Investigation of Long-Term Oxidation Resistance of Titanium Alloys with a Coating Based on Ti–Al-C System Nanocomposites

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Abstract Physical and mechanical properties of thin sheets (0.5 mm) of titanium grades VT1-0 and OT4-1 in the operating conditions of intermedium-temperature fuel cell were compared. It is established that the heat and oxidation resistance of the OT4-1 alloy was dominated by titanium VT1-0, which allows it to be considered as a promising substrate material for the manufacture of thin interconnects of solid oxide fuel cell. The oxidation resistance of Ti–Al-C coatings obtained by magnetron deposition under different modes has been studied. The 2.5 μm thick coating obtained by the method of magnetron deposition having the Young's modulus close to the OT4-1 alloy substrate can be considered promising for this purpose.

1 Introduction

Nowadays, solid oxide fuel cell (SOFC) interconnects are traditionally made of sheets (0.3…0.5 mm thick) of Crofer steels, which contain 20…24% Cr [1]. However, it is known that due to the diffusion of chromium from the interconnect to the cathode, functional properties of the interconnect deteriorate. Due to oxidation, the surface electrical conductivity of such interconnects is lost. This requires the creation of special coatings on their surface [2]. In addition, the high density of Crofer steels ($\gamma \sim 8$ g/cm^3) causes a significant weight of a SOFC.

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An alternative to Crofer steels is composites based on the titanium MAX phases ($\gamma \sim 4.1 \ldots 4.3$ g/cm^3) [3–5], especially in the case of intermediate temperature (550–650 °C) SOFC. Here, the MAX phase of Ti_2AlC is preferred over the MAX phase of Ti_3AlC_2. Oxidation resistance of Ti_3AlC_2 at 600 °C in contrast to Ti_2AlC is abnormally lowered due to the formation of TiO_2 oxide of the anatase type [6–8]. Higher oxidation resistance of Ti_2AlC is probably due to the ability of oxygen to penetrate the crystal lattice of Ti_2AlC, forming a solid solution of $Ti_2Al\,(C_{1\text{-}x}O_x)$ and inhibiting the formation of titanium and aluminum oxides in the near-surface layers [5, 9, 10]. However, like Crofer steels, during long-term exposure to air at 600 °C, the MAX samples of the Ti_3AlC_2 and Ti_2AlC phases lose their electrical conductivity [11–13].

Interconnects made of thin (0.2…0.5 mm) titanium sheets with coatings based on MAX phases of the Ti–Al–C system can be more efficient [14]. Behavior of coatings obtained by vacuum-arc deposition under conditions of long-term exposure to oxidizing media at 600 °C was studied in [15]. Here, a thin sheet of titanium grade VT1-0 was used as a substrate. It is known [16] that this material is not oxidation-resistant, so for the interconnects of fuel cells with an operating temperature of 550… 650 °C, it is necessary to change the substrate material. In this paper, the influence of technological parameters of coatings on their long-term oxidation resistance depending on the substrate material was investigated.

2 Materials and Methods

Mechanical characteristics σ_B (ultimate tensile strength) and $\sigma_{0.2}$ (yield strength) were determined on standard fivefold flat specimens 0.5 mm thick and 2 mm wide of the working part, in air at 20 °C and after heating to 600 °C.

Oxidation resistance tests of the material were performed during 4 stages. Each stage involved heating of a polished sample to 600 °C in air, holding for 250 h and cooling to room temperature. The weight gain of the sample Δm was measured on analytical scales of the brand Radwag-AS after each stage of the test with an accuracy of ± 0.1 mg. Oxidation resistance of the material was evaluated by the ratio $\Delta m/S$, where S is the initial surface area of the sample.

The Nano Indenter G200 system (Agilent Technologies, USA) equipped with a Berkovich diamond tip was used to determine the nanohardness H (10 mN) and the elastic modulus E of the coatings [17]. Ten indentations were made on each sample. The maximum load was 10 mN, for which the depth of indentation was approximately 200…300 nm.

Planar rectangle target based on Ti_2AlC MAX phase of 180×90 mm and 6 mm thick was used for the coatings deposition by DC magnetron sputtering. Preliminary evacuation of the setup was carried out until the vacuum in the chamber was at least 10^{-3} Pa. Ar was used as a working gas at a pressure of 2 Pa. The distance between the target and rotating substrates was 120 mm. A negative bias potential of 50 V was applied to the substrate. The deposition of coatings was carried out at different power of the magnetron discharge. The discharge power was controlled by varying the discharge voltage 320 to 430 V.

Zeis EVO-40XVP scanning electron microscope was used for microstructural studies, where SEM EDX analysis of local content of alloying elements was also performed using INCA Energy 350 system.

3 Results and Discussion

In order to improve the oxidation resistance of SOFC interconnects, titanium alloy grade OT4-1, the properties of which were compared to those of titanium grade VT1-0, was chosen as a substrate material. The chemical composition of these materials is given in Table 1.

It is found that tensile strength and yield strength of OT4-1 alloy in the temperature range of 20…600 °C significantly exceed those of VT1-0 titanium. At the operating temperature of the fuel cell (600 °C), it meets the requirements for interconnect materials ($\sigma_{0.2}$ > 100 MPa), in contrast to titanium grade VT1-0 (Fig. 1, Table 2).

In the previous stage of the work, the efficiency of vacuum-arc coating was substantiated. However, this method is technologically complex and of high-energy

Table 1 Chemical composition (wt.%) of the studied titanium alloys

Titanium grade	Ti	Al	Mn	C	Fe	Si	Zr
VT1-0	Balance	–	–	0.03	0.20	0.10	–
OT4-1	Balance	1.83	1.54	0.04	0.09	0.14	0.11

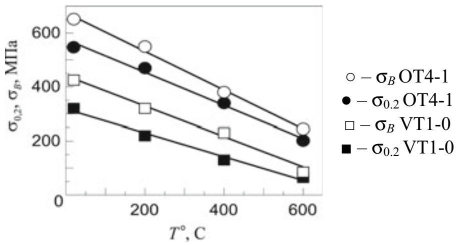


Fig. 1 Temperature dependence of strength characteristics of titanium grades VT1-0 and OT4-1

Table 2 Strength characteristics of titanium grades VT1-0 and OT4-1 at different temperatures

Titanium grade	$\sigma_{0.2}$, MPa		σ_B, MPa	
	20 °C	600 °C	20 °C	600 °C
OT4-1	547	202	652	244
VT1-0	320	65	425	85

consumption [14, 15]. To simplify the technology of coating the interconnects, the method of magnetron deposition in different modes was chosen (Table 3).

It was also found that the OT4-1 alloy is twice superior to titanium grade VT1-0 in long-term (based on 1000 h) oxidation resistance (Fig. 2), which for both alloys vary in parabolic dependence. Thus, according to the obtained results, a OT4-1 titanium alloy substrate with a coating resistant to high temperature oxidation can be used for the manufacture of thin-walled (0.5 mm) interconnects for intermediate temperature (550…650 °C) SOFC.

The study of oxidation resistance of coatings on OT4-1 titanium alloy substrate at 600 C on the basis of 1000 h has showed that the ones based on Ti–Al–C composite, formed by high-energy deposition (MAX-1) has the best oxidation resistance ($\Delta m/S = 0.22\ mg/cm^2$). Coatings formed by medium-energy magnetron deposition (MAX-2 and MAX-3) had oxidation resistance at the level of OT4-1 alloy, and oxidation resistance of the coating obtained by low-energy deposition (MAX-4) was intermediate (Fig. 2).

Table 3 Technological modes of coatings deposition

Sample No	Mode	P, W	t, min	δ, μm
MAX-1	HP+Mo	2800	90	9
MAX-2	MP	960	180	9.5
MAX-3	MP	930	120	4.8
MAX-4	LP	612	120	2.5

Comment HP+Mo: high power mode; LP: low power mode; MP: medium power mode; P is the power applied; t is the deposition time; δ is the thickness of the coating

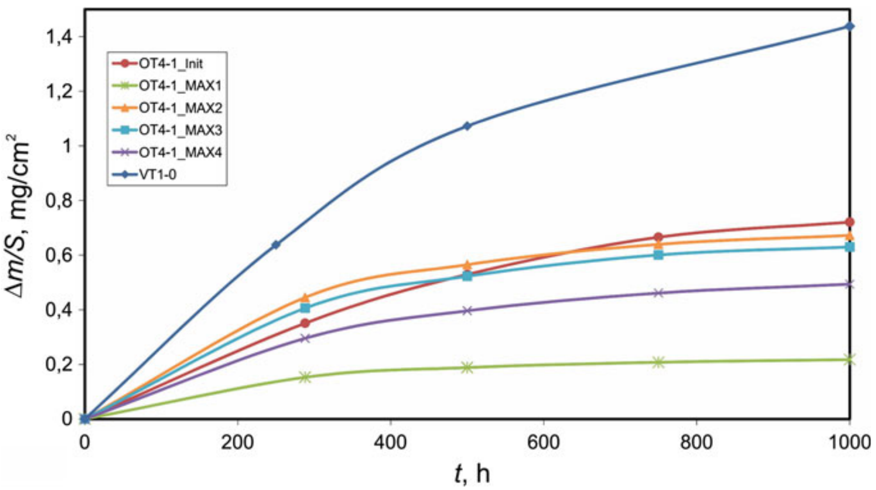


Fig. 2 Oxidation resistance of titanium grades VT1-0 and OT4-1 and coatings based on Ti–Al-C composite at 600 °C on the basis of 1000 h

Microstructural analysis showed that all coatings have a columnar structure with high adhesion to the substrate (Fig. 3).

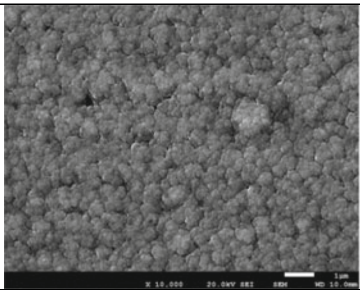
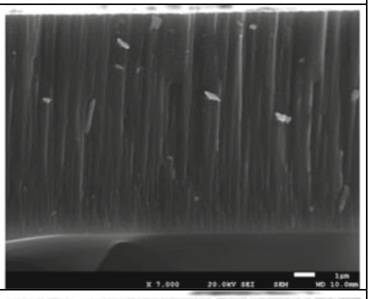
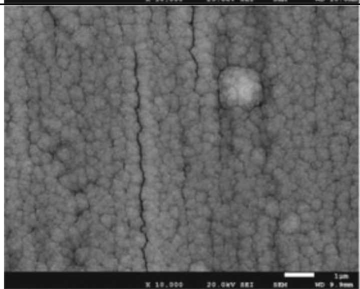
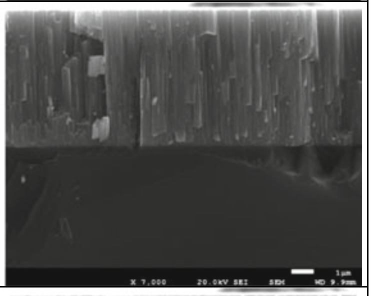
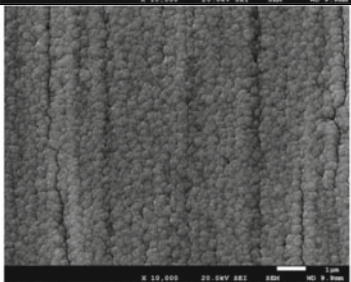
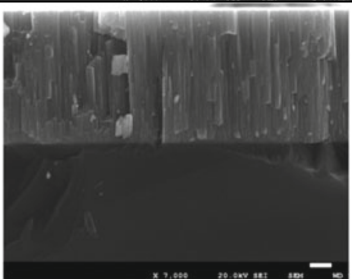
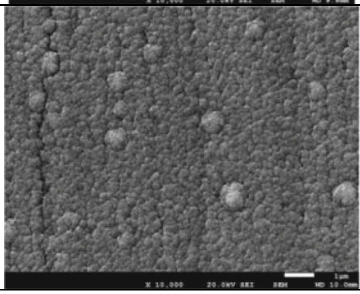
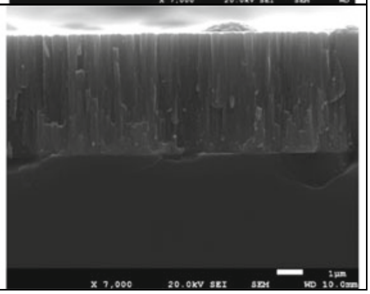
Sample No.	SEM microstructure	
	Surface	Cross section
MAX-1		
MAX-2		
MAX-3		
MAX-4		

Fig. 3 SEM microstructure on the surface and in the cross section of the coatings

Table 4 Influence of substrate material on chemical composition and mechanical properties of coatings based on MAX phases of titanium

Substrate material	Sample No	Chemical composition, at %			δ, μm	H, GPa	E, GPa
		Ti	Al	C			
OT4-1	MAX-1	45	22.7	32.3	9	15 ± 1	240 ± 10
OT4-1	MAX-2	46	22.1	31.9	9.5	11 ± 1	200 ± 10
OT4-1	MAX-3	53	20.1	26.9	4.8	10 ± 1	170 ± 10
OT4-1	MAX-4	57.6	22.2	20.2	2.5	9 ± 1	150 ± 10
VT1-0	MAX-5 [15]	51.7	21.8	26.5	6	5, 5 ± 1	132 ± 10

In high-energy and long-term medium-energy deposition modes (MAX-1 and MAX-2), a coating thickness of ~ 9 μm with high hardness and Young's modulus was obtained, but local microcracking zones were detected on the coating surface (Fig. 3, Table 4). With decreasing both power and deposition durations (MAX-3), the coating thickness decreased by half with some decrease in hardness, Young's modulus, and surface microcracking. With further reduction in power (MAX-4), the coating thickness became 2.5 μm, nanohardness H = 9 GPa, and Young's modulus E = 150 GPa, which is closest to the characteristics determined for the titanium alloy OT4-1 substrate material (H = 4.2 GPa; E = 145 GPa). In this case, the proximity of the physical and mechanical characteristics of the coating material and the substrate determines the minimum surface microcracking of the sample MAX-4 (Fig. 3).

Local chemical analysis of the surfaces of coatings obtained in different technological modes (MAX-1… MAX-4) showed (Table 4) that their phase compositions present MAX phases of different structural type, obviously Ti_2AlC and Ti_3AlC_2, which provide high conductivity of the coatings ($3…4·10^5$ Sm/m).

In addition, it should be noted that the characteristics of the material of the sample MAX-4 are close to those of a coating obtained earlier [15] by vacuum-arc deposition on a titanium substrate grade VT1-0 (Table 4), according to which a fuel cell interconnect material with high functional properties was obtained [15].

Thus, according to the obtained results, the 2.5 μm thick coating obtained by the method of magnetron deposition having Young's modulus close to that of the OT4-1 alloy substrate can be considered promising for fuel cell interconnects.

4 Conclusions

According to the obtained results, a OT4-1 titanium alloy substrate with a coating resistant to high temperature oxidation can be used for the manufacture of thin-walled (0.5 mm) interconnects for intermediate temperature fuel cells (550…650 °C). The 2.5 μm thick coating obtained by the method of magnetron deposition having

Young's modulus close to the OT4-1 alloy substrate can be considered promising for this purpose.

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