**Formation of periodic layered structure during
reaction between Co_2Si and liquid Zn**

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Abstract: Reactions of Co_2Si alloy with liquid zinc for annealing time up to 720 minutes were studied by means of scanning electron microscope, energy-dispersive X-ray spectroscopy and electron backscattered diffraction techniques. The results showed that periodic patterns, $\text{Co}_2\text{Si} / (\gamma_2 + \eta\text{-Zn})$, were observed in the reaction zone, and its thickness and morphology were dependent on the crystallographic orientation of Co_2Si grain. The relationship between anisotropy growth of the periodic patterns and crystal structure was explained with the concept of dangling bonds. The thermodynamic foundation and mechanism of formation of the periodic layered structure were elaborated in this paper.

Keywords: Hot-dip galvanizing; Co-based alloy; Periodic layered structure; Anisotropy; Thermodynamics

1 Introduction

Galvanizing has been widely used to protect steels from corrosion for more than 200 years [1]. In a hot dip galvanizing process, a steel article is cleaned, fluxed and then immersed in a molten zinc bath at a temperature of about 450 °C. Thus formed zinc coating corrodes preferentially than the steel substrate by a cathodic reaction that prevents steel from undergoing anodic corrosion reaction [2]. In this process, equipment exposed to liquid in the bath suffers from corrosion, wear, and thermal-mechanical fatigue at elevated temperature. Sink roll, usually made of 316L stainless steels, is immersed in molten zinc tank and attacked by the liquid zinc leading to pitting and builds up [3]. Cobalt based alloys are conventional bearing materials used for the bushing of sink rolls, however, Al added in zinc bath of continuous galvanizing line reacts with Co to form Co-Al particles, which degrade life-span of bearing [3-5]. Performance of zinc pot hardware can be improved with optimized microstructure or by introducing protecting layers or coating [6-8]. In recent years, CoCrMoSi alloys were developed to enhance bearing's performance at high temperature by introducing Laves phase net in the microstructure [6]. Intermetallic compounds, such as FeCrSi [7], Fe₃Si [9], Fe₃Al [7], Fe-B [10-11], which were used as structural material in various metal surface engineering process, are considered as candidate structural materials in the hot dip galvanizing industry. Research relating to reaction between metallic alloy and liquid zinc bath have important impacts on hardware equipment in industry. So reactivity between Zn and Co₂Si alloy was experimentally investigated in this study. Microstructure evolution was identified, and the reaction mechanism was proposed with the aids of diffusion path theory and thermodynamic calculation.

2 Method

2.1 Experimental procedures

Materials used were cobalt rod (99.99%), silicon powder (99.99%) and zinc bulk (99.9%) (Beijing Mountain Jingdian Technical Development Center, China). Co₂Si alloy was prepared by repeated argon arc melting. They were sealed and annealed at 1000 °C for 30 days to obtain homogeneous alloys. Annealed sheet specimens were mechanically polished and cleaned. After that, plates of Co₂Si alloys were then immediately sealed separately together with the Zn (99.999 wt. %) bulk in a vacuum quartz tube. In this study, 14 samples were prepared. 8 of them were kept at 450 °C for 50 minutes to 80 minutes with intervals of 5 minutes, and the others was kept at 450 °C for 120 minutes to 720 minutes

with intervals of 120 minutes, followed by water-quenching.

Small specimens (5 mm × 5 mm × 3 mm) were cut from annealed and quenched samples. Fig.1 (a) shows specimen position within the electron backscattered diffraction (EBSD) (Oxford Instruments, Oxfordshire, U.K.) specimen chamber. ND refers to the normal direction, RD and TD refer to subsequent longitudinal and transverse directions. ND, RD and TD are axes of the specimen coordinate axis, and ND parallels to the growth direction of the reaction products. The ND-RD plane of the sample were mounted by using silicon carbide wet polishing papers (up to #4000-grit) and then mechanically polished using 9 μm, 3 μm and 1 μm diameter of diamond paste, and finally 0.05 μm diameter of colloidal silica suspended solution to remove any surface damage and most of the strain on surface layer. The ND-RD plane was exposed to the EBSD detector. In this position the EBSD map was collected and analyzed under the following conditions: e-beam accelerated voltage 20 kV, beam current 20 nA, working distance of 10 mm and the sample tilt angle of 70°. The samples were also examined by a JSM-6510 scanning electron microscope (SEM) (JEOL, Japan) equipped with OXFORD INCA energy dispersive X-ray spectroscopy (EDS) (Oxford instrument, UK)). The phase identities of reaction products were analyzed by X-ray diffraction (XRD) patterns generated using a D/max 2500 PCX-ray diffractometer (Rigaku, Japan) with Cu K α -radiation and a step width of 0.02° (2 θ).

2.2 Theory analysis

Schematic diagram relating the sample coordinate system to the crystal coordinate system is illustrated in Fig. 1 (b). [100], [010] and [001] are axes of the Co₂Si crystals in the crystal coordinate system. As growth direction of reaction products is vertical to the interface between Co₂Si substrate and reaction zone (the RD-TD plane), ND is the growth direction of the reaction products regardless of the crystal orientation of the Co₂Si substrate alloy. Project Manger module in the Channel software developed by HKL Company was utilized to obtain the ND direction of the specimens, then the normal direction of the plane where the reaction products formed can be determined.

Crystal structure parameters of the Co₂Si alloy has been listed in Table 1. Co₂Si belongs to be orthorhombic system. Indices of the plane where the reaction products formed can be calculated with the following equation:

$$[uvw] = \begin{pmatrix} 1/a^2 & 0 & 0 \\ 0 & 1/b^2 & 0 \\ 0 & 0 & 1/c^2 \end{pmatrix} (hkl) \quad (1)$$

where a, b and c are lattice parameters, $[uvw]$ are the orientation indexes perpendicular to the plane where the reaction products formed, and (hkl) are this plane's indices. The interplanar spacing of the Co_2Si substrate alloy can be calculated by equation (2):

$$d_{hkl} = \frac{1}{\sqrt{\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2}} \quad (2)$$

3 Results and discussion

3.1 Microstructure and phase constituents of interaction layer

Figure 2 (a) shows a backscattered electrons (BSE) image of the Co_2Si alloy dipped in liquid zinc at 450 °C for 12 hours. The reaction zone exhibits a periodic layered structure perpendicular to the diffusion direction. Periodic pattern consists of one dark layer and one bright layer. The thin dark layer contains 49.1 at.% Co, 50.3 at.% Si and 0.6 at.% Zn. In the bright layer, average composition of the bright blocks is 6.9 at.% Co, 91.3 at.% Zn and 1.8 at.% Si, and composition of the matrix is 99.4 at.% Zn, 0.5 at.% Co and 0.1 at.% Si. To identify the phase formed during reactions of Co_2Si and molten zinc at 450 °C, thermodynamic model proposed by Wang et al. [13] was used to construct the 450 °C isothermal section of the Co-Si-Zn ternary system, as presented in Fig. 3. Based on the information from EDS compositional analyses with the calculated isothermal section, the thin dark layer were identified as the CoSi phase, and the bright layer comprised of the $\gamma_2(\text{CoZn}_{13})$ phases and the liquid phase, respectively. It is worth to mention that the liquid phase transformed to the η -Zn phase while quenching, so the η -Zn phase evidenced in the microstructure corresponds to the liquid phase at 450 °C. The dark CoSi layer and bright ($\gamma_2 + \eta$ -Zn) layer are represented as D layer and B layer, respectively, in the text below. XRD analysis of the ground powders of the reaction products confirmed that the reaction zone is composed of CoSi, γ_2 phases and η -Zn (Fig. 2 (b)).

Thickness of periodic pattern, one D layer with one B layer, varies from 5 μm (minimum) up to 15 μm in the reaction zone. The width of the D layer is from 0.6 μm to 1 μm . In each zone the spacing of periodic structure is nearly constant. The thickness ratio between the bright and dark layers is significantly higher in the zone with thicker periodic layers because of more zinc in bright layer. The thicker periodic layer, the more zinc in the reaction zone. However, the thickness of reaction products

with smallest spacing is widest and more substrate is consumed, i.e. they have grown faster.

3.2 Periodic layered structure evolution

Figure 4 (a) - (f) show SEM micrographs of reaction zone between Co_2Si and liquid Zn that had reacted at 450°C for 50 minutes to 80 minutes with intervals of 5 minutes respectively. As presented in Fig. 4 (a), one bright layer consists of large grains and one dark grey layer were found between the molten zinc and the Co_2Si substrate after 50 minutes of reaction. The compositions of the bright grains and the dark grey layer were determined to be γ_2 and CoSi , respectively.

Seen from Fig. 4 (b), when the reaction time was extended to 55 minutes, the CoSi layer was split off the Co_2Si substrate, and some other γ_2 phase was formed between them. When the diffusion time reached to 65 minutes, two periodic patterns were formed at the interface, as shown in Fig. 4 (c). 5 minutes later, the third γ_2 phase layer partially merged between the CoSi layer and the Co_2Si substrate, as shown in Fig. 4 (d). When the reactions that had lasted for 75 minutes, up to three pairs of $\text{CoSi} / \gamma_2 + \text{liq.}$ periodic patterns were observed (see Fig. 4 (e)). As the reaction time increased to 80 minutes, as shown in Fig. 4 (f), the number of the $\text{CoSi} / (\gamma_2 + \text{liq.})$ periodic patterns continuously increased while the liquid phase was simultaneously consumed. From the liquid zinc to the Co_2Si substrate, the diffusion path across the interface is liquid / γ_2 / CoSi / liquid / γ_2 / CoSi ... liquid / γ_2 / CoSi / Co_2Si , as presented in Fig. 3 (a).. In the diffusion path, the periodic layers are connected with the tie-lines across the mass-balance line.

3.3 Effect of substrate alloy orientation on morphology of interaction layer

Anisotropy growth of periodic layered structure due to crystallographic orientation of the Co_2Si grains is shown in Fig. 5 (a). Misorientation of two grains close to the Co_2Si /reaction zone interface is nearly 70° (see Fig. 5 (b)). The relationship between the morphology and crystal structure is the concept of dangling bonds [14]. By using method introduced in session 2, surfaces where periodic patterns formed on grain A are parallel to (323), while that on grain B is perpendicular to (123). According to Equ. (2), $d_{(323)}$ of grain A is less than $d_{(123)}$ of grain B, suggesting that atomic density of (323) on grain A is lower than that of (123) on grain B. Because of the large number of dangling bonds on the less-packed planes [12], the atoms on the {323} surfaces are not as well bonded as those on {123} surfaces. It also means that the Zn atoms will attach to the {323} surfaces more easily to {123} surfaces. Therefore, the growth velocity of periodic patterns on {323} of grain A is faster than that on

{123} of grain B. That's why more substrate close to grain A were consumed than that close to grain B. It also agrees well with the general rule relating morphology to growth velocity, which says the fast-growing faces disappear and the slow-growing faces remain [14]. In addition, difference in surface roughness on various crystallographic planes can contribute to the anisotropic growth of periodic layered structure.

3.4 Growth kinetic of interaction layer

Figure 6 (a) presents the width of reaction zones as a function of annealing time at 450 °C. At this temperature the growth of reaction zone starts without any incubation period. The growth velocity is linear with time, implying surface reaction controlled kinetics. The linear growth can also be distinguished by the morphology [15], as shown in Fig. 6 (b), typical “Maltese cross” type figure forms from the sharp corners of the substrate. This differs from that of diffusion-controlled periodic layered structure formation [16-20], where the substrate was completely covered by the reaction layer.

Actually, Rijnders and Loo had reported anisotropy growth of periodic layered structure in Co₂Si/solid zinc diffusion couples annealed at 390 °C, where reaction products were γ_1 (11.0 at.% Co ~ 12.8 at.% Co) at the Co₂Si side, γ_2 (11.0 at.% Co ~ 12.8 at.% Co) at the zinc side and CoSi [20]. In the present study, phase constituents are γ_2 , CoSi and liquid, the γ_1 phase is not evidenced. This may attributed to impact from the physical state of zinc. In the solid state reaction, reaction layer grows parabolic with time, indication diffusion-controlled kinetics [20]. The γ_1 phase is the product of diffusion process. As indicated in Fig. 6 (a), the reaction between Co₂Si / liquid zinc is controlled by interfacial reaction, the liquid phase (or the η -Zn phase in the solidify microstructure) is the main phase in the periodic layered structure.

3.5 Formation mechanism of periodic layered structure

In the ternary diffusion couples, three kinds of morphology, i.e. simply-layered structure, rod-aggregate structure and interwoven-aggregate structure are often observed. In 1982, Osinski found another structure, named periodic layered structure, in Fe₃Si/Zn solid state diffusion couple. δ layer and FeSi phase layer presented periodically in the reaction zone [16]. Till now, the periodic layered structure has been evidenced in the other systems [16-29]. Not only in the solid state reaction [16-24], but also in the solid-liquid reaction [25-28], even solid-vapor reaction [29]. In this kind of structure, phase layers appears periodically in time and space. The periodic pattern can be the assembly of the layer with a single-phase α and a single-phase β , such as in the systems SiC / Ni [21] and Sn / (Ni-7% V)

[22]. And it can also be composed by two-phase layer of $\alpha+\beta$ and single-phase layer of α , as identified in the systems SiO_2/Mg [23] and CuTi/Zn [28]. Apart from above mentioned aspects of periodic layer formation, morphology of periodic layered structure being sensitive to the grain orientation of substrate as revealed in this study deserves attention. Though Rjnders and Loo [20] reported this phenomenon in the Co_2Si and solid Zn diffusion system, and inferred that the anisotropic morphology should be dependent on the crystallographic orientation of the Co_2Si , no quantitative relationship has been established yet.

Up to now, several mechanisms have been proposed for particular cases. The first model proposed by Osinki [16] considered the periodic build-up and release of stressed at the substrate/product interface, which has been employed in the system with “cracks” in the microstructure [16, 23-24]. The second model advised by Kao and Chang [30] proposed a chemical-potential instability model, however, this model did not consider the layers consisting of two-phases. In our group’s series work on periodic layered structure, diffusion-controlled precipitation and growth model was elaborated [25, 27, 31]. In the following discussion, this model has been put forwarded to explain the formation mechanism of alternating layers in the Co-Si-Zn system. Analyses has been conducted with aids of chemical potential diagram calculated by CALculation PHase Diagram (CALPHAD) [32] thermodynamic modeling, with emphasis on the impact of anisotropy growth of periodic layered structure.

The overall process of periodic structure formation at the $\text{Co}_2\text{Si}/\text{Zn}$ interface is described by reaction (3),

As a result, the CoSi and γ_2 phases form simultaneous according to above reaction. Since no stable equilibrium exists between Co_2Si and γ_2 according to the ternary Co-Si-Zn diagram (see Fig. 3), only CoSi can form a layer adjacent to Co_2Si substrate.

Figure 7 schematically shows the evolution of the periodic layered structure formation in the reaction between Co_2Si and liquid zinc at 450°C . When liquid phase contacts with Co_2Si phase, it will react with Co_2Si phase to form D layer. Once a continuous D layer forms on Co_2Si phase surface, its growth will rely on Co diffusion. According to the stability diagram of Co in Co-Si-Zn system at 450°C (Fig. 3 (b)), the chemical potential of Co decreases continuously from Co_2Si phase to the Zn substrate (or η -Zn liquid phase), which is the driving force of Co diffusion. Similar analyses have also

been performed for Si and Zn. Since the Si diffusion direction is opposite to its chemical potential gradient, Si is immobile. Zn also migrates by down-hill diffusion. Since Zn, present in the form of liquid, is highly mobile and easily transport through the reactive zone to the D/B interface, the growth of B layer will depend on the diffusion of Co through the initial-formed D layer (Fig. 4 (a) and Fig. 7 (a)). With the increase of D layer thickness, the diffusion of Co becomes difficult, leading to the slower growth of B layer. Due to higher Zn mobility in D layer than Co [21], Zn diffuses through the initial-formed D layer and enriches at the $\text{Co}_2\text{Si}/\text{D}$ interface. When Zn concentration reaches a critical value of γ_2 nucleation, γ_2 phase will precipitate at the $\text{Co}_2\text{Si}/\text{D}$ interface as shown in Fig. 4 (b) and Fig. 7 (b), leading to Co depletion and Si enrichment. Under this circumstance, CoSi phase will form between γ_2 phase and Co_2Si matrix. With the continuation of γ_2 growth, a new layer pair (D_1 / B_1) will form as presented in Fig. 7 (d) and evidenced in Fig. 4 (c). At the same time, the previous D / B layer pair ceases to grow. With the reaction goes on, as presented in Fig. 7 (d), the D_1 layer becomes thicker, Co diffuses through the D_1 layer becomes more difficult, Zn consumption become less. However, as said before, Zn supply is sufficient, Zn aggregates in the B_1 layer, thus liquid occurs (see Fig. 4 (e)). These processes will repeat and repeat, leading to periodic layered structure formation. Since the formation of periodic layered structure is dependent on crystallographic orientation of the Co_2Si grains, the morphology of periodic layered structure varies.

Though the growth of reaction zone varies linearly with reaction time, formation of periodic layered structure is a diffusion-controlled process. At 450 °C, Zn present as liquid in B layer of periodic pattern, which serves as a fast channel for Zn supply in periodic layered structure formation and growth. This counts for linear growth of reaction layers. Although Co diffusion has a large driving force as shown in Fig. 3 (b), Co supply will depend on decomposition of Co_2Si and transport distance. The diffusion mobility of Co is much lower than Zn [21], which causes limited growth of B layer in periodic layered structure. As layers form periodically, distance of Co diffusion change from 0 to a final D layer thickness periodically and it does not increase with the increasing of periodic layer pairs. For the growth rate of each periodic layer pair is nearly constant, time-dependent growth of full periodic layered structure would be linear. And also, due to grain orientation of Co_2Si substrate, the planes served for periodic layered structure formation differ in dangling bonds and nucleation of γ_2 is influenced in the interface controlled reaction. This will lead to the anisotropy growth of periodic layered structure in the reaction zone.

4. Conclusion

Interfacial reactions between Co₂Si and liquid zinc at 450°C were investigated by means of SEM-EDS and EBSD. The following conclusions can be drawn:

1) Reactions between Co₂Si and Zn at 450°C resulted in the formation of periodic patterns consisting of CoSi / (γ_2 + η -Zn). From the liquid zinc to the Co₂Si substrate, the diffusion path across the interface is liquid / γ_2 / CoSi / liquid / γ_2 / CoSi ... liquid / γ_2 / CoSi / Co₂Si

2) Thickness of periodic pattern varies from 5 μm (minimum) up to 15 μm in the reaction zone, and the width of the CoSi layer is from 0.6 μm to 1 μm . Anisotropy growth of the periodic patterns was attributed to number of dangling bonds on the crystal surfaces.

3) The width of the reaction zone in solid-liquid reaction is linear with annealing time, suggesting a surface reaction controlled kinetics.

4) Mechanisms of the alternating layers' formation, as well as the reaction zone morphology, are explained based on the thermodynamics of the Co-Si-Zn system and diffusion path analysis.

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Figure captions:

Fig. 1: Schematic diagram showing the position of specimens in the EBSD specimen chamber (a) and diagram relating the sample coordinate system to the crystal coordinate system (b)

Fig. 2: backscattered electrons (BSE) image of the Co_2Si alloy dipped in liquid zinc at 450°C for 12 h (a) and XRD patterns of the reaction products (b).

Fig. 3: Calculated (a) isothermal section and (b) stability diagram of Co at 450°C of the Co-Si-Zn ternary system

Fig. 4 : SEM micrographs of reaction zone between Co_2Si and liquid Zn that had reacted at 450°C for (a) 50 minutes, (b) 55 minutes, (c) 60 minutes, (d) 65 minutes, (e) 75 minutes and (f) 80 minutes

Fig. 5: (a) [010] (growth direction) inverse pole figure-map of the Co_2Si substrate and (b) misorientation of two grains close to the Co_2Si / reaction zone interface

Fig. 6: Linear growth of reaction layer of the Co_2Si / Zn diffusion couples reacted at 450°C vs. annealing time (a) and SEM image (b)

Fig. 7: Schematic diagram of the interfacial phase evolution in the $\text{Co}_2\text{Si}/\text{Zn}$ couple reacted at 450°C

Table caption:

Table 1: Crystal structure parameters of the Co_2Si alloy [12]

Table 1: Crystal structure parameters of the Co₂Si alloy [12]

ICSD	Crystal parameters (nm)	Space group	Crystal system
#44858	a=4.918, b=7.109, c=3.738 $\alpha=\beta=\gamma=90^\circ$	Pnam	Orthorhombic

Fig.1(a)

Fig.1(b)

Fig.2(a)

Fig.2(b)

Fig.3(a)

Fig.3(b)

Fig.4(a)

Fig.4(b)

Fig.4(c)

Fig.4(d)

Fig.4(e)

Fig.4(f)

Fig.5(a)

Fig.5(b)

Fig.6(a)

Fig.6(b)

Fig.7