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Lower-temperature aluminizing behaviors of a ferritic–martensitic steel processed by means of surface mechanical attrition treatment

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ABSTRACT

By means of surface mechanical attrition treatment (SMAT), a gradient nanostructured surface layer was fabricated on a ferritic–martensitic (F–M) steel plate. Its aluminizing behaviors were investigated during a packed aluminization process and a subsequent diffusion annealing treatment at lower temperatures. In comparison with the initial sample, a much thicker Al_5Fe_2 layer was formed on the SMAT sample after the packed aluminization, with a growth constant of ~3 times higher at 600 °C. The transformation kinetics from Al_5Fe_2 phase into AlFe phase and α-(Fe,Al) solid solution are also enhanced in the subsequent annealing treatment at ~700 °C. The enhanced aluminizing kinetics originates from the increased atomic diffusivities by numerous grain boundaries and a higher concentration of vacancies in the nanostructured surface layer. With the determined growth kinetics, a duplex aluminizing process was demonstrated for achieving a gradient surface layer with lower-Al containing aluminides below the tempering temperature of F–M steel.

1. Introduction

Elevating steam conditions to higher pressures and temperatures has been proven to be the most efficient solution to increase fuel efficiency and to improve environmental protection [1,2]. For example, an increment in the steam temperature from 535 to 635 °C and the steam pressure from 18.5 to 30 MPa would reduce fuel consumption and CO_2 emission by more than 25% [3].

Ferritic–martensitic (F–M) steels containing 9–12% Cr are designed for the application in ultra-supercritical power plants up to 650 °C. However, their applications suffer from low oxidation resistance in service. Formation of volatile Cr oxy-hydroxides leads to promoted oxidation kinetics and unacceptable material losses in the presence of water vapor [2,4–6]. It is known that Al_2O_3 is thermodynamically more stable than Cr_2O_3 or SiO_2, and Al_2O_3-base protective scales are virtually immune to water-vapor effects. Various aluminide coating processes, such as chemical vapor deposition (CVD) and packed aluminization processes, have been developed to form Al-rich coatings for improving oxidation resistance of F–M steels in steam environments [1,3,4,7–13]. Most aluminizing processes are carried out at high temperatures of 900–1050 °C, which are above the final tempering temperature (~775 °C) for 9–12% Cr F–M steels. Thereby their mechanical properties (e.g. creep rupture strength and fracture toughness) are degraded by the aluminizing processes. Lowering aluminizing temperatures is desired, but it not only considerably slows down the processing kinetics but also leads to the formation of brittle Al-rich aluminides such Al_5Fe_2 and Al_3Fe [3,4,8,9,12]. To eliminate the Al-rich aluminides, a post-aluminizing diffusion heat treatment was employed, yet with very long durations [4,10]. Alternatively, the pure Al master alloy was replaced by a binary one in aluminization processes, but either rather thin or non-uniform coatings were resulted [4,9,12]. All these difficulties are originated from limited atomic diffusivity at low temperatures.

Surface mechanical attrition treatment (SMAT) has been demonstrated to be an effective method to fabricate gradient nanostructured surface layers on various metallic materials [14,15]. With the help of significantly enhanced diffusion and chemical reaction kinetics in the formed nanostructures, chromizing, nitriding, boronizing, and galvannealing have been achieved at much lower temperatures than the conventional processing temperatures in the coarse-grained (CG) counterparts [16–22]. Moreover, the synthesized compounds by the reactive diffusion processes were usually with much smaller grain sizes than those formed in the CG samples. This was expected to further enhance atomic diffusion after the formation of compound layers [17,19,20]. Therefore, combining SMAT with the conventional aluminization process may provide an effective approach to form a surface layer of lower-Al containing phases at lower temperatures.

The formation of a nanostructured surface layer has been applied to achieve lower-temperature aluminization previously [23–25]. For example, an aluminide surface layer of ~52 μm thick was formed on a SMAT low carbon steel after a packed aluminization treatment at 600 °C, more than 3 times thicker than that on the aluminized CG counterpart [23]. An enhancement effect of shot peening on the growth kinetics of aluminide coating on the P92 steel was revealed at temperatures below 675 °C [24]. The authors found the enhancement is larger at lower temperatures and progressively diminished as temperature

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increased. However, these studies only observed the formation of Al-rich aluminides (mostly Al_5Fe_2) and the nanostructure effect on the growth kinetics of Al_5Fe_2. Formation of lower-Al containing aluminides, which is desired for a better protection, has not been dealt with.

In this study, a commercial Fe–9Cr–1Mo F–M steel (P92) sample was subjected to SMAT. The aluminization behaviors in the gradient nanostructured surface layer were investigated quantitatively at temperatures below 750 °C. Therefore, the possibility of achieving a thicker lower-Al containing aluminides surface layer has been demonstrated by employing a duplex aluminization process at lower temperatures on the SMAT sample.

2. Experimental

2.1. Sample preparation

The as-received (AR) P92 steel with a chemical composition of Fe–0.1C–9Cr–0.5Mo–1.8 W (wt.%) was austenitized at 1070 °C for 1 h and tempered at 775 °C for 2.5 h. A plate sample ($100 \times 50 \times 4$ mm^3 in size) was subjected to the SMAT processing in order to achieve a nanostructured surface layer [14,15,26]. In brief, a large number of steel balls were placed at the bottom of a cylinder-shaped chamber and vibrated at a high frequency by a generator. The plate sample to be treated was fixed at the upper side of the chamber and impacted by flying steel balls multi-directionally and frequently. The sample surface layer was plastically deformed with high strains and strain rates (10^2–10^3 s^{-1} [15]), in which grains were significantly refined. In this work, the sample was treated for 60 min at ambient temperature in vacuum under a vibrating frequency of 50 Hz by steel balls with a diameter of 8 mm. No detectable contamination was introduced into the surface layer during the SMAT.

The SMAT samples were cut into small dimensions ($10 \times 10 \times 4$ mm^3 in size) and were ultrasonically cleaned in ethanol and pickled in a 10 vol.% HCl aqueous solution. Then the samples were aluminized in a packed powder mixture, which contains Al powders (50 wt.%), NH_4Cl (2 wt.%) as the activator, and Al_2O_3 powders (48 wt.%) as the inert filler. The average particle sizes of Al and Al_2O_3 powders were about 45 μm and 60 μm, respectively. Pieces of samples were embedded in the packed powder mixture filled into a double container designed by Meier et al. [27]. The distance between two neighboring pieces was at least 50 mm to ensure sufficient aluminizing source supply. The container was first heated at 380 °C for 30 min to allow a partial dissociation of NH_4Cl to prevent the oxidation of sample surface, and then heated to the designed temperatures (within 520–640 °C) at a heating rate of 10 °C/min for aluminization. The temperature was controlled with an accuracy of ±2 °C. After aluminization, the samples were ultrasonically cleaned in water and acetone.

A post-coating diffusion annealing treatment was performed on the aluminized samples at different temperatures from 680 to 740 °C in a vacuum furnace subsequently, at heating and cooling rates of ~10 °C/min.

2.2. Structure characterization

Microstructures of the top surface layer of the as-SMAT sample were characterized by using a JEOL 2010 transmission electron microscope (TEM) operated at a voltage of 200 kV. Thin foils for TEM observations were cut by electro-spark discharge technique from the SMAT surface layer, and then mechanically polished, dimpled and finally ion-milled from the untreated side. Cross-sectional morphologies of the as-SMAT and the aluminized samples were observed on an FEI Quanta-200 scanning electron microscope (SEM). Al distribution in the aluminized surface layer was monitored by an Oxford INCA X-ray energy dispersive spectroscope (EDS). A protective layer of pure Ni of ~50 μm thick was electro-deposited onto the sample surface for preparing the cross-sectional specimens.

X-ray diffraction (XRD) analysis was carried out to identify the phase constitutions in the aluminized surface layer, by using a Rigaku D/max 2400 X-ray diffractometer (12 kW) with Cu K_α radiation, with a step size of 0.02°.

2.3. Hardness measurement

The microhardness variation along depth from the aluminized surface was measured on cross-sectional specimens by using a Hysitron TriboIndenter fitted with a Berkovich indenter. The nanoindenter was calibrated by using a SiO_2 standard specimen. Measurements were performed at a loading rate of 500 $\mu N \cdot s^{-1}$ to a maximum load of 2500 μN, and then with a holding duration of 5 s, finally at an unloading rate of 500 $\mu N \cdot s^{-1}$. The distance between any two neighboring indentations was larger than 5 μm. The load–displacement data obtained during the first unloading were analyzed using the Oliver–Pharr method to determine the hardness value [28].

3. Results and discussion

3.1. Microstructure and thermal stability of the SMAT sample

Clear evidences of microstructure refinement induced by plastic deformation are observed in the SMAT surface layer of ~100 μm in thickness, as shown in the cross-sectional SEM image (see Fig. 1(a)). The initial microstructure of the sample before SMAT (i.e. the matrix in Fig. 1(a)) is a typical martensitic structure with numerous precipitates (mostly rod-like $M_{23}C_6$) at lath/subgrain boundaries [29]. With decreasing depth from the treated surface, the microstructure becomes more and more distorted and refined in the deformation layer. Extremely fine equiaxed ferrite grains (~8 nm) with random crystallographic orientations are formed in the top surface layer, as revealed by TEM morphologies and the corresponding selected area electron diffraction (SAED) pattern in Fig. 1(b and c).

Detailed microstructure observations [29] showed a gradient nanostructured surface layer in which the mean grain size of ferrite decreases with decreasing depth has been formed on the SMAT sample. And the top 40 μm surface layer is nanostructured, i.e., with mean grain sizes below 100 nm. Meanwhile, sizes and volume fraction of the $M_{23}C_6$ particles in the nanostructured surface layer has also been decreased evidently. The refinement of martensite/ferrite and carbides in the SMAT surface layer was discussed to be resulted from a series of dislocation activities during severe plastic deformation [29–31].

Thermal stability of the nanostructured surface layer has also been investigated on the SMAT samples in the previous work [29]. The results showed that the size of ferrite grains at the surface layer in the SMAT sample increases slightly with the increasing annealing temperature below 650 °C, from ~8 nm at room temperature to ~18 nm after annealing at 650 °C in the topmost surface layer. The fairly stable microstructure at elevated temperatures is due to the presence of a large number of dispersive carbides and M(C,N)-type precipitates, which act as strong pinning obstacles to the growth of ferrite grains [17,29].

3.2. Growth kinetics of Al_5Fe_2 layer

The growth kinetics of the Al–Fe compound layers on the SMAT and the AR samples was studied after isothermal aluminization in the packed powder mixture at different temperatures within 520–640 °C, at which the nanostructures are stable and the aluminization medium is activated enough to deposit Al atoms onto the sample surface. As shown in Fig. 2, a continuous and dense Al–Fe compound layer is formed on both samples after aluminization at 600 °C for 4 h. The layer thickness on the SMAT sample is ~50 μm, more than twice that on the AR sample (~23 μm), indicating a significant enhancement in aluminization kinetics on the SMAT sample. Measured Al-concentration profiles on both samples (see Fig. 2(c)) show that the Al

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