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Solid-State Displacement Reactions in the Fe-Ni-S and Cu-Ni-S Systems Between 400 and 500°C

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Solid-state displacement reactions of the type $A + BS \rightarrow B + AS$ have been studied in the systems Fe-Ni-S and Cu-Ni-S. In diffusion couples, mainly of the type Fe/Ni₃S₂ and Cu/Ni₃S₂, the layer sequence, morphology, and growth rate of the reaction products have been investigated. The layer sequence of the reaction products in the couples appears to be just the reverse of that found previously in displacement reactions in some couples of oxide systems like Ni/Cu₂O and Co/Cu₂O. We find the sequence A/B/AS/BS, whereas in the oxide systems the sequence A/AO/B/BO has been found. This means that the metal atoms exchange and sulfide ions practically stand still in the first case, whereas in the oxide system the transport of oxygen is essential. For a correct interpretation of the results it was necessary to determine the isothermal cross-section through the Fe-Ni-S system at 460 and 500°C. At 500°C the iron stabilized high-temperature modification β -Ni₃S₂ was found.

KEY WORDS: Fe-Ni-S system; Cu-Ni-S system; displacement reaction; diffusion path; ternary diffusion; multiphase diffusion.

INTRODUCTION

The kinetics of solid-state displacement reactions of the type $pA + B_qX \rightarrow qB + A_pX$ have been extensively studied by Rapp *et al.*¹ for the case where X stands for oxygen. In planar diffusion couples with the metal A and the oxide B_qX as starting materials, they examined the morphologies of the reaction layers and determined their growth rate experimentally. On the

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other hand, they predicted these morphologies and rates from a knowledge of pertinent thermodynamic and diffusion data. Their theory, in fact an extension of the well-known Wagner's oxidation theory, can be summarized as follows.

In the diffusion couple A/B_qX , two reaction product morphologies are possible: a layered structure as shown schematically in Fig. 1a, or an aggregate structure as shown in Fig. 1b. Which of these possibilities will show up depends on the stability of the interface between the products B and A_pX . A perturbation in this interface will disappear if the flux of X atoms through the B layer exceeds the flux of A ions through the A_pX layer, with the result that the layered structure will be stable. If, however, the reverse is true, then an accidental perturbation will grow out, eventually leading to a two-phased aggregate layer of B and A_pX .

From this model Rapp *et al.*¹ and Yurek *et al.*² predicted layer morphologies, which were confirmed by their experiments, and layer thicknesses, which agreed within an order of magnitude. Vosters *et al.*³ also investigated some of these systems and arrived at the same conclusion, although they pointed out the important role of minor impurities on the reaction product morphology and reaction rate. Shatynski *et al.*⁴ applied the same model on displacement reactions in a number of sulfide systems. In all cases they predicted from the foregoing model an aggregate morphology which indeed they found experimentally. However, these experiments were done at temperatures where liquid phases were present in the diffusion couples, which made the results unreliable. We have carried out experiments on these and other sulfide systems at temperatures where only solid phases occur. In this

Fig. 1. Schematic illustration of a displacement reaction $pA + B_qX \rightarrow qB + A_pX$ according to the model of Rapp *et al.*¹

paper special emphasis will be put on the investigation of the couples Fe/Ni₃S₂ and Cu/Ni₃S₂ between 400 and 500°C.

In order to interpret the experimental results it is necessary to know the isothermal cross-sections through the Fe-Ni-S and Cu-Ni-S phase diagrams at the relevant temperatures. Data about the binary systems are given by Romig *et al.*⁵ and Kubaschewsky⁶ on Fe-Ni, Kubaschewsky⁶ on Fe-S, Lin *et al.*⁷ on Ni-S (see Fig. 2), and Sharma and Chang⁸ on Cu-S. The rather simple 500°C cross-section through the Cu-Ni-S phase diagram is given by Moh and Kullerud.⁹ The Fe-Ni-S phase diagram is more intricate. Shewman and Clark¹⁰ give a number of cross-sections at several temperatures through this system with special emphasis on the homogeneity region of pentlandite, (Fe, Ni)₉S₈, and the (Fe, Ni)_{1-y}S phase. The other cross-section data for these two systems were taken from earlier investigations of Kullerud *et al.*^{11,12} Since we found some discrepancies with our experiments, we determined the 460 and 500°C cross-sections between 0 and 50 at.% S by the analysis of equilibrated ternary alloys and diffusion couples.

EXPERIMENTAL METHODS

For the preparation of the various sulfides, we have used Fe powder (1–5 μm Riedel de Haën or Drijfhout, 99.1% purity), Cu powder (Merck 99.5% purity), and S powder (Merck p.a.). The pure compounds Ni₃S₂,

Fig. 2. Temperature-composition diagram for the binary Ni-S system according to Lin *et al.*⁷

NiS, Cu_2S , and $(\text{FeNi})_9\text{S}_8$ were made very simply and successfully by heating the appropriate mixtures of powders of the various elements in a silica tube under a He atmosphere to prevent oxidation. After the exothermal reaction the product was melted in the same tube, except for NiS because of the loss of sulfur at the melting point. The various ternary alloys, which were used for the determination of the isothermal cross-sections through the Fe–Ni–S phase diagram, were made by cold-pressing Fe powder and powders of NiS, Ni_3S_2 , or pentlandite. These pellets were then heated either in a nitrogen stream or in an evacuated silica tube at the appropriate temperature for one week.

For the preparation of the diffusion couples, we used slices of the dense sulfides sawn from bars obtained in the above-mentioned way after a heat treatment at the same temperature as the diffusion annealing. The other couple halves were recrystallized slices of Fe (1 cm diam, 0.15 cm thick from MRC, 99.9%) and Cu (MRC, 99.998%). Couples were made in three different ways: (a) by clamping the couple halves in a vice and heating them in an evacuated silica capsule or in a N_2 atmosphere; (b) by pressing the halves together using a spiral spring in order to keep a constant pressure on the couple during diffusion annealing under a N_2 atmosphere; (c) by means of a vacuum furnace in which a controlled external load can be applied on the couple halves.

After heat treatment the couples were quenched in water when using preparation method (a); the other methods did not permit a rapid quenching procedure. The experimental results were not affected by the origin of the starting materials or the preparation technique used for the diffusion couples. The metallographic preparation of the alloys and couples implied the usual sawing, embedding, grinding, polishing, and etching procedures. The samples were investigated using microscopic, X-ray, and electron microprobe analyses. In the latter case the BAS correction procedure was used for the conversion of relative intensities to concentrations.¹³ Pyrite, FeS_2 , was used as a standard for Fe and S and Ni_3S_2 as a standard for Ni, whereas for Cu the pure element was used. Other standards were also used in order to check the correction procedure, but no important differences were found.

EXPERIMENTAL RESULTS

Phase Relations in the Fe–Ni–S System

We determined the 460 and 500°C cross-sections through the phase diagram by analyzing alloys of the compositions given in Figs. 3 and 4. These results have been supplemented by the investigation of various

Fig. 3. Phase relations and diffusion paths ($\times-\times$ and $\bullet-\bullet$) in the Fe-Ni-S system at 460°C. Triangles and ellipses denote the compositions of the investigated three-phased and two-phased alloys.

diffusion couples, measuring the compositions in adjacent phases, as discussed below. The compositions of the coexisting α - and γ -(Fe, Ni) phases could not reliably be determined because equilibrium was not obtained at these low temperatures. Therefore, these data in Figs. 3 and 4 have been taken from Romig and Goldstein.⁵

Fig. 4. Phase relations and diffusion path ($\times-\times$) in the Fe-Ni-S system at 500°C. Triangles and ellipses denote the compositions of the investigated three-phased and two-phased alloys.

At 500°C we found in equilibrated alloys as well as in diffusion couples an iron stabilized high-temperature modification, β -Ni₃S₂, which could not be retained during the quenching procedure; this phase decomposed into the low-temperature β' -Ni₃S₂ modification, pentlandite, Fe_{4.5}Ni_{4.5}S₈, and γ -(Fe₂₂Ni₇₈). From Fig. 2 it can be seen that in the binary Ni-S system, a high-temperature modification of Ni₃S₂ exists above 522°C. According to Kullerud *et al.*,¹¹ this phase is unquenchable and may dissolve a considerable amount of iron. Obviously the presence of iron extends the stability towards lower temperatures. The dashed lines in Fig. 4 represent parts of the section based on the data of Kullerud,¹² not verified by our experiments. By our techniques it was not possible to detect the presence of a superstructure of ordered FeNi₃. This is, therefore, omitted in Figs. 3 and 4, the more so as the literature data are not consistent in this respect.⁶

Layer Morphology in Fe/Ni₃S₂ and Fe/NiS Diffusion Couples Between 400 and 460°C

The diffusion layer morphology found in the Fe/Ni₃S₂ couples between 400 and 460°C was quite different from the one predicted by Rapp *et al.*¹ and Shatynski *et al.*⁴ In Fig. 5 an optical micrograph is presented showing two reaction layers, viz., a γ -(Fe, Ni) layer containing about 36 at.% Fe and a pentlandite layer of constant composition Fe_{4.5}Ni_{4.5}S₈. Figure 6

Fig. 5. Optical micrograph of the layered product morphology in a diffusion couple, Fe/Ni₃S₂, annealed for 144 hr in a N₂ atmosphere at 460°C.

Fig. 6. Concentration-penetration curves of the elements Fe, Ni, and S in the diffusion couple shown in Fig. 5.

represents the concentration-penetration curves of the three elements; the diffusion path is given in Fig. 3. The sequence of these layers is just the reverse as postulated by Rapp *et al.* in Fig. 1. At large magnifications, scanning electron microprobe pictures show very small sulfur-rich precipitates to be present in the γ -layer, probably along (sub)grain boundaries. X-ray analysis revealed the γ -layer to consist of textureless, small crystallites giving rise to continuous, somewhat diffuse diffraction lines in contrast to the very coarse-grained iron starting material on which the layer grows.

The Fe/NiS couple reacted much faster and was, in fact, not semiinfinite: after 72 hr at 460°C all the NiS had disappeared. The layer sequence was α -Fe/FeS/pentlandite/ Ni_6S_5 /(NiS). The diffusion path is shown in Fig. 3. We tried to make Fe/ Ni_6S_5 couples, but we did not succeed in preparing purely single-phased Ni_6S_5 ; the sample always contained some NiS. The reaction products formed in these couples were, however, interesting because composition analysis enabled us to construct the three-phase field pentlandite/ Ni_6S_5 /(Fe, Ni)S as shown in Fig. 3.

Reaction Kinetics in the Fe/ Ni_3S_2 Diffusion Couple Between 400 and 460°C

In couples of the type Fe/ Ni_3S_2 at 400, 430, and 460°C both the γ -(Fe, Ni) layer and the pentlandite layer grew parabolically with time, although the latter was quite irregular owing to pores and cracks both in this layer and in the adjacent starting material, Ni_3S_2 . The ratio between

the thicknesses of the γ -(Fe, Ni) and pentlandite layers was 0.54 ± 0.08 , as expected from the chemical reaction (discussed below). In Fig. 7 the squares of the γ -layer thickness d are plotted as a function of time for the three temperatures. In Fig. 8 the logarithm of the parabolic rate constant $k_p = d^2/2t$ is plotted as a function of $1/T$, from which the relation

$$k_p = \exp - (3.4 \pm 1) \exp - (16000 \pm 700)/T \text{ cm}^2/\text{s}$$

can be derived, and an activation energy of 133 ± 6 kJ/mole for the growth process is found.

Layer Morphology and Growth in Fe/Ni₃S₂ Couples Between 460 and 600°C

At temperatures above 460°C the reaction zone consisted of a γ -(Fe, Ni) layer containing about 31 at.% Fe and a three-phased layer consisting of pentlandite, β' -Ni₃S₂, and γ -(Fe, Ni). At 470 and 477°C both β' -Ni₃S₂ and γ -(Fe, Ni) were present as precipitates along cracks and grain boundaries of a pentlandite matrix. Above 480°C the three phases were closely intermixed on a fine scale; the overall composition of the layer was about Fe₉Ni₅₁S₄₀. Since this kind of structure is not allowed in solid ternary diffusion couples because of Gibbs' phase rule, we looked for possible

Fig. 7. Plot of the square of the layer width d of γ -(Fe, Ni) vs. diffusion time in Fe/Ni₃S₂ couples.

Fig. 8. Plot of $\log k_p$ vs. $1/T$ for the γ -(Fe, Ni) reaction layer in Fe/ Ni_3S_2 couples. The parabolic rate constant k_p is defined by $k_p = d^2/2t$.

reasons for this behavior. The occurrence of liquid phases can be ruled out at these temperatures, the more so as no melting phenomena was observed in the couples. From the analysis of very rapidly quenched alloys, it turned out that at the diffusion temperature, the layer was indeed single-phased and that on cooling, decomposition took place on a very fine scale (see above). The diffusion path at 500°C is given in Fig. 4. The ratio between the thicknesses of the γ -(Fe, Ni) layer and the " $\text{Fe}_9\text{Ni}_{51}\text{S}_{40}$ " layer was about 0.14 at this temperature. The parabolic rate constant k_p of γ -(Fe, Ni) was $1 \times 10^{-10} \text{ cm}^2/\text{s}$.

Layer Morphology and Growth in Cu/ Ni_3S_2 and $\text{Cu}_{70}\text{Ni}_{30}/\text{Ni}_3\text{S}_2$ Couples at 500°C

The diffusion layer sequence in the Cu/ Ni_3S_2 couple was in line with the one found in the Fe/ Ni_3S_2 couple (Fig. 9). Concentration-penetration curves are given in Fig. 10, whereas the diffusion path is shown in Fig. 11. The thickness ratio between the (Cu, Ni) layer and the Cu_2S layer was 1 ± 0.1 . The latter layer was quite irregular but dense, contrary to the pentlandite layer in Fe/ Ni_3S_2 couples. The parabolic rate constant of the (Cu, Ni) layer was about $1 \times 10^{-11} \text{ cm}^2/\text{s}$, although it was not as reproducible as the γ -(Fe, Ni) layer in the Fe-Ni-S system. The (Cu, Ni) layer had no fixed composition; a clear concentration gradient was present, giving rise to an average content of about 60 at.% Cu. The sulfide precipitates in the (Cu, Ni) layer were larger than in the γ -(Fe, Ni) layer and microscopically

Fig. 9. Optical micrograph of a Cu/Ni₃S₂ couple, annealed for 48 hr at 500°C in an evacuated silica capsule.

Fig. 10. Concentration-penetration curves of the elements Cu, Ni, and S in the diffusion couple shown in Fig. 9.

Fig. 11. Phase relations and diffusion path (x-x) in the Cu-Ni-S system at 500°C.

visible, especially near the boundary with Cu and along the grain boundaries. The grains in the (Cu, Ni) layer were much smaller than those in the Cu starting material, but larger than those in the γ -(Fe, Ni) layer discussed above.

In order to gain an insight into the reaction kinetics, we also investigated some couples of the type $\text{Cu}_{70}\text{Ni}_{30}/\text{Ni}_3\text{S}_2$. We found a Cu_2S layer with a thickness of about $\frac{1}{3}$ of the layer formed in a Cu/ Ni_3S_2 couple during the same annealing time, and a (Cu, Ni) layer with a concentration varying between 70 and 37 at.% Cu. This layer could be distinguished from the $\text{Cu}_{70}\text{Ni}_{30}$ starting material because of the much smaller grain size and the small sulfide precipitates along the grain boundaries. Its thickness was about the same as found in Cu/ Ni_3S_2 couples for comparable annealing times.

DISCUSSION OF THE LAYER SEQUENCE, MORPHOLOGY, AND GROWTH RATE IN Fe/ Ni_3S_2 AND Cu/ Ni_3S_2 COUPLES

We will focus our discussion on the couples in which the following reactions occur:

where the numbers under the reactions are the calculated volume ratios. In all cases the reaction products appear as single-phased layers bounded by planar interfaces, apart from the small sulfide precipitates in the grain boundaries of the metallic product layer. The experimentally found thickness ratio of the metallic and sulfidic layers is in agreement with calculations based on the chemical reactions given above, using the appropriate molar volumes. From the volume data it can be seen that Cu_2S occupies a larger volume than the original Ni_3S_2 , contrary to the pentlandite phase in the Fe-Ni-S system. This difference undoubtedly accounts for the difference in porosity between the Cu_2S and pentlandite layers.

In relation to the layer sequence and morphology two questions arise. Why are they different from the results found and predicted by Shatynski *et al.*,⁴ and why are they different from those found in displacement reactions on oxides by Rapp *et al.*¹ and Vosters *et al.*?³ The first question can be answered quite easily. Shatynski *et al.*⁴ performed their reactions in sulfidic systems at temperatures at which liquid phases are formed in the diffusion couples. This leads to intricate structures in noninfinite couples, further complicated by transitions occurring during the cooling procedure. The morphology found by them in the reaction layers cannot, therefore, be simply related to or predicted from the solid-state model as given in Fig. 1.

The second question is far more interesting. Obviously, with Rapp's model in Fig. 1, a third possibility has been overlooked. In Fig. 12 a scheme is represented of the basic structures which are possible in displacement reactions; several morphological variants may occur in the two-phased aggregate structure as discussed by Rapp *et al.*¹ and Yurek *et al.*² Obviously, an initial layer sequence $A/A_pX/B/B_qX$ can lead to the development of a two-phased layer, $B + A_pX$, dependent on the various component fluxes. The initial layer sequence, $A/B/A_pX/B_qX$, however, does not lead to such a two-phased layer: the element X does not diffuse, and at the interfaces only an exchange of the elements A and B occurs.

In continuation of this paper we present in a separate, more general article a model stating that the initial layer sequence is a consequence of the thermodynamic properties of the system.¹⁴ More specifically, the immobility of the element X is related to the activity of this element: an element does not diffuse against its own activity gradient. In our case this means that sulfur practically stands still and the metallic elements diffuse.

Concerning the layer growth, it can be seen from Fig. 12 that the rate controlling step is either the interdiffusion of the metal atoms in the metallic product phase or the interdiffusion of the metal ions through the sulfide product layer, depending on which of these is the slowest process. It is clear that at these low temperatures interdiffusion in the metallic phase is by far the slowest. In fact, one can calculate that the layer thickness cannot

Fig. 12. Basic morphologies for the reaction zone in the displacement reaction $pA + B_qX \rightarrow qB + A_pX$. For more details see van Loo *et al.*¹⁴

exceed $1\ \mu\text{m}$ if pure volume diffusion is involved. However, from our experiments it can safely be concluded that the diffusion through the metal phase proceeds along the (sub)grain boundaries. Bastow and Wood¹⁵ assume that the bulk diffusion coefficient of Cu^+ through Cu_2S is 10^9 times larger than the grain boundary diffusion of the metal atoms in a Cu-Ni alloy. From this value it follows that the effective diffusion through the metal layer, which is a linear combination of the volume and the grain boundary diffusion,¹⁶ is the rate controlling step. This means that the overall layer growth is dependent on the grain size in the (Fe, Ni) or (Cu, Ni) layers. The grain size in the (Fe, Ni) phase is very small compared to the layer thickness which leads to a reproducible growth rate. In the Cu-Ni-S system the mean grain size in the (Cu, Ni) layer is larger and variable for every couple, which makes the material transport more dependent on this grain size and, therefore, less reproducible. In both systems, sulfur probably diffuses in ionic form through these grain boundaries, giving rise to sulfide precipitates.

This kinetic model is substantiated by the experiments on $\text{Cu}_{70}\text{Ni}_{30}/\text{Ni}_3\text{S}_2$ couples. If the transport through Cu_2S had been rate determining, then an equally thick Cu_2S layer should have formed in $\text{Cu}_{70}\text{Ni}_{30}/\text{Ni}_3\text{S}_2$ and $\text{Cu}/\text{Ni}_3\text{S}_2$ couples under equal circumstances. We find,

however, an almost equally thick (Cu, Ni) layer, and a much thinner Cu_2S layer in the first couple, leading to the conclusion that the transport through (Cu, Ni) is the rate controlling step.

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