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PHASE RELATIONS AND DIFFUSION PATHS IN THE SYSTEMS Cu-Ni-O AND Cu-Co-O AT 1000°C

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ABSTRACT

Morphology and composition of diffusion layers formed in multiphase ternary diffusion couples of the systems Ni-Cu-O and Co-Cu-O have been investigated by electronprobe microanalysis, X-ray diffraction and optical microscopy. Phase relations and diffusion paths are plotted on the isothermal sections of the ternary phase diagrams and discussed.

INTRODUCTION

Dalvi and Coates [1] reviewed the applicability of the diffusion path concept to the high-temperature oxidation of binary alloys, starting from alloy-oxygen interface studies. A different approach was followed by Rapp, Ezis and Yurek [2], who reported work on displacement reactions in metal-metaloxide systems. Our work is also based on the interactions of a metal or binary alloy with an oxide in multiphase ternary diffusion couples.

An important purpose of our work is to gain insight into the factors that determine the course of a diffusion path. For one particular couple nature always chooses one particular path. Let us consider this phenomenon more closely. Figure 1 shows the isothermal section of the hypothetical ternary phase diagram ABC. If we consider binary diffusion of a couple A/C, two intermediate phases will appear viz. A_2C and AC. The thicknesses of these layers are not interdependent. Suppose that the diffusion in AC is much faster than in A_2C . This means

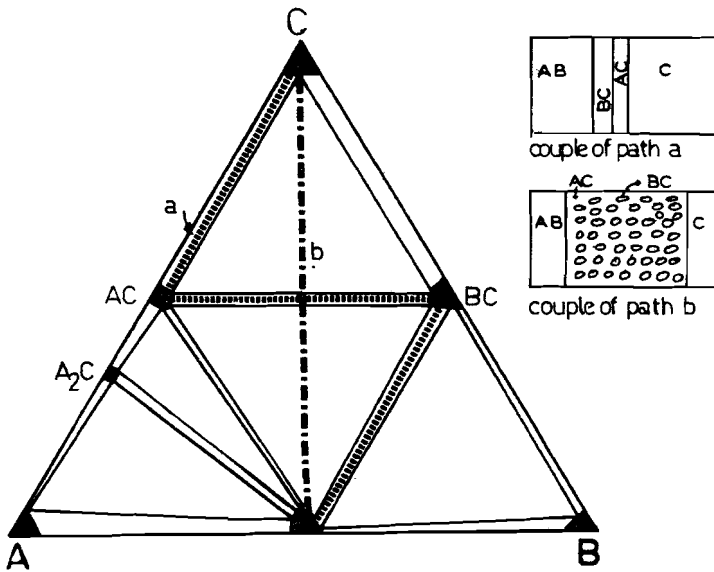


Fig. 1. Hypothetical ternary phase diagram ABC.

that the diffusion layer AC will be much thicker than A_2C in the case of a couple A/C.

Now consider a ternary diffusion couple AB/C and suppose, that diffusion in BC is equally slow as in A_2C . A number of diffusion paths are possible of which we plot two extremes. Path a represents the situation of two single-phase diffusion layers AC and BC. Path b represents the situation of a two-phase diffusion layer. The reaction product layer in case b is much thicker than the one in case a. This arises from the fact that in case b the fast diffusion through AC is rate-determining. In case a, however, the thicknesses of AC and BC are interdependent according to the followed displacement reaction. Therefore, the slow diffusion through the BC-layer is rate determining. Kirkaldy and Brown [3] suggest that "high-resistance series configurations" are favoured. In the case of AB/C this means that path a would be favoured. However, in literature there is a large number of cases described corresponding to path b. Yurek et al [4], for instance, found for the reaction between Fe and Cu_2O completely interwoven and continuous reaction products. They postulate that the product-morphology is such that the atom or ion fluxes through the reaction products are maximized. The systems Cu-Ni-O and Cu-Co-O are eminently suited for this kind of studies because of the relative simplicity of their phase diagrams at $1000^{\circ}C$. An advantage of the diffusion couple technique is that by analysing the co-existing

compositions a refinement of the isothermal section of the phase diagram is obtained.

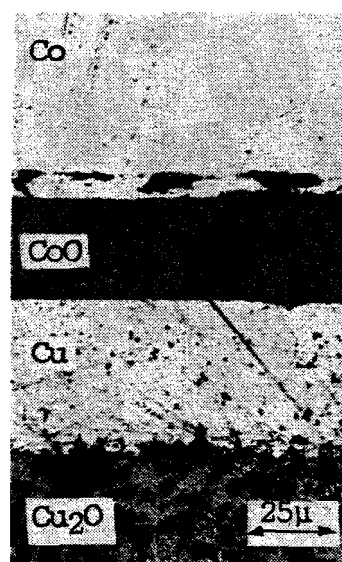
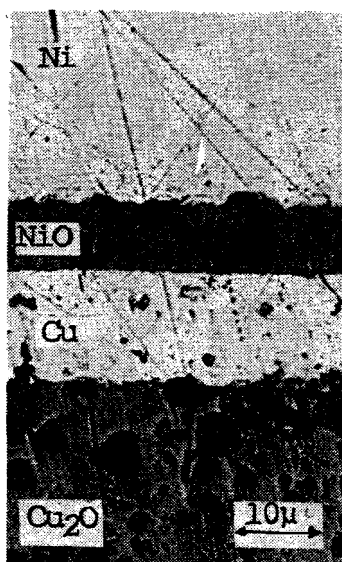
TECHNIQUE

The experimental technique of preparing the diffusion couples is extensively described in [5] where we reported work on phase relations in the system Fe-Cr-O at 1200°C. We will repeat this method briefly here. A polycrystalline pellet or powder of Cu₂O was compressed in a small cylinder of Ni, Cu or stainless steel together with a sheet of the metal Co or Ni or alloys of Cu and Ni. To avoid reaction of the Cu₂O with the cylinder material, the starting materials were wrapped in Pt foil.

The starting materials used were Ni 99,99% (M.C.R.), Cu 99,99% (Preussa) and Cu₂O (Merck).

RESULTS

Table 1 shows a survey of the investigated couples. All couples were reproducible. Figures 2 and 3 show photomicrographs of the morphology of couples I and II. It is clear that both reaction products have a layered arrangement. The ratios of the thicknesses, NiO/Cu and CoO/Cu, are in excellent agreement with the theoretical ratios. This is due to the fact that our



couples are annealed in closed systems so no additional oxygen can enter the reaction interface. Figures 4 and 5 show the

Table 1. Layers sequence and morphology of diffusion couples after annealing at 1000°C

No.	Starting materials (at. %)	Annealing time (h)	Morphology	Layer-sequence
I	Ni/Cu ₂ O pellet	20	single-phase layers	Ni/NiO/Cu/Cu ₂ O
II	Co/Cu ₂ O pellet	20	single-phase layers	Co/CoO/Cu/Cu ₂ O
III	Ni/Cu ₂ O powder	4	two-phase layer	Ni/NiO + Cu(Ni)/Cu/Cu ₂ O
IV	Co/Cu ₂ O powder	4.5	two-phase layer	Co/CoO + Cu(Co)/Cu/Cu ₂ O
V	Ni-Cu (74/26)/Cu ₂ O pellet	21	single-phase layers	NiCu/NiO/Cu/Cu ₂ O
VI	Ni-Cu (50/50)/Cu ₂ O pellet	21	intermediate	NiCu/NiO + CuNi/Cu ₂ O
VII	Ni-Cu (27/73)/Cu ₂ O pellet	21	two-phase layers	NiCu/NiO + CuNi/Cu ₂ O

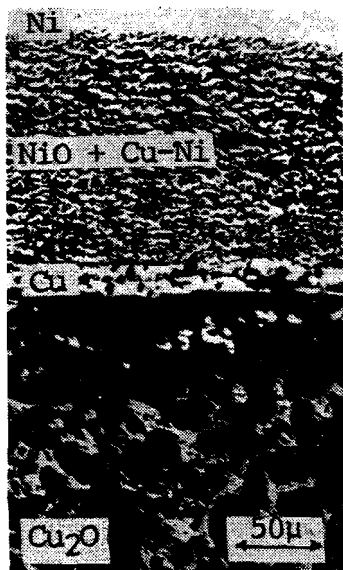


Fig. 4. Ni/Cu₂O powder.



Fig. 5. Co/Cu₂O powder.

morphology of couples III and IV. In these couples a striking difference is noticed with respect to the couples I and II. The reaction diffusion products have a clear two-phase aggregate microstructure and the reaction rate is much larger. In couples I and II the Cu₂O starting material was pretreated and sintered at 1000°C in a partial oxygen pressure of 8×10^{-2} atm and 10^{-5} atm, respectively, for 3 hours. After that, these pellets were quenched to room temperature. In couples III and IV the Cu₂O starting material was not pretreated. In Figs. 6a and 6b the diffusion paths of the couples mentioned above are plotted.

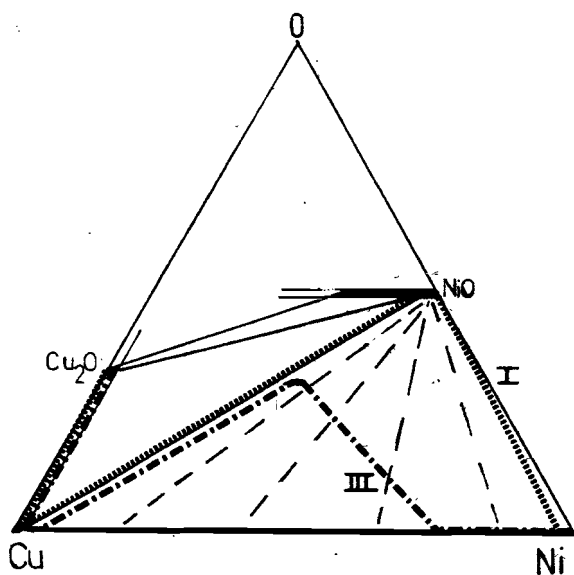


Fig. 6a. Ternary phase diagram Cu-Ni-O with diffusion paths.

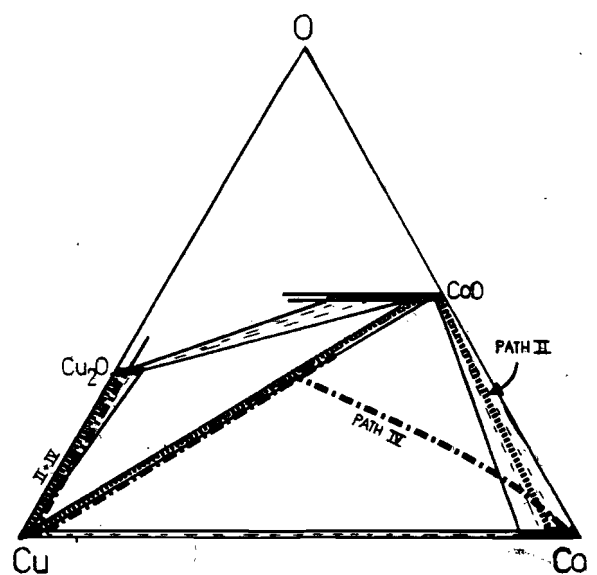


Fig. 6b. Ternary phase diagram Cu-Co-O with diffusion paths.

We also determined the interactions of Cu-Ni alloys with Cu_2O in ternary diffusion couples. Figures 7, 8 and 9 show the microstructure of the reaction products of three different alloys of Ni-Cu vs. Cu_2O pellets. The Cu-Ni alloys of these couples V, VI and VII were prepared in an argon-arc furnace. The Cu_2O pellets were sintered at 1000°C for 3 hours with $p\text{O}_2 = 3 \times 10^{-2}$ atm.

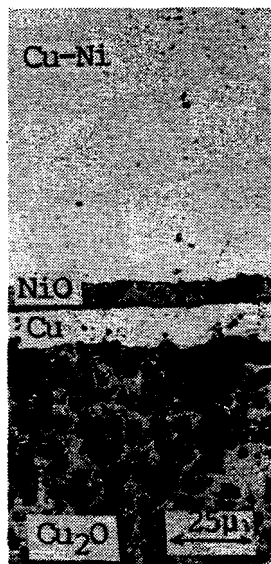


Fig.7. $\text{Cu}_2\text{O}/\text{Cu-Ni}$
(27/73).

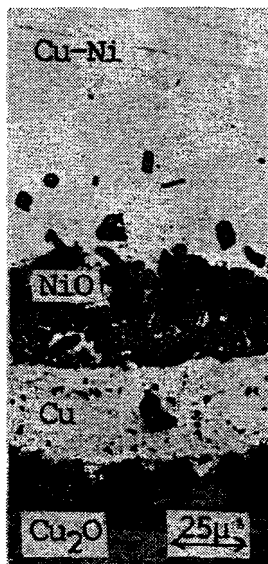


Fig.8. $\text{Cu}_2\text{O}/\text{Cu-Ni}$
(50/50).

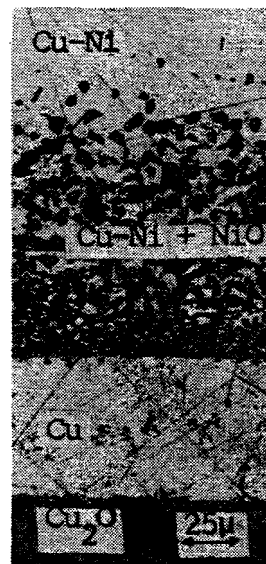


Fig.9. $\text{Cu}_2\text{O}/\text{Cu-Ni}$
(74/26).

DISCUSSION

The investigations give reliable information on phase relations in the systems and on the courses of diffusion paths. The study of the transition of a layered morphology to a two-phase structure is very interesting in the scope of the diffusion path concept. In the Cu-Ni-O system we see a transition of layered to aggregate structure for couples of Cu_2O vs. Cu-Ni alloys, with increasing Cu content. This can be compared with the phenomenon of internal oxidation in binary alloys. In couples I up to IV inclusive, a different effect is observed. We have found that the transitions of the layer-morphology in the couples I to III and II to IV are due to differences in preparation of the Cu_2O . For instance, it is known that the oxygen content of Cu_2O strongly depends on the preparation conditions. An excess of oxygen in the Cu_2O might form a diffusion barrier of NiO which can account for a low reaction rate and a layered microstructure. To solve this problem, further experiments are in progress.

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DISCUSSION

N. Birks. By pre-oxidizing a nickel sample to produce a thin surface layer of NiO and pelletizing this with your "normal" Cu₂O powder, it would be possible to check if the presence of such a layer caused by the effect found with "oxidized" Cu₂O could be reproduced. If so, this would confirm that the one-phase, layered, structure forms when a diffusion barrier is present in the nickel surface. Have you tried this?

M.A.J.Th. Laheij. Indeed, we have tried to do this but it is difficult to produce a thin layer of NiO on Ni without cracks and pores. Through these pores and cracks the reaction with "normal" Cu₂O proceeds and produces a two-phase morphology. Following your suggestions we succeeded in making better and denser NiO surfaces on Ni samples. But our samples are compressed in a reaction vessel in order to make good diffusion couples. During pressing cracks are formed. We found that in these couples there was a tendency to develop one-phase layers and that the reaction rate decreased sharply.

It is important to note here that by putting a Ni sample with a NiO surface layer versus Cu₂O we have introduced a new couple namely NiO/Cu₂O. So it is not fully correct to compare the results of this couple with those of the couple Ni/Cu₂O. We think that we can avoid this problem by plating the Cu₂O with Cu so that we start our annealing procedure with the couple Ni/NiO/Cu/Cu₂O. Experiments on this are in progress.