

Cyclic oxidation resistance of hot-dipping Al-5Si coating on 0Cr18Ni10Ti

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Abstract. 0Cr18Ni10Ti austenitic stainless steels were coated by hot-dipping in molten Al bath and molten Al-5 wt. % Si bath. The cyclic oxidation resistance behavior of both hot-dipping Al samples and hot-dipping Al-5Si samples at 900°C for 24 cycles have been investigated using muffle furnace. The element distribution, phase composition and morphology of the aluminide layer and the oxide film were characterized by SEM and EDS. The results show the coating layers on both hot-dipping Al samples and hot-dipping Al-5Si samples after 24 cycles at 900°C consisted of four layers, in the sequence of Al₂O₃ film, outer layer with black phase and grey phase, intermediate MAI layer, Al solution layer from the external topcoat to substrate. The thickness of intermediate MAI layer of hot-dipping Al-5Si samples was lower than the thickness of MAI layer of hot-dipping Al samples. Some cracks were found on intermediate MAI layer of hot-dipping Al samples after 24 cycles at 900°C. The cyclic oxidation resistance of Al-5Si samples is better than Al-5Si samples at 900°C for 24h.

Introduction

Hot dipping aluminizing is an effective method to improve the high temperature oxidation resistance due to fine, dense Aluminum oxide scale formed on the surface of the coating. The steel was dipped into molten aluminum or molten aluminum alloy and was keeping the appropriate time after preprocessing such as degreasing, descaling and plating. During the dipping process, Fe-Al intermetallic compound was generated due to interdiffusion between Fe from steels and Al of the molten aluminum. The Fe-Al intermetallic compound resulted in metallurgical bonding between the Al coating and steels, which resulted in the coating difficult to fall off [1]. After diffusion annealing, the thickness of Fe-Al intermetallic compound layer was increased, and then the high temperature oxidation resistance of hot dipped coating on steel was increased [2-4]. The intermetallic compound was brittle phase. Therefore, the increased thick of intermetallic compound layer would lead to generate crackles in Al coating. Then, Oxygen passed through Al coating to react with alloy atoms of steel, which means the high temperature oxidation resistance of hot dipping coating was decreased [5-6]. It was reported that the thickness of intermetallic compound layer was decreased with addition silicon in the melt and then Fe-Al-Si compound layer was formed on carbon steel [7-8]. Wang has studied the isothermal and cyclic oxidation of mild steel with Al-2.5Si, Al-5Si, Al-10Si at 750. The results of the cyclic oxidation showed that the steel with Al-5Si had the best cyclic oxidation resistance during Al-2.5Si, Al-5Si, Al-10Si [9]. Therefore, in order to increase the cyclic oxidation of 0Cr18Ni10Ti austenitic stainless steel, coating was formed on stainless steel by hot dipping Aluminum with addition 5wt%Si. To study the effect of Si in Al-Si coating, the cyclic oxidation resistance of hot dipping Al and hot dipping Al-5Si on 0Cr18Ni10Ti was researched at 900°C and the influence of Cr, Ni, atoms of 0Cr18Ni10Ti steel on the cyclic oxidation resistance was studied.

Experiment procedures

Materials.

The chemical composition of 0Cr18Ni10Ti austenitic stainless steel is given in table1.

Table1 Chemical composition of 0Cr18Ni10Ti austenitic stainless steel (mass, wt %)

C	Si	Mn	S	P	Cr	Ni	Ti	Fe
≤0.08	≤	≤2	≤0.03	≤	17-1	9-1	≤0.	Bal.
	1			0.035	9	2	4	

Specimens were cut to $\Phi 1\text{cm} \times 0.17\text{cm}$ by water-cooled cutting machine, and had a hole drilled 0.8 mm in diameter. Specimens were ground to 2000[#] sic paper and polished.

Commercial grade pure aluminum with a purity of 99.97 % and Commercial grade pure Silicon with a purity of 99.7 % were used as the molten alloy bath. The aluminum ingots and the silicon ingots were heated to 700 °C in a graphite crucible using a resistance furnace SG-5-12, and keep 7 days. The 0Cr18Ni10Ti samples were degrease at 85 °C for 15 min, rinsed with hot water, and then descaled in 15 % HCl at 30 °C for 8 min, rinsed with hot water again, and then promoted in a molten salt mixture at 90 °C for 2min. After being surface-preheated at 270 °C, the steel specimens were immersed in the pure aluminum ,Al-5Si(wt%) molten baths at 800 °C for 2 min and then cooled in water. After aluminizing, the specimens were diffused in resistance furnace at 950°C for 2h and were cooled inside furnace to room temperature. The outer rough surfaces of aluminized samples were removed to improve the oxidation resistance using steel file [5, 10]. Hereafter, the hot dipping Al samples were termed HDA samples and the hot dipping Al-5Si samples were termed HDA5Si samples.

Cyclic-Oxidation.

Cyclic oxidations of HDA samples and HDA5Si samples were conducted at 900 °C in static air for 24 cycles. Each sample was putted in corundum crucible. Then, the crucibles with samples were placed in muffle furnace. Each cycle consisted of oxidation for 50 min in the furnace followed by 10 min outside the furnace to room temperature. The weight changes of specimens after cyclic oxidation were measured together with crucibles by electronic balance (0.1mg accuracy).

Analysis Method.

The surface morphology and cross-section of oxidized specimens were examined by scanning-electron microscopy (SEM) with energy-dispersive spectrometry (EDS). Surface morphologies were observed by SEM in secondary electron mode (SE2). The samples after cyclic oxidation were prepared for cross-sectional observation using standard grinding and polishing. Cross-section specimens were observed by SEM in black scattered electron mode (BSE). Chemical compositions of the phase observed from SEM were analyzed by EDS. Phase on oxidized samples was identified by-ray diffraction (XRD).

Result and discussion

Oxidation kinetics.

Mass-gain as a function of the number of 1-hr cycles at 900°C was presented in figure.1. As shown in figure.1, the oxidation mass gain of HDA samples and HDA5Si samples were unstable at the initial stage, and then both HDA samples and HDA5Si samples retained a relatively stable value at a later stage. This means that dense and protective Al₂O₃ films were formed on both HDA samples and HDA5Si samples at the later stage. Mass gain value of HDA samples at 24 cycles was 0.727 mg/cm², while Mass gain value of HDA5Si samples at 24 cycles was lower with 0.0786 mg/cm². The lower mass gain might due to denser oxide Al₂O₃ scale was formed on HDA5Si samples.

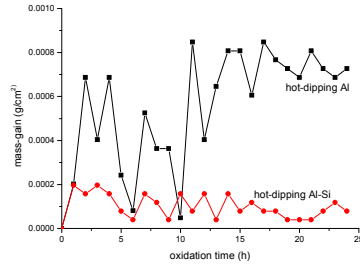


Figure.1 The cyclic oxidation kinetics of hot-dipping aluminum and GH169 at 900°C for 24 cycles

Surface and Cross-section morphology.

X-ray diffraction analysis revealed that Al_2O_3 oxide scales were formed on HDA samples and HDA5Si samples after 24 cycles at 900°C. Observations of the top surface of the scale shown that the Al_2O_3 oxide scale on HDA samples (figure.2 (a, b)) after 24 cycles was irregularity with little white oxides included in the oxide scale (figure2 (a)). The white oxides on HDA samples was analysis by EDS, which was composed of O 80.95 at%, Ti 14.04 at%, Al 4.70 at%, Fe 0.32 at%. This means the white oxide is mainly the oxide of Ti, so the white oxide in Al_2O_3 oxide film is TiO_2 . TiO_2 distributed in Al_2O_3 oxide scale might destroyed the continuity of oxide scale [11]. The Al_2O_3 oxide scale on HDA5Si samples in figure.2(c) after 24 cycles was smoother and denser than the Al_2O_3 oxide scale on HDA. There are some white oxides scattered on Al_2O_3 oxide scale of HDA5Si samples in figure2(c). EDS analysis illustrate the white phases on HDA5Si samples consisted of Fe oxide and Ti oxide. The denser oxide scale samples was consistent with lower weight gain on HDA5Si after 24 cycles at 900°C.

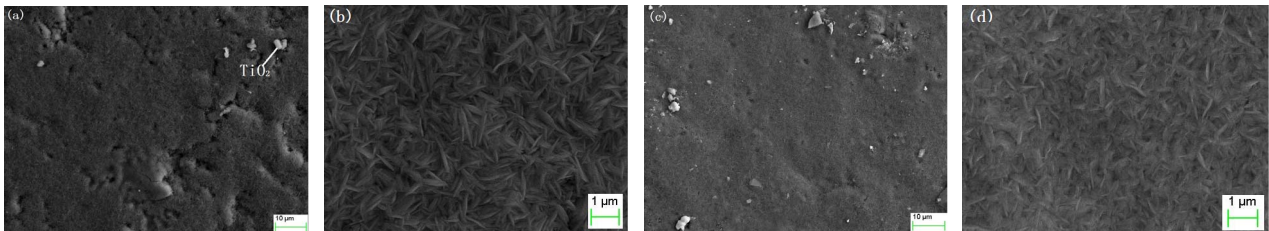


Figure.2 The morphology of surface hot dipping Al samples and hot dipping Al-5Si samples after cyclic oxidation at 900°C for 24 cycles (a) (b)hot dipping Al (c)(d) hot dipping Al-5Si

Observation of the cross-section morphology of HDA samples (figure 3(a)) and HDA5Si samples (figure 3(c)) after 24 cycles at 900°C shown that similar microstructure was formed: Al_2O_3 oxide film, outer layer, intermediate layer and inner layer. The outer layer composed of black phase and gray phase. Element analysis revealed that the alloy atom content was different as shown in table 2. The line scan analysis of HDA samples and HDA5Si samples by EDS were shown in figure3 (b) and figure3 (d), respectively. Observation of figure3 (b) and figure3 (d) shown that the Al distribution in outer layer was rugged due to the different Al content in black phase and grey phase. The Al content of intermediate was uniform and the Al content in inner layer was gradually reduced.

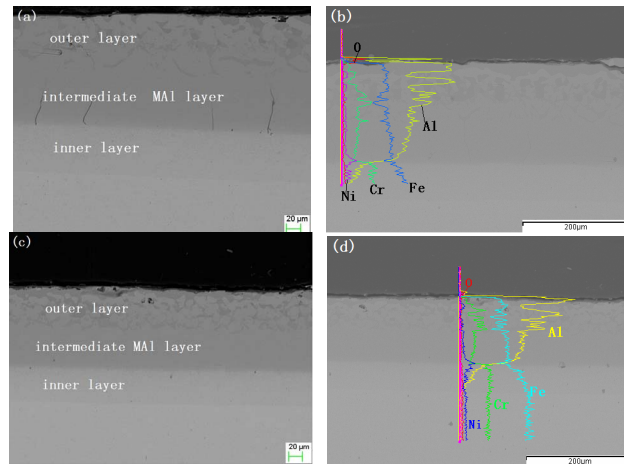


Figure.3 cross-section morphology and element distributions of hot dipping Al samples and hot dipping Al-5Si samples after cyclic oxidation at 900°C for 24 cycles (a) (b)hot dipping Al (c)(d) hot dipping Al-5Si

As shown in table 2, Al content of black phase is higher than Al content of grey phase in outer layer; the component of grey phase of outer layer was similar to the component of intermediate layer. This means Al diffused into matrix during oxidation process and the black phase would transformed to gray phase. Then the outer layer would disappeared with increasing time. According to Al atomic ratio of metal atoms, the intermediate layer was composed of MAI (M on behalf of Fe, Cr, Ni et al). The Al content gradually reduce in inner layer revealed that Al diffused into matrix gradually and Al dissolve in steel. So, the inner layer was called Al solution Fe(Al) layer. The distribution of Fe and Cr atom of steel gradually reduce from matrix to outer layer in Table 2. This distribution means the alloy atoms diffused outward.

Table 2 Chemical compositional of coating on hot dipping Al samples and hot dipping Al-5Si samples

sample		Al (at %)	Cr (at %)	Fe (at %)	Ni (at %)	
HDA samples	Outer layer	Black phase	66.07	3.57	28.67	1.18
		Grey phase	52.00	7.74	32.73	6.05
	Intermediate layer		50.78	8.40	34.56	4.88
	Inner layer		14.24	19.56	54.40	0.53
HDA5Si samples	Outer layer	Black phase	64.48	3.74	30.42	1.00
		Grey phase	51.24	8.09	35.17	4.69
	Intermediate layer		50.04	8.47	35.66	4.41
	Inner layer		13.19	20.39	55.59	7.68

The formation of intermediate layer was due to interdiffusion of Al and alloy atoms of steel. With increasing time, the thickness was increased. Compare figureure3 (a) and figureure3 (c), the thickness of intermediate layer of HDA samples (figure3 (a)) was more than the intermediate layer of HDA5Si samples (figure3 (c)). And some cracks were found in intermediate layer of HDA samples, because of different coefficient of thermal expansion of steel and MAI layer. The thin intermediate layer on HDA sample due to silicon in the moleten aluminum helps in reducing the thickness of MAI layer [12, 13].

According to Wang' study on hot dipping Al-Si coating on mild steels, voids were found at the

interface between the compound layer and the steel substrate and the study point out that voids were formed due to Kirkendall effect. In this work, No voids were formed between the MAI compound layer and inner solid solution layer in HDA samples and HDA5Si samples. It might be that during oxidation Fe, Cr, Ni diffused outward in HDA samples and HDA samples and the Cr, Ni reduces the diffusion rate of Fe.

Conclusions

1) During cyclic oxidation process at 900 °C, mass-gains of hot dipping Al-5Si samples and hot-dipping aluminum were unstable at the early stage, and then retained a relative stable value due to formation protective Al₂O₃ scales. After 24 cycles, mass-gains of hot dipping Al-5Si samples was lower than mass-gain of hot dipping Al samples resulting from denser oxide scale on hot dipping Al-5Si samples.

2) After 24 cycles at 900 °C, Similar microstructures were formed on hot dipping Al-5Si samples and hot dipping Al samples: Al₂O₃ film, outer layer conclude black phase and grey phase, intermediate MAI layer and inner solid solution Fe(Al) layer. The thickness of MAI layer on hot dipping Al-5Si samples was lower than hot dipping Al because of silicon in the molten aluminum helps in reducing the thickness of MAI layer.

3) The cyclic oxidation resistance of Al-5Si samples is better than Al-5Si samples at 900 °C for 24h.

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