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Effect of fluxes on wettability between the molten Galfan alloy and Q235 steel matrix

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ABSTRACT

Effect of fluxes on wettability between the molten Galfan alloy and steel matrix was studied by modified sessile drop method. Five fluxes were selected and numbered as Z1-($ZnCl_2$, NH_4Cl), Z2-($ZnCl_2$, NaF), Z3-($ZnCl_2$, NaCl, $CaCl_2$, $SnCl_2$, $CeCl_3$), Z4-($ZnCl_2$, NH_4Cl, KCl, $BiCl_3$), Z5-($ZnCl_2$, NH_4Cl, $SnCl_2$, KF). Results show that some components in fluxes react with zinc oxide and alumina on the alloy surface, thus reducing the interfacial energy and improving wettability between molten alloy and steel matrix. Initial contact angles between molten alloy and steel matrix decrease from 122.3° to 99.7°, and the interfacial energy (σ_{sl}) decreases from $0.92\sigma_G$ J/m^2 to $0.79\sigma_G$ J/m^2 when the flux varies from Z1 to Z5. The wettability of Z5 flux was the best, which shortened the incubation period before the interface reaction due to its rapid decomposition and volatilization. The main chemical factors determining wettability of each flux are Z1-NH_4Cl, Z2-NaF, Z3-$CaCl_2$ and $SnCl_2$, Z4-NH_4Cl and $BiCl_3$, Z5-KF, $SnCl_2$ and NH_4Cl respectively.

1. Introduction

Hot-dip galvanizing is one of the most effective methods of corrosion protection for steel products with low cost. However, with the variety of application environment, hot-dip galvanizing has not been able to meet the market demand for high corrosion resistance of coatings. Many alloying elements have been added to liquid zinc to improve properties of the coatings, such as magnesium and manganese which can improve corrosion resistance of the coating, yet nickel and bismuth are used to refine the coating grain and to reduce the coating thickness [1–6]. Aluminum is usually added to conventional hot-dip galvanized liquid to obtain Zn-Al alloy coating on steel matrix [7]. In 1984, the international lead and zinc research group developed the Galfan (Zn-5%Al-RE) alloy, of which the corrosion resistance was 2–3 times of pure zinc coating [8,9]. This coating has broad application prospects in the field of automobile body, the inner panel and building keel industry. However, due to the high content of aluminum in Galfan alloy, it is very sensitive to the surface conditions of metals. Therefore, coating defects, such as leakage, pinholes and bulges appeared after pretreating by the traditional flux [10–12]. In order to obtain high quality Zn-Al alloy coating, several researches have been done. Yuttanant et al. [13] and N. Pistofidis et al. [14] studied effects of flux composition on the structure and thickness of hot-dip coating. They found that the growth of coating thickness and brittle phase-ζ was inhibited when a certain amount of $NiCl_2$ was added into the flux, whereas $SnCl_2$ and $CdCl_2$ had little effect on the structure of the coating. Rare earth elements were added to fluxes to obtain thinner zinc coating with refined grain, better plasticity and corrosion resistance [15].

The formation of hot dipping coatings is a process of solid-liquid reaction, for which good wetting at solid-liquid interface is essential. Wetting occurs when two metals can be mutually miscible or form intermetallic compounds [16]. The study of factors affecting the wettability of interface reaction is still a hot topic.

Some researchers [17–20] pointed out that with the increase of test temperature, the interfacial reaction between droplets and substrate was more severe, and the corresponding wetting rate became faster, but the final degree of wettability changed little. A. Mortensen et al. [21] pointed out that the main factor affecting wettability is the surface tension of droplets, and the wettability between droplets and matrix can be improved by reducing the surface tension of droplets. The addition of rare earth La to Zn-Al based filler metal can effectively improve the wettability of solder. Besides, the wetting force and contact angle of hot-dip galvanized alloy (0.05–1.10% Al, Mn and Si) on 23 wt% Mn steel were analyzed by Marc Blumenau [22] through Wilhelmy plate methodology. It was found that the wettability between alloy and steel matrix was the best when the content of Al was 0.12–0.22 wt%. M.L. Giorgi et al. pointed out that a small amount of Al (about 0.12–0.25 wt %) should be added to the zinc bath, and the Fe_2Al_5 interface layer can

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be formed on the steel substrate during reaction wetting process, thus promoting the adhesion of Zn coatings to steel substrates [23–24]. The wettability of two kinds of liquid metals (one reactive -Sn, the other non-reactive-Pb) with iron was determined by P. Protsenko, et al. [25] under the same experimental conditions, it was found that the formation of intermetallic compounds seem to improve wetting of a solid metal strongly by a liquid one. In the study of AgCu eutectic alloys/Cu and AgCuTi/Al wetting systems, Mao Wu [26] found that the substrate roughness has a great influence on reaction wetting. L. Wojciechowski, et al. [27] found that the higher the surface roughness of the substrate, the better wettability properties in term of oil spreading on such surface. The equilibrium contact angle decreased from 19° to 15°, when the mean slope of roughness motifs Kr varied from 40 to 85.

Based on the influence of fluxes on the wettability between zinc bath and steel substrate, researches showed that fluxes can reduce the surface tension between workpiece and liquid zinc, and improve the wettability of liquid zinc on the steel matrix surface [28]. Mingyi He and other studies [29–30] found that the surfactant in flux can be selectively adsorbed on the surface of the liquid to reduce the surface tension. Therefore, the wettability of the bath can be improved during hot dipping, and the wetting angle of the flux can be reduced by 15–20°. Zhongbao Luo et al. [31] reported that when the content of $FeCl_2$ in flux was < 60 g/L, the wettability between liquid alloy and steel matrix was the best. G.A. Lopez [32] and Takahashi Juniehi [33] found that the addition of sodium fluoride in flux can dissolve the oxide on the surface of molten zinc-aluminum alloy, which reduced the surface tension of liquid zinc and improved the wettability of molten zinc to the workpiece.

There are relatively few researches on wettability of liquid alloy during hot dipping, and most of them are concerned with temperature and alloy elements in liquid metal, which affect the wetting behavior of zinc bath on steel substrate. Researches about the influence of flux compositions on the wettability of both flux and molten alloy are not very thorough. Most studies described the phenomena of observation without providing reliable theoretical data and mechanisms. Therefore, effects of different fluxes on wetting behavior of molten Galfan alloy and steel matrix were studied by modified sessile drop method in this paper in order to provide a theoretical basis for the selection of Galfan alloy flux.

2. Experimental procedure

2.1. Experimental materials and samples preparation

The substrate material was made of 50 mm × 40 mm × 3 mm Q235 steel plate (composition as shown in Table 1), which was rinsed with water after pickling in dilute hydrochloric acid of 18% concentration at 25 °C for 20 min to remove iron fines and oxides, and then soaked in anhydrous ethanol in reserve (the surface roughness of all the steel plates used in the study are 1.4 μm).

The Torch brand Galfan alloy used in the experiment was produced by Zhuzhou smelting Group. This company had obtained the production patent license of international lead and zinc organization. And the chemical composition of Galfan alloy in the factory inspection report is shown in Table 1. The Galfan alloy was put into a graphite crucible and heated into the molten state at 460 °C in a box furnace.

Table 2
Classification and composition of five fluxes.

Classification	Z1	Z2	Z3	Z4	Z5
Composition	$ZnCl_2$ NH_4Cl	$ZnCl_2$ NaF	$ZnCl_2$ NaCl $CaCl_2$ $SnCl_2$ $CeCl_3$ HCl	$ZnCl_2$ NH_4Cl KCl $BiCl_3$ HCl	$ZnCl_2$ NH_4Cl $SnCl_2$ KF HCl

In Table 2, five fluxes were selected by comparing the smoke, slag and coating quality in a large number of hot-dip Galfan alloy tests. First of all, the traditional zinc ammonia flux with the worst effect was selected as the contrast, and the common hot-dip galvanizing aluminum alloy flux - $ZnCl_2$ + NaF was also selected. The other three are self-developed fluxes suitable for hot-dip Galfan alloy. Five fluxes were numbered as Z1–Z5 according to the coating quality. All fluxes were configured as solutions and were statically placed for 12 h.

2.2. Experimental methods

Contact angles of the flux solution to steel matrix were measured by using contact angle measuring instrument (DSA30, measuring range: 0–180°; resolution ≤0.01°, Kruss, Germany) coupled with image analysis system. 10 μL flux solution was dropped onto the steel matrix by a syringe in the measurement, and the droplet shape was photographed with a high definition digital camera after the solution touched the steel matrix for 25 s. Subsequently, contact angles can be calculated automatically with the system software.

An automatic surface tension instrument (SFT, measuring range: 0–1000 mN/m; resolution: 0.01 mN/m, Peking) was adopted at room temperature, and the surface tension values of five flux solutions were measured by wilhelmy plate method.

Influences of five fluxes on the wetting behavior of molten Galfan alloy/steel matrix were investigated by sessile drop method, and the whole process was carried out in a box-type reheating furnace. The Galfan alloy was heated above the melting point (382 °C) and exhibited a molten state under the condition of air, then it was heated to 460 °C for 1 h in the furnace. Firstly, the steel plate was fluxed for 25 s and dried at 200 °C, then it was put into the heating furnace with the pipetting spoon to preheat for 2 min. After that, an appropriate amount of liquid alloy was dripped into the high temperature funnel with the pipette, and the shape of the droplet was photographed immediately with the photographic equipment. Finally, the initial contact angle between the liquid alloy and the steel matrix was measured. Each flux was repeatedly tested with six times for the most concentrated values, and the average of six measurement results was the final value of the wetting angle.

The surface topography and roughness of steel matrix pretreated by Z1–Z5 fluxes was examined using an atomic force microscope (AFM5500, maximum scanning range: 90 μm, maximum roughness: 7 μm, Agilent, USA). Atomic force microscopy was used to observe the

Table 1
Composition of the starting materials (wt%).

Q235 steel					
0.12–0.20 C	0.30–0.67 Mn	≤0.045 P	≤0.30 Si	≤0.045 S	Balance Fe

Galfan alloy						
4.2–7.2 Al	0.03–0.10 La + Ce	<0.075 Fe	<0.015 Si	<0.005 Pb	<0.060 Other elements	Balance Zn