Periodic structures in ternary diffusion couples

PERIODIC STRUCTURES IN TERNARY DIFFUSION COUPLES

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Introduction

During the reaction in the ternary diffusion couples Fe_3Si-Zn and Co_2Si-Zn reactionlayers with periodic structures develop[1]. Fig. 1 and 2 give examples of the observed reactionlayers. The thin bands consist of resp. FeSi and CoSi precipitates and are in fact two-phase bands composed of metal-silicides and metal-zinc intermetallics (see fig. 3). The different "cells" in the reactionlayer of the Co_2Si-Zn couple correspond with different grains in the Co_2Si substrate which points to a relation between the observed periodicity and grain-orientation. Co_2Si has a hexagonal structure. In the Fe_3Si-Zn couple such a relationship is not to be expected because Fe_3Si is cubic. This paper deals only with the results of the Fe_3Si-Zn couples. First we will discuss the diffusion mechanism of the formation of a two-phase band. Finally we will discuss two models which might explain this unusual phenomenon.

Diffusion mechanism of formation of the two-phase band

Zinc is the only diffusing component in the $FeZn_{10}$ ($=\delta$) and $FeZn_{13}$ ($=\zeta$) intermetallic compounds[2]. This means that the two-phase band is formed at the Fe_3Si substrate. With EPMA we were able to measure the total concentration of a two-phase band viz. $Fe_8Si_7Zn_{10}$. When we suppose the two-phase band to be composed of FeSi and $FeZn_{10}$ the molar ratio of these two compounds in a band will be 7:1. (N.B. the stoechiometric ratio is 1:2). We can now draw a diffusionpath[3] of a Fe_3Si-Zn couple on the 395°C Fe-Zn-Si isotherm. This has been done schematically in fig. 4. Every two-phase band in the δ or ζ layer should correspond

with a loop of the diffusionpath into the FeSi-δ and FeSi-ζ two-phase regions. For clarity this has not been drawn in fig. 4.
From fig. 4 we can see that the diffusion path crosses the α-FeSi-δ three-phase triangle to the measured band composition marked by 1 almost horizontally. So there is only a weak Si concentration gradient across the substrate/two-phase band interface and consequently hardly any Si diffusion will occur across this interface. The consequence of this immobility of Si is (see also fig. 5) that when Zn reacts with the substrate at position I the amount of FeSi in the two-phase band will be dictated by the amount of Si in the Fe_3Si substrate. The quantity of δ formed between the FeSi in the two-phase band is now too little to satisfy the mass-balance. So Fe is forced to diffuse through the two-phase band and reacts with Zn at position II to form the δ phase behind the two-phase band. (Note: the δ phase in the two-phase band and the δ phase behind this band are formed in a different way). Thus both half-reactions occuring resp. at I and II are:

$$7Fe_3Si + 10Zn \rightarrow Fe_8Si_7Zn_{10} + 13Fe$$

$$13Fe + 130Zn \rightarrow 13FeZn_{10}$$

The diffusion velocity of Fe through this two-phase band is probably very low, the consequences of which we will discuss in the next chapter.
Summarizing we can say that the main characteristic diffusional features of the reaction in a Fe_3Si-Zn couple are:
- there is a very fast diffusing component viz. Zn
- there is a component which is almost immobile viz. Si
- there is a component which is forced to diffuse but its diffusion velocity is very low viz. Fe.

Discussion

In this section we will give some general remarks on this phenomenon and discuss two models which might explain the observed phenomena.
The question is why the reaction does not proceed by a continuous growth of the different reaction layers but rather proceeds in this disconti-nuous way. This problem has been schematically visualized in fig. 6.

In our view there are two models which can account for the observed phenomena, in both cases it will appear that events at the substrate/ two-phase band interface play an important role.
The first model is that when the two-phase band, which is formed at the substrate reaches a critical thickness it is lifted of the substrate due to mechanical stresses accompanying the growth of the two-phase band. After this lift-off we have a "fresh" surface on which the reaction can start afresh. Experiments in which we used diffusion couples prepared from thin (200μ) Fe_3Si substrates and a vapour-deposited Zn layer as Zn source confirmed this model because a remarkable change in band thickness was observed (see fig. 7). However, the lack of cracks at the interface may refute this model.
The second model is that after a fixed time a sudden formation of the δ-phase occurs at the interface due to an enrichment of Fe (see fig. 8). After this sudden δ formation the whole process of band formation could start from the beginning. This enrichment may arise because the excess Fe which is formed during the development of the two-phase band cannot diffuse away anymore owing to its low diffusion velocity.
We believe that an explanation of the observed phenomena lies in one of these two models or a combination of both.
At the moment other techniques (TEM) are being applied in order to give a more clear image of the processes occuring at the interface.

References

1) K. Osinski, A.W. Vriend, G.F. Bastin and F.J.J. van Loo, Z. Metallkde. 73 (1982) 258.
2) M. Onishi, Y. Wakamatsu and H. Miura, Trans. Jap. Inst. Met. 15 (1974) 331.
3) J.B. Clark, Trans. Met. Soc. AIME 227 (1963) 1250.

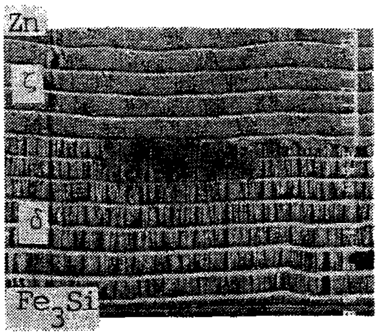

Fig. 1. Fe_3Si-Zn, 24^h, 395°C (BEI) ═══:100μ

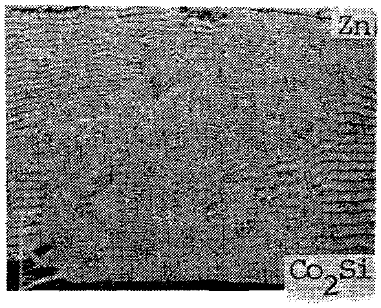

Fig. 2. Co_2Si-Zn, 44^h, 395°C (BEI) ═══:100μ

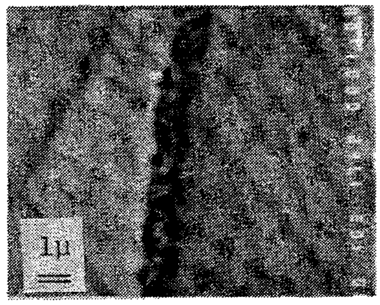

Fig. 3. Magnification of a band in a Fe_3Si-Zn couple

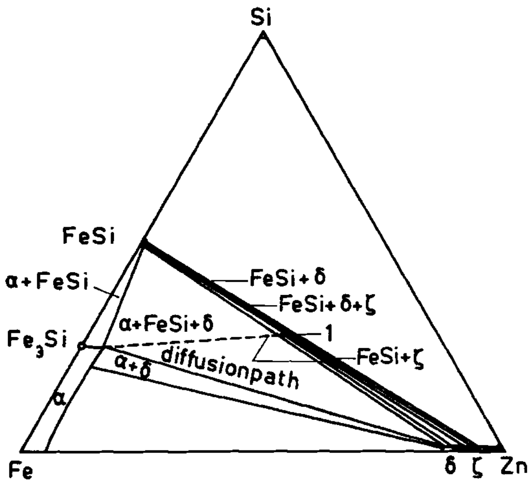

Fig. 4. Fe-Zn-Si 395°C isotherm with diffusion path of Fe_3Si-Zn couple (schematic drawing)

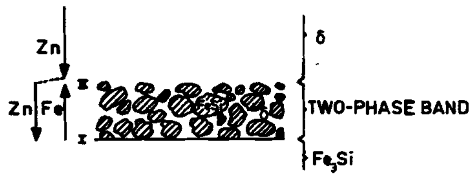

Fig. 5. Diffusion mechanism at Fe_3Si substrate (see also text)

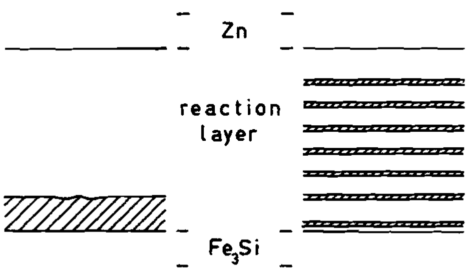

Fig. 6. Expected (left) and observed (right) morphology in Fe_3Si-Zn couple

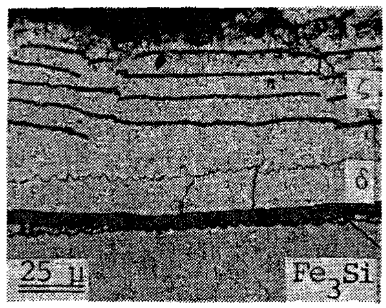

Fig. 7. Thin substrate Fe_3Si-Zn, 20^h, 395°C

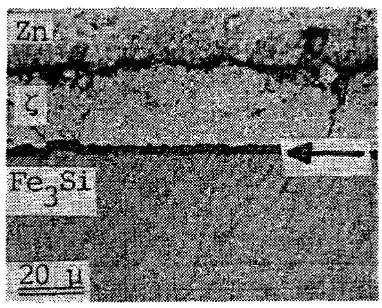

Fig. 8. Fe_3Si-Zn, 2^h, 395°C Supposed sudden δ formation at arrow