' surface during the test allows us to state that no significant changes took place on the surface of the materials being tested, such as peeling off, exfoliation or cracks,
2. The volatile chromium chlorides being formed may undergo secondary reactions, which cause chlorine release and oxide formation. The released chlorine changes the equilibrium pressure of the atmosphere and, as a result, creates an internal chlorination zone with $NiCl_2$ creation in the areas with aluminium depletion. X-ray analysis of corrosion products has confirmed the presence of small amounts of nickel chlorides on the surface of materials being examined after only 48 hours of performing the test, besides large quantities of chromium and aluminium oxides.

In accordance with the foregoing, at the initial stage of reaction we deal with the creation of oxide coatings, growing thanks to cation diffusion from the core and "sucking out" the aluminium from the coating. Therefore, the initial excess of aluminium is advantageous as it becomes a motor for the creation of a continuous protective lamella of aluminium oxide. Moreover, the NiAl phase in the initial stage is not depleted of aluminium, and so nickel does not diffuse towards the material's surface. The depletion takes place in a later period, when the growing oxides start to form a continuous protective film of aluminium oxide. The diffusion of nickel is then quicker than that of aluminium, which means a larger supply of nickel to the boundary phases of coating/scale than that of aluminum, and transport of nickel towards the scale's surface. Cation diffusion may take place only via privileged ways, for example, along the intergranular boundaries. According to Wagner's theory, the diffusion activation energy on the grains' boundaries is lower than the activation energy of the lattice diffusion. There is some analogy here to the formation of FeS sulphides on the surface of FeAl-Al_2O_3 coatings [14-18]. The assumption of the above theses means that part of the nickel becomes bonded with chlorine on the substrate/scale interface as a result of the internal chlorination zone creation, and the remaining part is bonded with the sulphur coming from the aggressive action of the gaseous environment. Therefore, the appearing nickel sulphide grows as a result of cation diffusion from the core. It should be noted than in both zones discussed, the creation of continuous lamella, respectively of nickel chloride or sulphide chloride, is impossible. The presented mechanism is compliant with the results obtained. This can be explained by the fact that on the surface of the materials being examined, after the completion of a corrosion test lasting 500 hours, neither chlorides nor sulphides were identified. $NiCl_2$ and NiS phases were identified after only 48 hours of the test, on the border of detectability, by the probe with a simultaneous large fraction of oxide phases.

Diffractogram analysis of coatings with NiAl intermetallic phase has shown that after 48 hours of oxidation, aluminium oxide, nickel sulphides (NiS and NiS_2) and the created $NiCl_2$ chlorine phase are formed on the surface of the materials tested. Sulphide phases showed non-shaped, weak peaks, which confirms the slow development of corrosion products on the surface of materials tested. On the other hand, the $NiCl_2$ phase was identified based on very minute, however unambiguous, peaks (that is, peaks of this phase did not overlap with peaks of other phases, as often happens in the case of surface texturation). This means that $NiCl_2$ phase probably developed as one of the first ones, and its increase was inhibited by the formation of continuous aluminium oxide coating.

On the other hand, X-ray microanalysis confirmed that the phases discussed did not create a continuous lamella (only single concentrations of sulphide phases have been identified Figs. 13-14. It needs emphasizing that further formation of compact oxide lamella of lamellar structure inhibits the reacting substances' diffusion, so the increase of both successive oxide lamellas and the sulphide lamellas depending on them, is scanty. This confirms that on the surface of the formed scale, oxide phases are present after 500 h of operation (Table 1) and the course of corrosion process changes from the initial linear one to one consistent with cubic law (Fig. 13). The results are also compliant with the suggested mechanism for the nickel oxide phase, whose presence has not been confirmed. This means that modification of the coating with aluminium causes, in accordance with Fick's law, the initial growth of aluminium oxide, and not a formation of nickel oxide which is also stable in the discussed conditions (Figs. 8-9). In the case being discussed, the formation of continuous and compact scale, counteracting the oxide diffusion to the coating's surface, prevented the creation of additional oxide lamella of nickel when the nickel supply became higher.

In this scope, compliance with results presented by P. Saltykov et. al. in the Journal of Alloys and Compounds was obtained [27]. The tabular data presented by the author suggest unambiguously the initial formation of chromium oxide and not the nickel oxide which is also stable in the given conditions.

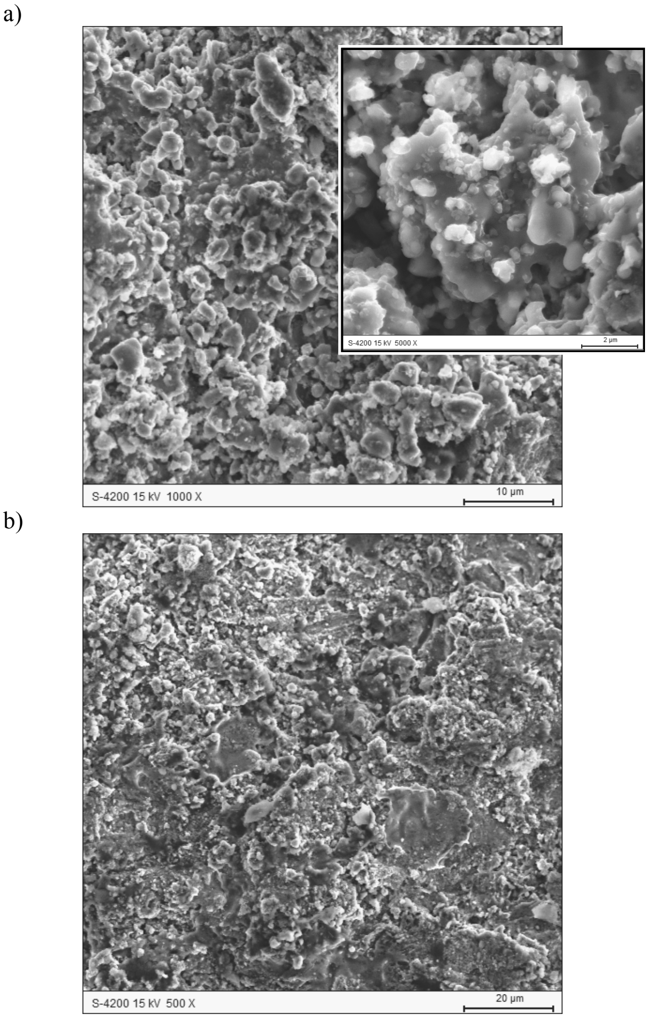

Fig. 13. Morphology of NiAl(Cr)-Al_2O_3 coating a) –after 48 h exposure time, b) 500 h exposure time

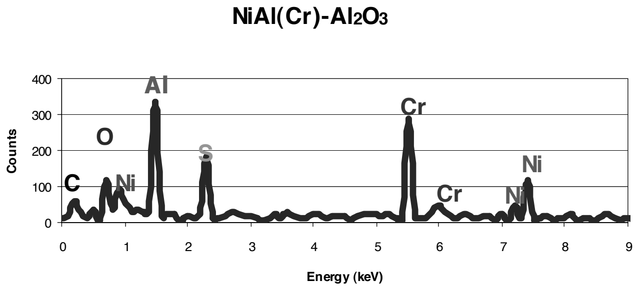

Fig. 14. EDX of NiAl(Cr)-Al_2O_3 coating –after 48 h exposure time

Considerations in this chapter concerning the mechanisms of forming the scales on the NiAl(Cr)-Al_2O_3 coating lead to the conclusion that the curves of samples' mass increase as registered during the kinetic measurements are connected with several processes running simultaneously.

First of all, the initial rapid increase of samples' mass is connected with the processes of mass transport in the oxide heterogeneous Cr_2O_3 scale being formed. This opinion is correct only until a continuous film is formed from oxides with a lamellar structure, consisting of aluminium and chromium oxides on the surface of the investigated materials, which inhibits the diffusion processes. Therefore, this lamella determines the course of corrosion processes which initially take place according to the linear law and then, to the cubic law, which explains the change of registered curves of mass measurements in time. The mechanism of oxide coating growth, taking place through the simultaneous transport of metal cations and oxygen anions is modified since finely dispersive atoms of admixtures counteract the diffusion of metal cations. Inhibiting the aluminium oxidation will also cause the prolongation of the period after which the alloy stops being able to form a protective coating.

The assumption that in the initial reaction chlorides in the gas form, which periodically change the composition of the corrosive atmosphere, explains the fact of finding no corrosion products in the form of chromium chloride on the surface of NiCrAl-Al_2O_3 coatings being examined. The volatile chromium chlorides being formed, while reacting with oxygen, may give stable corrosion products in the form of Cr_2O_3 phases and gas products in the form of Cl_2. In this scope, some analogies to the corrosion processes taking place in steels may be noticed (Fig. 15). The formation of chromium oxides was registered, among others, during tests of nickel-chromic steels in complex atmospheres [1-4]. The authors obtained stable corrosion products in the form of chlorides (lower process temperature and various partial pressures of the individual gas components).

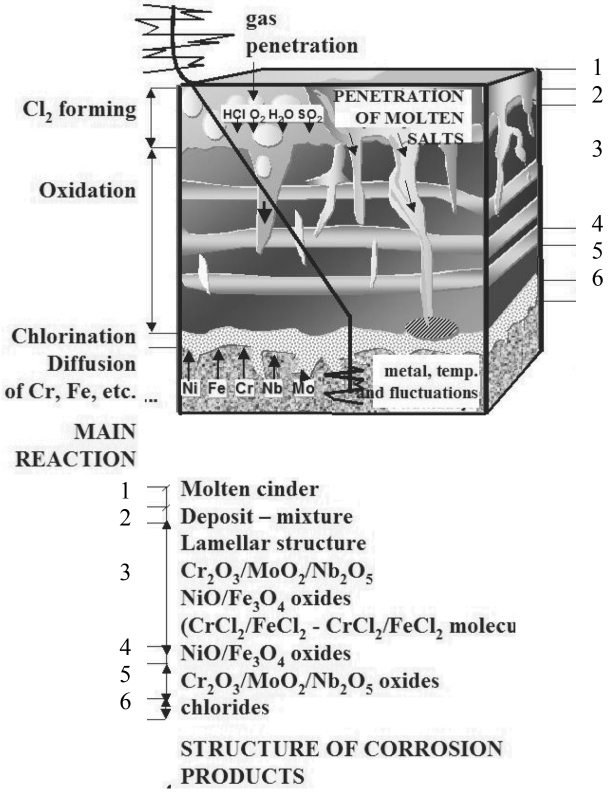

Fig. 15. Diagram of high-temperature corrosion course in an environment containing a mixture of gases: HCl; O_2 and SO_2 [4]

Assuming the formation of chromium chlorides and not nickel or aluminium chlorides in the initial reaction is complaint with the obtained stability diagrams of these phases, as well as with test results presented around the world. The authors of a study, Y.S.Li, M. Spiegel et al. [5-6] have proven that in an environment containing chlorine nickel shows lower reactivity with chlorine than chromium, so the surface of intermetallic phases alloys of NiAl type is notexposed to such an aggressive influence of the environment in the initial stage as took place in the case of non-modified intermetallic phases.

In accordance with the above thesis, the course of reactions in the suggested mechanism is the following:

$$4CrCl_2(g) + 3O_2(g) \rightarrow 2Cr_2O_3(s) + 4Cl_2(g) \qquad (2)$$

$$8CrCl_2(g) + 3SO_2(g) + O_2 \rightarrow 2Cr_2O_3(s) + 2CrO + 8Cl_2(g) + \\ + Cr_2S_3(s) \qquad (3)$$

Simultaneously, the initial "reserve" of aluminium diffuses towards the surface, where it bonds with oxygen and a lamella of aluminium oxide begins to form. At this moment, in the areas with aluminium depletion, an excess of nickel is present. It should be noted that together with the increase of nickel supply (in accordance with Fick's law), the chlorine concentration increases. The chlorine release takes place in accordance with formulas (2) and (3). In these thermodynamic conditions, a stable nickel chloride phase may be formed (Fig. 10). Therefore, chlorine again reacts with nickel in accordance with formula (4):

$$2Ni + Cl_2(g) \rightarrow 2NiCl_2(s) \qquad (4)$$

Analogous reactions, connected initially with the chromium chlorides' formation, before nickel chloride formation, and also the increase of heterogeneous Cr_2O_3 scale as a result of secondary reaction of chromium chlorides with oxygen, were reported by A. Zahs et al. in Corrosion Science magazine [26]. The authors of the study also noted some analogies in the scope of the chlorination of intermetallic phases alloys from the Fe-Al and Ni-Al system, connected with the initial influence of chlorine on the materials' surfaces. However, they underscore here the advantage of modified alloys of Ni-Al over Fe-Al since, in their opinion, the affinity of nickel to chlorine evidently lowers with the fraction of other metals.

Whereas, on the surface of the corrosion lamella being formed, the initially formed sulphides react in accordance with formula (3) with the oxygen contained in the corrosive atmosphere, giving as a result stable corrosion products – chromium oxides and sulphur released in gas form.

$$2Cr_2S_3(s) + 3O_2 \rightarrow 2Cr_2O_3(s) + 3S_2(g) \qquad (5)$$

The released sulphur reacts in accordance with formula (5) with nickel, which is diffused towards the surface through intergranular boundaries in the growing scale. As a consequence, NiS compound is created. The reaction is analogous to the mechanism of sulphuration of coatings with Fe-Al system phases, as suggested by S.C. Kung and w.T. Bakker [19]. The authors of the study have suggested that in the initial corrosion stage they may have been dealing with the intensified process of sulphur's influence on the surface of FeAl alloy tested by them. In the authors' opinion, as a result of the reaction of the iron sulphides with oxygen, sulphur is released, which may again react. The process of releasing gas products in the form of chlorine and sulphur, in accordance with the reactions shown, cause constant fluctuations of these components in the corrosive environment and changes of their partial pressures [15-20]. In turn, the formation of chromium oxide Cr_2O_3, as a result of the various reactions shown, causes its initial non-uniform increase, which leads to the formation of heterogeneous Cr_2O_3 scale, enabling initially the nickel diffusion. Therefore, when nickel's supply is increasing, it can quite easily diffuse towards the surface of the scale being formed, and it does not manage to react totally with chlorine in the internal chlorination zone. In the situation described above, no continuous lamella of nickel chloride is formed, which would weaken the connection between the growing scale and substrate.

Independently of the formation of compounds in the form of iron chlorides and oxides, as well as sulphides in the incubation period, a continuous lamella of aluminium oxide starts to be formed. This lamella, independently of the changes of partial pressures of the corrosion components being discussed, is thermodynamically stable in almost the entire range of concentrations (Fig. 8). It is formed as a result of two phenomena:

- aluminium diffusion from the core, which, in a reaction with oxygen, gives a stable aluminium oxide,
- as a result of modification of the discussed coating with aluminium oxide.

The finding of aluminium oxide growing on the surface of the examined scale may be explained by the diffusive nature of changes taking place in the lamellar structure built of Cr_2O_3, NiS and an initially small amount of Al_2O_3. It should be noted that in the initial stage the aluminium concentration lowers and the nickel concentration increases towards the scale's surface. Aluminium diffusion takes place all the time in accordance with the concentration gradient of this element in the lamellar film; that is, in accordance with Fick's law. This is confirmed by the fact of identifying both chromium and aluminium phases on the surface of growing oxide scale. In the scope of protective lamella of aluminium oxide formation, there are some analogies to the so-called "poisoned interface mechanism" and "dynamic segregation mechanism", connected with oxidation of dispersively modified alloys of intermetallic phases, described in the literature [23-25]. In both cases there is a deceleration of scale's growth, as a result of which a thin layer is formed, which is characterized by lower stresses and, consequently, better adherence to substrate than a layer formed on a non-modified alloy [23-24]. In the mechanisms presented, the clear connection between the formation of an oxide lamella with modification of alloy with a given element on the surface of substrate or of protective scale is underscored. However, the mechanisms presented concern the alloys being in an oxidizing environment and modified with only one type of element, so they cannot be uncritically accepted as a whole. The creation of a continuous lamella of aluminium oxide causes the inhibition of diffusion processes of reacting substances coming from the environment towards the coating's surface, and it explains the transformation of the initial non-cubic increase of samples' mass into a cubic process, characterized by a low increase of tested materials' mass during operation. The process running in accordance with the cubic law is characterized by a so-called stabilization period. It needs emphasizing that in this period, the fraction of intergranular diffusion in the total nickel transport process through the scale decreases to the advantage of lattice diffusion, which determines the reaction rate in the stabilization period being discussed [18-20]. The length of incubation period depends on the process temperature and the speed of crystallite growth, forming the passive oxide layer.

Moreover, as a result of aluminium diffusion from the core, which begins in the incubation period, there is a possibility of forming a continuous aluminium oxide layer below the layer of lamellar structure, comprised of aluminium oxide, chromium oxide and sulphide phase. In the period when the course of corrosion processes shows deviations from the cubic law, the factor determining the speed of the corrosion process is (in accordance with the previous assumptions) diffusion within the grains' boundaries. So, grain boundaries show tendencies to form an open microchannel, allowing the oxidizer to access the coating's surface, and the creation of the internal oxide layer [16, 19-20]. With this assumption, it is possible to state that the corrosion resistance of coatings depends, among other things, on the initial aluminium content in the coating. This conclusion is analogous to the conclusions presented, among others, by Bakker, during tests of the corrosion resistance of intermetallic phases to oxidation in high temperatures and to hot corrosion (oxygen's and sulphur's influence) [19, 20].

Formation of continuous aluminium oxide lamella (under the layer of lamellar structure) on the coating/scale interface surface causes an increase of the adhesion of scale to the substrate, and explains why no weight losses, exfoliation or peeling off of the growing scale were found. It needs emphasizing that the corrosion processes are still recorded, although they are very limited. The growing of a protective aluminium oxide coating on the surface of materials slows down these processes, hence their course is compliant with the cubic law and not the parabolical one, and the reaction rate constants are very low. Formation of a continuous aluminium oxide lamella below the forming oxide layers of lamellar structures is the reason for "inhibiting" corrosion processes.

In order to better visualise the suggested corrosion mechanism, in Fig. 16 its model is presented. Taking into consideration changes taking place in the corrosion environment as a result of the reactions (Fig. 17), stable and volatile/molten corrosion products are determined and the modification with aluminium oxide is taken into consideration.

Summing up, the mechanism suggested above assumes the presence of two periods: the initial one, running in accordance with the linear corrosion law, comprising the incubation process and the initial increase of corrosion products, and a subsequent stabilisation period, whose course is approximated with the cubic corrosion law. In the incubation period, the suggested mechanism takes into consideration: ① the course of reaction connected with chlorides' formation (in gaseous and molten form), ② a slow growth of aluminium and chromium oxide ③-④ reactions connected with the formation of nickel chlorides, sulphides and subsequent oxide layers until the formation, on the surface of a lamellar oxide structure, of: aluminium and chromium oxide (designations in accordance with Fig. 16). It also assumes in this period an intensified process of chlorine's and sulphur's influence, which are released as a result of reaction and constant fluctuations taking place in the corrosive environment. This confirms Wagner's theory on the sulphuration process. Explaining partial pressure changes of reacting substances in the corrosive atmosphere, it elucidates the apparent departures from the thermodynamic course of the corrosion process. Moreover, it explains changes of corrosion process kinetics, elucidating its initial non-stable and then, stable course.

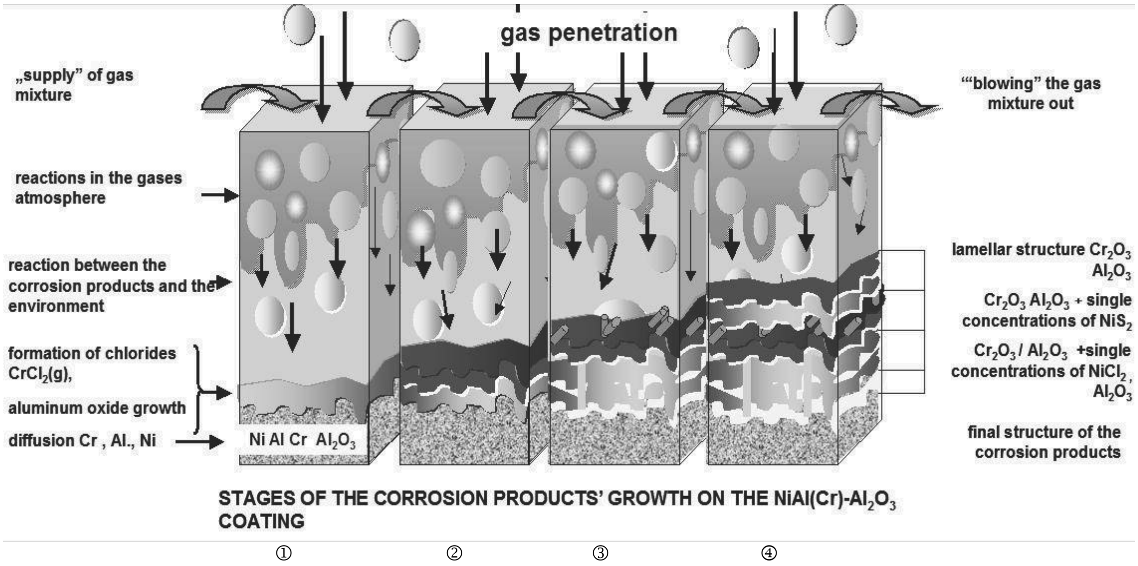

Fig. 16. Suggested mechanism of coating's corrosion: Growth of corrosion products on the surface of NiAl(Cr)-Al_2O coating during the corrosion process: ①the course of reaction connected with chlorides' formation (in gas and molten form), ②slow growth of aluminium and chromium oxide ③-④ reactions connected with the formation of nickel chlorides, sulphides and subsequent oxide layers

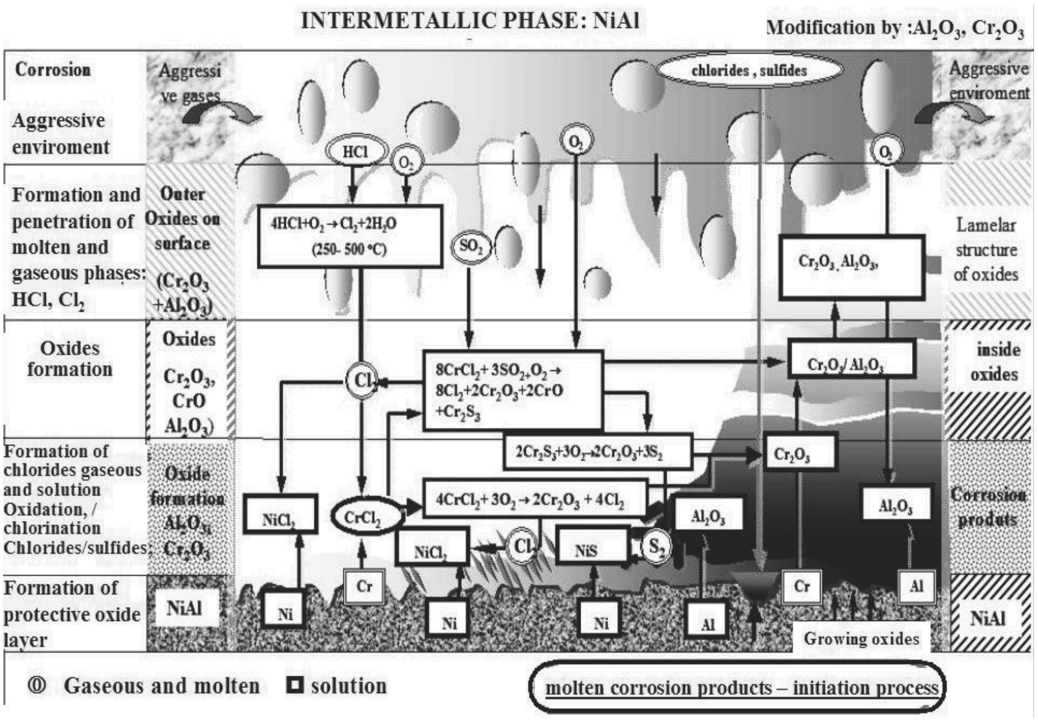

Fig. 17. The corrosion mechanism of NiAl(Cr)-Al_2O_3 coatings in aggressive environments: N_2+9%O_2+0.2%HCl+0.08%SO_2

5. Conclusions

Based on the literature data, as well as the test results obtained and analysed, it is possible to formulate the following conclusion:

- the coatings, sprayed using the supersonic method with intermetallic NiAl phase and aluminium oxide, are characterised by high corrosion resistance in an aggressive atmosphere which contains oxygen, sulphur and chlorine at a temperature of 600°C;
- the composite dispersive powders, obtained with a self-propagating high-temperature syntheses SHS, of a complex phase composition and morphology containing intermetallic NiAl phases and finely dispersive emissions of aluminium oxide (Al_2O_3) meet the requirements of powder materials designed for thermal spraying of coatings with high corrosion resistance;
- the kinetics of the growth of corrosion products' layers on coatings in the complex atmosphere: N_2 + 9 % O_2 + 0.2 % HCl + 0.08 % SO_2 may be determined with the linear law in the initial period and then, with the cubic one, in the conditions of the conducted test. In the incubation period of the corrosion products' growth in a complex atmosphere, volatile chlorides and sulphides are created with the simultaneous formation of heterophase oxie scale, Al_2O_3 and Cr_2O_3. Thermodynamically stable oxides, formed on the coatings' surfaces, determine their corrosion resistance. The suggested mechanism presented here is in accordance with the obtained test results and the results of other authors' tests on the oxidization and sulphuration processes of intermetallic phases of the nickel – aluminium system. In the period of stable increase of corrosion products, it assumes the diffusive dislocation of components of nickel, chromium and aluminium in accordance with Fick's diffusion law. Thermally sprayed coatings with NiAl intermetallic phase are preferred for work in high temperatures and complex, aggressive corrosion atmospheres, as well as for the protection of construction elements in the power engineering industry;
- the carried out tests allow the characterisation of the properties of coatings with NiAl phase, and supplement the state of knowledge in the scope of their high temperature corrosion resistance [20-25]. The proposed mechanism of the corrosion process presented in Figure 9 takes into account the chemical composition of coatings and the phase composition of corrosion products.

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