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Estimation of adhesion energy of alumina scales on FeCrAl alloys: effect of the TiO_2 sol-gel coating

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Abstract. In this work, the effect of sol-gel TiO_2 coating on adhesion energy of alumina scales formed on FeCrAl alloys was investigated. The adhesion energy was evaluated by means of a tensile test in the SEM chamber for the samples oxidized in air at 850 and 950°C during 72 h.

In addition, the spallation rate of alumina scales was studied as a function of the imposed longitudinal strain.

1 Introduction

FeCrAl alloys are extensively used to combat the degradation mechanism where they are exposed to high temperature oxidation. The α-alumina scale developed on FeCrAl alloys is known to be protective against high temperature oxidation [1]. Nevertheless, the α-alumina scale can be subjected to cracking and spalling under thermal cycling oxidation [2]. Previous works have shown that reactive elements can improve the protective feature of α-alumina and its adherence on the substrate. Efforts have been made in the last years to suppress or reduce the formation of transition aluminas in the temperature range 800-1000°C. One the effective ways to overcome this problem is to deposit TiO_2 films on the oxidized samples from FeCrAl alloys. This surface treatment promotes the formation of a stable $\alpha-$alumina scale. To form the TiO_2 coatings, the sol-gel technique was adopted in this study since it has an advantage of low cost and rapidity [3]. Among the properties of oxide layers, the adhesion plays an important role since it affects the protective feature of oxide layers. It is well known that doping the alloys with small additions (< 0.1wt%) of so called reactive elements (RE) such as Y or Zr improve the resistance against spallation. It is also known that, in the absence of RE, a few ppm of sulphur, which exists as a natural impurity in these materials, has a detrimental effect on the scale adhesion [4].

In the current work, the FeCrAl alloys are oxidized in air at 850 and 950° C under an atmosphere of (Ar +15% O_2). TiO_2 sol-gel coating was applied on some oxidized alloys to study its effect on adhesion energy of oxide layers. Adhesion energy of oxide layers were then determined by means of tensile test working in the SEM chamber.

2 Experimental details

The investigated materials used for the oxidation tests are from FeCrAl alloys. They are supplied by Thyssen Krupp VDM and Kanthal. Their chemical compositions (in wt. %), are diplayed in Table 1.

Table 1. Chemical compositions (in wt. %) of FeCrAl alloys.

Alloy	Cr	Al	Si	Hf	Ti	Y	Zr
YHfAl	20.15	6.02		0.045	0.004	0.065	0.058
YHf	19.65	5.53	0.29	0.031	0.0098	0.046	0.054
M_1	19.9	5.0	0.002	--	--	--	--
APM	21	5.8	0.4	0.00011	0.021	0.00001	0.11

TiO_2 sol-gel films were prepared from the TIPT precursor using a procedure close to that proposed in reference [5]. Oxidation of treated FeCrAl samples was carried out in a horizontal furnace under an atmosphere of (Ar + 15%O_2). Non-treated samples were also systematically oxidized in all runs. The adhesion energy G (J/m^2) given by Equation (1) was determined by a forced spallation of the oxide scale from the tensile test in the SEM chamber.

$$G = W \times e \quad (1)$$

where W represents the elastic energy stored per volume unit (J/m^3) in the oxide layer and e is the oxide layer thickness (m).

The samples, used for estimating the quantity G, were oxidized in air at 850 and 950 °C for 72 h. The oxidized samples were cooled down to ambient temperature and placed in the SEM chamber for the tensile tests at a deformation speed of $20\ \mu$m/s.

3 Experimental results

In Figure 1 is shown the top-view of SEM micrograph of the surface of the oxidized YHf alloy in air at 850°C during 72 h after a unidirectional tensile test.

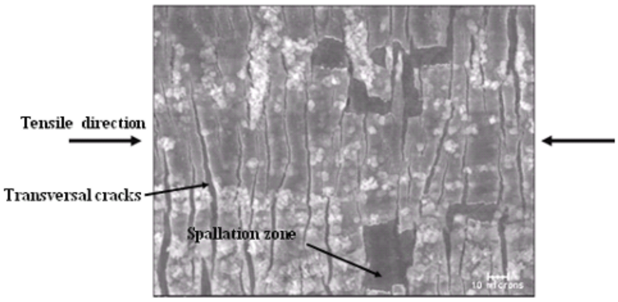

Figure 1. SEM micrograph of the surface of the YHf sample oxidized in air at 850°C for 72 h after a unidirectional tensile test.

The variation of the estimated value of rate spallation at each imposed strain is presented in Figure 2 for the oxidized samples from FeCrAl alloys at two temperatures: 850 and 950°C during 72 h.

Figure 2 (A) shows that the spallation rate determined on the oxidized YHf sample is almost stationary. The low rate spallation at 950°C (Figure 2 (B)) compared to that obtained at 850°C can be explained by the rapid relaxation of the induced stresses in the oxide layer [6].

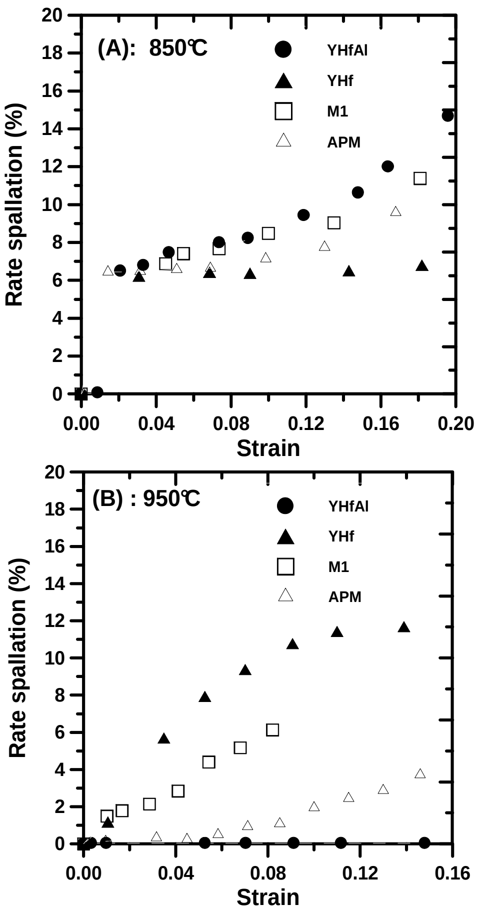

Figure 2. Evolution of the rate spallation as a function of the imposed strain: (A) oxidation in air at 850°C, (B) oxidation in air at 950°C.

The first scales appeared on the surfaces of oxidized samples (YHf, YHfAl, APM and M_1) at 950°C for the low values of imposed longitudinal strains contrarily to those observed on the surfaces of oxidized samples at 850° C. As an example, the results of spallation rates, obtained for an imposed strain of 5%, on the oxidized samples at 850 and 950°C are gathered in Table 2.

Table 2. Values of spallation rates obtained for an imposed strain of 5%.

FeCrAl Alloys	850°C	950°C
YHf	6.23	7.86
YHfAl	7.41	0
APM	6.46	0.43
M1	7.41	4.35

The critical spallation strain is an important characteristic when evaluating the adhesion energy. In Table 3, it is noticed that the values of adhesion energy of the formed oxides at 950° C are lower than those of the formed oxides at 850°C, excepted for the oxidized YHfAl alloy. The high value of adhesion energy (1263 J/m^2) estimated at 950°C on the oxidized YHfAl alloy is in contradiction with the result obtained on other oxidized samples.

This fact can be attributed to the progressive transformation of transition aluminas to stable $\alpha-$aluminas, caused by the volume contraction. After the oxidation tests in air at 850°C for 65 h, two YHfAl samples with and without the TiO_2 coating are subjected to the tensile test in the SEM chamber.

SEM micrographs of the surfaces of the oxidized YHfAl alloys in air at 850°C for 65 h with and without TiO_2 film are displayed in Figure 3.

Table 3. Values of elastic and adhesion energies of the aluminas scales formed on FeCrAl alloys at 850 and 950°C.

T (°C)	FeCrAl Alloys	Elastic energy (MJ/m^3)	Adhesion energy (J/m^2)
850	YHf	181	253
	YHfAl	212	339
	APM	977	1271
	M_1	415	332
950	YHf	827	15
	YHfAl	901	1263
	APM	195	411
	M_1	18	7

The transversal cracks after the tensile tests are visible on the both oxidized surfaces. The density of theses cracks is found to be important when applying the TiO_2 film on the surface of the oxidized YHfAl alloy.

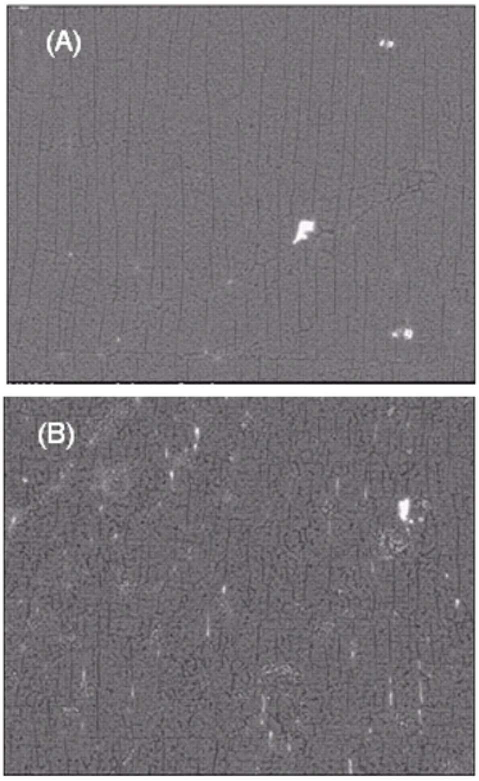

Figure 3. SEM micrographs of the surfaces of the YHfAl alloys oxidized in air at 850°C for 65 h after a tensile test: (A) Non coated sample, (B) coated sample with TiO_2 film.

Evolution of the spallation rate versus the imposed strain for the two samples (with and without the TiO_2 coating), is shown in Figure 4.

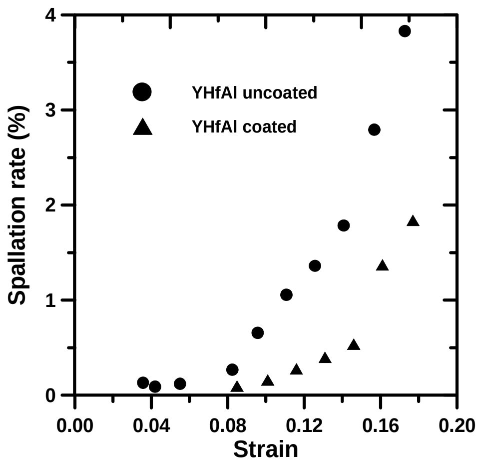

Figure 4. Influence of TiO_2 coating on the variation of spallation rate of YHfAl samples as a function of the applied longitudinal strain.

It is found that the oxidized samples without TiO_2 film spalled at a strain lower than 4 %. The scales appeared at a strain value of 8.6 % for the coated sample. The application of TiO_2 film contributed to reduce the transition aluminas by forming the $\alpha -$ aluminas which are adherent to the substrate [**7**]. The value of adhesion energy was estimated as 2145 J /m^2 for the coated sample with TiO_2 film, while it was only 475 J/m^2 for the non-coated sample oxidized at 850°C during 65 h.

4 Conclusion

From the present work, the following concluding point can be drawn as follows:
1) TiO_2 sol-gel deposit on FeCrAl alloys constitutes an efficient surface treatment to reduce the presence of transition aluminas.
2) The aluminas formed on the FeCrAl alloys at 950° C exhibited a low adhesion on the substrate.
3) The value of adhesion energy was estimated as 2145 J /m^2 for the coated sample with TiO_2 film, while it was only 475 J/m^2 for the non-coated sample oxidized at 850°C during 65 h.

References

1. T. Biegun, M. Danielewski, Z. Skrzypek, Oxid. Met. **38** 207 (1992)
2. V.K. Tolpygo, Oxid. Met. **51** 449 (1999)
3. L.V. Ramanathan, M.F. Pillis, S.M.C. Fernandes, J. Mater. Sci**. 43**(2) 530 (2008)
4. C. Mennicke, E. Schumann, C. Ulrich, M. Ruhle, Mater. Science Forum **251-254** 389 (1997)
5. M. Langlet, M. Burgos, C. Coutier, C. Jimenez, C. Morant, M. Manso, J. Sol-Gel Sci. Technol. **22** 139 (2001)
6. R. Chegroune, M. Keddam, E. N’Dah, A. Galerie, Mater. et Tech. **2013** (2013)
7. R. Chegroune, M. Keddam, Y. Wouters, A. Galerie, E.Salhi, Applied Surf. Sci. **257** 3929 (2011)