Influence of V–Cr–W–Zr alloy microstructure on features of oxidation during chemical-heat treatment

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Abstract. Investigation results of microstructure influence on oxidation coefficient during chemical-heat treatment of V–Cr–W–Zr alloy are presented. It is shown that the formation of a high defect structural state in the alloy leads to a twofold increase in the oxidation coefficient and a significant increase in the oxygen concentration. The maximum effects of the microstructure on the oxidation processes are detected at short treatment times.

1. Introduction
The use of oxidation in the process of chemical heat treatment (CHT) is one of effective ways of modifying the structural-phase state of vanadium alloys, which significantly improve their physical-mechanical and chemical characteristics [1–6]. It was shown in [6] that, as a result of CHT, high density of fine-disperse high-stable particles of the second phases provide an increase in thermal stability of microstructure and mechanical properties of V–Cr–W–Zr system alloy. As is known [7], the formation of high defect structural states in metallic materials contributes to a significant acceleration of diffusion processes and the associated mass transfer effects. Thus, for the controlled production of the required volume fraction of particles of the desired dispersion, the questions of structural state influence on the processes of oxidation and redistribution of oxygen remain topical.

In the present work, we studied the influence of V–Cr–W–Zr alloy structural state on the oxidation coefficient during CHT.

2. Experimental materials and procedures
V–Cr–W–Zr vanadium alloy produced by SC "VNIINM" was used, the chemical composition of which in weight (wt. %) and atomic (at. %) percent is given in Table 1.

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

| Element | wt. % | V | Cr | W | Zr | O | C | N |
|---------|-------|---|----|---|----|---|---|---|
|         |       | Base | 4.23 | 7.56 | 1.69 | 0.02 | 0.02 | 0.01 |
| at. %   |       | Base | 4.41 | 2.23 | 1.00 | 0.07 | 0.09 | 0.04 |

Samples of this alloy were subjected to thermomechanical treatment by mode II (TMT II) [8] without annealing (No. 1) and with one-hour stabilization annealing at temperatures (Tₛₐ.) 1200 °C (No. 2) and 1400 °C (No. 3). The samples had the same shape and surface area (S ≈ 175 mm²). Chemical heat treatment by internal oxidation method [6] was carried out on samples after various
combinations of TMT and stabilizing annealing (No. 1 – 3). The duration of oxidation (formation of surface scale) in air at 600 – 700 °C was 3 and 6 hours. The redistribution of oxygen inside the material was carried out by vacuum stepwise (from 600 to 1000 °C) annealing for 9 hours.

Electron backscatter diffraction (EBSD [9]) analysis was performed with scanning electron-ion microscope FEI Quanta 200 3D (30 kV). The Kikuchi patterns formed by backscatter electrons were automatically indexed by the program “TSL OIM data collection”. The collected data was processed with the use of “TSL OIM analysis” software. Microstructural investigations were conducted using a transmission electron microscope Philips CM30 TWIN (300 kV).

Total oxygen concentration \( C_O \) (at. %), achieved during CHT, was determined by the ratio
\[
C_O \approx 100\Delta m(0.295m_i + \Delta m)^{-1} + C_{O_i}^{-1},
\]
where \( m_i \) – sample mass before CHT, \( \Delta m \) – mass change during CHT, 0.295 – normalization coefficient for conversion to atomic percent, taking into account the alloy chemical composition before oxidation, \( C_{O_i} \approx 0.07 \) at.% – initial concentration of oxygen in the studied samples before CHT (Table 1).

3. Results and discussion

It was established that after treatment No. 1, the material is characterized by grains elongated in the rolling direction (RD) of more than 100 μm in length (\( d_{||} \)) and 5 – 20 μm in width (\( d_{\perp} \)) (Figure 1 a). Gradient color is observed inside these grains, indicating the presence of small-angle misorientations. The dislocation density \( (\rho_d) \) reaches \( 4 \times 10^{10} \) cm\(^{-2} \) (Figure 1 d).

![Figure 1](image_url)  
**Figure 1.** Orientation mapping of V–Cr–W–Zr alloy subject to TMT conditions: No. 1 (a), No. 2 (b), No. 3 (c) and corresponding defect substructure No. 1 (d), No. 2 (e), No. 3 (f).

Structural state No. 2 is characterized by the formation of fine \( (d \approx 5 – 20 \mu m) \) almost equiaxed grains on the background of interlayers of coarse \( (d_{\perp} \approx 10 – 20 \mu m; d_{||} \approx 20 – 50 \mu m) \) grains elongated in RD (Figure 1 b). In large and small grains, the alignment of the gradient color is observed. The dislocation density decreases to \( 2 \times 10^{10} \) cm\(^{-2} \) (Figure 1 e).
Processing No. 3 leads to a significant increase in grain size ($d \approx 20 – 130 \mu m$) (Figure 1 c) and defect substructure relaxation (Figure 1 f). In all grains there is no gradient color; the dislocation density (Figure 1 f) does not exceed $10^{10} \text{cm}^{-2}$.

The parameters of grain and defect structure depending on TMT conditions are summarized in Table 2.

### Table 2. Parameters of grain ($d, d_\parallel, d_\perp$) and defect ($\rho_d$) structure depending on TMT conditions.

| Treatment                     | Grain sizes ($\mu m$)          | $\rho_d$ (cm$^{-2}$) |
|-------------------------------|-------------------------------|----------------------|
| No. 1 - TMT II (without annealing) | $d_\perp \approx 5 – 20$ | $4 \times 10^{10}$     |
|                               | $d_\parallel \approx 30 – 300$ |                       |
|                               | $d_\perp \approx 10 – 20$    |                       |
| No. 2 – TMT II ($T_{s.a.} = 1200 ^\circ C$) | $d_\perp \approx 20 – 50$ | $2 \times 10^{10}$     |
|                               | $d \approx 5 – 20$           |                       |
| No. 3 – TMT II ($T_{s.a.} = 1400 ^\circ C$) | $d \approx 20 – 130$ | $10^{10}$              |

$d$ – equiaxied grain diameter;
$d_\parallel$ and $d_\perp$ – elongated grains length along and perpendicular to RD.

Table 3 shows the values of $C_O$, depending on TMT conditions (structural state) and oxidation duration in air.

### Table 3. Influence of TMT conditions and CHT duration ($t_0$) on mass change ($\Delta m$), oxygen concentration ($C_O$) and oxidation coefficient ($k$).

| Treatment before CHT          | $t_0$ (h) | $\Delta m \times 10^{-6}$ (kg) | $C_O$ (at. %) | $k \times 10^{-10}$ (kg$^2$·m$^{-4}$·s$^{-1}$) |
|------------------------------|-----------|-------------------------------|---------------|----------------------------------|
| No. 1 – TMT II (without annealing) | 3         | 1.75                          | 1.41          | 1.4                              |
|                               | 6         | 2.39                          | 1.84          |                                  |
| No. 2 – TMT II ($T_{s.a.} = 1200 ^\circ C$) | 3         | 1.42                          | 1.12          | 1.0                              |
|                               | 6         | 2.20                          | 1.60          |                                  |
| No. 3 – TMT II ($T_{s.a.} = 1400 ^\circ C$) | 3         | 1.07                          | 0.89          | 0.7                              |
|                               | 6         | 1.72                          | 1.38          |                                  |

It was established that during 3 and 6 hours of oxidation, the maximum mass increase ($\Delta m$) occurs in samples No. 1 (Table 3) without stabilization annealing, which are characterized by the most defect structural state (Table 2). In samples No. 2 (Table 3), stabilized at 1200 °C, $\Delta m$ after 3 hours of oxidation is lower by 20 %, and after 6 hours – by 15 %. The minimum values of the mass increase are observed during the oxidation of samples No. 3 (Table 3), annealed at 1400 °C. Compared with state No. 1, $\Delta m$ after 3 hours of oxidation is lower by 40 %, and after 6 hours – by 30 %.

According to [10], the consequence of oxygen concentration increase in the oxidation process is an increase in the sample mass normalized to a unit surface ($\Delta W = \Delta m/S$), which is described by formula

$$\Delta W = \sqrt{k t_0},$$

where: $t_0$ – duration of heat treatment in air, $k$ – oxidation coefficient.

Figure 2 shows the straight and quadratic dependences of the normalized mass change of samples after different treatments on the duration of oxidation in air. Inclination angles tangents of the approximated straight lines (Figure 2 b) represent the oxidation coefficients ($k$) of samples with different structural states.
The presented results (Figure 2, Table 3) indicate that the oxidation coefficient \(k\) is sensitive to microstructure parameters (Figure 1, Table 2). The most intensive processes of internal oxidation occur in the high defect state No. 1, averaged (in the time interval from 0 to 6 hours) oxidation coefficient \(k\) of which is 1.4 times higher than after annealing at 1200 °C (No. 2) and 2 times higher than in state after annealing at 1400 °C (No. 3). Comparison of the data presented in Table 3 suggests that the maximum effect of the microstructure on the oxidation processes is detected at short treatment times \((t_0 = 3 \text{ h})\).

4. Summary
The formation of a high defect structural state in V–Cr–W–Zr alloy at the TMT stage contributes to a significant increase in the oxidation coefficient during CHT in air. At the same time, the oxidation coefficient is 1.4 times higher than in the structural state, stabilized at 1200 °C, and 2 times higher as compared to the state after recrystallization at 1400 °C.

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