CATASTROPHIC OXIDATION OF AISI M4 ALLOY

KATASTROFALNA OKSIDACIJA ZLITINE AISI M4

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In the annealing of some pure metals and various alloys, the phenomenon of accelerated oxidation is known, which is due to the fact that the resulting surface oxides fail to inhibit or completely stop the oxidation process. Vanadium ferrous alloys are rapidly oxidized during high-temperature annealing in oxygen atmospheres. The rate of oxidation is so great that it is considered a catastrophic oxidation. In this work, the AISI M4 alloy was investigated. The mechanism and model of the oxidation of alloy AISI M4 were developed on the basis of an analysis of the oxidation in a temperature range of 700–1000 °C. The holding time was 6 h. The alloy was analysed with an optical microscope and scanning electron microscopy equipped with EDS, WDS and EPMA detectors. It was found that below 850 °C, molten oxide is formed, which is predominantly of V_2O_5 composition. Above 850 °C, the oxide layer is multi-layered. The oxide layer consists of complex oxides, which formed with other elements. The X-ray analysis confirmed the presence of the following oxides in the oxide layer: Fe_2O_3, Cr_2O_3, $FeVO_4$, V_2O_3 and Fe_2WO_6; and the second oxide may additionally be: V_2O_5, Cr_2O_5 and $FeWO_4$.

Key words: catastrophic oxidation, internal oxidation, vanadium, iron alloys, diffusion, kinetics

Pri žarjenju nekaterih čistih kovin in različnih zlitin je poznan pojav pospešene oksidacije, ki je posledica dejstva, da nastali površinski oksidi ne uspejo zatreti ali povsem ustaviti proces oksidacije. Pri zaviranju oksidacije ali popolni pasivaciji so pri čistih kovinah ali različnih zlitinah uspešni oksidi kroma, aluminija, silicija ipd., nasprotno pa nekatere kovine, ki tvorijo hlapne okside (Mo) ali staljene okside, te sposobnosti nimajo in zelo pospešijo oksidacijo tudi do stopnje, ki se okarakterizira kot katastrofalna oksidacija. Tak primer so tudi zlitine železa z vanadijem, ki sicer kot binarne zlitine niso posebej poznane, so pa zelo pomembne kot večkomponentne zlitine kot orodna ali hitrorezna jekla, v katerih je več vanadija (3–6 w/%), ki ima pomemben vpliv na stanje oksidne plasti. Železove zlitine z vanadijem pri žarenju na visokih temperaturah v atmosferah s kisikom pospešeno oksidirajo. Zato so pri vročem preoblikovanju in toplotni obdelavi jekel velike izgube kovine, če se jekla ne žare v zaščitni atmosferi ali soleh. Hitrost oksidacije je tako velika, da jo štejemo v skupino katastrofalne oksidacije. Ta način oksidacije je poznan pri večjem številu zlitin in tudi čistih kovinah. V zlitini AISI M4 smo analizirali fazne sisteme in termodinamične parametre za nastanek možnih oksidov. Izvedli smo raziskavo z optičnim mikroskopom in SEM opremljenim z EDS, z EPMA opremljenimi z WDS, napravo za rentgensko strukturno analizo in s sistemom naprav za termično analizo. S pomočjo teh raziskav smo okarakterizirali produkte visokotemperaturne oksidacije zlitine AISI M4 in določili mehanizem pospešene površinske oksidacije za to zlitino.

Ključne besede: katastrofalna oksidacija, notranja oksidacija, vanadij, železove zlitine, difuzija, kinetika

1 INTRODUCTION

Vanadium has a high affinity for oxygen, with which it forms oxides. The natural role of these oxides is to protect the metal from reacting or to slow down its reaction with the environment. Vanadium oxides, however, are unable to do this because some of them have a very low melting point, for example, V_2O_5 (647 °C) and $V_{12}O_{16}$ (670 °C). These vanadium oxides are the cause of catastrophic oxidation, advancing at a very high speed. This phenomenon is not only characteristic of pure metals but also of many alloys (for example, AISI M4 alloy). The AISI M4 alloy oxidizes rapidly at high temperatures in oxygen atmospheres. Therefore, there are large metal losses during hot forming and heat treatment of steels if they are not annealed in a protective atmosphere or salts.

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The rate of oxidation can be so great that it leads to a catastrophic oxidation. This form of oxidation is known for a large number of alloys as well as pure metals. Zinchenko[1] observed the role of catastrophic oxidation in austenitic steels designed to work at elevated temperatures. Leslie and Fontana[2], however, found that on molybdenum a volatile oxide is formed, which cannot protect the metal from oxidation and therefore the metal surface is in contact with the atmosphere at all time, with the oxidation rate being at its maximum.

Catastrophic oxidation is also characteristic of alloys in which molten oxidation products are formed.[3–9] This was first observed by Rathenau and Meijering.[10] They found that different alloys oxidize rapidly in contact with MoO_3. In the case of the Fe-25Cr steel, this effect occurs at the temperature at which MoO_3 reacts with the Cr_2O_3 layer. Oxidation of steels alloyed with more than 1 w/% vanadium already shows the characteristics of catastrophic oxidation. After a few hours of oxidation of

Table 1: Chemical composition of alloy AISI M4 in *w*/%

Alloy designation	Fe	C	S	Si	Cr	Ni	V	Al	Cu	Mn	Mo	W	P
AISI M4	79.53	1.26	0.013	0.33	4.10	0.14	3.90	0.013	0.14	0.29	4.63	5.63	0.022

such steels at relatively low temperatures (800–900 °C), they can oxidize to a depth of more than 10 mm. This is a result of the vanadium oxide formed in the layer, which has a very low melting point and does not melt other oxides. At higher temperatures, which are typical for the transformation of these steels (1100–1200 °C), oxidation no longer has the characteristics of catastrophic oxidation, as the other oxides dissolve at these temperatures, which increases the melting point of vanadium oxide (V_2O_5).

Indirect effects of vanadium or V_2O_5 from ash (or fly ash) on the instability of surface oxides on steels for boiler parts and their accelerated oxidation are well described in reference.[11] The negative effects of V_2O_5 on the Inconel-X alloy as well as AISI 347 (PK11NB)[11] stainless steel were noted. This influence of V_2O_5 was investigated on copper alloys by Belousov.[12,13] Later, based on the obtained results, he presented a new model[14] of catastrophic oxidation, the basis of which is the formation of the liquid phase at the grain boundaries (LGBs). The occurrence of catastrophic oxidation in Fe-V alloys is explained with the formation of low-melting eutectics between iron and vanadium oxides. "Normal oxidation" at high temperatures is explained with the formation of a solid oxide layer.[15] If the oxides of an alloying component react with each other and form more stable complex oxides (double oxides, etc.), these oxides will also be present in the oxide layer (scales).[16,17] The formation of complex oxides is important for the oxidation of many alloys; in particular, it was investigated for technologically important alloys containing iron, nickel and chromium.[18]

Diffusion rates in double oxides are usually lower than in single oxides. The protective layers of temperature-resistant alloys are therefore composed of complex oxides. The formation of complex oxides depends on the composition of the alloy, temperature, oxygen pressure in the atmosphere and oxidation time. Rahmel[8] investigated the oxidation of a binary iron alloy with one of the alloying additives of V (< 7.1 %), Cr (< 5 %), Si (< 2.2 %) or Mo (< 5.6 %). The alloys consisted of the outer oxide layer (FeO, Fe_3O_4 and Fe_2O_3 oxides) and the layer between FeO and the alloy, consisting of complex oxides (FeO + Fe_yX_zO, X=V, Si or Mo). Iron alloys with vanadium are characterized by surface and internal oxidation. Iron oxides are first formed on the surface, and the oxygen dissolved in iron also causes an internal oxidation of vanadium. At the metal-oxide interface, vanadium oxide is enriched, reacting with iron oxides to form complex oxides. The same mechanism as for the Fe-V system also applies to Fe-Cr alloys and to the Fe-Ni[19] system.

2 EXPERIMENTAL PROCEDURE

The AISI M4 alloy[20] was oxidized in a tunnel furnace in air at temperatures of (700, 800, 850, 950, 1000) °C. The holding time was 6 h. The chemical composition of the alloy is given in **Table 1**.

Multi-component alloy AISI M4 consists of several alloying elements, which are the common components of tool and high-speed steels. Among them, chromium increases the resistance of steels to oxidation the most. Since the cause of accelerated (catastrophic) oxidation is the formation of a melt, the interactions between the oxides of the elements from the alloy, or the sequence of the formation of simple or complex oxides, are also important. Accelerated oxidation is the result of a simple and rapid access of oxygen to the metal boundary either through molten oxides, oxide damage, or in another system-specific manner. Oxidation characteristics of selected alloys were determined with different methods. A microstructural analysis was performed, using optical and scanning electron microscopy (SEM) equipped with WDS, EDS and EPMA detectors.

3 RESULTS

During the oxidation of the AISI M4 alloy at the temperature of 800 °C, the top porous layer recedes because a porous oxide, consisting of Fe-rich grains, is formed and the V-rich melt is sucked inwards to the oxide-base interface. Vanadium carbides are present in the base metal (**Figure 1**).

The analysis of the first layer and the transition from oxide to the base alloy shows that just below the surface, the iron concentration decreased, while the molybdenum
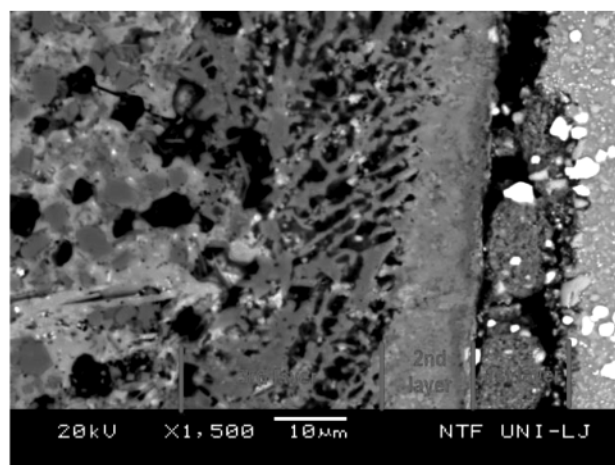

Figure 1: SEM micrographs of the oxides on the surface layers of AISI M4 steel oxidized at 800 °C in air, a holding time of 6 h
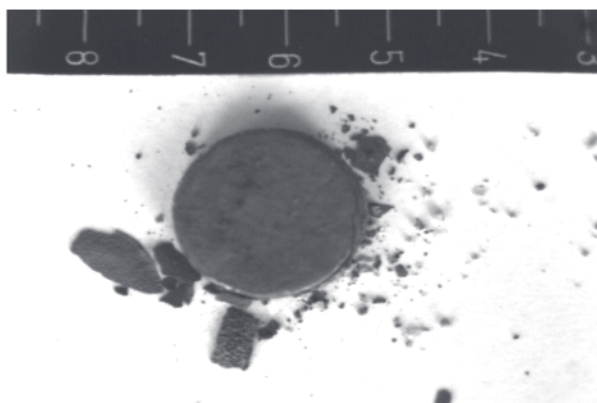
Figure 2: Catastrophically oxidized sample of AISI M4 steel oxidized at 850 °C in air, a holding time of 6 h

Figure 3: SEM micrograph of oxide on the surface of AISI M4 steel oxidized at 850 °C in air, a holding time of 6 h

concentration increased during the transition. In the whole layer, however, the concentration of tungsten and vanadium is increased, while chromium behaves in the same way as iron. The concentration of iron against the surface layer of the oxide increases.

During the oxidation of the AISI M4 alloy at the temperature of 800 °C, the scale consists of three layers (**Figure 1**). In the oxide-base alloy transition, oxide roots are present, rich in vanadium, chromium and tungsten, while the metal at the roots is rich in iron and molybde-

num. The first layer is porous and multi-phase, the middle and surface layers are two-phase, being separated from each other by a crack. A catastrophic-oxidation effect was observed on an AISI M4 sample that was oxidized at 850 °C (**Figure 2**).

The oxide layer is multilayered, and it is also very structurally heterogeneous (**Figure 3**). The skeleton of the oxide layer next to the steel is formed by polyhedral
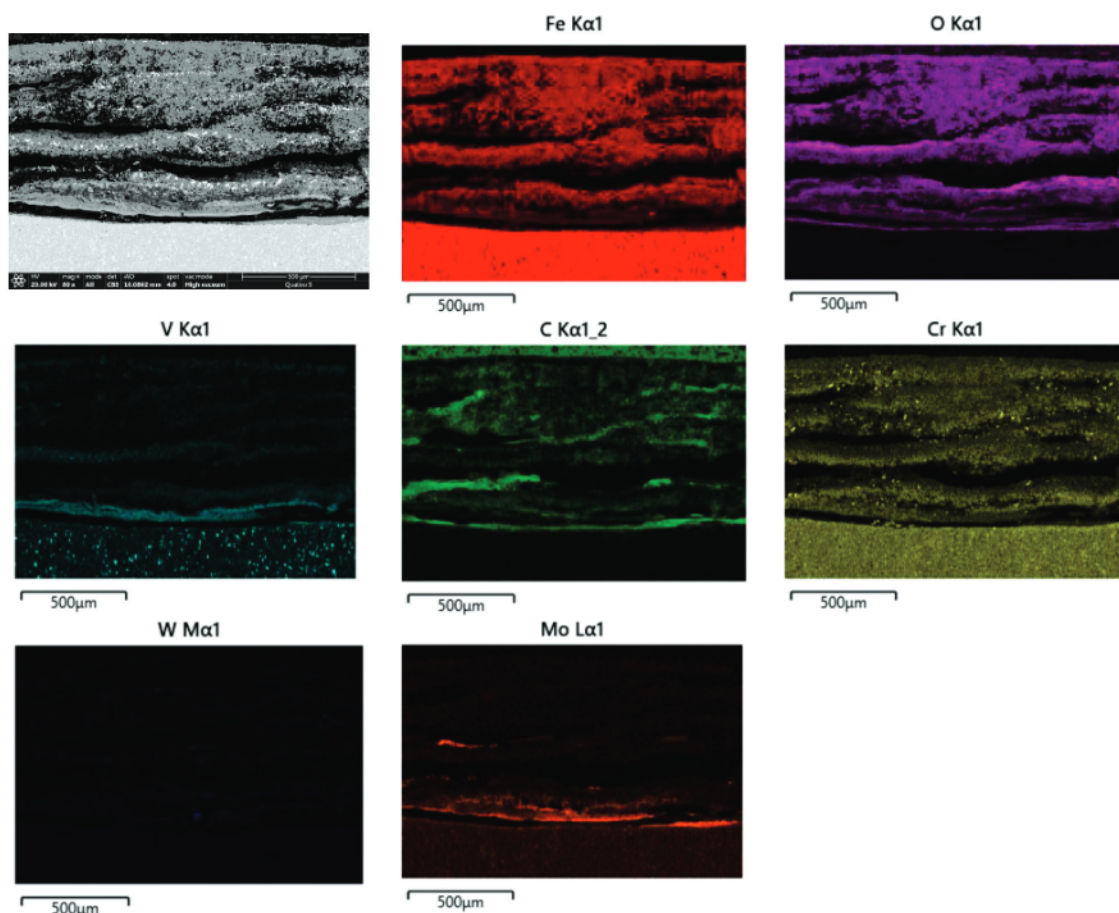

Figure 4: Mapping analysis of chemical elements C, O, Mo, V, Cr, W and Fe in AISI M4 alloy oxidized at 850 °C, a holding time of 6 h
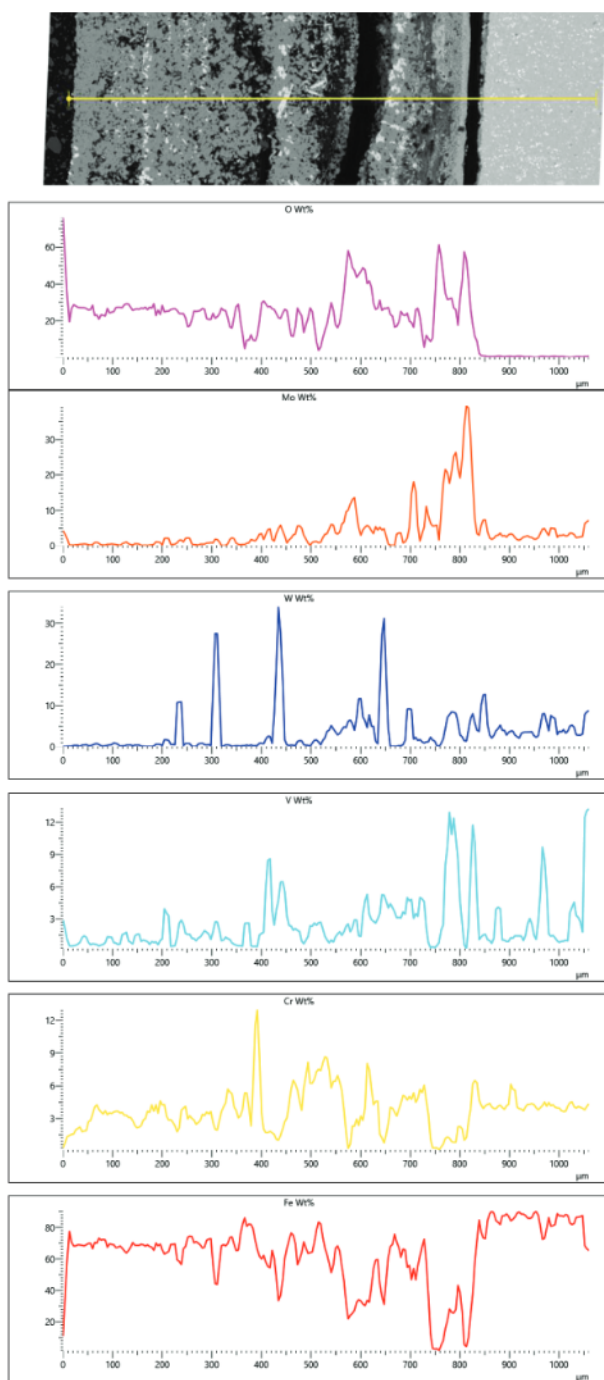
Figure 5: SEM micrograph of oxide and linear analysis of chemical elements O, Mo, W, V, Cr and Fe in AISI M4 alloy oxidized at 850 °C, a holding time of 6 h

grains of mixed oxides of iron, tungsten, molybdenum and chromium, in which individual oxides predominate, for example, iron, tungsten, silicon and molybdenum oxide.

At the boundary surface of steel, oxides do not have a single-phase transition; some oxides, especially those rich in tungsten, oxidize directly. Using a mapping analysis, we determined the distribution of the chemical elements such as carbon, nitrogen, oxygen, molybdenum, vanadium, chromium and iron over the entire structure of the AISI M4 alloy oxidized at 850 °C, with the holding time of 6 h (**Figure 4**).

A line analysis of an AISI M4 alloy sample oxidized at 850 °C, at the holding time of 6 h is shown in **Figure 5**. The following elements were analysed: oxygen, molybdenum, tungsten, vanadium, chromium and iron.

The line analysis showed that iron has the highest content in the base metal and the upper layer of the oxide, and in the oxide, it fluctuates depending on the oxide formation in the oxide layer. It reaches its lowest value in the first oxide layer where vanadium has the highest content. Vanadium and tungsten form carbides and complex oxides and oscillate throughout the oxide layer.

4 DISCUSSION

It is known that the AISI M4 steel has a relatively high concentration of vanadium. Vanadium has a high affinity with oxygen. Vanadium oxides have a more negative creative free energy than iron oxides, so we find vanadium oxides at the metal-oxide interface. Below 850 °C, a molten oxide is formed, which is predominantly of the V_2O_5 composition. Above 850 °C, complex oxides are formed including other elements (**Figure 6**).

Vanadium oxides usually also create an internal oxidation zone of the alloys, but in the case of AISI M4, no internal oxidation zone is formed. The internal oxidation zone is present especially in alloys with the vanadium content higher than 1 *w*/% and at high temperatures of 1000–1250 °C. Iron oxides were first formed on the surfaces of all alloys. Because the oxygen dissolved in the iron did not diffuse through the oxide to the metal boundary, it did not cause any internal oxidation of vanadium. These vanadium oxides, as already mentioned, react with the base-metal oxide and other alloying elements in the oxide, or at the interface with the metal. The complexity of the oxides formed increases with the diversity of the chemical composition. Among the alloying elements, chromium increases the resistance of steels to oxidation the most. Since the cause of accelerated (catastrophic) oxidation is the formation of a melt, the interactions between the oxides of the elements from the alloy, or the sequence of the formation of simple or complex oxides, are also important. Accelerated oxidation is due to a simple and rapid access of oxygen to the metal boundary either through molten oxides or through the cracks in the oxides. The condition for the catastrophic oxidation in the AISI M4 alloy is the formation of low-melting eutectic V_2O_5 at the temperature of 850 °C; above this temperature the causes of catastrophic oxidation, in addition to V_2O_5, are also complex oxides of iron and vanadium.

Phase systems and thermodynamic parameters for the formation of possible oxides were analysed. In the case of the catastrophic oxidation of the AISI M4 alloy, the
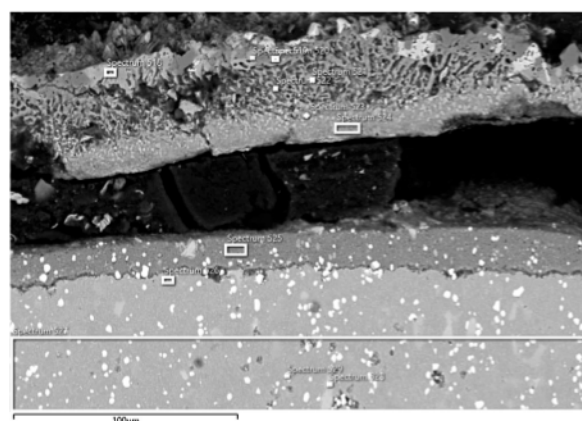
Result type	Weight w/%											
Spectrum label	Spectrum 518	Spectrum 519	Spectrum 520	Spectrum 521	Spectrum 522	Spectrum 523	Spectrum 524	Spectrum 525	Spectrum 526	Spectrum 527	Spectrum 528	Spectrum 529
O	20.31	20.66	22.34	25.07	37.69	22.53	27.34	27.33				
Si									0.30	0.15		
V	17.24	17.02	22.41	18.16	5.37	18.88	5.89	6.19	1.29	4.41	48.75	3.47
Cr	0.64	0.38	0.46	0.33		1.81	0.99	6.54	4.50	4.54	3.61	3.82
Mn	0.56	0.37	1.31	0.54					0.27	0.36		
Fe	28.97	29.12	32.95	30.42	25.17	17.73	37.82	48.12	88.22	78.12	2.77	34.05
Ni									0.22	0.14		
Cu									0.14	0.09		
Mo	11.24	12.21	12.71	17.96	20.24	13.78	22.71	6.07	2.29	4.73	18.04	21.26
W	21.04	20.24	7.83	7.52	11.52	25.27	5.24	5.76	2.78	7.46	26.83	37.40
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Statistics	O	Si	V	Cr	Mn	Fe	Ni	Cu	Mo	W
Max	37.69	0.30	48.75	6.54	1.31	88.22	0.22	0.14	22.71	37.40
Min	20.31	0.15	1.29	0.33	0.27	2.77	0.14	0.09	2.29	2.78
Average			14.09			37.79			13.60	14.91
Standard deviation			13.16			23.95			6.72	10.94

Figure 6: EDX point analysis of AISI M4 alloy oxidized at 850 °C, a holding time of 6 h

following oxidation products were observed: iron oxides (FeO, Fe_2O_3, Fe_3O_4), vanadium oxides (V_2O_3, V_2O_5), oxides of other alloying elements (Cr_2O_3, Cr_2O_5) and complex oxides ($FeVO_4$, Fe_2WO_6, $FeWO_4$).

The catastrophic oxidation of the AISI M4 alloy produces several oxide layers. The concentration of iron and chromium is considered to increase in the direction towards the surface, while the concentrations of vanadium, tungsten and molybdenum increase in the opposite direction (**Figure 7**). Vanadium and tungsten carbides are also present in the base metal. In the upper layer, there are iron oxides, which follow each other towards the surface of the oxide layer in the following order: FeO, Fe_3O_4 and Fe_2O_3.

The basic condition for determining the mechanism of catastrophic oxidation of the AISI M4 alloy is the assumption that one of the components forms a low-melting oxide. In our case, this component is vanadium. It is this small amount of melt in the oxide phase that causes catastrophic oxidation. The following conditions must be met for a catastrophic oxidation: a layer of melt is formed on the surface of the metal; reactions of grain boundaries with the melt result in channels along the grain boundaries formed as oxidation products; oxygen
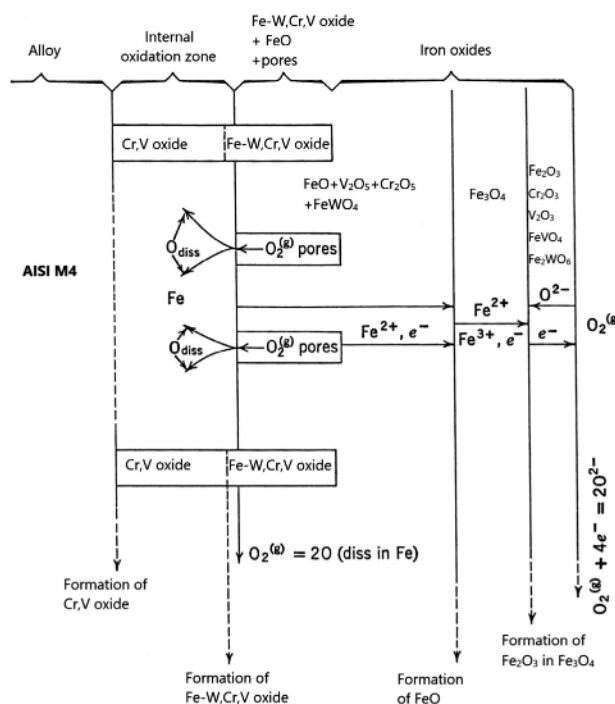

Figure 7: Schematic presentation of the mechanism of catastrophic oxidation of AISI M4 alloy

from the air dissolves in the melt and reacts with the metal; kinetics is determined by the diffusion of ions through the liquid phase and through the liquid channels along the grain boundaries. Thermodynamic equilibrium is established at the oxide/air and metal/oxide interfaces, preventing oxidation (for example, chromium) or with heat treatment in a protective atmosphere.

5 CONCLUSIONS

1. On the AISI M4 alloy, surface oxides are formed during oxidation in air. At low temperatures, oxides do not react with each other. Below 850 °C, a molten oxide is formed, which is predominantly of V_2O_5 composition. Above 850 °C, complex oxides are formed with other elements. The X-ray analysis confirmed the presence of the following oxides in the oxide layer: Fe_2O_3, Cr_2O_3, $FeVO_4$, V_2O_3 and Fe_2WO_6, and in the second oxide additionally: V_2O_5, Cr_2O_5 and $FeWO_4$.

2. The concentration of vanadium is reduced from the nominal value in the alloy to its minimum at the oxide boundary.

3. In oxidation, the ratio of vanadium to chromium, which oxidized internally, was very important, while molybdenum and carbon had no decisive influence.

4. Low-melting oxide V_2O_5 was formed in the AISI M4 alloy, causing catastrophic oxidation at the oxidation temperature of 850 °C.

5. There was no internal oxidation zone in the AISI M4 steel.

6. The scale on the AISI M4 alloy is formed due to the formation of oxides on the surface, due to the formation of an oxide melt, through which diffusion transport is rapid and due to the formation of a continuous, adhesive oxide layer.

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