

# Kinetics of corrosion on the intermetallic phase matrix FeAl in high temperature

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## Materials

### ABSTRACT

**Purpose:** Alloys on intermetallic phase matrix of iron and aluminium are considered the future materials for high-temperature applications as they are highly resistant to oxidation to temperature of 1100°C. The paper presents results of tests concerning kinetics of corrosion processes of alloy on intermetallic phase matrix FeAl type Fe40Al5CrTiB after vacuum casting and plastic treatment with the use of co-extrusion method and comparably for flameproof steel X12CrCoNi2120.

**Design/methodology/approach:** Corrosion tests were conducted in gas environment including 0.08% SO<sub>2</sub>, 0.02% HCl, 9% O<sub>2</sub> and nitrogen in temperature from 900°C to 1100°C in time of 100 hours. Kinetics of corrosion processes was marked, the condition of the surface of samples after tests was characterized with the use of electron scanning microscope and also the chemical composition of corrosion products was determined.

**Findings:** It was stated, on the basis of tests results that the increase of weight of corrosion products in time function has a parabolic character, where the highest mass was weighed for samples after test conducted in temperature of 1100°C. A significantly higher corrosive resistance of alloys was found in comparison with the resistance of flameproof steel types CrNi with austenitic structure.

**Practical implications:** The last feature is the reason to conduct the research for this group of materials as corrosion resistance materials. Especially FeAl intermetallic phase based alloys are objects of research in Poland and around the world in recent years.

**Originality/value:** The aim of this paper was to determine the influence of passivation in gas environment including 0.08% SO<sub>2</sub>, 0.02% HCl, 9% O<sub>2</sub> and nitrogen in temperature from 900°C to 1100°C in time of 100 hours on corrosion resistance of Fe40Al5CrTiB intermetallic phase based alloy.

**Keywords:** Metallic alloy; Corrosion; Microstructure

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## 1. Introduction

Development of technology with the aim of efficiency, reliability and productivity improvement of various products, forces the construction of new and/or modernisation of existing devices and installations. The choice of the proper technology in combination with the right material is the significant factor which

influences the improvement of productivity of industrial installations [1-3]. Significant possibilities in this area are created by the use of alloys and protective surfaces with intermetallic phases. In the last twenty years there has been a significant increase of interest in intermetallic phases meant for work in high temperature and complex environment, particularly after solving the technological problems connected with their manufacturing [4-9]. Alloys from Fe-Al system are applied in many different

branches of industry. They are applied in automotive, energy, petrochemical and aviation industries or in production of devices which function in elevated temperatures [10]. Such broad range of applications results from the fact that they have specific combination of resistance to the influence of oxidizing atmosphere up to temperature of 1100°C, particularly in environment which includes sulphur and chlorine, low density and resistance in elevated temperatures [11,12].

The disadvantages of them are: low ductility in ambient temperature and decrease of resistance in temperature above 700°C, resulting from susceptibility of those materials to being coarse-grained in crystallisation process [7,9,12]. However, there are methods of elevating the plasticity of those alloys and overcoming problems connected with small resistance to cracking in ambient temperature [13-15].

Different tests which have been conducted over the years prove that the improvement of properties can be achieved by the right choice of aluminium content, introduction of micro-addition of chromium and alloy-type micro-additions (mainly zirconium and boron), consolidating phase divisions, control of surface conditions and the structure of grains and maintaining the proper parameters of technological process [16-19].

Corrosion tests of those materials can be conducted in natural conditions by placing the samples in the area of influence of atmospheric factors and their observation (exploitation tests) or with the use of accelerated laboratory tests with the use of the proper climatic test chambers. In accelerated laboratory tests, one or a few corrosion factors are increased in order to speed up the corrosion process in comparison with standard exploitation. In most standardised tests there is elevated relative humidity and temperature applied. Such test may be used to initial assessment of the possibilities of application of newly developed construction materials [20, 21-23].

Unmodified materials on FeAl matrix are characterised with excellent resistance to corrosion in sulphur environment in temperature of 800-900°C and oxidation to temperature of 1200°C. FeAl phase in comparison with phase Fe<sub>3</sub>Al is characterised with higher resistance to the influence of oxidation and reduction environment. It was proved that the resistance of FeAl phase on sulphuration in gases containing H<sub>2</sub>S and SO<sub>2</sub> is better than in any other alloy based on iron and nickel. It is characterised with high resistance to oxidation up 1200°C and good corrosion resistance in aquatic environment. Moreover, phase FeAl shows significant resistance to influence of salty environment. Alloys on Fe<sub>3</sub>Al matrix are further characterised with high resistance to oxidation and influence of corrosive environments including sulphur and chlorine compounds. Intermetallic phases from FeAl system are particularly resistant to the influence of high temperature which appears on their surface due to the slowly forming layer of aluminium oxide Al<sub>2</sub>O<sub>3</sub>. The right adhesion of oxides to the surface is a protective barrier in diffusion process which guarantees intermetallic alloys a high resistance to both oxidation and reductive atmospheres which include oxygen and compound of sulphur and chlorine. The period after which the atrophy of the ability of alloy to create a protective layer of aluminium oxide Al<sub>2</sub>O<sub>3</sub> occurs together with appearance of so-called catastrophic corrosion is indirectly connected with technology of manufacturing of such alloy and directly with the amount of aluminium in the alloy. Selective oxidation of aluminium provides the creation of protective mill scale of Al<sub>2</sub>O<sub>3</sub> which prevents the diffusion of positive ions of

metal [10]. Modification of intermetallic phases is connected mainly with practical aspects. Application of intermetallic phases as construction materials, used in high temperatures, mainly results in an increase of their resistance to brittle cracking and increase of plasticity with maintenance of high corrosive resistance. Initial development of research on intermetallic phases from Fe-Al system led towards their modification with the proper alloy elements including zirconium, yttrium, boron, manganese, chromium, vanadium, titanium, cobalt, nickel or carbon. In most cases, simple configurations were tested by adding the right oxides or carbides which were the source of chemical element in its atomic form. On the basis of tests of modified intermetallic phase alloys with different amount of modifying elements, conducted by different scientific laboratories in the world, it was concluded that the most efficient additions which improve the resistance of intermetallic phases in elevated temperature, the plasticity and corrosive resistance to both isothermal and cyclic oxidation are: zirconium, boron and fine-dispersed yttrium oxide Y<sub>2</sub>O<sub>3</sub>. Moreover, a positive influence of modifying elements was found, both in oxygen environment and in the environment of aggressive gas mixtures including oxygen and sulphur, on the kinetics of oxidation of intermetallic phase alloys [10].

The results, achieved by authors of various papers, interchangeably prove the slowdown of the process of mill scale growth of Al<sub>2</sub>O<sub>3</sub> as a result of modification of FeAl phase with the right amount of given chemical element. It was shown that after addition of chromium and titanium the mass of the oxidation constituent of Fe-Al alloy increased. Additions of modifiers improved adhesion of mill scale and caused changes in its morphology. Moreover, as it can be found in literature analysis, the resistance of chromium modified alloys of Fe<sub>3</sub>Al is higher in reference to:

- oxidation in temperature 1000-1100°C in comparison with alloys type FeCrAlY and NiAl;
- influence of atmospheres containing H<sub>2</sub>S in comparison with alloys type Fe-18Cr-12Al;
- influence of melted nitrates KNO<sub>3</sub>-NaNO<sub>3</sub>-Na<sub>2</sub>O<sub>2</sub> and NaCl-Na<sub>2</sub>CO<sub>3</sub> in temperature up to 600°C [10].

It was also stated that the amount, size and shape of alloy additive influences the formation of mill scale. Presented results confirm that addition of fine-dispersed oxides positively influences the kinetics of corrosion whereas non-disintegrated particles diffusing to grain boundaries can be the source of micro-cracks in the material. Resistance tests were conducted of modified materials on intermetallic phase matrix to the influence of oxidising environments as well as chemically complex corrosive atmosphere in elevated and high temperatures and the results proved the influence of manufacturing technology on the corrosive resistance of alloys, the doping of other oxides, i.e.: Fe<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, or chemical elements zirconium (Zr), hafnium (Hf) on the properties of formed thin protective film of aluminium oxide [10].

The article presents the tests results of oxidation kinetics of alloy Fe40Al5CrTiB after plastic treatment based on extrusion in the environment including oxygen, sulphur and chlorine. A comparison was made between resistance to high-temperature corrosion of alloy Fe40Al5CrTiB and heat-proof steel X12CrCoNi2120. A change of mass caused by corrosion phenomena was determined in reference to surface of tested samples and the condition of surface, chemical composition of corrosion products as well as their phase composition.

## 2. Experimental procedure

Corrosion resistance test was conducted in temperatures of 700°C and 900°C for steel X12CrCoNi2120 as well as in 700, 900, 1000 and 1100°C for alloy Fe40Al5CrTiB in the environment: 9% O<sub>2</sub> + 0.2% HCl + 0.08% SO<sub>2</sub> + N<sub>2</sub>. Tests were conducted in time of 100 hours. Material for test was a set of samples made of alloy Fe40Al5CrTiB after crystallisation and plastic treatment with the use of extrusion and sample made of steel resistant to corrosion type X12CrCoNi2120. Tested samples had surfaces of 10 mm<sup>2</sup>. Mass of each of samples before and after corrosion test was determined with the use of laboratory scales with accuracy of

measurements of 10<sup>-4</sup> g. Chemical compositions of tested materials are presented in Table 1.

Microstructure of alloy on intermetallic phase matrix FeAl before corrosion tests was determined with the use of light microscope OLYMPUS GX51. The condition of surface after corrosion tests was checked with the use of scanning electron microscope (SEM) HITACHI S4200 with X-ray radiation detector EDS (Energy Dispersive Spectroscopy) with the use of which the chemical compositions of corrosion products were determined. Phase composition was marked with the use of X-ray phase analysis with application of X-ray diffractometer Jeol JDX 7-S.

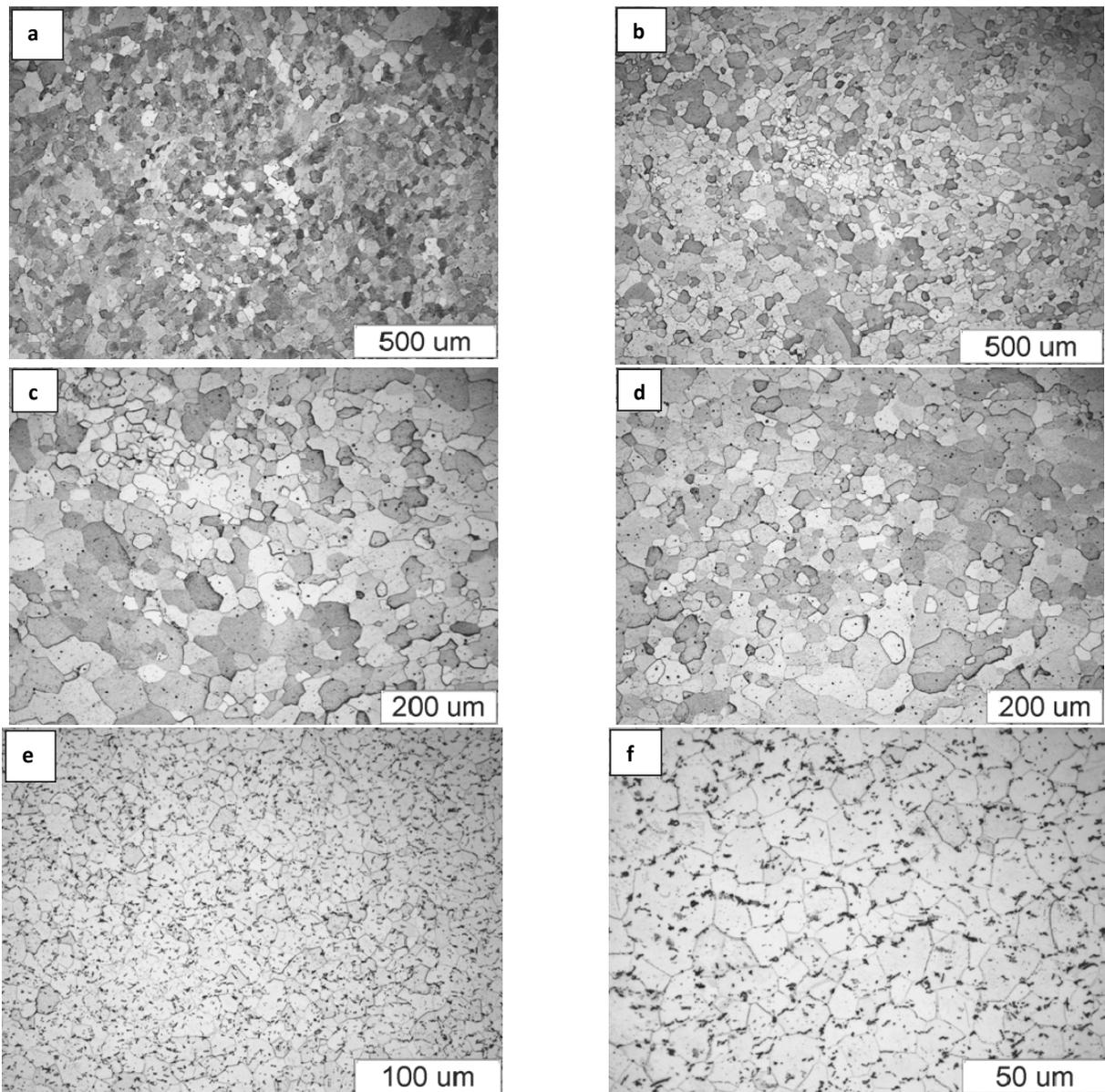


Fig. 1. Microstructure of alloy Fe40Al5CrTiB after plastic treatment, visible diversity of grain sizes and divisions, a, b) 100x; c, d) 200x; e) 100x; f) 50x

Table 1.  
Chemical composition of alloy Fe40Al5CrZrB and steel X12CrCoNi2120, %

	C	Cr	Mo	Ni	W
Fe40Al5CrZrB	-	5.3	-	-	-
	Co	Al	Zr	B	Co
	-	24.5	0.13	0.014	-
C	Cr	Mo	Ni	W	
X12CrCoNi2120	0.10	21.5	3.2	20	2.5
	Co	Al	Zr	B	Co
	20	-	-	-	20

### 3. Results and discussion

Alloy FeAl crystallises in the simplest out of intermetallic phases - structure B2. Microstructure of tested alloy Fe40Al5CrTiB after plastic treatment is characterised with diverse grain size with division (Fig. 1).

During the analysis of corrosion tests results of alloy FeAl and steel X12CrCoNi2120 the versatile changes of mass of samples for different materials were found (Figs. 2, 3). In case of samples of alloy Fe40Al5CrTiB only a slight change of mass was

observed in comparison to significantly bigger changes in samples of steel. Corrosion resistance of steel X12CrCoNi2120 meant for application on outlet valves of internal combustion engines is significantly smaller in comparison to corrosion resistance of alloy on intermetallic phase matrix FeAl (Fig. 2). Increase of mass of corrosion products of FeAl alloy has parabolic course and increases together with the test temperature (Fig. 3).

Tests of chemical composition of corrosion products of alloy FeAl samples with the use of X-ray microanalysis EDS have shown that, in the oxidation reaction, the compounds including mainly Fe compounds are formed, and as a result, the surface of the material is depleted from iron (Figs. 8-9).

Observations of surface of samples conducted with the use of electron scanning microscope (Figs. 5-9) and tests of chemical composition of corrosion products in FeAl samples with the use of X-ray microanalysis EDS (Figs. 10, 11) have shown that on the surface of samples there are areas which include aluminium oxides. The presence of passive layers of  $Al_2O_3$  give FeAl alloys a very high heat-resistance in oxidising environment. In the first stage of corrosion processes the oxidation of iron occurs in the surface layer and the heat-proof layer of  $Al_2O_3$  appears to isolate the rest of the material from the access of oxygen and sulphur. X-ray phase analyses of corrosion products have only shown the presence of  $Al_2O_3$  (Fig. 4).

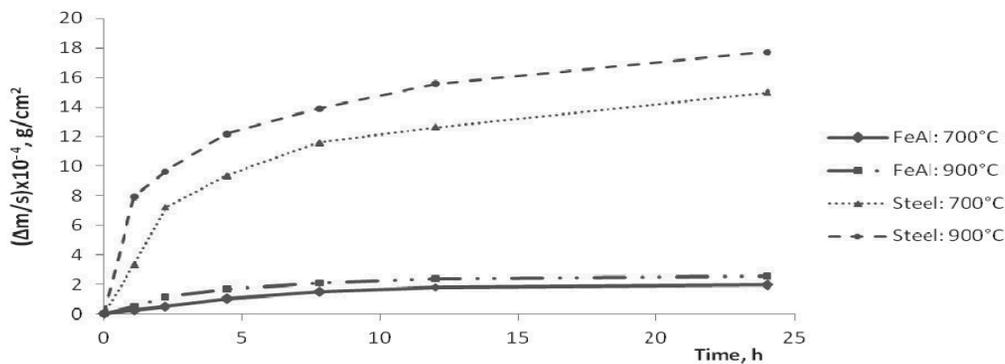


Fig. 2. Kinetics of corrosion in atmosphere: 9%  $O_2$  + 0.2%  $HCl$  + 0.08%  $SO_2$  +  $N_2$  for alloy Fe40Al5CrTiB (FeAl) and steel X12CrCoNi2120 in 700°C and 900°C

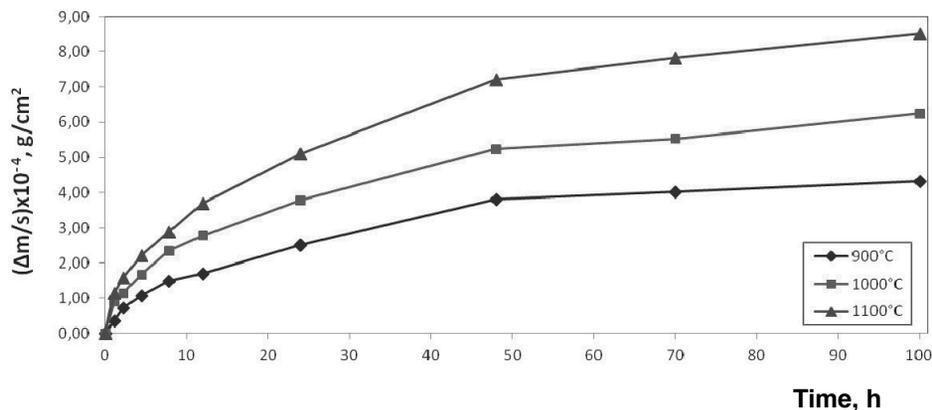


Fig. 3. Oxidation kinetics of alloy Fe40Al5CrTiB in atmosphere 9%  $O_2$  + 0.2%  $HCl$  + 0.08%  $SO_2$  +  $N_2$  in temperature 900-1100°C

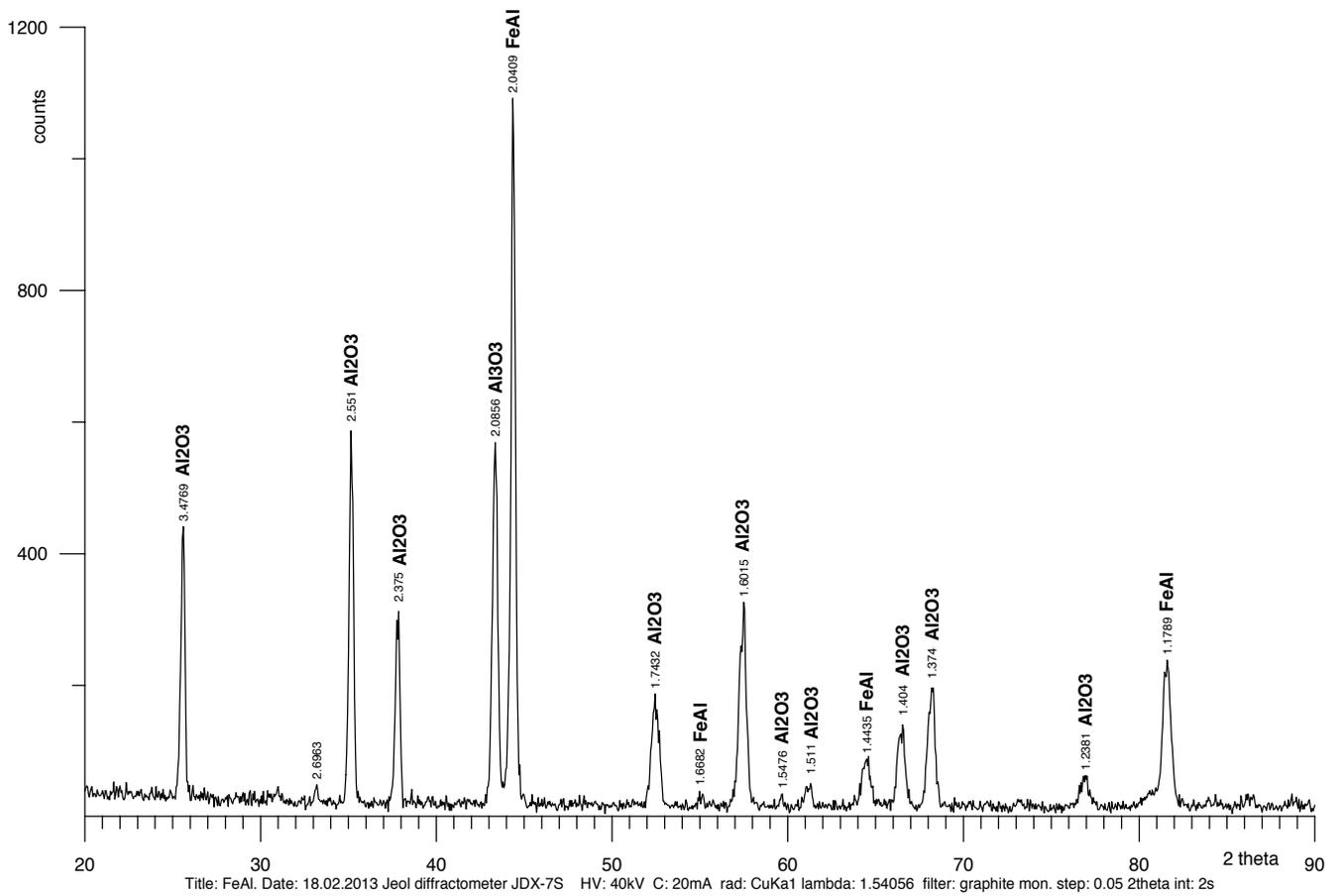


Fig. 4. Results of X-ray phase analysis of corrosion products of alloy Fe<sub>40</sub>Al<sub>5</sub>CrTiB after corrosion test in temperature of 1000°C in time of 100 hours

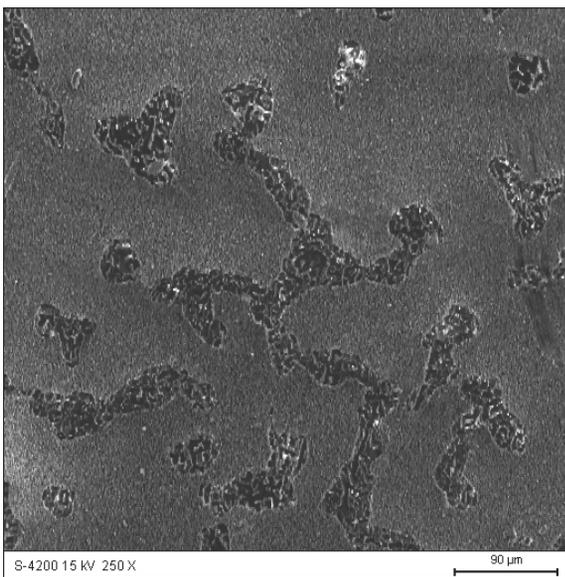


Fig. 5. Surface of alloy Fe<sub>40</sub>Al<sub>5</sub>CrTiB after corrosion tests in 900°C in time of 100h SEM

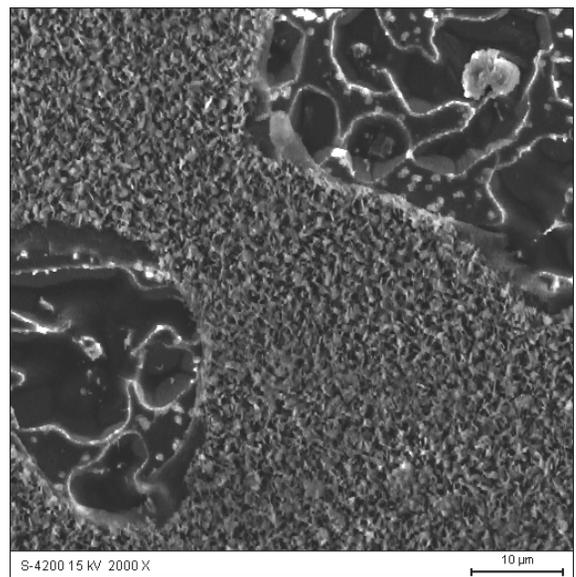


Fig. 6. Surface of alloy Fe<sub>40</sub>Al<sub>5</sub>CrTiB after corrosion tests in 900°C in time of 100h SEM

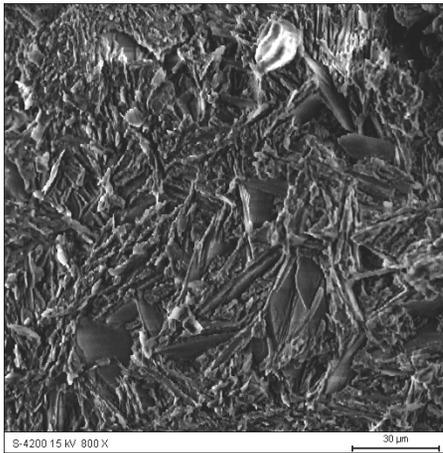


Fig. 7. Surface of alloy Fe40Al5CrTiB after corrosion tests in 1000°C in time of 100h SEM

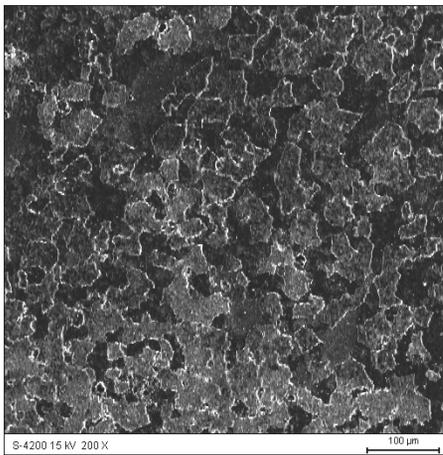


Fig. 8. Surface of alloy Fe40Al5CrTiB after corrosion tests in 1100°C in time of 100h SEM

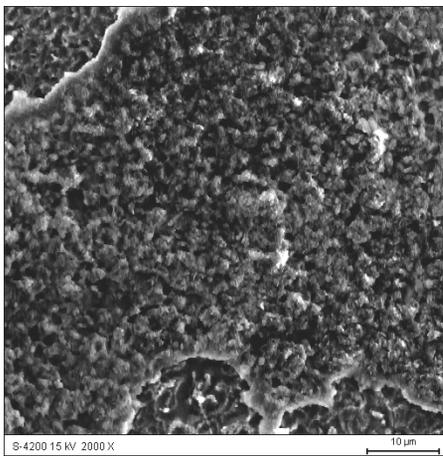


Fig. 9. Surface of alloy Fe40Al5CrTiB after corrosion tests in 1100°C in time of 100h SEM

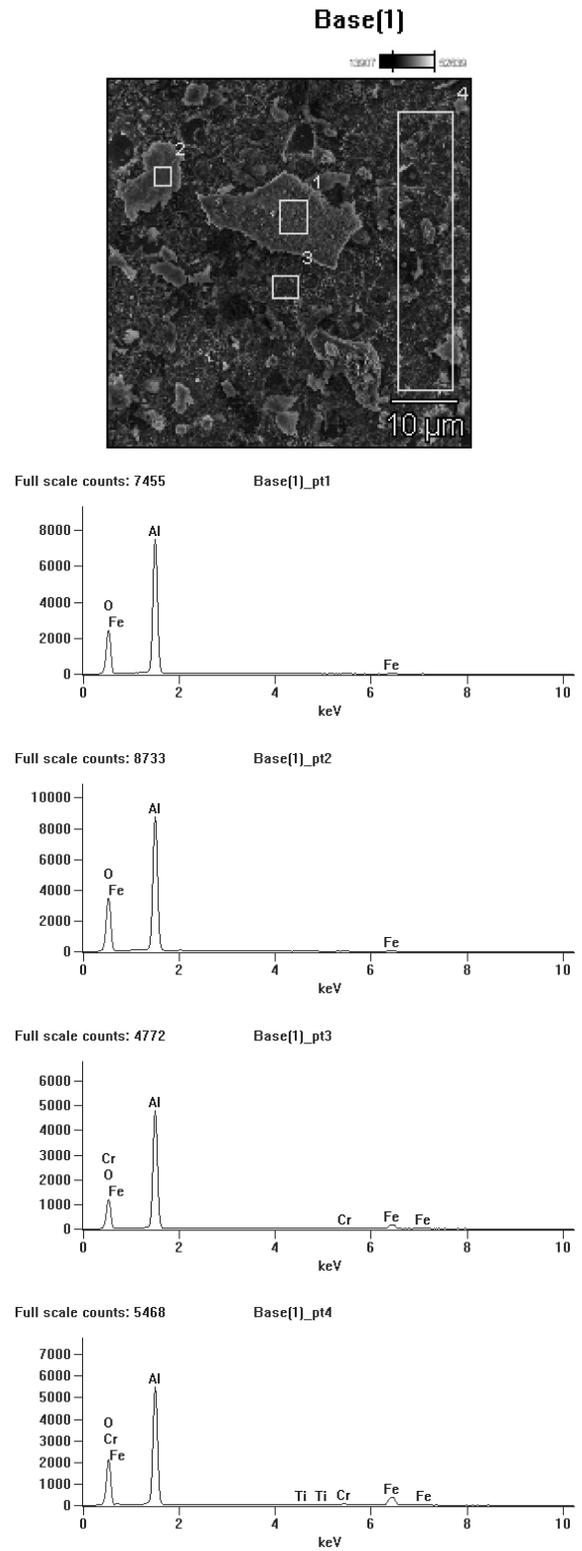


Fig. 10. X-ray radiation spectrum of chemical elements from the surface of sample from alloy Fe40Al5CrTiB after corrosion test in temperature of 900°C in time of 100h

### 4. Conclusions

Conducted tests and analysis of their results allow to conclude that the alloy on intermetallic phase matrix Fe40Al5CrTiB is characterised with high resistance to corrosion in the environment of 9% O<sub>2</sub> + 0.2% HCl + 0.08% SO<sub>2</sub> + N<sub>2</sub> to temperature of 1100°C. Corrosive resistance of this alloy in temperatures of 700°C and 900°C is significantly higher than the corrosive resistance of steel X12CrCoNi2120 applied on the valves of internal combustion engines. Increment of mass of corrosion products in FeAl alloy has a parabolic course and increases together with the temperature of the test. Good corrosive resistance of alloy Fe40Al5CrTiB is provided by the passive layers of Al<sub>2</sub>O<sub>3</sub> which form on its surface. Detailed explanation of the phenomena of high-temperature corrosion on intermetallic phase matrix FeAl needs conduction of further analysis.

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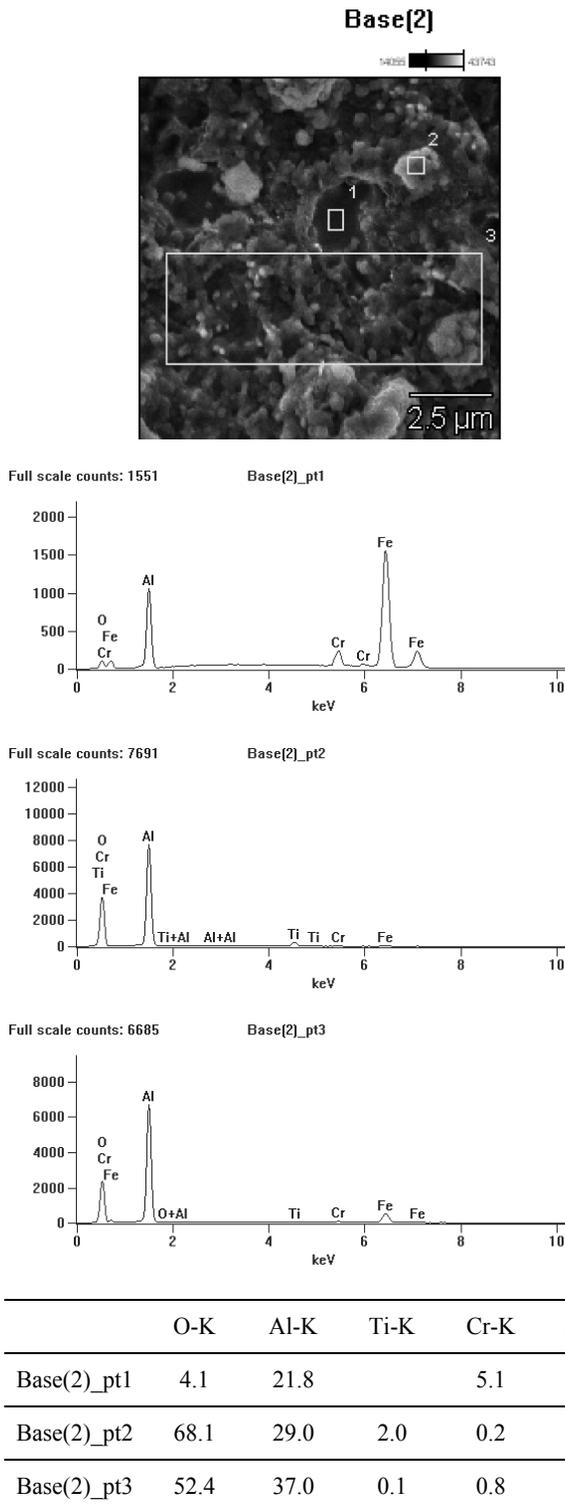


Fig. 11. X-ray radiation spectrum of chemical elements and results of chemical composition analysis from the surface of alloy sample Fe40Al5CrTiB after corrosion test in temperature of 900°C, in time of 100 hours

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