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MECHANISM OF THE OXIDATION OF THE Fe-C-Si-Al-Zr ALLOYS

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Mechanism of the oxidation of the thermal-resistant Fe-C-Si-Al-Zr alloys was investigated at high temperatures. For the analysis three series samples: L1, L2 and L3, had been annealed at 1100 °C, were cast. After annealing the samples were investigated on the oxide thickness increase. They were observed and analysed by optical and electron microscopes. In case of the small zirconium content in the L1 sample, the graphite lamellae and only a significant amount of zirconium carbide in the ferrite matrix have been observed. At higher zirconium content (the L2 and L3 samples) graphite lamellae and particles of ZrC have been observed. During annealing an oxidation of graphite and ZrC took place. The oxidation of ZrC into ZrO_2 is direct and progressive. Evolving CO gas formed the pores around ZrO_2. Under sufficient amount of the dissolved oxygen the oxidation of aluminium was taking place too. Al_2O_3 was precipitating in the CO-ferrite interface filling up the formed pores. Finally the interaction between ZrO_2 and Al_2O_3 were taking place and formation the compound of $ZrO_2 \cdot Al_2O_3$ retarded further oxidation.

Key words: *oxidation at high temperatures, iron-carbon alloys, oxide layer*

Mehanizam oksidacije legura Fe-C-Si-Al-Zr. Ispitivao se mehanizam oksidacije termički otpornih legura Fe-C-Si-Al-Zr na visokim temperaturama. Za analizu su izlivena tri serijska uzorka L1, L2 i L3, i žarena na 1100 °C. Nakon žarenja uzoraka ispitivana je debljina oksidnog sloja. Promatrani su i analizirani optičkim i elektronskim mikroskopom. Kad je količina cirkonija bila mala u uzorku L1 uočene su grafitne lamele i čestice ZrC. Tijekom žarenja došlo je do oksidacije grafita i ZrC. Oksidacija ZrC u ZrO_2 je vanjska i progresivna. Razvija se plin CO, koji oko ZrO_2 formira pore. Kad je količina rastopljenog kisika postala dovoljno velika došlo je također do oksidacije aluminija. Al_2O_3 se istaložio u CO-feritnom međuprostoru i popunio postojeće pore. Konačno je došlo do interakcije između ZrO_2 i Al_2O_3 te se stvorio spoj $ZrO_2 \cdot Al_2O_3$ koji je usporio daljnju oksidaciju.

Ključne riječi: *oksidacija pri povišenoj temperaturi, legure željezo-ugljik, oksidni sloj*

INTRODUCTION

In oxidizing atmosphere and at elevated temperatures the surface and the internal oxidation take place respectively. Oxide thickness and its growing velocity depend on the alloying elements addition.

By addition of the alloying elements the protective oxide layer [1-4] can be formed. Progress of the oxidation can be reduced under the following conditions:

- alloying elements are less stable as the base metal;
- alloying metal is added in sufficient quantity to enable the formation of the compact and continuous oxide layer;
- protective oxide layer must be tightly adhered to the specimen;
- oxygen must be soluble in the base metal;
- diffusion rate of the oxygen into the base metal must be much higher as through the alloying element.

Process of the oxidation of the Fe-C-Si-Al-Zr alloys was investigated. Alloying elements as Al, Si, Zr are less stable than the base metal. Those alloys are thermal resistant at high temperatures. By addition of the zirconium a carbide (not carbon!) was precipitated. Thus alloys presented as the composite materials have been made, which are wear resistant at high temperatures.

EXPERIMENTAL

Various alloys have been prepared for our experiments. The burden has been molten in the electric induction furnace. It was composed of low-carbon steel, silico-zirconium and the carburizing agent. The molten alloy was mixed by aluminium, and immersed into the melt. Such

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melt was cast into the bar shape moulds by the CO_2 - process. The surface of the cooled bars was cleaned by turning. Then the samples of the length of 10 mm were cut out and weighed, and annealed at 1100 °C for 24 hours. Three different samples of L1, L2 and L3 were prepared. In Table 1. the chemical compositions of the investigated alloys are presented.

Table 1. **Chemical composition of the investigated iron alloys [mas %]**
Tablica 1. **Kemijski sastav istraživanih legura [mas %]**

Alloy	Fe	Zr	Si	Al	C
L1	Rest	1.9	2.4	2.2	3.1
L2	Rest	5.1	6.2	5.1	2.5
L3	Rest	10.6	11.2	9.3	2.4

During the annealing the mass increase of L1, L2 and L3 alloys was established. The results of our measurements are shown in Table 2. and in Figure 1..

Table 2. **The mass increase of the alloys after the annealing at 1100 °C**
Tablica 2. **Porast mase proba žarenih na 1100 °C**

Alloy	Mass of the annealed samples [g]		Mass increase	
	before	after	[g]	[%]
L1	12.3	13.2	0.9	7.5
L2	13.3	13.5	0.2	1.5
L3	16.0	16.2	0.2	1.2

METALLOGRAPHIC INVESTIGATIONS OF THE ANNEALED SAMPLES

The specimens have been prepared for metallographic investigations. They have been examined by optical microscope and by the electron probe microanalyzer. The distribution of iron, aluminium, silicon, zirconium and carbon in the oxidized and unoxidized sections of the investigated alloys has been observed. Compositions of the single phases were determined by the point analysis. The line and X-ray analyses were done, next to micrographs, and SEM images.

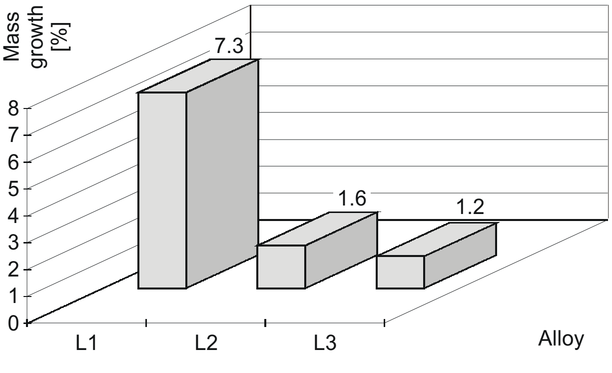

Figure 1. **The mass increase of the samples at 1100 °C, the annealing time: 24 hours**
Slika 1. **Porast mase proba žarenih na 1100 °C, vrijeme žarenja: 24 sati**

Microstructure and the distribution of the elements in the L1 alloy

The microstructure of the not-annealed L1 alloy (Figure 2.), which contains 2.2 % Al, 2.4 % Si, and 1.9 % Zr is composed of the graphite lamellae and zirconium carbide. The matrix of the alloy is the ferrite phase.

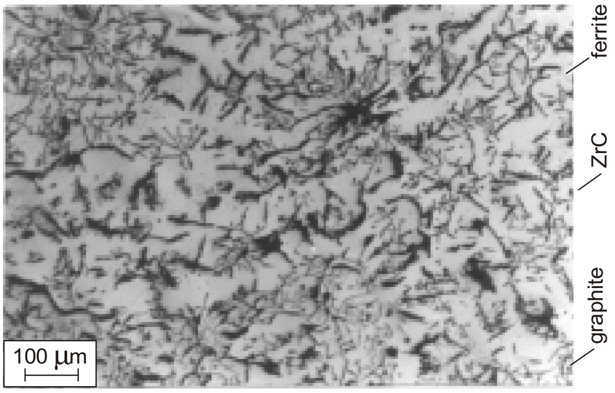

Figure 2. **The microstructure of the not-annealed L1 alloy of (magnif. 100 x)**
Slika 2. **Mikrostruktura nežarene legure L1 (povećanje: 100x)**

After the annealing at 1100 °C for 24 hours the oxidation of the graphite lamellae was observed on the microstructure. By microanalysis of the graphite lamellae, Al_2O_3 phase was observed. The interface transition from the metal phase to the scale is compact and not porous. On the interface of the metal and multiphase scale, Al_2O_3 reacted with iron oxide into a new complex oxide with the composition of 60 % FeO, 38 % Al_2O_3 and 2 % SiO_2.

On the interface of the metal/scale the oxidation of ZrC into ZrO_2 took place. The amount of ZrC is insignificant.

Two phases were observed on the interface of the scale-magnetite layer: the first one was dark, and the second one bright. Both phases were distributed evenly. The transition into the magnetite layer is porous.

The EDS analysis of the dark $FeO.Al_2O_3$ phase showed the composition of 63 % FeO and 35 % Al_2O_3 and 2% SiO_2. The bright phase consisted of 96 % of iron oxides and 4 % SiO_2.

External part of the scale was very porous and was composed of magnetite and hematite layer, which was confirmed by the point EDS microanalysis of the single phases.

Microstructure and the distribution of the elements in the alloy of L2

The increased amount of the alloying elements in the not-annealed L2 alloy (5.1 % Al, 6.2 % Si and 5.1 % Zr) caused the graphite phase and the zirconium carbide in the microstructure, which can be seen also in Figure 3.. By the point EDS microanalysis the amount of 90 % Zr in ZrC was established. The aluminium and the silicon were evenly distributed in the ferrite matrix.

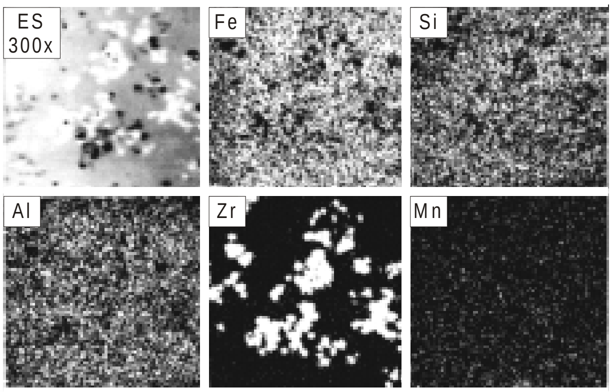

Figure 3. **The distribution of the elements in the not-annealed L2 alloy)**

Slika 3. **Raspored elemenata u nežarenoj leguri L2**

The L2 alloys were annealed at 1100 °C for 24 hours. Oxidation of the graphite lamellae on the surface has begun. On these spots the voids were formed, where Al_2O_3 was deposited afterwards. On the metal/subscale interface the oxidation zirconium carbide was carried out.

During the oxidation of ZrC the products of ZrO_2 and CO were formed. The aluminium oxidation has been followed after the oxidation of ZrC. Al_2O_3 and precipitated on the interface of ferrite/gas CO. Thus the ZrO_2 phase was surrounded by Al_2O_3.

Due to the aluminium oxidation the amount of aluminium in the matrix decreased. Thus the concentration of the aluminium dropped from 5.1 % in the middle to 1.5 % on the edge of the sample. The concentration of the silicon remained unchanged.

The external part of the scale is the thin oxide layer composed by the iron oxides (magnetite and hematite).

Microstructure and the distribution of the elements in the L3 alloy

The microstructure of the not-annealed L3 alloy was composed of the ferrite phase, where the particles of the zirconium carbides, ZrC were found. The fine granular graphite has the net structure. After the annealing of the L3 alloy on 1100 °C for 24 hours, the particles of the zirconium carbides and the fine fragments of graphite on the edge of the metal oxidized. On the REM-micrograph (Fig. 4.) the transition boundary of the alloy oxidized/non-oxidized section is shown. The oxidation of ZrC into ZrO_2 proceeded directly and gradually (Figure 4.).

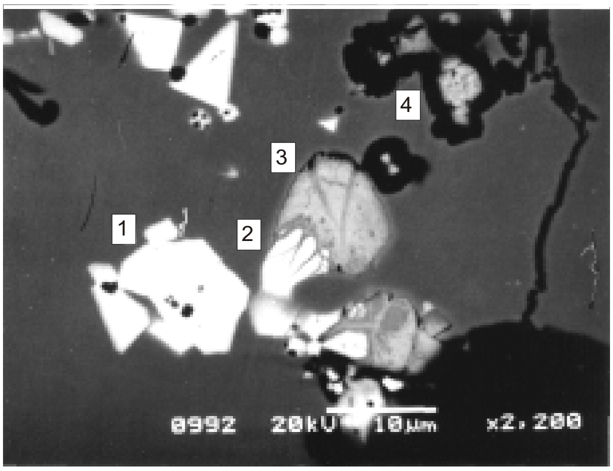

Figure 4. **REM-micrograph of the direct oxidation section of the zirconium carbide of the L3 alloy:**
1 - not-oxidized particle of ZrC
2 - transition of the oxidized and non-oxidized section
3 - precipitation of Al_2O_3
4 - complete surrounded ZrO_2 grains by Al_2O_3

Slika 4. **REM snimak izravne oksidacije površine cirkonijevoga karbida legure L3:**
1 - neoksidirani dio ZrC
2 - prijelaz oksidiran in neoksidiran dio
3 - precipitacija Al_2O_3
4 - mjesto gdje je ZrO_2 potpuno obložen sa Al_2O_3

The gradual transition of the oxidation of ZrC particles was confirmed also in Fig. 5 and 6. In the dark phase the amount of aluminium is increased and the presence of oxygen in the middle of ZrC particles is not observed due to the precipitation of Al_2O_3 around the partly oxidized zirconium carbide, ZrC (Figure 5. and 6.).

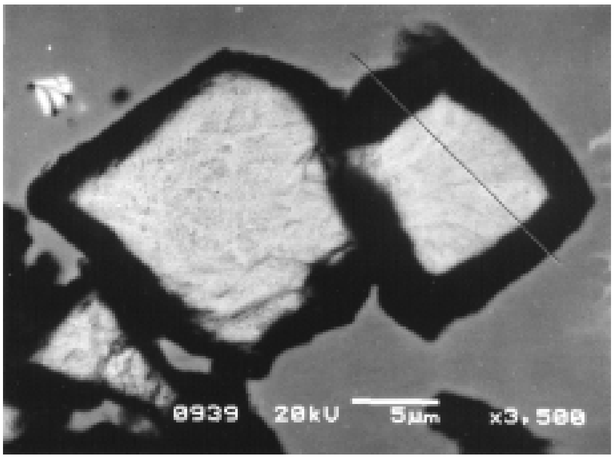

Figure 5. **The line analysis through the partly oxidized ZrC particle of the L3 alloy**

Slika 5. **Linijska analiza oksidiranog dijela ZrC legure L3**

DISCUSSION

The base chemical reaction of the oxidation is presented by the following reaction:

$$aMe + 0.5\ O_2 = Me_aO_b \qquad (1)$$

Initially the oxygen was adsorbed on the metal surface, then it reacted with the metal, formed the compound which overlapped the entire surface of the metal as the thin film.

The formed oxide film overlapped the metal and protected it against the oxygen atmosphere. The oxide film can be compact or porous [1]. In case of the compact oxide film the oxidation was controlled by diffusion of the reactants through it. The reaction through the porous film is proceeded on the metal-oxide interface.

During the oxidation the metal ions were diffussed through the cation vacancies in the oxide film into the oxide-gas phase boundary, where the reaction with the oxygen took place.

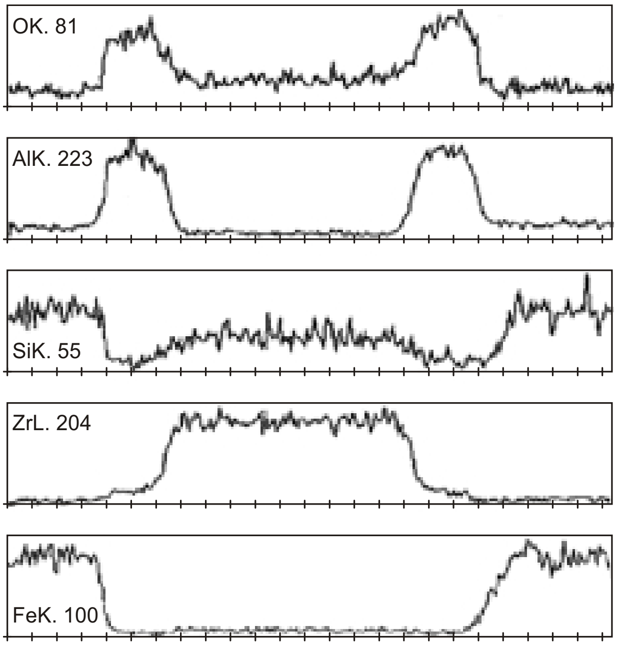

Figure 6. **The line analysis of the partly oxidized ZrC particle of the L3 alloy**

Slika 6. **Linijska analiza djelomično oksidiranog djela ZrC legure L3**

By Wagner [5] model of oxidation the diffusion of metal through the lattice defects controlled the reaction velocity. Both the electrons and ions migrated independently of each other.

Reactions on the phase boundaries were so fast, that the thermodynamic equilibrium was reached on the phase boundaries of oxygen/oxide and oxide/metal respectively.

The constant of the oxidation rate that obeys the parabolic law at high temperatures can be determined by the Wagner theory.

During the iron oxidation above 570 °C various oxide layers were formed [6-7] (Fe_2O_3, Fe_3O_4, and FeO). Oxides closer to the metal phase consisted mostly of the metal, and other ones closer to the gas phase had less metal. Closer to the metal phase the wustite is prevailing, followed by hematite and magnetite phases.

The rate of iron oxidation at 570 °C obeyed the parabolic law; therefore the process depended on the diffusion of the ions through the scale. Diffusions of the iron ions through the layers of FeO and Fe_3O_4 and the diffusion of the oxygen ions through the Fe_2O_3 layer were prevailing.

Above 850 °C the diffusion of iron and oxygen ions took place, while below it only the iron ions were diffused through the wustite layer [8].

During the oxidation of the grey cast iron, the oxide layers of Fe_2O_3, Fe_3O_4, FeO, and the intermediate layer (or multi-phase scale) [1, 9, 10] were formed and oxidation of the graphite lamellae distributed in the matrix were simultaneously took place.

Oxide layer (subscale) represents the barrier between unoxidized matrix and the multiphase oxidized section. The consequence of internal oxidation of the grey cast iron above 850 °C could be the diffusion of the oxygen ions [8] or the formation of the gaseous products [7] of CO and CO_2 as the result of the oxidation of the graphite lamellae respectively. Carbon oxides can be built up in the interface of the metal/oxide under the following condition: $p_{CO} + p_{CO_2} = P$ (P = 1 bar). In case that above condition should be exceeded, as $p_{CO} + p_{CO_2} > P$ the microcracks could be formed.

In order to obtain wear-resistant alloys applied at higher temperatures the grey cast iron with lamellar graphite and alloyed with zirconium, aluminium and silicon was made for our investigation. All applied alloying elements are less stable then the basic metal.

Iron alloys containing aluminium and silicon are known as heat resistant alloys at high temperatures. The addition of zirconium affects positively on the oxide layer growth [11], first of all in cases when the annealing temperature is below 1600 K (on account of the spalling resistance).

Mechanism of the grey cast iron oxidation with different quantity of zirconium, aluminium and silicon was investigated. The following course was established:

- Carbon in the base alloy was mainly in form of ZrC. Therefore the amount of the precipitated graphite was very low. With addition of more then 5 % zirconium the graphite clusters were observed.
- Oxidation of ZrC started at sufficient quantity of the dissolved oxygen in the metal after the following equation:

$$ZrC_{(s)} + 3\ [O]_{Fe} = ZrO_{2(s)} + CO_{(g)} \qquad (2)$$

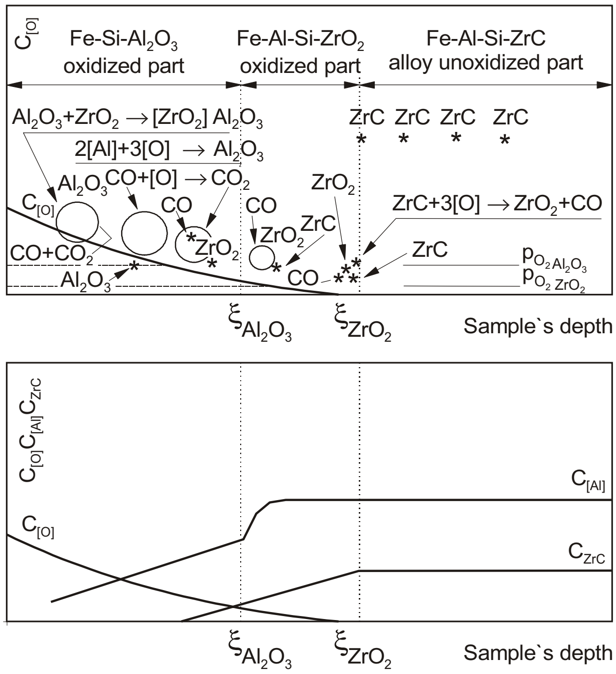

Figure 7. **The model of oxidation of ZrC in the Fe-C-Si-Al-Zr alloy in the air, on the phase boundary of unoxidized / oxidized section**

Slika 7. **Model oksidacije ZrC u leguri Fe-C-Si-Al-Zr pri slobodnom pristupu zraka na granici faza neoksidiran / oksidiran dio**

In the certain distance from the surface (Figure 7., at ζ_{ZrO_2}) the ZrO_2 phase appeared in the microstructure and the carbon monoxide was formed simultaneously.

- The oxidation of ZrC into ZrO_2 proceeded, but the decreased diffusion of the oxygen through the ZrO_2 compound layer caused the increased concentration of oxygen on the phase boundary of ZrO_2/base metal.
- Thus the oxidation of aluminium and the precipitation of the primary aluminium oxide on the surface boundary of gaseous pore of CO/ferrite was enabled (Figure 7., at $\zeta_{Al_2O_3}$). The oxidation of aluminium can be represented by the following equation:

$$2/3\ Al + [O]_{Fe} = Al_2O_3 \tag{3}$$

- By the progress of the oxidation the thickness of the formed oxide increased. At the same time the diffusion of the oxygen through ZrO_2 into unoxidized ZrC was took place. ZrC oxidized progressively and entirely into ZrO_2.
- During the oxidation the gas of CO was formed, which could react further at the sufficient quantity of the oxygen into CO_2 by the following equation:

$$CO + [O]_{Fe} = CO_2 \tag{4}$$

In this case the gaseous mixture of CO and CO_2 surrounded the particle of ZrO_2.

- The compound of Al_2O_3 filled existing pores, therefore the formed oxide particles were not porous. By further oxidation the compound of ZrO_2 was entirely surrounded by Al_2O_3.
- Finally the interaction between both oxides of aluminium and zirconium and the formation of the solid solution of oxides were took place.
- The amount of the zirconium carbide, which was distributed in the base metal, depended upon the quantity of the alloyed zirconium. The observation of the oxidation of the alloy of L1 was difficult, due to the presence of the graphite lamellae and some particles of ZrC. ZrC oxidized into ZrO_2. Then the oxidation of the graphite lamellae was followed. Al_2O_3 filled the formed voids. In the multi-phase scale on the boundary layer of magnetite, the oxides of aluminium, silicon and iron were evenly distributed. In the external part of the scale only the iron oxides were present.
- By the increased amount of zirconium, silicon and aluminium (in the alloy of L2) the quantity of graphite decreased, and after the oxidation the thickness of the oxide layer decreased too. The oxidation of ZrC into ZrO_2 took place directly before the oxidation of aluminium. Al_2O_3 precipitated on the phase boundary of CO/ferrite, on the particles of ZrO_2 or on the cluster sites of the burnt graphite lamellae. In the multiphase part of the scale the layer consisted of the oxides of the base metal, the alloying elements (FeO, SiO_2, Al_2O_3) and the compound of $FeO{\cdot}Al_2O_3$.
- The oxidation of the silicon in the L3 alloy with high content of the alloying elements was not so distinctive at 1100 °C for 24 hours of annealing. The typical oxide layers of iron, as hematite, magnetite and wustite have not been formed but only the subscale.

CONCLUSIONS

At high temperatures the surface of Fe-C alloy was overlapped by the iron oxides of FeO, Fe_3O_4 and Fe_2O_3.

The Fe-C alloys containing alloying elements, as aluminium and silicon, formed the layer of iron oxides and combine oxides of the base metal and alloying elements during the oxidation. Thus the layer of hercynite, $FeO{\cdot}Al_2O_3$ and fayalite, $2FeO{\cdot}SiO_2$ were formed which suppressed the oxidation of the base metal.

Aluminium and silicon dissolved in the solid base metal alloy (ferrite) oxidized under the mechanism of the oxidation of the solid solutions. If the concentration of these elements was higher than of the critical value, the surface oxidation was taking place.

Zirconium in the examined alloys was bonded in ZrC. Particles of ZrC oxidized directly without their previous dissolution in ferrite.

At direct oxidation of the particles of ZrC, ZrO_2 oxide and the gas CO phase were forming. Gas CO was depositing on the phase boundary between the compound of ZrO_2 and the metal base, thus the voids surrounding the particles of ZrO_2. ZrO_2 occupied the same site as ZrC before the oxidation.

If the metal was also alloyed with aluminium, the Al_2O_3 was precipitated in the voids formed after the oxidation of ZrC. In this way the formed pores were filled with Al_2O_3. Al_2O_3 was also precipitated on the interface of ZrO_2/ferrite and on the cluster sites of the burnt graphite lamellae.

In Fe-C-Si-Al-Zr alloys the particles of ZrC or ZrO_2 were the sites of the precipitation of the compound of Al_2O_3. Formed oxides bonded mutually and suppressed the oxidation. For the alloys with the high quantity of the alloying elements of aluminium and zirconium the oxidation of the silicon was not so distinctive.

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