Preparation and high temperature oxidation behaviors of (Al-Y)-dipped TiO₂/Al₂O₃ composite coatings on the surface of Fe-Al alloy

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Abstract: Sol-gel method combined with dipping process was used to prepare (Al-Y)-dipped TiO₂/Al₂O₃ composite coatings on the surface of Fe-Al alloys. Oxidation thermodynamic results show the composite coatings caused lower oxidation weight gain than the sample without this coating. Combination of XRD and SEM results illustrates that the cross section morphology composed of an outermost layer of loosen Al and then a thick layer of Fe₂O₃, and a continuous Al₂O₃ innermost layer. This work shows that through appropriate designing of the composite coatings, better high temperature oxidation resistance alloy which can be prepared rapidly and simply can be obtained.

1. Introduction
In modern engineering society, metallic materials are widely used in many fields, and more and more concentrations are focused on the modification of metals, especially on the surface preparing. For example, in gas turbine applications, the operation temperature of engine is getting higher to improve engine efficiency and performance, thus the oxidation resistance of alloys at higher service temperature is becoming an important issue. Usually, the works for the high-temperature alloys include doping active elements (Al, Si, Cr, et.al) into the matrix, which will be oxidized firstly and the obtained thin films (Al₂O₃, Si₂O₃, Cr₂O₃, et.al) on the outermost layer of the alloys can prevent the further oxidation of the inner matrix[1-3]. The research also includes the surface modification of the high-temperature alloy, which means protective thin films (Al₂O₃, Si₂O₃, Cr₂O₃, et.al) will be prepared on the surface of the alloy by magnetron sputtering[4], plasma spraying[5], thermal spraying[6], as well as sol-gel method[7]. The sol-gel method has distinctive advantages, but the process usually needs long time to repeat the dipping and pulling procedure to obtained the required thickness of the film. The research in this work, dipping of the Y-doped Al powders on the TiO₂/Al₂O₃ composite coatings obtained by the sol-gel method was used, in order to improve the efficiency of the sol-gel method, meanwhile the protective function of (Al-Y)-doped TiO₂/Al₂O₃ composite coatings obtained on the surface of the Fe-Al alloys.

2. Experimental
Fe-Al alloys used in this work were melted in non consumable vacuum arc furnace from the Fe (99.99%) and Al (99.99%) powders, and then were cut to pieces with surface area of 2 cm². X-ray diffraction (XRD) was used to analyse the phase compositions of the materials obtained on the surface of Fe-Al
alloy after oxidation at the temperature of 800 °C. Scanning electron microscope (SEM) and energy spectrometer (EDS) were used to observe the surface profile of the samples.

After washed in ethanol and acetone, the Fe-Al alloy was dipped into Al2O3 gel for 600 seconds, then pulled up with a speed of 2000 mm·s-1 and following by being kept in air for 60 seconds. Then the same operation was carried out just with the difference of dipping into TiO2 gel. These two steps as a cycle was then operated for 5 times. In the next step, the sample was dipped into Al powders in order to obtained well dispersed Al powders on each surface of the sample, then put the alloy into muffle furnace kept on 500 °C for 10 minutes. The above processes were repeated for 2 times to prepare the expected coatings.

To investigate the protective function of the composite coating, the sample obtained with and without the coating were dealt with cyclic oxidation at 800 °C for 10 h.

3. Results and Discussion

3.1. Oxidation thermodynamics

Figure 1 shows the Oxidation thermodynamics of Fe-Al alloys with and without (Y,Al)-doped TiO2/Al2O3 composite coating oxidized at 800 °C for 10 h. The results indicate that the mass gain of the sample covered by the composite coating was smaller. Composite coating improves the high-temperature oxidation resistance of the alloy more obviously. The sample with coating appears negative weight gain at the beginning stage which might attributed to the decomposed of the organic component in the coating and the oxides peeled from the alloy surface.

3.2. XRD analysis

Figure 2 shows the XRD patterns of samples with and without composite coating oxidized at 800 °C for 10 h. The analysis of the results indicates that the oxidation products of the sample without coating are mainly composed of Fe2O3(33-0664) and a little Al2O3(10-0173). Coating on the surface of the alloy leads to more complex forms of the oxidation, which includes more Al2O3, less Fe2O3 and TiO2(33-1381) and a little amount of non-oxidized Al(01-1180) powders. Analysis of these results shows that when coated with a composite coating, more Al2O3 is formed and the product of oxidation of the matrix, here is the Fe2O3, is decreased, which might means that a protective function of the coating on the matrix is gained.
Figure 2. The XRD patterns of samples oxidized at 800 °C for 10 h

3.3. SEM morphology
Fig. 3 shows the cross-section morphology of the TiO$_2$/Al$_2$O$_3$ composite coating modified Fe-Al alloy with dipping into the mixture of Y and Al powders once (A) and twice times (B) after oxidized at 800 °C for 10 h. From the results we can see that, the oxide films on the surface of the sample that dipped the mixed powders once, which means getting less Al, are composed of two Al$_2$O$_3$ layers, between which there is a thick layer of Fe$_2$O$_3$. The innermost Al$_2$O$_3$ layer is continuous but not compact enough. On the other side, the morphology for the other sample that dipped into the powders twice is more disordered, because the overmuch Al powders clustered together and even not completely oxidized, so an continuous Al$_2$O$_3$ layer can be obtained on the outermost layer. Still, the continuous Al$_2$O$_3$ innermost layer is not compact enough to protect the matrix best. Designing better dipping process of TiO$_2$/Al$_2$O$_3$ composite coating modified Fe-Al alloy into the mixed powders of Al and Y, can obtain continuous Al$_2$O$_3$ layer, which is desired for the high-temperature alloys.
4. Conclusions
(1) Dipping process combined with sol-gel method was successfully used to prepare TiO$_2$/Al$_2$O$_3$ composite coating modified Fe-Al alloys.
(2) Composite coating improves the high-temperature oxidation resistance properties of the Fe-Al alloy.
(3) In order to get the most effective protective coatings, the dipping process must be appropriately designed.

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