

# Effect of gas corrosion on the character of phase boundaries in Ni<sub>3</sub>Al / WC composite

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## Abstract

In view of quite specific physico-chemical and performance properties, the composite based on an intermetallic Ni<sub>3</sub>Al compound reinforced with tungsten carbides (WC) was selected for investigations. The said composite is characterised by very good mechanical and tribological properties within a wide range of temperatures, combined with good corrosion resistance. In fabrication of the Ni<sub>3</sub>Al/WC composite, a modified variant of the SHS process was applied. It is the SHSB process, i.e. the Self- Propagating High-Temperature Synthesis in Bath. The said method enables obtaining pure products of reaction, unoxidised and free from the precipitates of alien phases. The main goal of this study has been determination of the susceptibility of the Ni<sub>3</sub>Al/WC composite to gas corrosion. To examine the microstructure and chemical composition of both the composite and the scale, the metallographic and structural examinations were made, using optical and scanning microscopy.

**Keywords:** Composite in situ, Phase Ni<sub>3</sub>Al, SHSB Process, Carbide of WC, Gas corrosion .

## 1. Introduction

Dispersed particulate-reinforced metal matrix composites are considered products of the advanced technology, and as such raise vivid interest of numerous scientific and research centres. Among these materials, an interesting and important group form „*in situ*” composites, also known as composites of the second generation. In *in situ* composites, the reinforcing phases are formed in one single metallurgical process as a result of various reactions proceeding in liquid metal [1,2]. Often, the composite material fabricated by this route is assigned for elements, which should offer high mechanical properties and good corrosion resistance within a wide range of service temperatures. Owing to a specific complex of physico-chemical and service properties, composites based on an intermetallic Ni<sub>3</sub>Al phase are the material of choice for extra-heavy duty parts operating under

the conditions of load, friction, high temperature and aggressive media. Applications of these composites include aircraft and engineering industries, and various automotive parts, e.g. parts of the drive mechanism and engine system (pistons in I.C. engines, cylinder sleeves, slide bearings), parts of suspension system, steering system and brake system (brake discs and drums) [3]. Often, elements of various mechanisms made from composite materials are expected to run under the most extreme operating conditions and in strongly aggressive environments. Composites based on Ni<sub>3</sub>Al aluminide offer a number of beneficial properties, but the presence of reinforcing phase introduced to this material may change in a substantial way their behaviour in aggressive media, resulting in higher susceptibility to corrosion process [4 - 6]. Besides its composition, one of the main factors that determine the properties of a composite material is the character of the matrix-reinforcement interface [2]. The type of bond between the

composite components affects both the mechanical properties and corrosion resistance. The physico-chemical condition of phase boundary directly affects also the type of bond between the reinforcing phase and matrix, the vibration damping capacity, and the crack formation mechanism, the latter regarding both volume and intercrystalline cracks that occur in the whole material or in the sole matrix, respectively [7,8]. In materials exposed to excessive wear, especially in contact with water, the bond between the reinforcing phase and matrix may disappear totally and, as a consequence, the particles will detach and the matrix will suffer progressive degradation, uncovering the successive layers of particles, all of these effects depriving the composite of its high service properties. The aim of the studies described in this article was to determine the susceptibility of the Ni<sub>3</sub>Al/WC composite to gas corrosion. The study describes a composite material in which the matrix has been formed of an intermetallic Ni<sub>3</sub>Al compound, modified for better toughness with microadditions of boron in an amount of 0,05 wt.%, while the reinforcing phase is high melting point tungsten carbide, generated by a genuine technique of SHSB (Self- Propagating High-Temperature Synthesis in Bath ) [9]. The choice of Ni<sub>3</sub>Al aluminide as a matrix material was dictated, among others, by the possibility of making this phase more ductile. Other factors taken into consideration included the high specific strength ( $\gamma/R_m$ ), high resistance to oxidation within a wide range of temperatures, and a characteristic increase of mechanical properties with temperature raising from 923 to 1123 K. The fabricated composite material is suitable for elements operating under the variable conditions of temperature and environment. The aim of the research was to determine the composite susceptibility to gas corrosion at a temperature close to the operating temperature of elements made from the Ni<sub>3</sub>Al/WC system.

## 2. Methods of investigation

Investigations of gas corrosion resistance were carried out on the Ni<sub>3</sub>Al/WC composite fabricated by SHSB process. The properly prepared and weighed samples of composite were placed in a thermobalance measuring the increase of sample weight during the process of corrosion in active gas. The gas composition corresponded to the composition of an exhaust waste gas emitted by a car engine, containing: steam, carbon monoxide and sulphur dioxide (10% steam and 1% SO<sub>2</sub>). The time of sample exposure to the effect of this atmosphere was 24 and 50 hours, respectively. The samples were weighed on an analytical balance at an accuracy of +/- 2,0 · 10<sup>-4</sup> g, and were placed next in a through-flow tubular furnace in the atmosphere of reactive gas. After the sample exposure to the previously established conditions, it was weighed again, and the change of weight was determined along with the corrosion constant A, calculated as a change in the sample weight before and after the corrosion process. Knowing the value of corrosion constant enabled the corrosion rate to be determined in the examined material. The higher values of the constant A indicate that in the material undergoing degradation additional corrosion paths are formed, enabling gas to penetrate inside the sample.

To examine the microstructure and chemical composition of the scale, metallographic and structural examinations

were carried out, using for this purpose a Leica metallographic microscope and a Jeol scanning microscope with attachment for the EDX analysis. A series of photographs were taken from the scale surface and scanning examinations were made directly on the scale surface at the composite-corrosive atmosphere and scale-composite interfaces.

## 3. The results

The results of the studies of corrosion effect in reactive gas made for the Ni<sub>3</sub>Al/WC composite at temperatures of 800°C and 700°C are compared in Table 1. Hence it follows that the highest increase in sample weight, amounting to 0,45684g, has occurred at a temperature of 800°C after 50h exposure, the lowest, amounting to 0,00384g, at a temperature of 800°C and 24h exposure.

Table 1. The results of investigations of the Ni<sub>3</sub>Al/WC composite oxidation rate at temperatures of 800°C and 700°C

| Exposure temperature | S* [cm <sup>2</sup> ]     | m <sub>0</sub> * [g] | m <sub>1</sub> * [g]       | Δm* [g] |
|----------------------|---------------------------|----------------------|----------------------------|---------|
| 800 <sup>0</sup> C   | 5,76                      | 5,11840              | 5,12224                    | 0,00384 |
|                      | 5,61                      | 4,08116              | 4,53800                    | 0,45684 |
| 700°C                | 6,57                      | 4,54680              | 4,64425                    | 0,09745 |
| Exposure temperature | Δm/S [g/cm <sup>2</sup> ] | t* [h]               | A* [g/cm <sup>2</sup> · s] |         |
| 800 <sup>0</sup> C   | 6,67 · 10 <sup>-4</sup>   | 24                   | 7,72 · 10 <sup>-9</sup>    |         |
|                      | 8,14 · 10 <sup>-2</sup>   | 50                   | 4,52 · 10 <sup>-7</sup>    |         |
| 700°C                | 1,48 · 10 <sup>-2</sup>   | 24                   | 1,72 · 10 <sup>-7</sup>    |         |

where:

\*S – the total surface of sample,

\*m<sub>0</sub>, m<sub>1</sub> – the starting and final sample weight, respectively, counted together with platinum holder,

\*Δm – the sample weight increment,

\*t – the exposure time,

\*A – the corrosion constant  $\left(\frac{\Delta m}{S \cdot t}\right)$

The obtained results of the oxidation process were confirmed by images in Figure 1, showing samples after the 24h and 50h exposure at a temperature of 800°C – Fig. 1 (a) and (b), respectively. The sample staying for 24 hours in corrosive atmosphere forms a thin and non-homogeneous scale. A considerable increase of the scale thickness has been observed after 50h exposure to the effect of corrosive atmosphere. The topographic images show changes that have occurred on the surface of the Ni<sub>3</sub>Al/WC composite due to gas corrosion, and relate them to time and temperature. To better illustrate this phenomenon, a series of examinations have been made using scanning microscope and X-ray microanalyser (Figs. 2 to 8). Figures 2 and 3 show the topography of external layer of the scale formed on the Ni<sub>3</sub>Al/WC composite after corrosion testing at a temperature of 800°C and the exposure time of 24h and 50h. A microanalysis of the sample exposed to reactive gas for the time of 24h indicates that the scale formed in the atmosphere of hot gas

is of an oxide character. The chemical analysis of the scale made in a region marked in Fig. 2b gave the following results: aluminium 0,2%, sulphur 0,8%, nickel 27,2%, tungsten 62,4%, and oxygen 9,3% In the case of the sample exposed to the effect of corrosive environment for the time of 50 hours at a temperature

of 800°C, the chemical analysis of the scale made in region 1 marked in Fig. 3 gave the following results: aluminium 12,7%, sulphur 0,7%, nickel 72,5%, tungsten 0,7%, and oxygen 12,8%..

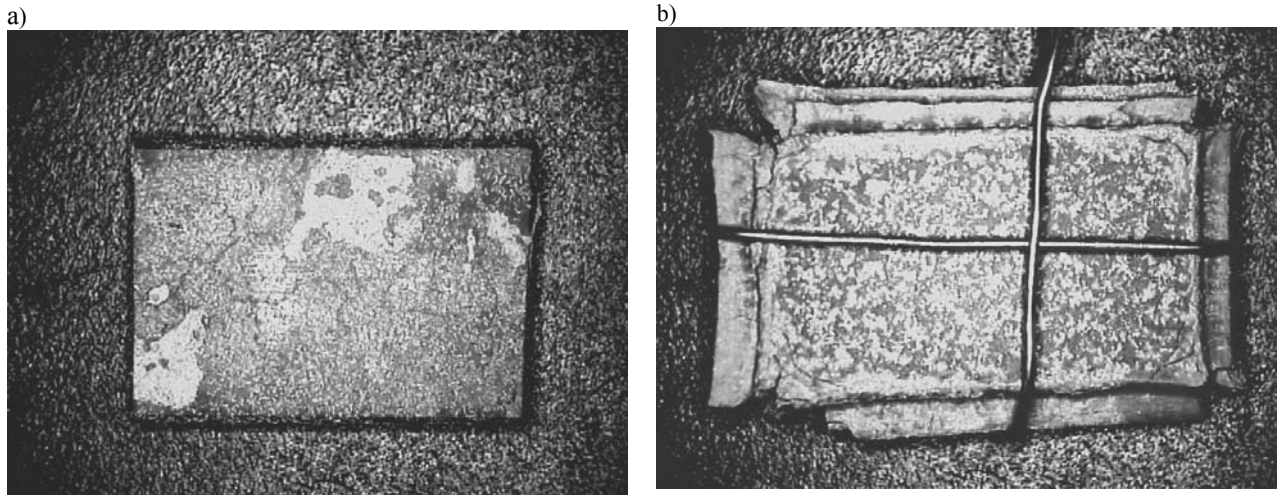


Fig. 1. Sample of Ni<sub>3</sub>Al/WC composite after corrosion process; exposure time: 24 hours (a) and 50 hours (b) in the atmosphere of air + 10% H<sub>2</sub>O + 1% SO<sub>2</sub>; temperature: 800 °C.

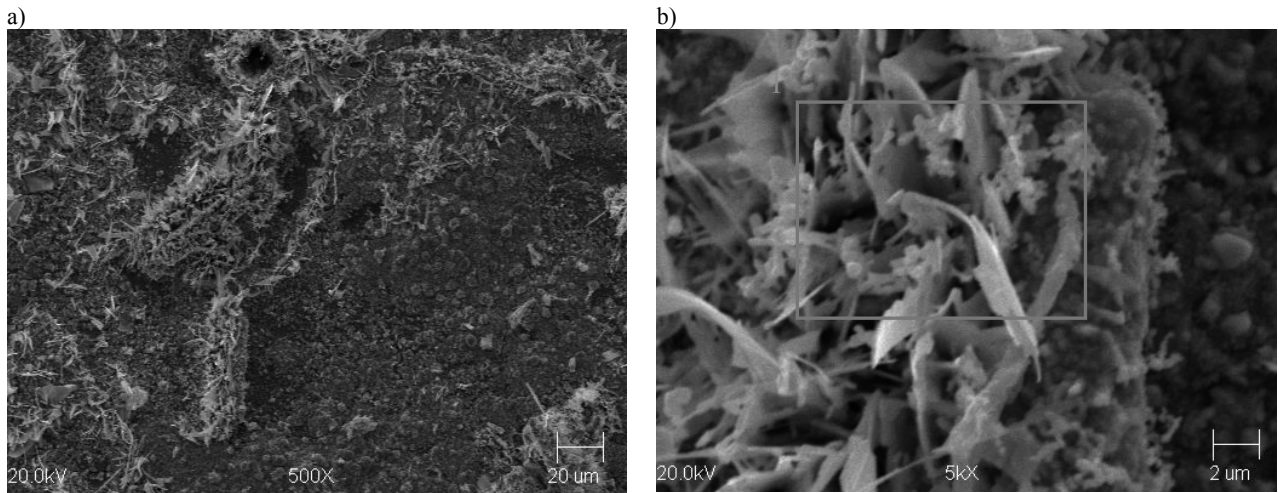


Fig. 2. Sample of Ni<sub>3</sub>Al/WC composite after corrosion process; exposure time : 24 hours in the atmosphere of air + 10% H<sub>2</sub>O + 1% SO<sub>2</sub>; temperature: 800 °C. Magnification: 500x (a) and 5000x (b)

The presence of sulphur compounds has not been traced, and the reason is weak chemical affinity of nickel and aluminium for this element. Sulphur does not enter into reaction with tungsten and carbon, either, both these elements constituting the reinforcing phase. In this situation only matrix undergoes the process of oxidation.

To examine changes at the composite-scale interface, polished metallographic specimens revealing microstructure of the scale, formed due the presence of reactive gas atmosphere, were prepared. As a next step, the quantitative chemical analysis was carried out in the Ni<sub>3</sub>Al-WC interface region, using for this purpose an X-ray microanalyser. The results of the examinations are shown in Figures 4 to 8.

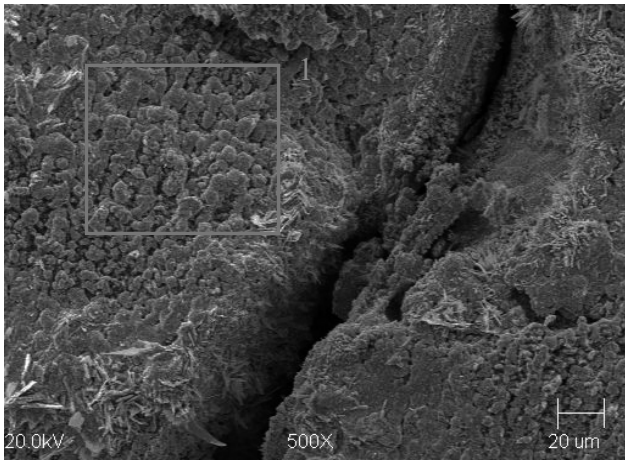


Fig. 3. Sample of Ni<sub>3</sub>Al/WC composite after corrosion process; exposure time: 50 hours in the atmosphere of air + 10% H<sub>2</sub>O + 1% SO<sub>2</sub>; temperature: 800 °C. Magnification: 500x

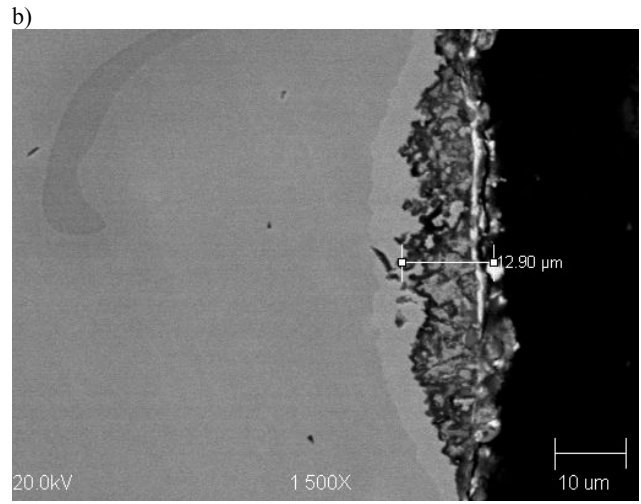
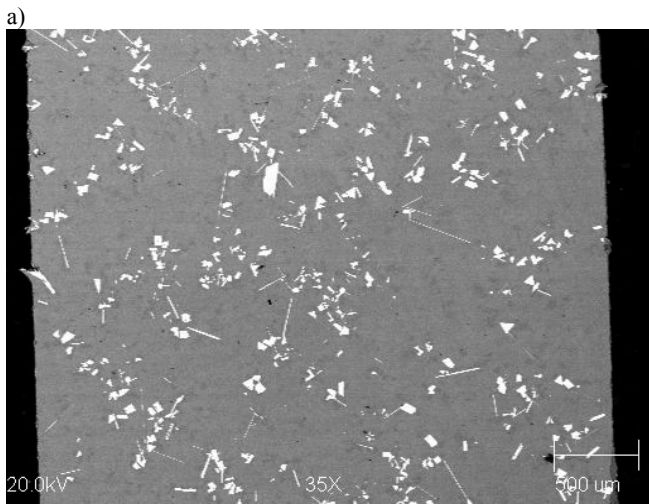


Fig. 4. The Ni<sub>3</sub>Al/WC composite after corrosion process; exposure time: 24 hours in the atmosphere of air + 10% H<sub>2</sub>O + 1% SO<sub>2</sub>; temperature: 800 °C. Magnification: 35x (a) and 1500x (b)

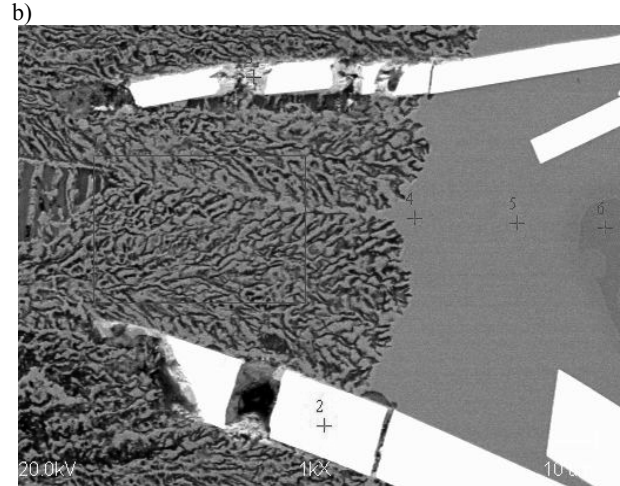
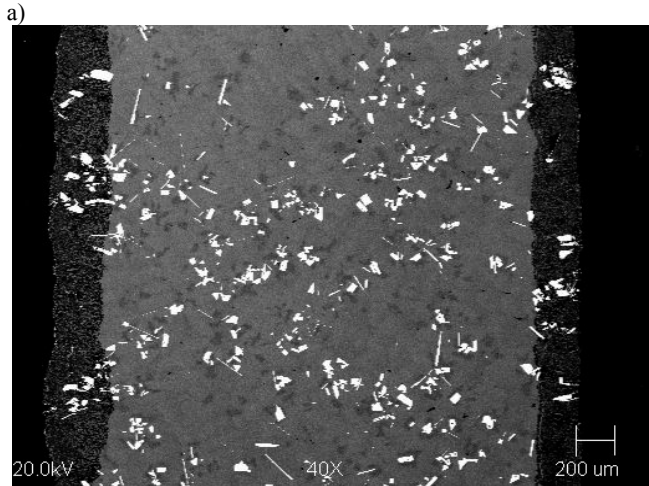


Fig. 5. The Ni<sub>3</sub>Al/WC composite after corrosion process; exposure time: 24 hours in the atmosphere of air + 10% H<sub>2</sub>O + 1% SO<sub>2</sub>; temperature: 700 °C. Note the layer of scale (a) with marked points where the quantitative analysis was made (b). Magnification: 40x (a) and 100x (b)

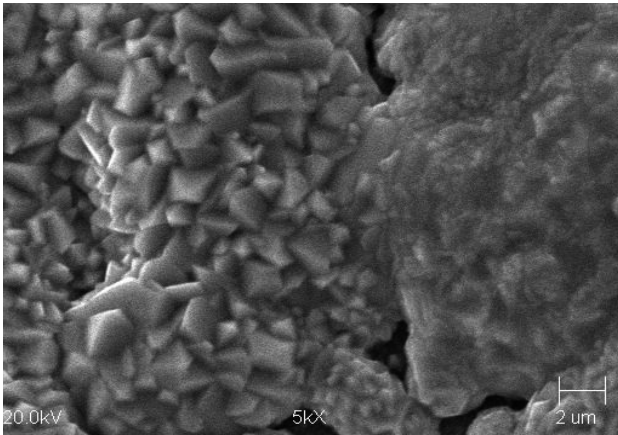


Fig. 6. The Ni<sub>3</sub>Al/WC composite after corrosion process; exposure time: 24 hours in the atmosphere of air + 10% H<sub>2</sub>O + 1% SO<sub>2</sub>; temperature: 700°C. Magnification 5000x.

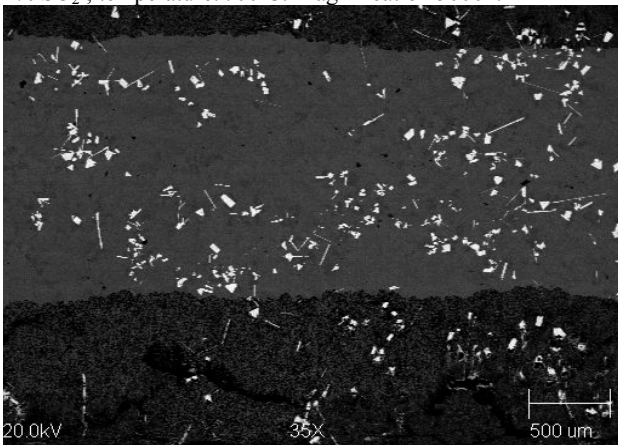


Fig. 7. The Ni<sub>3</sub>Al/WC composite after corrosion process; exposure time: 50 hours in the atmosphere of air + 10% H<sub>2</sub>O + 1% SO<sub>2</sub>; temperature: 800°C. Magnification: 35x

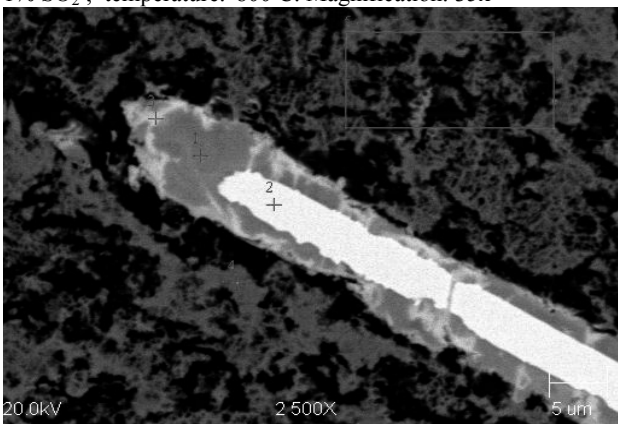


Fig. 8. The Ni<sub>3</sub>Al/WC composite after corrosion process; exposure time: 50 hours in the atmosphere of air + 10% H<sub>2</sub>O + 1% SO<sub>2</sub>; temperature: 800°C. Carbide-scale interface with marked points where the quantitative analysis was made. Magnification: 2500x

The kinetics of the formation of corrosion layer in the examined specimens varied and depended on the time of the composite exposure to the effect of corrosive gaseous environment. The thickness of the layer of corrosion products was comprised in a range from several dozen micrometres, observed in the specimen after 24h exposure (Fig. 4b), up to several hundred micrometres for the specimen after 50h exposure (Fig. 7-8). A highly destructive effect of both the temperature and gaseous environment on the matrix material, i.e. on the Ni<sub>3</sub>Al compound, was reported. Figure 8 shows the presence of carbide phase in the scale. The phase can suffer mechanical degradation, especially in the region of the composite-scale interface. After 24h exposure in the gaseous atmosphere, the quantitative microanalysis of the Ni<sub>3</sub>Al/WC composite (Fig. 5a, b) revealed a very interesting phenomenon, viz. the nickel concentration increasing locally at the metallic material-scale interface ( columns 5 in table 2). The said effect may reduce the rate of scale formation, creating a protective barrier in the form of a thin film of the nickel-rich Ni-Al alloy arresting the corrosion process.

Table 2 compares the results of local quantitative analysis in the region of the scale-composite interface.

Table 2. Chemical analysis in microregions at the scale-composite interface.

| measuring point. | O <sub>2</sub> wt% | C wt% | Al wt% | S wt% | Ni wt% | W wt% |
|------------------|--------------------|-------|--------|-------|--------|-------|
| 1                | 13,8               | 4,4   | 12,5   | 0,1   | 64,5   | 5,0   |
| 2                | -                  | 17,7  | 0,2    | 0,4   | 0,3    | 81,4  |
| 3                | 36,0               | 2,5   | 0,7    | 0,9   | 43,0   | 12,0  |
| 4                | 0,1                | 0,2   | 14,0   | -     | 85,9   | 0,5   |
| 5                | -                  | 0,7   | 14,1   | -     | 85,0   | 0,4   |
| 6.               | -                  | -     | 23,9   | -     | 72,1   | -     |

Figures 7-8 shows the Ni<sub>3</sub>Al/WC composite after 50h exposure at a temperature of 800 °C. From Figure 7 it follows that now the thickness of the scale amounts to several hundred micrometres, which proves the very high rate of corrosion layer growth, indicating, moreover, further critical and destructive effect of temperature, responsible for severe degradation of the composite material surface.

Table 3 compares the results of quantitative local analysis in the region of the reinforcing phase (WC) - scale interface

Table 3. Chemical analysis in microregions at the matrix-Ni<sub>3</sub>Al/WC composite particle interface

| Measuring point. | O <sub>2</sub> wt% | C wt% | Al wt% | S wt% | Ni wt% | W wt% |
|------------------|--------------------|-------|--------|-------|--------|-------|
| 1                | 0,5                | 14,4  | 1,0    | 0,1   | 72,3   | 12,6  |
| 2                | 17,9               | 0,1   | 0,5-   | -     | 4,5    | 77,5  |
| 3                | 9,5                | 8,7   | 1,8-   | 0,1   | 14,0   | 67,5  |

## Conclusions

1. The investigations of the resistance to gas corrosion of the Ni<sub>3</sub>Al/WC composite indicated changes in microstructure and chemical composition of this material, depending on the corrosive medium temperature and exposure time. The said changes result from different kinetics of the synthesis of corrosion layer, an immediate effect of which is the different thickness of the layer of corrosion products. For the examined material, the thickness of the layer of corrosion products at a temperature of 800 °C amounted to several dozen micrometres and several hundred micrometres after the exposure time of 24h and 50h, respectively.
2. It is mainly the matrix material that suffers degradation; the carbides seem to be left untouched by this harmful effect.
3. Due to back diffusion, the effect of nickel enrichment has been observed to occur in a thin subsurface layer near the matrix-scale interface.
4. The boundary temperature at which the resistance of the Ni<sub>3</sub>Al/WC composite to high-temperature corrosion decreases is 800°C.

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