Effects of adding aluminium in zinc bath on Co-Zn interfacial reaction

Yongxiong Liu [a,b], Fucheng Yin [a,b]*, Zhi Li [a,b], Zhu Chen [a,b], Manxiu Zhao [a,b] & Zhaohui Long [a,b]

[a]Key Laboratory of Materials Design and Preparation Technology of Hunan Province, School of Materials Science and Engineering, Xiangtan University, Hunan 411105, PR China

[b]National-Provincial Laboratory of Special Function Thin Film Materials, School of Materials Science and Engineering, Xiangtan University, Hunan 411105, PR China

Effects of adding 0.3 wt.% Al in Zn bath on the microstructure and reaction kinetics of intermetallic compounds have been studied using Co/Zn and Co/Zn-Al solid/liquid diffusion couples by means of scanning electron microscopy (SEM) and wave dispersive spectrometry (WDS). The intermetallic compounds in the Co-Zn interface have been identified and the diffusion process of Al in zinc bath has been analyzed. The diffusion constants of intermetallic compounds have been evaluated. The chemical potential of Al and standard Gibbs free energy of intermetallic compounds have been calculated using the Co content as a variable based on the calculation of phase diagram (CALPHAD) method. The results show that the chemical potential of Al decreases with increasing Co. At the solid/liquid interface, the Co content is high, the chemical potential of Al atoms is lower than that in other areas, uphill diffusion of Al atoms occurs, and an Al-rich metastable phase forms. The Gibbs free energy of the CoAl phase is lower than that of Co-Zn compounds; therefore, the Co atoms diffuse through the γ2 layer into the Al-rich area and nucleate to form a shape-stable CoAl layer at the solid/liquid interface and significantly inhibit the Co-Zn interfacial reaction.

Key words: Interfacial reaction, Galvanizing, Co-based alloy, Aluminium

1 Introduction

Hot-dip galvanizing is one of the major methods used for improving the corrosion resistance of steel[1-2]. In continuous hot dip galvanizing, pot hardware, including rolls and supporting bearings, is used to guide incoming steel strips passing through a zinc bath during the coating process and is therefore submerged in molten zinc. The Zn melt can erode most of the metals. When continuous galvanizing is used in industrial applications, 0.25–55 wt.% of Al[3-5] is often added to the zinc bath in order to control the Fe-Zn reaction or increase the corrosion resistance ability of the coating[6-9]. The corrosion of the equipment in the Zn-Al bathwill reduce its service life and result in the formation of dross in the bath, which scratch the surface of the coatings. The arduous working environment of elevated temperatures (450–480°C) and corrosive medium (molten zinc) makes it rather challenging to select suitable hardware materials that can be used for longer operations. It is not uncommon that galvanizers must stop continuous galvanizing lines (CGLs) within 2–4 weeks to replace the degraded pot hardware. Therefore, the control of

the corrosion is a key factor that decides the effectiveness of the galvanizing line and the coating quality. In recent times, corrosion-resistant materials such as heat-resistant steel and Co-based superalloys are being used in the molten Zn bath. In fact, Co-based superalloys are the most commonly used corrosion-resistant materials.

There are some reports on the corrosion of Co-based superalloys in Al-Zn molten bath. Zhang *et al.* [10] researched a Co-based alloy (Stellite® 6) for application in a CGL and observed that some CoAl particles form outside the seriate CoAl layer, causing severe abrasion. Yao *et al.* [11] investigated the corrosion of four alloys (Stellite 6, Tribaloy T-400, Tribaloy T-800, and Tribaloy T-401) in 0.22 wt. % Al-Zn bath at 470 °C, and found that the increase of the reaction layer thickness follows a parabolic rate law, indicating a solid diffusion process. Seong *et al.* [12] studied the corrosion of WC-12 wt. % Co coated sink roll in the Zn-Al bath of a CGL. They reported that it is mainly aluminium, rather than zinc, that diffuses into the WC-Co coating along the cracks and forms the reaction product Fe_2Al_5 between the molten bath and the coating layer, even though the zinc bath contains less than 0.23% aluminium. The enrichment

*Corresponding author (E-mail: fuchengyin@xtu.edu.cn)

of Al in the zinc bath can restrain Zn diffusion along the cracks. Scheid *et al.* [5,13] reported that the reactivity of a Co-based alloy immersed in 55 wt.% Al-Zn molten bath depends on the Al-Co reactions.

There are also some reports on the Co-Zn reaction. Yang *et al.* [14] and Duchenko *et al.* [15] studied the microstructure and reaction kinetics of intermetallic compounds of the Co-Zn interface by solid/solid diffusion couples, and reported γ, γ_1, and γ_2 diffusion layers. They also calculated the growth coefficient of the intermetallic compounds. However, these results were obtained at a temperature much lower than the hot-dipping temperature, which could not be used as a guidance of the Co-Zn reaction in the galvanizing process.

In this work, pure Zn and 0.3 wt. % Al-Zn were chosen to investigate the effect of Al on the interfacial reaction of Co-Zn at hot-dipping temperature. The diffusion process of Al in the zinc bath was analyzed and the reaction-diffusion constants of intermetallic compounds were evaluated. These researches on the interfacial reaction of the superalloy in the Zn-Al melt are both scientific and commercial interest for the galvanizing industry.

2 Experimental Methods

Al, Co and Zn with purity >99.9 wt. % were used in this work. Instead of pure Al, Zn-5 wt. % Al alloy was added to zinc bath in order to prevent oxidation and promote homogeny. The Co blocks were smelted from 25g Co chips, and were divided to 4 mm×1.5 mm×20 mm sheets by wire-electrode cutting. The Co sheet as substrate was dealt with pre-galvanizing. It was dipped in a Zn bath at the designed temperature for different immersion times and intermetallic compounds formed at the interface of Co-Zn. The metallographic samples were prepared and examined by means of JSM-6360LV scanning electron microscopy (SEM). Some samples were measured using OXFORD type INCA wave dispersive spectrometer (WDS) under the back scattering model for accurate determination in each phase composition. The thicknesses of the intermetallic compound layers were measured. The thickness of each layer was determined based on the mean value of at least 20 thickness values.

3 Results and Discussion

3.1 Interfacial Reaction of Co and Pure Zn

Figure 1 shows the microstructure of the reaction interface of pure Co in the pure Zn bath. Three intermetallic phases were observed from the substrate to the solidified structure: γ (75.2 – 85.4 at. % Zn), $\gamma1$ (87.4 – 88.6 at. % Zn), and $\gamma2$ (91.0 – 92.8 at. % Zn). The composition of the three intermetallic compound agrees well with the results of Duchenko *et al.* [15]. A list of symbols and abbreviation in this work is in Table 1.

As shown in Fig. 1a, the $\gamma2$ layer shows dendrite growth at 450 °C, along the direction perpendicular to

Table 1 — List of symbols and abbreviation in this work.

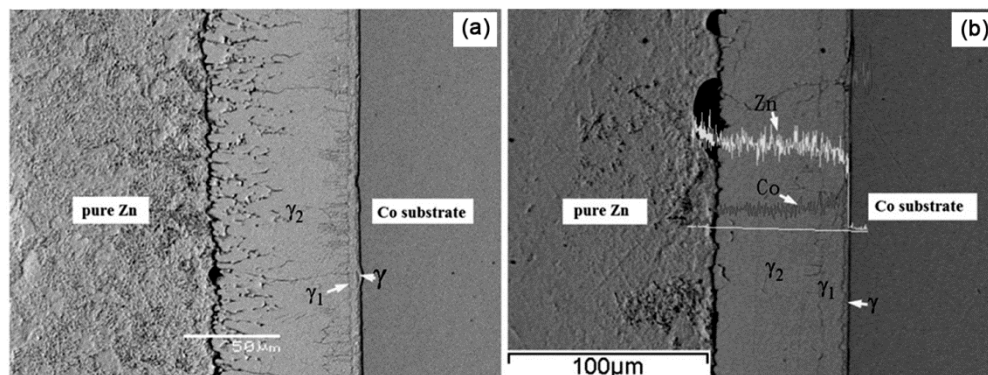| symbols and abbreviation	implication
γ	Co_5Zn_{21}
$\gamma1$	$CoZn_{7.5}$
$\gamma2$	$CoZn_{13}$
x	intermediate layer thickness
K_1	growth factor
t	reaction time
t_0	incubation time
T	temperature
K	Kelvin
°C	degree centigrade
wt.%	weight percent
at.%	atomic percent
min	minute
m	meter
s	second

Fig. 1 — Microstructure of Co/Zn interface in pure Zn bath at (a) 450 °C and (b) 480 °C, for 20 min.

the solid/liquid interface with the fastest growth rate. The thickness of γ1 increases obviously on increasing temperature from 450 °C to 480 °C (Fig.1a and b). The growth of intermetallic compound layer in interface reaction is mainly controlled by atomic diffusion of reactants[16-18]. When the temperature is increased to 480°C, the consumption and diffusion resistance of the Co atoms in the γ1 layer increase because of the rapid growth of the γ1 layer; therefore, the thickness of the γ2 layer becomes lesser than that obtained at 450 °C. Hence, the thickness of the total compound coating layer reduces at 480 °C. The thickness of the γ layer does not show any obvious change, and remains within the 2 μm width, which proves that the growth rate of the γ layer is very slow within the tested temperature range.

3.2 Effect of Al on the Growth Kinetics of Co-Zn Interfacial Reaction

Figure 2 shows the relationship between total thickness of intermetallic compounds and immersion times in the two baths: pure Zn and 0.3 wt.% Al-Zn.

It can be seen that the total thickness of intermetallic layers in pure Zn bath is bigger than that in 0.3 wt.% Al-Zn bath at both 450 °C and 480 °C. It shows that the addition of Al significantly inhibits the Co-Zn interfacial reaction. Moreover, the total thickness of the intermetallic layers at 450 °C is bigger than that at 480 °C in the two baths. The growth rate of the γ1 phase increases with the immersion temperature, and hence, the thick γ1 layer hinders the diffusion of Co atoms from the substrate, resulting in a slower growth rate for the γ2 phase.
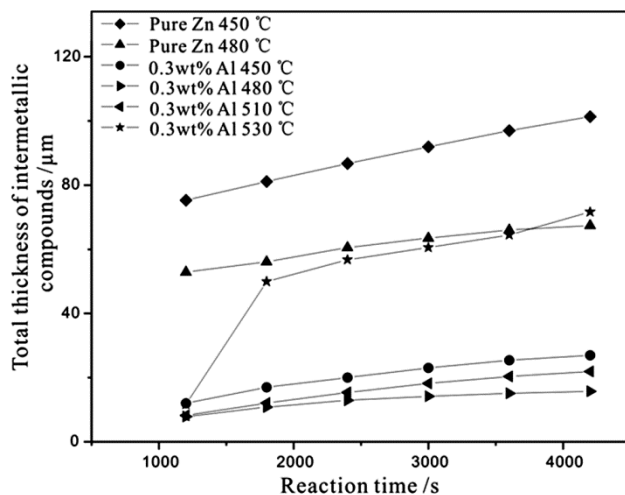

Fig. 2 — Relationship between total thickness of intermetallic compounds and different immersion time in the two baths.

As the γ layer is very thin in all samples, it cannot be clearly distinguished from the γ1 phase during the measurement. Hence, the total thickness of the γ and γ1 layers was recorded. According to the literature[10,19,20], the relationship between the intermediate layer thickness and the reaction time is in accordance with the following formula:

$$x^2 = 2K_1 \cdot (t - t_0) \qquad \qquad …(1)$$

where x is the intermediate layer thickness, K_1 is the growth factor, t is the reaction time, and t_0 is the incubation period. The coefficients of layer growth in 0.3 wt. %Al-Zn bath at different temperatures are obtained by data processing (Table 2). As the table shows, the growth rate of the γ2 layer is much faster than that of the γ1 layer.

3.3 Effect of Al on the Microstructure of Co-Zn Interfacial Reaction

The microstructures of the reaction interface as pure Co dipped in the 0.3 wt.% Al-Zn bath at 450 °C for 20 and 90 min are shown in Fig. 3. The γ2 phase still shows the dendrite growth in the Al-added Zn bath; it is thinner than that in the pure Zn bath at 450 °C, which shows that the added Al strongly inhibits the growth of the γ2 layer (Fig. 3a). In the line scan, the Al enrichment phenomenon can be seen in the left section of the γ2 layer; gaps in the γ2 layer dendrite can also be clearly seen. Furthermore, in the left section of γ2 layer, the Al content in the position of the peaks, the Co content in the peak position. Therefore, the Co atoms and Al atoms are found in the same area. When the immersion time was extended to 90 min, some dark textures form near the Zn-0.3 wt.%Al bath, as shown in Fig. 3b. WDS proves that these dark textures are CoAl phases[21]. The CoAl particles are distributed in the front of the dendrite γ2 layer, which strongly inhibit the growth of the γ2 layer. The CoAl particles are also generated in the liquid zinc bath solidification microstructure. As CoAl has higher microhardness (about 1064HV) than cobalt-based alloys[7]. The existence of CoAl particles

Table 2 — Reaction-diffusion constants of intermetallic compounds at different temperature.

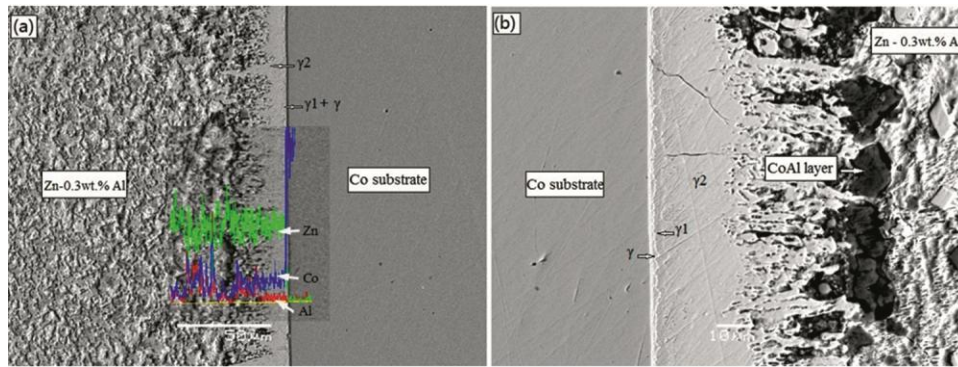| Temperature	$K_1 (\times 10^{-13} \text{ m}^2 \cdot \text{s}^{-1})$		
	γ+γ₁ layer	γ₂ layer	three layers
450 °C	—	—	0.7945
480 °C	0.01822	0.11385	0.2246
510 °C	0.0932	0.28605	0.706
530 °C	1.2695	2.526	7.375

Fig. 3 — Microstructure of Co-Zn interface in Zn bath with 0.3wt% Al at 450 °C for (a) 20 min and (b) 90 min.
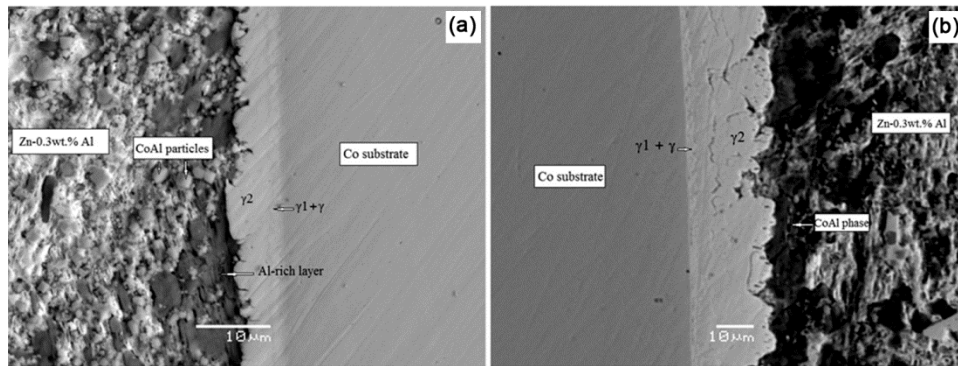

Fig. 4 — Microstructure of Co-Zn interface in Zn bath with 0.3wt% Al at 480 °C for (a) 20 min and (b) 70 min.

in the zinc bath is the main reason for the serious abrasive wear of the roll and bearing in continuous galvanizing. This result agrees well with Zhang *et al.* research [9].

Figure 4 shows the microstructure of the reaction interface of pure Co immersed in the 0.3 wt.% Al-Zn bath at 480 °C for 20 and 70 min. In Fig. 4a, many CoAl particles are formed at the solid/liquid interface. And big black grey areas outside the γ2 layer which comprise Al 17.07 at.%, Co 9.52 at.%, and Zn 73.41 at.% is confirmed as metastable phase, based on the Zn-Al-Co ternary phase diagram[21]. When the dipping time is extended to 70 min, the metastable phase area disappears and a dense CoAl layer forms. Similar phenomenon occurs at 510 and 530 °C.

3.4 Discussion

According to the thermodynamics database of alloy system, the CALPHAD method can be used to calculate the thermodynamic properties of the alloy system and the results are of help to analyze the growth of the coating process. The phase diagrams of Co-Zn[22], Al-Zn[23] and Co-Al[24] have be optimized by scholars. Based on the results of the above three binary systems, parameters of thermodynamic model

of the ternary system (Co-Zn-Al) can be obtained. Then, the thermodynamic data of every phase in the ternary system can be calculated by Thermo-Calc software.

Figure 5a shows that when the Co content in the liquid phase increases, the chemical potential of Al atoms decreases. Following the Co-Zn interfacial reaction, the Co atoms move from Co substrate to the liquid phase, and increase the Co content in the interface. Then, uphill diffusion of Al atoms occurs; as a result, they spread to the interface (which contains a high concentration of Co) from the central area of the zinc bath (which has a low concentration of Co). Therefore, the process through which the Al atoms enrich the interface can be expressed as follows. The Co matrix firstly reacts with liquid zinc to form a Co-Zn phase, which leads to the consumption of Zn atoms at the solid/liquid interface; then, the Al atoms added into the Zn bath diffuse to the region, leading to the enrichment of the bath with the Al atoms. Figure 5b shows that the Gibbs free energy of the CoAl phase is much less than that of the Co-Zn compounds. Therefore, a large amount of Co atoms will diffuse through the γ2 layer into the Al-
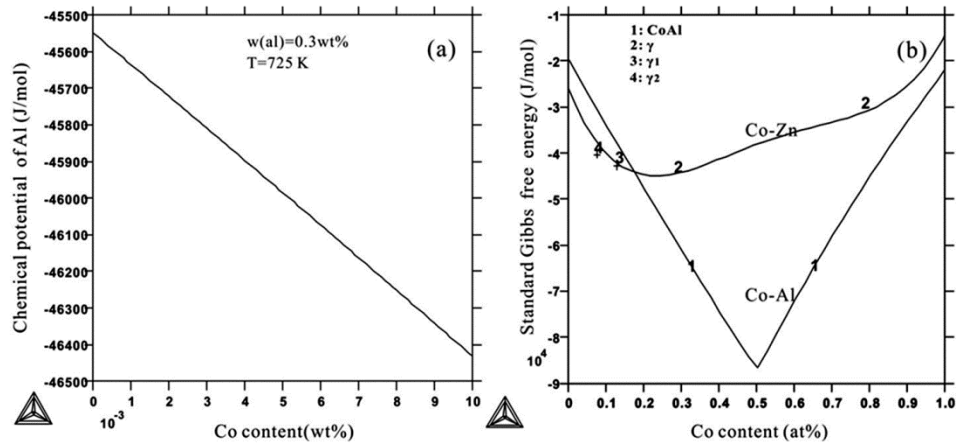
Fig. 5 — (a) Relationship between chemical potential of Al and (b) standard Gibbs free energy of intermetallic compounds, with Co content at 450 °C.
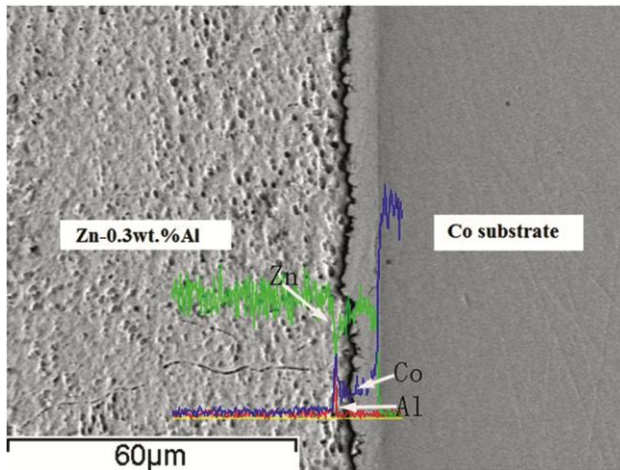

Fig. 6 — Line scan of EDS for the interface in Zn bath with 0.3wt.% Al at 480 °C for 10 min.

rich area, and nucleate to create a CoAl layer. On further increasing the temperature, denser and thicker CoAl layers formed. The generation of CoAl compound hinders the diffusion of Co and Zn atoms, significantly inhibiting the Co-Zn reaction.

The component analysis result of EDS line scanning at the interface of the Co substrate dipping in 0.3 wt.%Al-Zn bath for 10 min at 480 °C is shown in Fig. 6. The contents of Al and Co atoms increase abruptly, with Zn content reducing near the solid/liquid interface.

4 Conclusions

(i) The intermetallic compounds formed at Co-Zn interface are γ, γ1 and γ2. The γ2 layer shows dendrite growth at 450 °C and grows very fast. When the temperature increases, the growth rate of the γ_1 layer also increases, and its thickness increases significantly. The γ layer shows a very slow growth rate from 450 to 480 °C.

(ii) The intermetallic layer grows and follows a parabolic law in 0.3wt.%Al-Zn bath. The growth coefficients are 0.7945×10^{-13}, 0.2246×10^{-13}, 0.706×10^{-13} and 7.375×10^{-13} m^2 s^{-1} at 450, 480 , 510 and 530 °C, respectively.

(iii) At the solid/liquid interface, the Co content is high, and the chemical potential of Al atoms is lower than that in other areas. Uphill diffusion of Al atoms occurs at the solid/liquid interface, and an Al-rich metastable phase is formed. The Gibbs free energy of the CoAl phase is much less than that of Co-Zn compounds; therefore, the Co atoms will diffuse through the γ2 layer into the Al-rich area and nucleate to form a shape-stable CoAl layer in the area, significantly inhibiting the Co-Zn reaction.

References
1   Berto F, Razavi S M J, Ayatollahi M R & Mutignani F, *Procedia Structural Integrity*, 3 (2017) 135.
2   Berto F, Mutignani F & Guido E, *Int J Fatigue*, 93 (2016) 168.
3   Marder A R, *Progress Mater Sci*, 45 (2000) 191.
4   Xue Q, Sun C Y, Yu J Y, Huang L & Zhang J, *J Alloy Compound*, 699 (2017) 1012.
5   Scheid A & D'Oliveira A S C M, *Mater Sci Technol*, 26 (2010) 1487.
6   Soog J H & Kim H J, *Wear*, 210 (1997) 291.

7   Kim H J, Yoon B H & Lee C H, *Wear*, 254 (2003) 408.

8   Zhang K, *Wear*, 255 (2003).

9   Wang W J, Lin J P & Wang Y L, *Rare Met Mater Eng*, 36 (2007) 994.

10   Zhang K & Tang N Y, *Mater Sci Technol*, 6 (2004) 739.

11   Yao M X, Wu J B C & Liu R, *Mater Sci Eng A*, 407 (2005) 299.

12   Seong B G, Hwang S Y, Kim M C & Kim K Y, *Surf Coat Technol*, 138 (2001) 101.

13   Scheid A, Schreiner W H & D'Oliveira A S C M, *Corrosion Sci*, 55 (2012) 363.

14   Yang Z L, Song Y Q & Li S C, *Phys Test*, 43 (2007) 59.

15   Duchenko O V, Vereshchaka V M & Dybkov V I, *J Alloys Compound*, 288 (1999) 164.

16   Liberski P, Gierek A & Kania H, *Archive Foundry Eng*, 8 (2008) 93.

17   Li Y, Wei X J & Fen F L, *Mining Metall*, 10 (2001) 49.

18   Meng R X & Yang X Z, *J Chinese Soc Corrosion Protect*, 7 (1987) 8.

19   Zhang J H & He P, *Welding J*, 21 (2000) 84.

20   Pan J S, Tong J M & Tian M B, Tsinghua University Press, Beijing, 1998.

21   Zhao M X, Yin F C, Li Z, Liu Y X, Long Z H & Su X P, *J Phase Equilibria Diffusion*, 3 (2010) 183.

22   Vassilev G P & Jiang M, *J Phase Equilibria Diffusion*, 25 (2004) 259.

23   Mey S, *Z. Metallkd.*, 74 (1993) 451.

24   Ohtani H, Yamanoz M & Hasebe M, *Calphad*, 28 (2004) 177.