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Effect of rare earth oxide nano-additives on the corrosion behavior of Fe-based hardfacing alloys in acid, near-neutral and alkaline 3.5 wt.% NaCl solutions

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ABSTRACT

In this paper, effect of rare earth oxide nano-additives on the corrosion behavior of Fe-based hardfacing alloys was studied. The corrosive solutions were 3.5 wt.% NaCl + 0.01 mol/L HCl solution, 3.5 wt.% NaCl solution and 3.5 wt.% NaCl + 0.01 mol/L NaOH solution. The deep-etched microstructure of the hardfacing alloys was observed. The potentiodynamic polarization curves and electrochemical impedance spectra were used to study the corrosion behavior of the hardfacing alloys. The polarization test results showed that nano-additives shifted the corrosion potentials of the hardfacing alloys towards the noble direction in corrosive solutions. The values of the equivalent circuit elements for the impedance spectra of the hardfacing alloys indicated that nano-additives increased the corrosion resistance of the hardfacing alloys. When the content of nano-additives was 0.3 wt.%, the hardfacing alloy possessed the maximum charge transfer resistance in acid NaCl solution. The hardfacing alloy with 0.6 wt.% nano-additives had the maximum charge transfer resistance in near-neutral and alkaline NaCl solutions. The change in volume fraction of the primary and eutectic carbides and refinement of primary carbide influenced the corrosion behavior of the hardfacing alloys.

1. Introduction

Corrosion is defined as the deterioration and failure of materials due to reactions with their environment [1]. Corrosion is one of the most common three failure modes causing failure of materials. Corrosion of metal and alloys causes huge economic losses in the industrial development [2]. Ordinarily, the corrosion of metals and alloys includes chemical corrosion and electrochemical corrosion. Surface engineering technologies are developed to improve the corrosion resistance of metals and alloys [3–5]. Even though surface engineering technologies have many advantages in enhancing corrosion resistance of material surfaces, they are not capable of improving corrosion resistance of the materials fundamentally.

The corrosion resistance of materials can be improved by optimizing their organization and structure. For example, the preparation of the composites containing ceramic particles of different size can decrease corrosion rate of single materials significantly [6]. At present, nanoparticles have been widely used to prepare nanocomposites to improve corrosion performances of materials. Dehgahi et al. added nano SiC and nano Al_2O_3 into the plating solutions and electrodeposited nanocomposite Ni coatings [7]. Nano particles in the coatings improved their corrosion resistance [7]. Sadreddini et al. added SiO_2 nanoparticles into Ni-P composite coatings and improved their protection ability [8]. Nanoparticles like TiO_2 [9], ZnO [10], Al_2O_3 [11] and Fe_2O_3 [12] have been also used to improve the corrosion resistance of coating materials. Rare earth oxide nanoparticles particularly attracted researchers' attention among different types of nanoparticles [13,14]. Cerium oxide (CeO_2) nanoparticles exhibit attractive properties in many applications, including luminous materials, catalysts, electronic ceramics, and glass polisher [15]. Besides, nano ceria can be used as antioxidant in biomedicine [16]. The unique redox property of nano ceria can protect against diseases caused by the reactive oxygen species or intermediates [16]. CeO_2 nanoparticles have been used to improve the mechanical properties and wear performances of high chromium cast irons [17–19]. But the effect of CeO_2 nanoparticles on the corrosion behavior of high chromium cast irons is still unclear.

In this paper, Fe-based hardfacing alloys with different content of rare earth oxide nano-additives was prepared. The electrochemical measurements including polarization curve and electrochemical impedance spectrum were used to study the effect

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Table 1
Composition of the Q235 steel substrate (wt.%).

Element	C	Si	Mn	Al	Cr	Ni	Cu	P	S
Content	0.15	0.18	0.71	0.007	0.023	0.004	0.007	0.019	0.006

Table 2
Compositions of the core powders in the self-shielded flux cored wire without REO nano-additives (wt.%).

Powders	High carbon ferrochrome (69%Cr, 8%C)	Ferrosilicon (73%Si)	Electrolytic manganese (pure)	Ferroboron (19%B)	Graphite (pure)	Al-Mg alloy (50%Al, 49%Mg)
Content	72–85	2–6	1–4	4–8	2–6	2–4

Table 3
Sources of the raw materials used in the experiments.

Raw materials	Brands	Country of origin
high carbon ferrochrome	Sichuan Kehui Industrial Co., Ltd	China
ferrosilicon	Sichuan Kehui Industrial Co., Ltd	China
electrolytic manganese	Sichuan Kehui Industrial Co., Ltd	China
ferroboron	Sichuan Kehui Industrial Co., Ltd	China
graphite	Sichuan Kehui Industrial Co., Ltd	China
Al-Mg alloy	Sichuan Kehui Industrial Co., Ltd	China
Q235 steel	Minmetals Yingkou Medium Plate Co., Ltd	China
SiC abrasive paper	Tianjin Namkyung Abrasive Ind. Co., Ltd	China
diamond polishing slurry	Wuxi Gangxia Precision Abrasive Paper Factory	China
ferric chloride	Shanghai Aladdin Bio-Chem Technology Co., Ltd	China
hydrochloric acid (38 wt.%)	Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd	China
sodium chloride (NaCl)	Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd	China
sodium hydroxide (NaOH)	Shanghai Aladdin Bio-Chem Technology Co., Ltd	China

of rare earth oxide nano-additives on the corrosion behavior of the Fe-based hardfacing alloys. The factors influencing the corrosion resistance of the hardfacing alloys were discussed in detail.

2. Experiment materials and methods

Self-shielded flux cored wires were used to prepare Fe-based hardfacing alloys. The substrates were Q235 steel with a dimension of 200 mm × 150mm × 25 mm, the composition of which was shown in Table 1. Self-shielded flux cored wires were prepared in our laboratory. The outer was low carbon steel strip. First, the core powders were mixed to ascertain their even distribution. Second, the core powders were filled into the steel strip by a wire rolling mill. Third, the wires with core powders were drawn, the diameter of which was reduced to 2.8 mm. The compositions of the core powders in the wire without rare earth oxide (REO) nano-additives were shown in Table 2. The sources of raw materials are shown in Table 3. Different content of REO nano-additives was added into the core powders of the wire to improve performances of hardfacing alloys. The contents of the REO nano-additives in the wires were 0.3 wt.% and 0.6 wt.%. The compositions of the REO nano-additives in hardfacing alloys were nominal composition, which were equal to their compositions in the wires. The main substance of the REO nano-additives was ceria. REO nano-additives was prepared in our lab. Arc welding technique was used to melt the wires and deposit hardfacing alloys. Each type of self-shielded flux cored wire was used to prepare five layers of hardfacing alloys. Fig. 1 shows the schematic of the hardfacing layers. The bottom three layers were two beads per layer. The top two layers were one bead per layer. The top two layers of the hardfacing alloys were studied in order to avoid dilution of the deposited alloys by the substrate metal.

Microstructure of the hardfacing alloys was observed by a scanning electron microscope (SEM, FEI Quanta 200, FEI Company, America). The hardfacing specimens were ground with SiC waterproof type abrasive paper and polished with 0.5 μm diamond polishing slurry. Then the polished specimens were deep-etched. The etching reagent was 10% hydrogen chloride in methanol. The etching time was 24 h.

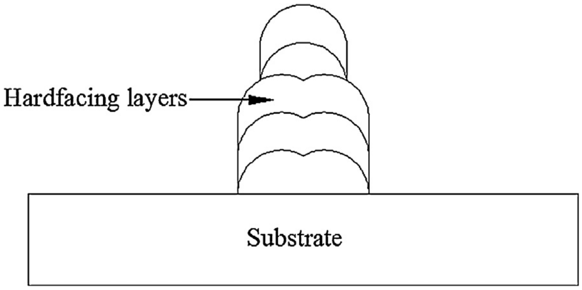

Fig. 1. Schematic of hardfacing layers.

Potentiodynamic polarization curve tests were performed by a CS350H electrochemical workstation (Wuhan Corrtest Instruments Corp., LTD, China). A traditional three-electrode cell was used. The reference electrode was a saturated calomel electrode (SCE). The counter electrode was a platinum sheet. The scanning range was in the range of −0.5 V to 1 V (vs. open circuit potential, OCP) with a scanning rate of 0.5 mV/s. The scan rate affects the extent of distortion of the potentiodynamic polarization curves [20]. The distortion of potentiodynamic polarization curves can lead to obvious error in corrosion current density. Corrosion reactions may not approach the steady state during the potentiodynamic test conducted at a high scan rate [20]. Our previous experiments demonstrated that scan rate of 0.5 mV/s was appropriate for testing potentiodynamic polarization curves of the hardfacing alloys. Impedance spectra were tested by a Zahner Impedance Analyzer (ZAHNER-elektrik GmbH & Co. KG, Germany). The reference electrode was an Ag/AgCl electrode. The counter electrode was a platinum sheet. All electrochemical measurements (polarization curves and impedance spectra) began after stabilization of OCP. The hardfacing specimens used to test potentiodynamic polarization curves and impedance spectra were immersed in corrosive media for 30 min for the stabilization of OCP. The stabilization of OCP meant that the change

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