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ON THE SEQUENCE OF THE PRODUCT LAYERS IN SOLID-STATE DISPLACEMENT REACTIONS

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Displacement reactions of the type \( A + BX \rightarrow AX + B \) have been investigated. Experiments have been carried out which affirm on the one hand the relation between the phase diagram of the system \( A-B-X \) and the layer sequence in a diffusion couple \( A/BX \), and on the other hand permit to identify the rate-limiting step in the reaction process. To this end one of the reaction products has been applied as an initial layer on one of the couple halves before the heat treatment. In a sandwich couple arrangement the effect of this initial layer on the morphology and thickness of the reaction zone has been directly compared with a true couple \( A/BX \). The couples investigated up to now are Ni/CuO at 1000°C, Fe/Ni3S2 at 460°C and Cu/Ni3S2 at 500°C.

1. INTRODUCTION

In a solid-state displacement reaction of the type \( A + BX \rightarrow AX + B \) the reaction products are formed at the contact interface between A and BX. Fig. 1 shows some possible morphologies if polished faces of discs of the starting materials A and BX are pressed upon each other as a so-called semi-infinite diffusion couple and heated at the desired temperature. The initial sequence of the reaction product layers can be either \( A/AX/B/BX \) or \( A/B/AX/BX \). In some former papers\(^1,2\) we have given evidence that this initial sequence depends upon the shape of the isothermal cross-section of the ternary phase diagram \( A-B-X \). The basic idea is, that an element can only intrinsically diffuse into a direction in which its own thermodynamic activity is lowered. In the phase diagrams as given in Fig. 1, the metals A and B form a complete solid solution, in which the third element \( X \) (metal or non-metal) has an only very limited solubility. The compounds \( AX \) and BX have a small homogeneity range. In Fig. 1a,b) the tie lines between the \( (A,B) \) solid solution and the compounds \( AX \) and BX all have the same sign of slope. This means, that in the two-phase regions \( (A,B)/AX \) and \( (A,B)/BX \) the activity of \( X \) is a continuously decreasing function of the mole fraction of B.

It has been shown\(^1,2\) that in that case the initial layer sequence \( A/AX/B/BX \) develops. Depending on the diffusion mechanism, the straight boundary between the layers \( AX \) and B can become wavy, finally leading to one two-phased layer \( (AX + B) \) (Fig. 1c).

In Fig. 1d,e) the slope of the tie lines from the solid solution \( (A,B) \) towards \( AX \) have a sign different from those connecting \( (A,B) \) with BX. Then, the activity of \( X \) shows a maximum as a function of the mole fraction of \( B \) in the three-phase region \( (A,B)-AX-BX \). It has been shown that in that case basically the layer sequence \( A/B/AX/BX \) develops (Fig. 1f). Sometimes precipitates of \( AX \) in the B-layer are found\(^3\).

The overall growth rate of the layer is governed by the rate-determining step in the process. In a previous paper\(^2\) we have shown that this step can sometimes experimentally be determined by investigating the reaction product layers arising through the gas phase at the side or rear faces of the couple halves. In this paper we describe an experimental method which on the one hand affirms our theory on the relation between phase diagram and layer sequence, and on the other hand permits to find...
Basic morphologies for the reaction zone in the displacement reaction $A + BX \rightarrow B + AX$ in relation to the isothermal cross-sections through the phase diagram of the A-B-X system. In a) and d) the so-called Gibbs triangle is represented; in b) and e) the same phase relations are shown in a rectangular configuration by another choice of variables; in c) and f) the possible morphologies corresponding to the phase diagrams are shown.
FIGURE 2
Phase relations in the systems:
(a) Ni-Cu-O at 1000°C;
(b) Fe-Ni-S at 460°C;
(c) Cu-Ni-S at 500°C.
The crosses represent the diffusion path in
the various diffusion couples.
the rate-determining step in the process. To this end we apply one of the reaction products as a thin layer on one of the couple halves, so that a couple A/AX/BX or A/B/BX is created. After diffusion annealing we investigate the morphology and the thickness of the product layer and compare this with the results of the true couple A/BX. As systems we have chosen Ni/Cu₂O, Fe/Ni₃S₂ and Cu/Ni₃S₂, from which the first preliminary results are presented here.

The phase diagrams of these systems are shown in Fig. 2, from which it can be seen that the system Ni-Cu-O belongs to the phase diagram type given in Fig. 1b), and the other two systems to the type given in Fig. 1e).

2. EXPERIMENTAL METHODS

The preparation of diffusion couples of the type Ni/Cu₂O in Ni or Cu cylinders has been described by Vosters et al. Sandwich couples were prepared in this way at 1000°C, viz. Ni(NiO)/Cu₂O/Ni and Ni/(Cu)Cu₂O/Ni. In the first one a pellet of Cu₂O is pressed between a pure disc of Ni at one side and a preoxidised disc of Ni at the other side. Pre-oxidation had taken place at 1000°C in an oxygen atmosphere, during which an 18-μm thick, regular and pore-free NiO layer was formed.

In the second couple an about 350-μm thick Cu-layer was formed around a Cu₂O pellet by reduction in a CO atmosphere at 1000°C, after which on one side the Cu-layer was ground off. This pellet was then pressed between two pure Ni discs. In this way the influence of the presence of a NiO or Cu layer on the reaction kinetics could be investigated directly by comparison with a true Cu₂O/Ni diffusion couple in the same sandwich couple. Diffusion couples in the sulphidic systems were prepared by clamping the couple halves in a vice as described by van Beek et al.

3. EXPERIMENTAL RESULTS

a. Couple Ni(NiO)/Cu₂O/Ni

In Fig. 3a) a schematic drawing of the diffusion couple after annealing 4 hours at 1000°C is shown. As can be seen, the deposited NiO barrier prevents the reaction between Ni and Cu₂O to a large degree without changing the layer sequence. This proves that the diffusion of Ni²⁺-ions through NiO is the rate-limiting step. This is in agreement with the layered morphology of the reaction products (see Fig. 1c).

b. Couple Ni/(Cu)Cu₂O/Ni

The result after 22.5 hours annealing at 1000°C is shown in Fig. 3b. The equally thick NiO layers on both sides again prove that the diffusion of Ni²⁺-ions through NiO is the rate-limiting step. This is in agreement with the layered morphology of the reaction products (see Fig. 1c).

c. Couple Fe(Ni)/Ni₃S₂/Fe

Fig. 3c) shows the morphology after 140 hours annealing at 460°C. Obviously the Ni-layer deposited on Fe acts as a diffusion barrier: the pentlandite layer is much thinner than in the case of the true Fe/Ni₃S₂ couple, whereas the total (Fe,Ni)-layers are almost equally thick. The Ni-barrier does not influence the layer sequence. This experiment shows, that the diffusion of Fe and Ni through the
FIGURE 3
Schematic representation of the reaction zones in some sandwich couples after diffusion annealing. In the left-hand row the situation is shown in which an extra layer is applied on one of the couple halves prior to the heat treatment. The shaded part shows this initial layer after the diffusion annealing. In the right-hand row the morphologies are represented as found in diffusion couples in which no extra layer has been applied. a) couple Ni(NiO)/Cu2O/Ni, annealed 4 hours at 1000°C. b) couple Ni/(Cu)Cu2O/Ni, annealed 22.5 hours at 1000°C. c) couple Fe(Ni)/Ni3S2/Fe, annealed 140 hours at 460°C. d) couple Cu(Cu2S)/Ni3S2/Cu, annealed 66 hours at 500°C.
(Fe,Ni)-layer is the rate determining step, possibly in ionic form through sulphide channels in this layer.

d) Couple Cu(Cu$_2$S)/Ni$_3$S$_2$/Cu

In Fig. 3d) the morphology is shown of a couple heated 66 hours at 500°C. The deposited Cu$_2$S layer does not influence the layer sequence nor the thickness of the developing (Cu,Ni)-layer. It may thus be concluded that diffusion of Cu- and Ni-ions through Cu$_2$S is very fast, and that the diffusion of Cu and Ni through the (Cu,Ni)-layer is the rate-limiting step, most probably as ions along the sulphide channels present in this layer.

4. CONCLUSIONS

It has been shown, that the layer sequence of the reaction products in displacement reactions is not influenced by the presence of a layer of one of these products at the start of the reaction. This strongly supports the idea that the thermodynamics of the system governs this sequence, more specifically the sign of the slope of the tie lines between the metal phase and the compounds AX and BX. The experimental results immediately show which is the rate-limiting step in the reaction process.

REFERENCES