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Glass coatings on stainless steels for high-temperature oxidation protection: Mechanisms

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The oxidation behavior of a martensitic stainless steel with or without glass coating was investigated at 600–800 °C. The glass coating provided effective protection for the stainless steel against high-temperature oxidation. However, it follows different protection mechanisms depending on oxidation temperature. At 800 °C, glass coating acts as a barrier for oxygen diffusion, and oxidation of the glass coated steel follows linear law. At 700 or 600 °C, glass coating induces the formation of a $(Cr,Fe)_2O_3$/glass composite interlayer, through which the diffusion of Cr^{3+} or Fe^{3+} is dramatically limited. Oxidation follows parabolic law.

1. Introduction

Glasses or glass–ceramics with good compatibility to certain metal substrates show good prospect to be used as coating materials for high-temperature corrosion protection [1–3]. It is well-known that glasses can easily form hermetic seals to the alloy substrates and insulate them from corrosive media. In addition to the superior high resistance to compressive stresses and chemical attack, glass coatings stand out with the ease of processing [4–8]. By controlling crystallization of the parent glasses or incorporation of a second phase (metals or ceramics), the thermophysical properties of the glass matrix composite coatings would be tailored in a wide range to match better with the alloy substrates [9,10].

The protection mechanisms of glass coatings for titanium alloy and superalloy substrates against high-temperature oxidation have been studied previously [11–14]. Interfacial reactions forming an inert interlayer play an important role in the oxidation behavior of the glass coated alloy system. For the glass coated titanium alloys, oxidation proceeds at a constant rate after the formation of a silicide interlayer, of which the limiting step is transportation of oxygen through the glass coatings [11,12]. In case of superalloy substrates, the glass coatings decrease oxygen partial pressure in contact to the underlying superalloy and alter the composition of alloy at surface after interfacial reactions. These two factors promote selective oxidation of aluminum at interface to form an alumina interlayer. The alumina interlayer provides better protection for the superalloy substrates from oxidation than the glass coating due to the lower diffusion coefficient of oxygen (and Al^{3+}) in Al_2O_3. It grows at a very slow speed, which becomes the controlling step for oxidation of the glass coated superalloy system [13,14].

Numerous studies have been conducted on enameling steels. They focused mostly on the improvement of chemical or corrosion resistance at moderate temperature [15–23]. However, some steels are exposed as well to elevated-temperature environments, for which the low oxidation resistance is one of the fatal shortcomings [24–27]. Lefort and Friedberg [28] have firstly reported the application of glass coatings for oxidation protection of steels at elevated temperature. It was found that the oxidation of enameled steel followed linear law and the rate was much lower than that of the bare one. The limiting step of oxidation was attributed to oxygen diffusion through glass coatings. Ritchie et al. [29] also reported that oxidation of the glass coated steel developed at a constant rate, and that the glass was supersaturated with iron oxides at the glass/steel interface. In terms of dissolution and diffusion of iron oxides in glass, Borom and Pask [30] found that the dissolution of iron oxides was controlled by their diffusion in the molten glass. Considering that Fe^{3+} diffuses in silicate glass at a much lower rate than that of O_2 [31,32], it is uncertain whether the long-term oxidation of the glass coated steel is controlled by diffusion of oxygen or of iron cations through the glass coatings. Moreover, the definition of interlayer and its influence on oxidation behavior of the glass coated steels needs to be clarified as well.

The primary aim of the present work is to analyze the oxidation kinetics, as well as microstructures, of the system of glass coating/stainless steel substrate at 600–800 °C. The interlayer is identified and its influence on oxidation is discussed depending on the

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oxidation temperature. From these experimental results, protection mechanisms of glass–ceramic coatings on stainless steels against high temperature oxidation are schematically illustrated. The glass system investigated has been previously demonstrated good as protective coating material against high temperature oxidation for superalloy and titanium alloys. As a result, estimating the protective properties of this glass coating on steel substrates is another aim of this paper.

2. Experimental procedure

Table 1 shows the chemical composition of the glass. The preparation process of the glass frit has been described in detail elsewhere [33]. After homogenization, the raw materials used for preparation of the glass frit, SiO_2, Al_2O_3, ZnO, $CaCO_3$, ZrO_2, TiO_2, $Na_2B_4O_7{\cdot}10H_2O$, Na_2CO_3 and KNO_3, were loaded into an alumina crucible and heated up to 1450 °C to form molten glass. The molten glass was then transformed into glass granules after quenching in water. The glass transition temperature and soften point of this glass system are 585 °C and 675 °C. Wet milling operations were carried out in a ball milling machine, where the frit granules and ethanol (in ratio of 10 g:160 ml), combined with agate balls were sealed in an agate container. The vitreous frit granules were reduced in size to less than 10 μm after ball milling and then the suspension of glass frit was obtained.

The 1Cr11Ni2W2MoV martensitic stainless steel with dimension of $15 \times 10 \times 2.5$ mm^3 was selected as the substrate. Table 2 shows the nominal composition of the steel substrate. After grinding with 400# SiC paper, blasted under pressure of 0.3 MPa with quartz sand, and cleaned with acetone in an ultrasonic cleaner, they were sprayed at room temperature with the glass suspensions, dried at 250 °C for 15 min and finally heat-treated at 870 °C for 3 min. The firing of glass coatings on stainless steel substrates were carried out in air. Generally, the firing temperature of glass coating is about 150–250 °C higher than its soften point, where the glass coating would flow and spread well on the alloy substrate. The soften point of this glass system is 675 °C, this is the reason why we choose the heat-treatment temperature as 870 °C. Considering the steel substrate will be oxidized very fast during the firing process of glass coating, the firing temperature should be as short as possible in order to minimize the thickness of steel oxide at interface. So it was controlled in the range from 3 to 5 min. A manual painting gun was used to spray the glass suspension. By connecting the painting gun with an air compressor, the air pressure of spaying was fixed at 0.2 MPa. The glass suspension was transformed to spray mist under this spraying pressure by the painting gun. The alloy specimen was placed about 15 cm in front of the gun mouth, which ensured that it was in the central of spray mist. In such a case, the spray mist deposited homogeneously on the surface faced to the gun mouth. For each spray, all the six surfaces of the alloy substrate were deposited with the glass coating by continuously changing the surface faced to the gun mouth. In order to obtain a thicker glass coating, the deposition and firing process of the glass coating was conducted twice.

Isothermal oxidation was carried out in static air at 600–800 °C for different times with weight measurement performed at appointed intervals. Three parallel specimens placed in alumina crucibles were used. The alumina crucibles were all heat-treated in furnace at 1000 °C for enough time to ensure that their weight would not be changed in the following oxidation test. The weight change of the specimen together with the alumina crucible was recorded using an electronic balance (0.01 mg precision, Sartorius BP211D).

The phase constituent was characterized by using X-ray diffraction (X' Pert PRO, PANalytical Co., Almelo, Holland, Cu Kα radiation at 40 kV). The obtained XRD patterns were recorded in 2θ range 20–90° and, a step-scanning mode was employed with a step size of 0.02°. Morphologies and microstructures were examined by scanning electron microscopy (SEM, Inspect F 50, FEI Co., Hillsboro, Oregon) coupled with an energy dispersive spectrometer (EDS, X-Max, Oxford instruments Co., Oxford, UK), electron probe microanalysis (EPMA-1610, Shimadzu, Kyoto, Japan), and by transmission electron microscopy (TEM, JEM-2100F, JEOL, Tokyo, Japan) in conjunction with energy-dispersive X-ray spectroscopy.

Table 1
Nominal composition of the glass frit (wt%).

SiO_2	Al_2O_3	ZnO	CaO	ZrO_2	TiO_2	B_2O_3	Na_2O	KNO_3
58.26	5.98	9.00	3.66	5.29	2.75	4.66	3.40	7.00

3. Results

3.1. As-fired

Fig. 1 shows the microstructures of the as-fired glass coated stainless steel. Due to the low firing temperature and short sintering time, the glass did not spread well on the steel surface and the remaining gases had not been released out completely. Though many closed pores are found, the steel substrate is still successfully insulated from oxidizing atmosphere by the glass coating. From the cross-sectional view, the glass coating is about 35 μm thick, and bonds well with the steel substrate. As shown in Fig. 1B, no spallation of glass coating and no distinct interlayer are found at the glass/steel interface. Generally, a porous interlayer of steel oxide will decrease the bonding strength of glass coating on steel substrate. XRD pattern (Fig. 2) shows that the as-fired glass coating is still vitreous. A very broad peak near 25° is present. The only crystallite detected in the XRD pattern is Fe, which is attributed to the steel substrate.

Fig. 3 shows the bright field TEM image at interface of the as-fired glass coated stainless steel. EDS composition analyses at areas from 1# to 3# are summarized in Table 3. After firing, the glass has already been phase separated (as denoted in Fig. 3, the phases “H” and “L”) though the firing time was very short. Heavy elements, such as Zr, Ti and Zn, are enriched in the grey phase (phase “H”), while they are denuded in the bright phase (phase “L”). Certain amounts of Fe have been dissolved into the glass coating. At a distance of about 200 nm away from the interface, the Fe concentration is 14.7 at.%, as shown in Table 3 (at area 1#). However, selected-area diffraction (SAD) pattern reveals that the glass coating is still vitreous, indicating that Fe dissolved into glass by taking part into the glass network rather than by precipitating out from glass as crystallites. To be noticed, the Cr content immediately at the interface of glass/steel increased noticeably after firing. It accounts up to 40.7 at.% according to the EDS analysis (at area 2# in Table 3).

3.2. Oxidation at 800 °C

Fig. 4 shows the oxidation kinetics of the bare and glass coated stainless steels at 800 °C. The oxidation rate of the stainless steel is decreased clearly by the glass coating. For the bare stainless steel, the weight gain accounts up to 4.57 mg/cm^2 after 50 h oxidation. This is more than six times of that of the glass coated one. As denoted by arrow in Fig. 4A, the oxide scale formed on the surface of the bare steel is so fragile that it spalls off easily once it is cooled down in air for the weight measurement. The oxidation kinetic of the bare steel follows roughly parabolic law, which differs largely