JOURNAL OF IRON AND STEEL RESEARCH, INTERNATIONAL. 2016, 23(11): 1127-1133

Periodic Layered Structure Formed during Interfacial Reaction

Xian-man ZHANG, Hong-feng LUO, Liu-yong SHI

(Institute of Electrical and Mechanical Engineering, Hainan University, Haikou 570228, Hainan, China)

Abstract: A review of the periodic layered structure (PLS) formed during reactive diffusion was presented. The formation of PLS is a very interesting and complex phenomenon during the reactive diffusion process. It was firstly discovered occasionally. The formation of PLS has been reported in various solid state diffusion couples such as Zn/Ni_3Si, Mg/SiO_2, Zn/Cu_xTi_y and so on, and some controversial theoretical models and formation mechanism of PLS were put forward. However, there have been few reports about the PLS formed during hot dip. The development of PLS was reviewed, and the recent progress referring to the formation of PLS during the hot dip aluminizing of a novel Fe-Cr-B cast steel was especially introduced. However, not all of the borides could form PLS in their interfacial reaction with molten Al. PLS only formed at the Cr-rich Fe_2B/Al interface, while Mo-rich Fe_2B fractured. A general qualitative description for the interfacial reaction of Fe-Cr-B cast steel with molten Al was represented. Further investigation on the constituents of the alternating phases and formation mechanism of PLS needs to be done. At last, the development trends of PLS were proposed.

Key words: periodic layered structure; interfacial reaction; reactive diffusion; formation mechanism; Fe-Cr-B cast steel

The interesting periodic layered structure (PLS) formed during interfacial reaction was firstly discovered in 1982 by Osinski et al.[1], where two single-phase layers displayed periodically in the reaction zone of the solid state diffusion couple of Fe_3Si/Zn. Since then, the PLS, which was different from the three common types of morphology (single layered, rod-aggregate structure, interwoven-aggregate structure) formed during a solid state reaction, attracted a lot of attentions from researchers. During the past 30 years, the PLS was observed in many multi-component diffusion couples, and several different theoretical models were reported to explain the formation processing. In summary, the formation mechanism of PLS could be divided into two types: thermodynamic instability and kinetic instability. The PLS formed during reactive diffusion is a complex self-organized structure, and research on the mechanism of PLS is of great importance to design some in-situ multilayer composites, which would have significant potential for the preparation of novel energy conversion materials and magnetic materials. However, the formation of PLS is discovered occasionally, the nature of the formation is not clear, and even some of its formation mechanism remains controversial; most of the materials systems are mainly focused on where solid Zn participated, and the PLS formed in the solid/liquid interface is seldom reported. And the effect of alloying element on the formation of PLS has never been investigated yet. It is therefore highly desirable to learn more about it in order to explore a new material system that can form PLS in the interfacial reaction in future. To the end, some solid diffusion couples were introduced firstly, various materials systems, especially Zn involved, were summarized, and corresponding formation mechanism of the PLS was explained briefly, then the PLS formed at the solid/liquid interface was also presented, some of which were supported by the recent work of the authors. The development trend of PLS was also discussed.

1 Periodic Layered Structure Formed at Solid/Solid Interface

1.1 Solid diffusion couples

Until now, most of the solid state diffusion

Foundation Item: Item Sponsored by National Natural Science Foundation of China (51404084); Scientific Research Foundation of Hainan University of China (hyqd1629); Opening Project of Guangdong Key Laboratory for Advanced Metallic Materials Processing (South China University of Technology) of China (GJ201609)

Biography: Xian-man ZHANG, Doctor; **E-mail**: xianman213@163.com; **Received Date**: May 31, 2016

couples that can form the PLS during diffusion reaction are composed of Zn and other metal, cermet or ceramics, and others conclude Mg-M, Al-M (M represents the phase except the pure metal in the diffusion couple), and so on.

1.1.1 Zn-M

In the Zn-M system, M includes many materials, such as Ni_3Si, Cu_xTi_y, Co_2Si, and so on. And solid state Zn/Ni_3Si diffusion couple has been studied comprehensively. Su et al.[2] discovered the PLS formed in the solid state Zn/Ni_3Si diffusion couple, as shown in Fig. 1, which was composed of Ni_2Zn_3Si (T phase) and Zn_3Ni (γ phase). And the physical state of Zn had no influence on the appearance of PLS, but it had effect on the amount of Zn supplied to the reaction zone and changed the reaction path[3]. The different diffusion coefficients of Zn, Si and Ni were the main reason for the formation of PLS: the pair of T/γ was firstly formed at the Zn/Ni_3Si interface, then Ni atoms accumulated at this interface because of its low mobility; when the concentration of Ni reached a certain critical value, γ phase would nucleate and precipitate from the T phase. The formation of PLS was attributed to the number of the previously precipitated γ particles inside the T phase[4], which was controlled by the thermodynamic instability mechanism. Different from the PLS consisting of single-phase layer, Chen et al.[5] clarified that the PLS in the Zn/Ni_3Si diffusion couple was composed of single Ni_2Zn_{11} phase layer and the two-phase ($Ni_2Zn_{11}+Ni_2SiZn_3$) layer. Furthermore, evident split-off phenomenon existed in the reaction zone, so it was in accordance with the kinetic instability mechanism proposed in the diffusion-induced stresses model. They also used diffusion-induced stresses model to explain the formation of PLS in Zn/Fe_3Si and Zn/Co_2Si systems[6,7]. As for the Zn/Co_2Si system, different patterns were formed on different grains of Co_2Si substrate. Clearly, the morphology and thickness of PLS were strongly dependent on the crystallographic orientation of substrate[8,9]. Generally speaking, the stress resulted from the difference between the interface growth rate of the two phases within the PLS. However, the derivation of theoretical diffusion-induced stresses model was very complicated[9,10]. Chen et al.[11-13] also found the PLS formation during solid state reaction between Zn and Cu_xTi_y (i.e. CuTi, $CuTi_2$, and Cu_4Ti). Besides the Zn/Fe_3Si, Kodentsov et al.[14] also found the PLS in Zn/Co_2Si solid diffusion couples, and they owed the formation of periodic structure to a manifestation of the Kirkendall effect accompanying reactive phase formation. Based on the diffusion thermodynamics, kinetics and diffusion path theory, Wu et al.[15] studied the TiCu/Zn diffusion couples, and three kinds of periodic layers were observed in the reaction zone. The interfacial reactions of FeCr alloys (containing 5, 30, 70 and 95 at.% Cr)/Zn diffusion couples were investigated by Liu et al.[16]. Surprisely, PLSs were observed at the interfaces of Fe-30Cr/Zn and Fe-70Cr/Zn, which were attributed to the periodic thermodynamic instability in these two FeCr alloys. And the PLSs consisted of Cr and Fe-Zn intermetallics.

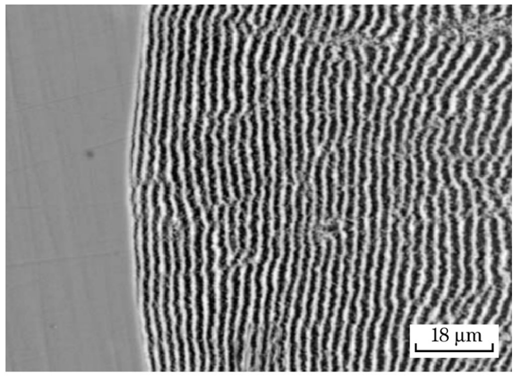

Fig. 1 Periodic layered structure formed in the reactive diffusion zone in Ni_3Si/Zn

1.1.2 Mg-M

According to the evidences available from the literature, the formation of PLS in the Mg-M system is mainly reported on $Mg\text{-}SiO_2$. Gutman et al.[17-20] found PLS formation consisting of alternating MgO and Mg_2Si-rich layers in SiO_2-Mg system, which was the first oxygen-containing system reported to produce a PLS. The growth of reaction zone also obeyed the parabolic law, controlled by Mg diffusion to SiO_2 substrate. Moreover, a qualitative model describing the formation of PLS in the Mg/SiO_2 system was presented based on the Fick's diffusion law and conservation of matter. Chen et al.[21] concluded that the PLS formed in the Mg/SiO_2 system consisted of the single Mg_2Si phase and the two-phase layer of ($Mg_2Si+MgO$), in line with the diffusion-induced stresses model; a quantitative description of this PLS formation was given and the computer simulation results coincided well with the experimental data. Shi et al.[22] also discovered the formation of PLS in the interface of Mg/SiO_2, i.e. the PLS consisted of Mg_2Si and MgO, and the formation mechanism was discussed based on thermodynamics and kinetics. However, there was no PLS forma-