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Influence of oxidation duration on features of surface scale of V–Cr–Ta–Zr alloy

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Abstract. Investigation results of surface oxide scale features during the oxidation of V–Cr–Ta–Zr alloy in air are presented. Intensive oxidation processes in time interval under study lead to an increase in the scale thickness. Oxide scale structure is characterized by open porosity formed as a result of sticking together of small flakes of plate-shaped oxides (V_2O_5).

1. Introduction

In papers [1 – 3], high efficiency of chemical heat treatment (CHT) of vanadium alloys of different systems was demonstrated. Such processing contributes to a significant increase in high-temperature strength values and a significant (by several hundred degrees) increase in thermal stability of microstructure and properties. An integral stage of CHT is the formation of surface scale [4, 5], which can be formed during oxidation in air or in an oxygen-containing medium. The scale thus obtained is a source of oxygen diffusing deep into the metal during high-temperature vacuum annealing, the duration of which usually ranges from several hours to several hundred hours [4, 5]. At the same time, insufficient attention has been paid to the study of the features of structure formation and thickness of surface scale, depending on oxidation duration. In [6], the influence of structural state of V–Cr–Ta–Zr alloy samples on the oxidation rate during surface scale formation in CHT process was studied.

In this paper, we studied the effect of the oxidation duration on structure and thickness of surface scale on V–Cr–Ta–Zr alloy samples.

2. Experimental materials and procedures

We used V–Cr–Ta–Zr vanadium alloy produced by SC "VNIINM", whose chemical composition in weight (wt. %) and atomic (at. %) percent is given in Table 1.

Table 1. Chemical composition of V–Cr–Ta–Zr alloy.

| Element | V | Cr | Ta | Zr | O | C | N |
|---------|------|------|------|------|-------|-------|-------|
| wt. % | base | 6.80 | 6.10 | 0.79 | 0.052 | 0.031 | 0.009 |
| at. % | base | 6.99 | 1.80 | 0.45 | 0.174 | 0.138 | 0.034 |

Samples of this alloy were subjected to thermomechanical treatment (TMT) by traditional mode [7, 8], which assumes alternating deformation by rolling (up to $\epsilon \approx 50$ %) at room temperature with one-hour anneals at 1000 °C in vacuum. After this treatment, one-hour annealing in vacuum at 1100 °C and deformation by rolling at room temperature ($\epsilon \approx 50$ %) were carried out. The subsequent heat



treatment of the samples in air, leading to surface scale formation, was carried out at a temperature of 620 °C, the oxidation duration was 10, 30, 60, and 90 minutes. At this temperature an intensive formation of a metastable oxide (V_2O_5) on the sample surface occurs. Oxide scale composition was identified by TEM electron diffraction analysis. Mass and concentration of introduced oxygen were determined by weighting of samples before and after oxidation on an electronic laboratory balance A&DCOLTD GH-200 with an accuracy of no worse than 10^{-4} g.

Structural studies were performed using Philips CM30 TWIN transmission electron microscope (300 kV), scanning electron-ion FEI Quanta 200 3D (30 kV) and electron Tescan Vega 3 SBH (20 kV) microscopes. Microhardness of surface scale was determined by the prints of a Vickers diamond pyramid on a Neophot 21 instrument with a load of 0.5 N and exposure time of 15 s. At least 10 prints were made at each oxide scale thickness.

3. Results and discussion

The results of a detailed study of V–Cr–Ta–Zr alloy grain and defect structure after TMT preceding oxidation are presented in [6]. As can be seen (Figure 1 a), the microstructure is characterized by anisotropic structural state. The grains are elongated in the rolling direction (RD), forming strips of length from several tens of microns to hundreds of microns, and their width is 10 – 15 microns. Inside some grains a strongly gradient color is observed, indicating the presence of structural states with a continuous change of crystal lattice orientation. In addition, the low angle misorientation boundaries break up the grains into fragments of almost equiaxed shape and microbands, like those shown in Figure 1 b. The characteristic sizes of microbands range from a few tenths of a micron to several microns. The dislocation density reaches $2.5 \cdot 10^{10} - 3.0 \cdot 10^{10} \text{ cm}^{-2}$ (Figure 1 c).

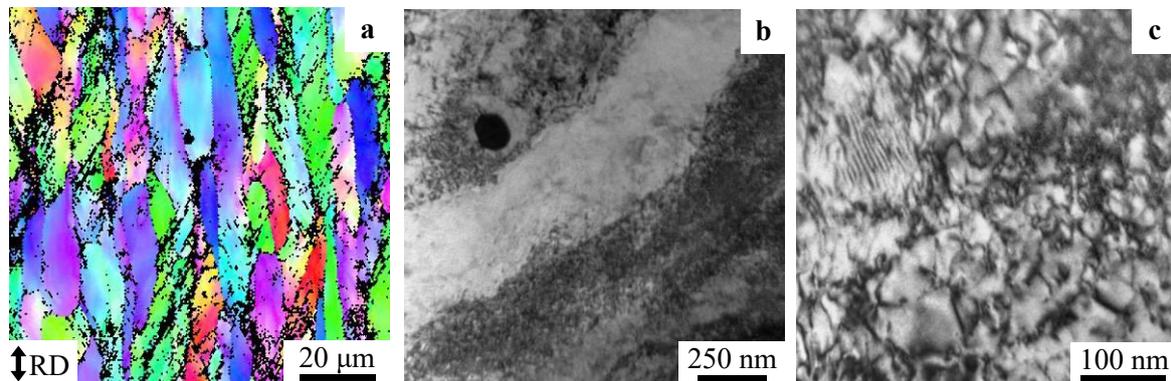


Figure 1. V–Cr–Ta–Zr alloy microstructure before oxidation [6].

Table 2 shows data on the change in mass (Δm) and concentration (C_O) of oxygen depending on the oxidation duration.

Table 2. Mass (Δm) and concentration (C_O) of introduced oxygen depending on oxidation duration (t).

| t (min) | 10 | 30 | 60 | 90 |
|-------------------------------|------|------|------|------|
| $\Delta m \cdot 10^{-6}$ (kg) | 0.40 | 1.15 | 2.20 | 3.40 |
| C_O (at. %) | 0.28 | 0.85 | 1.58 | 2.26 |

Figure 2 shows an example of the change in oxide scale thickness on V–Cr–Ta–Zr alloy samples, depending on the duration of oxidation in air. End sections were obtained by brittle fracture of samples with oxide scale at liquid nitrogen temperature.

It is established that the thickness of the oxide scale formed is significantly inhomogeneous. For example, after 60 minutes of oxidation, local areas are observed (Figure 2c), in which the scale thickness varies from 1.8 μm to 2.8 μm . At the same time, for this treatment the scale thickness is

mainly in the range from 2 μm to 2.2 μm . Moreover, on the frontal SEM images it can be clearly seen that the scale formed consists of flakes of plate-shaped V_2O_5 oxide, the dimensions of which are in length from 3 to 7 μm and from 1 to 3 μm in width, with thickness from 0.05 to 0.3 μm (Figure 3).

At the same time, the increase in the oxidation duration contributes to the sticking of the flakes among themselves, as a result of which a false impression can be created about their size increase.

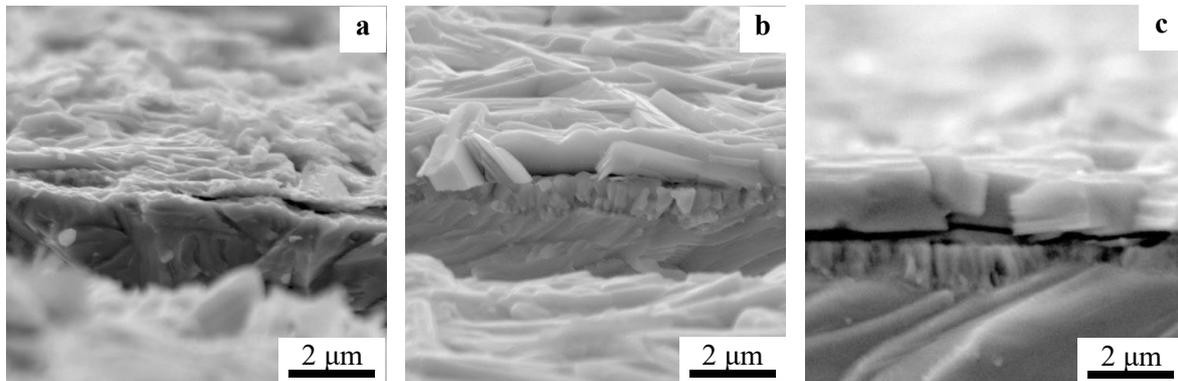


Figure 2. Electron-microscopic images of surface oxide scale end sections after different oxidation duration. a – 10 min; b – 30 min; c – 60 min.

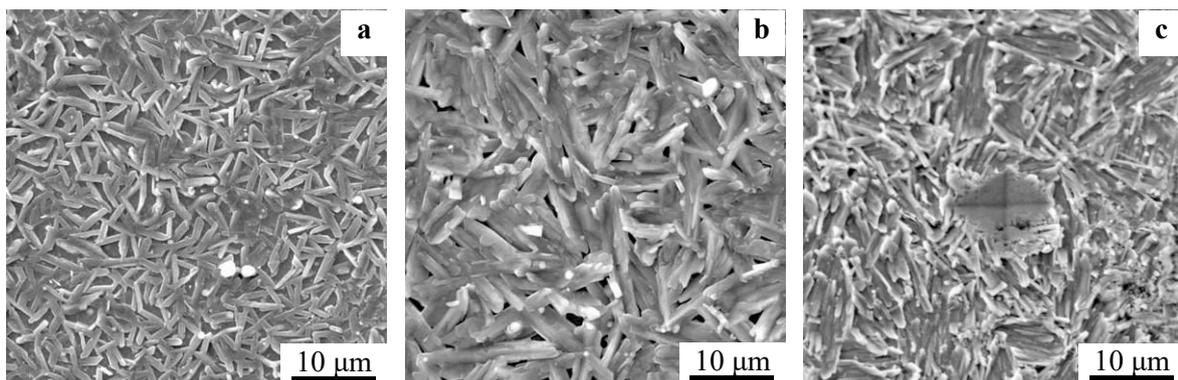


Figure 3. Frontal electron-microscopic images of surface oxide scale structure after different oxidation duration. a – 10 min; b – 30 min; c – 90 min.

Chaotic sticking of oxide flakes causes a non-uniform oxide layer to form. Note that the average thickness values are not informative at the above deviations. Thus, it is advisable to consider the characteristic intervals of the scale thickness depending on oxidation duration (Table 3).

Table 3. Thickness (h) of surface oxide scale depending on oxidation duration (t).

| t (min) | 10 | 30 | 60 | 90 |
|-----------------------|-----------|-----------|-----------|-----------|
| h (μm) | 0.4 – 1.0 | 1.0 – 2.0 | 1.5 – 3.0 | 2.5 – 4.0 |

In the process of end sections obtaining (Figure 2 and 4) by fracture at liquid nitrogen temperature, it was found that surface scale often cracks into thinner layers (Figure 4 a, b) or local chipping of some sites from the oxidized sample surface occurs (Figure 4 c). This fact testifies to its high brittleness and low adhesive strength with the surface. The averaged microhardness values of the scale after 90 minutes of oxidation reach 10 GPa with an indenter penetration depth of no more than 1.6 μm , which is 1.5 – 2.5 times lower than the scale thickness (Table 2). Note that the microhardness of the vanadium alloy prior to the oxidation does not exceed 2 GPa.

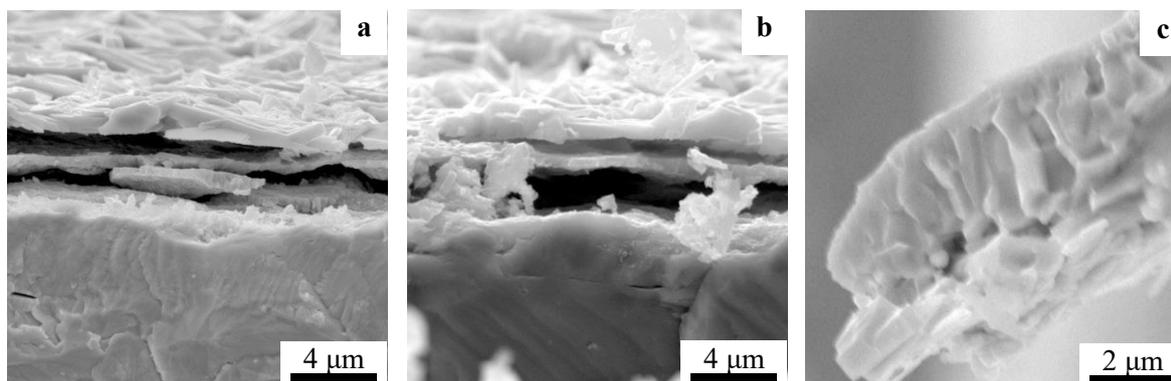


Figure 4. Electron-microscopic images of surface oxide scale end sections after different oxidation duration. a – 30 min; b – 60 min; c – 90 min.

One of the important features of surface scale formed during oxidation in air is the presence of open porosity, which is the result of the chaotic sticking of flakes together. This feature is clearly visible on the front (Figure 3) and end (Figure 4 c) SEM images. The pores on the faces in the depth of the Vickers pyramid imprint after measuring the microhardness (Figure 3 c) indicate the presence of porosity at different depths of surface scale. Moreover, the end electron microscopic image obtained from the breakaway fragment of scale shows pores throughout the entire thickness of the scale (Figure 4 c). The presence of open porosity ensures the supply of oxygen to the sample surface, on which the processes of nucleation and growth of flakes take place.

4. Summary

In the time interval studied, surface scale thickness on samples of V–Cr–Ta–Zr alloy significantly depends on the duration of oxidation in air. It is established that the surface scale consists of flakes of plate-shaped oxide (V_2O_5) and is characterized by the presence of open porosity, which provides oxygen supply to the sample surface

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