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Charging of V–4Cr–4Ti by oxygen to create *in situ* insulator coating

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Abstract

Oxidizing of V–4Cr–4Ti in flowing Ar–O_2 ($P_{O_2} = 1\text{–}5 \times 10^{-2}$ Pa) at 973–1273 K has been investigated. The mechanism of interaction between V-alloy and gaseous medium was found to change around 1011 K. At higher temperatures, $T > 1011$, the interaction is controlled by oxygen absorption in the alloy. At $T < 1011$ K, oxygen diffusion is accompanied by fine Ti–O precipitation with high density, limiting the depth of oxygen penetration into the alloy. Based on comparative analysis of the results obtained and reference data, the formation of an inner oxidizing zone at low temperature has been modeled. In the context of the model, the availability of this structure to produce Er_2O_3 on the V–4Cr–4Ti surface in contact with the Li(Er) melt is considered.

1. Introduction

One of the critical issues with a self-cooled V/Li blanket is the magneto-hydrodynamic pressure drop when Li flows through the duct. It can be eliminated by an electrically insulating coating applied to the inner wall of the ducts. Some *in situ* oxide insulating coatings (Er_2O_3, CaO, Y_2O_3) are currently being developed for application in the V/Li blanket [1]. Initially thermodynamic stability and electrical-insulating properties of the mentioned oxides in liquid Li were considered, later the feasibility of coating by exposure of V–4Cr–4Ti charged with oxygen in Li doped by Er (Ca, Y) was verified [1–3]. However, the durability of the oxide coating depends not only on its thermodynamic properties but also on oxygen delivery from the solid metal to the interface and, thus, kinetic factors deserve consideration as well. The efficiency of oxygen being delivered to the interface is directly dependent on the previous charging procedure of alloy by oxygen [4]. Nevertheless, up to now, this dependence has been ill defined. There is already experience of internally oxidizing of refractory alloys [5–11], which could be used. However, the essence of oxygen treatment of an alloy to support a continuous oxide coating is different and needs special investigation. Here, the aim is to study the kinetics of oxidation and the features of phase-structure transformation in V–4Ti–4Cr at 873–1273 K in flowing Ar–O_2 ($P_{O_2} = 1\text{–}5 \times 10^{-2}$ Pa).

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2. Experimental procedure

The samples ($7 \times 7 \times 0.5$ mm) of V–4Ti–4Cr (NIFS-HEAT-2, Ti – 3.98, Cr – 4.02 wt%, O – 148, N – 122, C – 69 wppm, the average grain size 20 μm) were pre-charged by oxygen at different temperatures (873–1273 K) and varied exposures in the Ar–O_2 (O_2 – 0.1 wppm; N_2 – 1.0; H_2O – 0.5) with oxygen partial pressure $P_{O_2} = 1–5 \times 10^{-2}$ Pa and flow rate of 400 ml/min. The weight gain was controlled by a thermo-gravimetric apparatus (TG). Subsequently the samples were annealed in vacuum ($\sim 10^{-5}$ Pa) at 973 K. The Vickers hardness (HV) in cross-section was measured with a 10 gf load. The microstructure of near-surface region was investigated by transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

3. Results

Under the given condition of pre-oxidation the main interaction consists of dissolution of oxygen into the alloy (with possibility of Ti–O precipitation) and formation of a thin surface oxide film VO_2 according to XPS results (V2p3 peak at 516 eV). The HV profiles are a direct function of oxygen distribution and state in the V-alloy. With increasing oxidizing temperature from 873 to 1073 K, both near-surface hardness and the depth to which hardening occurs increases regularly (Fig. 1(a), curves 1–3). However, this regularity is violated at 1173 and 1273 K: hardness decreases noticeably while depth of hardness alteration continues to increase (curves 4 and 5). This suggest a change in mechanism of interaction between alloy and oxygen at nearly 1073 K. To specify the value

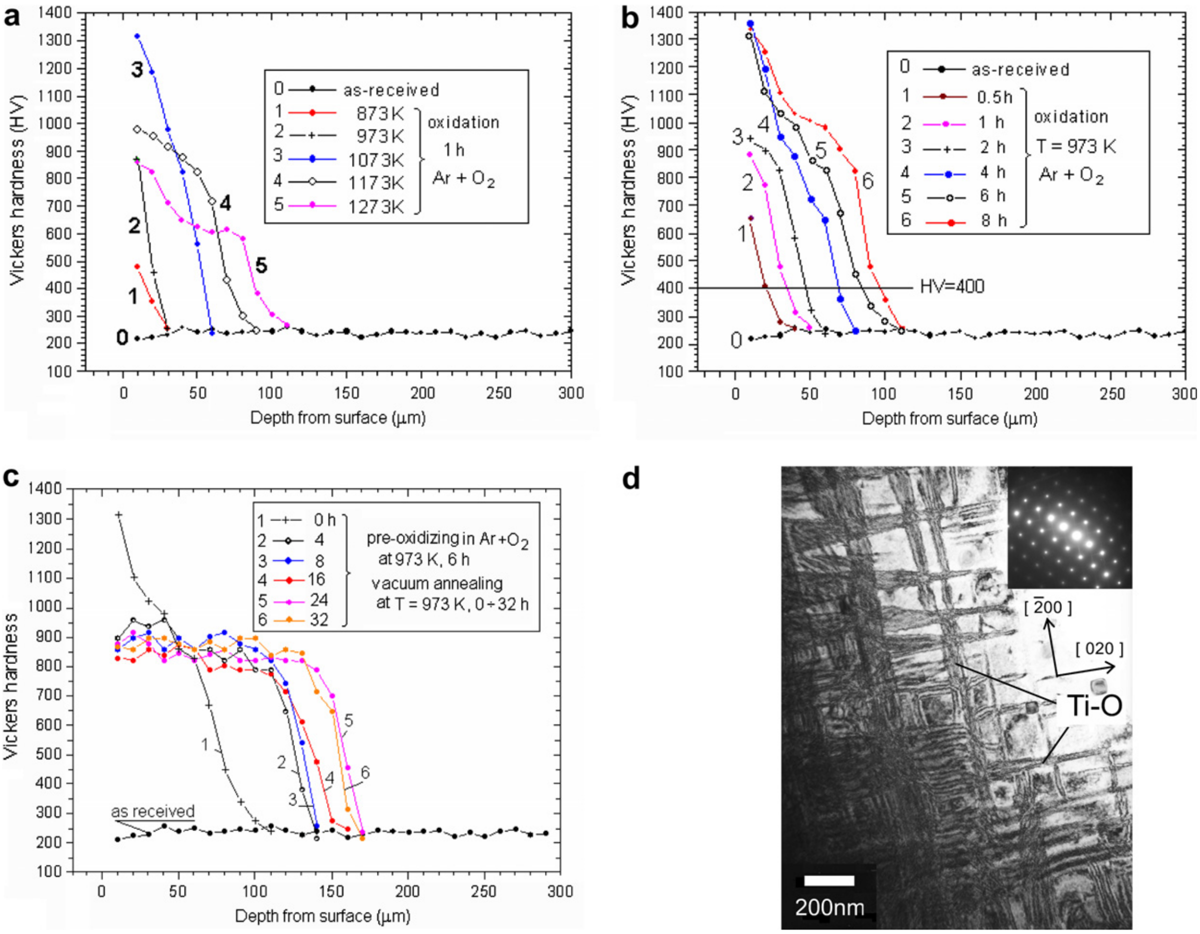

Fig. 1. The effect of temperature (a), time (b) of oxidizing in Ar + O_2 and annealing in vacuum (c) on the hardness profiles of V–4Ti–4Cr and TEM structure of alloy after oxidizing at 973 K, 6 h and vacuum annealing at 973 K, 16 h (d).

Table 1
Weight gain ($10^{-3} \times$ mg/mm^2) of V–4Ti–4Cr samples after exposures in Ar–O_2

t (h)	*T* (K)				
	873	973	1073	1173	1273
0.5		2.6			
1.0	0.8	3.7	6.1	8.8	11.3
2.0		5.6			
4.0		7.3			
6.0		9.0			
8.0		11.2			

of this temperature, the activation energy of the process was determined according to TG data (Table 1).

Natesan and Uz determined [11], that oxidation of V–4Ti–4Cr obeys a parabolic law at 673–973 K in rarefied O_2 which was used in a feed/bleed manner to maintain the constant pressure (5×10^{-6}, 5×10^{-4}, 1×10^{-1} torr). Therefore a weight gain (m/S) of alloy with time (t) is expressible by equation $(m/S)^2 = K \times t$, here K – parabolic rate constant of gas–metal interaction. Simultaneously $K = A\mathrm{e}^{-Q/RT}$, here Q – activation energy (J/mol), R – absolute gas constant, T – temperature. On the Fig. 2 logarithm of $K = (m/S)^2/t$ is shown as a function of $1/T$. There is an obvious break in the line at $T = 1011$ K and Q values on high and low temperature sides of it differ (67.493 and 178.75 kJ/mol, respectively.)

At higher temperature ($T > 1011$ K), oxygen essentially dissolves in the vanadium matrix. All oxygen, delivered to the surface from Ar–O_2, is taken by metal. The activation energy determined here (67.493 kJ/mol) is comparable to that of oxygen absorbed by pure vanadium (73.568 kJ/mol) [5].

At lower temperature ($T < 1011$ K), the rate of oxygen absorption by V-alloy diminishes. An activation energy of $Q = 178.75$ kJ/mol coincides well with one determined under oxidizing of V–4Ti–4Cr at $P_{O_2} = 5 \times 10^{-6}$ torr at 773–973 K (174.00 kJ/mol) [11]. Both these values are nearly three times greater than activation energy at higher temperature. Therefore, an extent of a temperature effect on the interaction between V-alloy and oxygen diminishes when $T > 1011$ K as seen in Fig. 2. Most likely, at low temperature, the process of interaction is controlled by oxygen diffusion through an inner oxidizing zone (IOZ), where coherent Ti–O precipitates with high density begin to form. In this case, the growth of an IOZ should obey a parabolic law with time [5].

The oxidation of the alloy in Ar + O_2 at $T = 973$ K is accompanied by an increase in hardness and a slight decrease in slope of the hardness profiles with time (Fig. 1(b)). This indirectly indicates oxide precipitation, though XRD and TEM show only VO, VO_2 in the near surface region. To determine kinetics, the depths at which HV = 400 was plotted versus $\sqrt{t}$ (Fig. 3(a)). The straight line suggests the parabolic growth of the IOZ. Gravimetric data demonstrates the same dependence on time (Fig. 3(b)).

In order to dissolve surface oxide film and extend the IOZ, vacuum annealing at 973 K of pre-oxidized samples was conducted. As a result, the IOZ increases to 140–170 μm, but its depth does not depend on time essentially (Fig. 1(c), curves 2–6). The uniform high hardness (~850), abrupt gradient, and hardness of the sample's core suggest the bound state of oxygen in this zone. The dispersed Ti–O

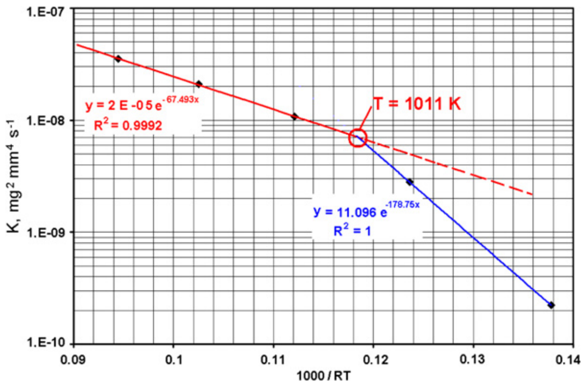

Fig. 2. Parabolic rate constant K as a function on reciprocal temperature for V–4Ti–4Cr oxidation.

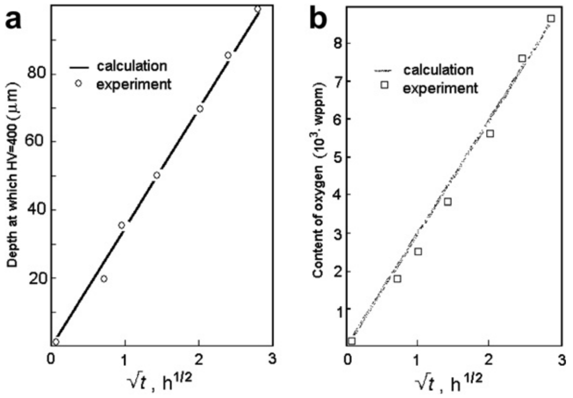

Fig. 3. Parabolic relationship of V–4Ti–4Cr oxidation in Ar + O_2 at 973 K: depth at which hardness HV = 400 (a) and content of oxygen in simples (b).

plates with preferred ⟨2 0 0⟩ orientation in the matrix were revealed using TEM (Fig 1(d)) and a Ti2p3 peak at 459 eV in the XPS spectrum conforms to TiO_2precipitation [2].

4. Discussion

Both thermodynamic and kinetic aspects of IOZ creation in V–4Ti–4Cr at 973 K in $Ar + O_2$ are considered below.

Thermodynamic estimation, TEM and XPS results, high hardness, and a parabolic dependence of oxidation on time indicate that in the low-temperature interval (873–1011 K), oxygen-diffusion into alloy is accompanied by Ti–O precipitation with high density. But these findings are in conflict with kinetic consideration. Specifically, at temperature $T < 0.6\ T_{\mathrm{melt}}$ the absolute inequality $D_{\mathrm{Ti}}C_{\mathrm{Ti}} \ll D_{\mathrm{O}}C_{\mathrm{O}}$ is satisfied (here D and C are diffusivity and concentration of Ti and O) [5]. It means that growth of IOZ should be controlled by titanium diffusion. Inasmuch as Ti-atoms are almost immovable at this temperature, the nature of mass transfer of components and mechanism TiO_2 growing in the IOZ must be clarified. Most likely formation of IOZ is caused by specific of oxygen transport into the alloy at low temperature.

It is well known that, at $T = 0.5–0.6\ T_{\mathrm{melt}}$, diffusion of interstitial impurities is predominately along boundaries [12]. Because of oxygen diffusion along boundaries, the grains are subjected to a specific osmotic pressure. Even at relatively low content of impurities (0.1–1.0%), this pressure is assessed to be tens or hundreds atmosphere [12]. It is sufficient to generate the mobile dislocations (flow $\boldsymbol{j}_{\mathrm{d}}$), which transfer the oxygen atoms (flow $\boldsymbol{j}_{\mathrm{O}}$) into the grain (Fig. 4). When oxygen attains its limit, the lattice becomes ordered ($\alpha \rightarrow \alpha'$) [2,3]. Ti-atoms are shifted no more than an interatomic distance. The ordered position of Ti- and O-atoms initiates coherent Ti–O oxides ($\alpha' \rightarrow TiO_2$). The coherent precipitates add inner stresses in the lattice and trigger an autocatalytic process of precipitation: fresh dislocations produced new oxides etc. As a result, a 'net-structure' with very high precipitate density is formed in the IOZ.

Considerable experimental data obtained for similar systems support the mechanism of $\alpha \rightarrow \alpha' \rightarrow TiO_2$ transformation, described above. For example, for different inner-oxidizing alloys (Nb–Zr, V–Zr, V–Ti, Ta–Hf), the *bcc*-lattice and lattice of newly growing oxide (ZrO_2, TiO_2, HfO_2) were observed to have definite mutual orientation [5]. Well-defined deformation contrast and high hardness is typical for growing Ti–O oxides in the V–4Ti–4Cr at 973 K and confirms their coherence (or semi-coherence) with the matrix [8,9]. At higher temperature (1073–1273 K) this effect disappears [8].

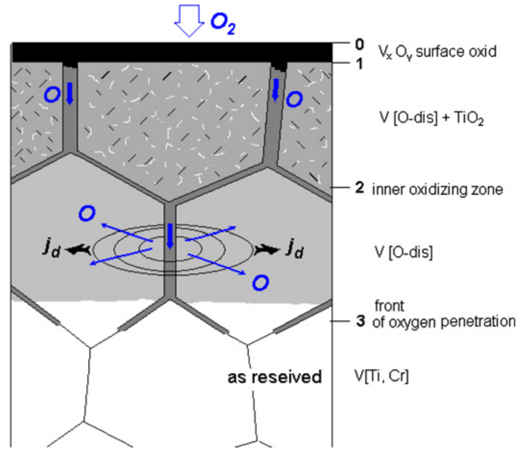

Fig. 4. Mechanism of inner oxidizing zone formation in V–4Ti–4Cr at low temperature ($T \approx 973$ K).

Under low-temperature oxidation of Nb-alloys, a tetragonal modification of oxide (ZrI_2, HfO_2) appears instead of monoclinic one, consistent with the equilibrium diagram [5]. This replacement is caused by unfavorable conditions, under which the oxide grows in *bcc*-lattice: tetragonal and *bcc*-lattices transform to create a new phase (Fig. 5) [5]. The oxides are usually plate-shaped, because they grow preferably in two directions of optimum coherence with the matrix. The growth in the third direction is suppressed by lattice mismatch. According to the proposed model (Fig. 5), the non-equilibrium defects play an important role in creation of IOZ. They promote oxygen's penetration into grain, contribute to the $\alpha \rightarrow \alpha' \rightarrow TiO_2$ transformation

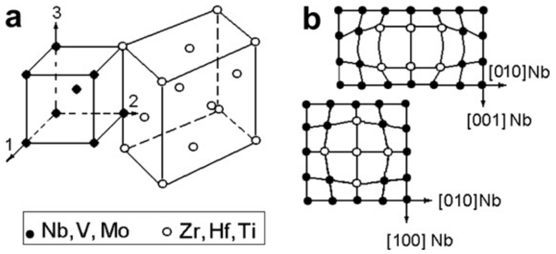

Fig. 5. The scheme of rearrangement of alloying atoms (Ti, Zr, Hf) in *bcc* lattice to create tetragonal coherent oxide (TiO_2, ZrO_2, HfO_2). (a) spatial pattern; (b) projection in (0 0 1) and (1 0 0) [5].

and keep oxygen in solid solution, perhaps as Ti-defect-O complexes. That is why the samples maintain a high level of hardness and abrupt gradient after prolonged vacuum annealing (Fig. 1(c)). Tentative tests in Li(Er) showed that only Ti–O net-structure could grow an Er_2O_3-layer on the surface of the charged V-alloy [13,14]. It can be supposed that the created Ti–O net structure provides the most efficient use of the oxygen accumulated in the vanadium alloy.

Consequently, as applied to *in situ* oxide coatings the essence of the V–4Ti–4Cr treatment by oxygen is to form the non-equilibrium structure containing both oxygen and defects. Therefore, the charging procedure of alloy should be implemented in the restricted temperature interval around 1011 K (923–1023 K). On the one hand, the lower temperature ($T < 923$ K) is unacceptable because of hampering of diffusion processes. This temperature should be sufficient for oxygen diffusion along grain boundaries, producing mobile dislocations and thereby Ti–O precipitation in the grains. On the other hand, such a structure cannot be formed at high temperature (1173, 1273 K), where the bulk diffusion is more active, osmotic pressure decreases and the recovery process does not allow accumulating the high level of defects in the grains.

5. Summary

Oxidation of V–4Cr–4Ti in the $Ar + O_2$ flow at 973–1273 K has been investigated. The mechanism of interaction between V-alloy and gaseous medium alters at around 1011 K. At $T \leqslant 1011$ K oxygen diffusion is accompanied with ultrafine Ti–O precipitation, limiting the deeper oxygen penetration into alloy. The growing of an oxidized zone and the content of oxygen in the alloy obeys parabolic law. At $T > 1011$ the interaction process is limited by oxygen absorption in the vanadium matrix as judged from activation energy.

The charging procedure of V–4Ti–4Cr by oxygen should be implemented in the restricted temperature interval (923–1023 K), where the diffusion of oxygen along the grain boundaries occurs producing the mobile dislocations and Ti–O precipitation in the bulk of grains.

Different combinations of charging procedure (pre-oxidizing + vacuum annealing) deserve further investigation to determine the optimum structure of V–4Ti–4Cr in context of oxide insulator coating formation at the interface.

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