The Influence of Impurities on the Kinetics and Morphology of the Displacement Reaction Between Ni or Co and Cu₂O

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By use of models given by Wagner and extended by Rapp et al., a layered structure is predicted for the reaction products resulting from the displacement reaction in diffusion couples (Ni–Cu₂O or Co–Cu₂O). Experiments at 1000°C confirm these predictions. However, when Cu₂O is contaminated with chlorine, the morphology changes completely from a layered to an aggregate structure. It is shown that the resulting increase in layer thickness can be well described by assuming that the diffusion of oxygen through the Cu matrix is the rate-determining step. This behavior is compared with the phenomenon of internal oxidation of Cu–Ni alloys.

INTRODUCTION

In 1980 we presented measurements of phase relations and diffusion paths in the systems Cu–Ni–O and Cu–Co–O at 1000°C.[1] These data were obtained from studies of the displacement reactions in diffusion couples of, for example, Ni–Cu₂O and Co–Cu₂O. Earlier these systems were investigated by Rapp et al.[2] Rapp et al. were especially interested in the morphologies and the reaction rates of the displacement reactions. For this purpose they extended the theory of oxidation kinetics of Wagner,[3] with

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the purpose of predicting the morphologies and reaction rates from a knowledge of pertinent thermodynamic and diffusion data. This theory can be summarized as follows.

Consider a displacement reaction of the type

$$y\text{Me} + \text{M}_x\text{O} \rightarrow \text{Me}_y\text{O} + x\text{M}$$
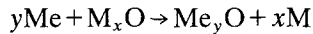
involving the metals Me and M and their lowest oxides. In the diffusion couple Me–M_xO two possible reaction product morphologies are possible: (1) a layered structure (as shown schematically in Fig. 1b), or (2) an aggregate structure (cf. Fig. 1c).

The criterion for the development of either of these structures can be derived from a consideration of Fig. 1a. Here, the interface between the M–Me_yO layers is tentatively assumed to be wavy. It is assumed that there is local equilibrium along the interfaces and that the reaction kinetics is determined solely by the diffusion rates of the reacting species in the product phases. If the diffusion of cations in Me_yO is rate-limiting, then the flux of Me^{z+} at position I exceeds the flux at position II. This leads to a flat interface between M and Me_yO. In case the oxygen ion flux in Me_yO is larger than the cation flux, the result is again a flat interface but now the Me_yO growth occurs at the interface Me_yO–Me.

If the growth of the Me_yO phase is limited by the oxygen diffusion in the M layer, the oxygen flux at position II will exceed the flux at position I. In that case a flat interface is unstable and the existing irregularities are reinforced. In the limiting case a lamellar structure of M and Me_yO results.

Four different couples were studied by Rapp *et al.*, viz. Ni–Cu_2O, Co–Cu_2O, Fe–Cu_2O, and Fe–NiO. After heat treatment at 1000°C the first two couples showed reaction layers with flat, parallel interfaces, while the
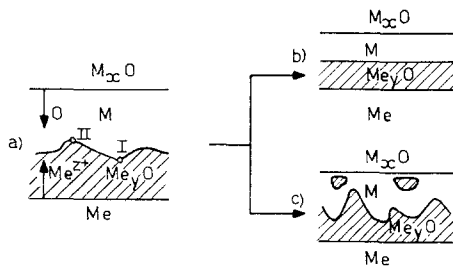

Fig. 1. Schematic illustration of the development of a layered morphology (b) or an aggregate morphology (c) for a displacement reaction with a wavy interface (a). Case (b) develops from (a) when $J^{\text{Me}_y\text{O}}_{\text{Me}^{z+}} < J^{\text{M}}_{\text{O}^{2-}}$; case (c) develops from (a) when $J^{\text{Me}_y\text{O}}_{\text{Me}^{z+}} > J^{\text{M}}_{\text{O}^{2-}}$.

latter two couples exhibited aggregate structures. These results correspond with the predictions of the model mentioned above.

For the layered arrangement the model also gives a quantitative expression for the layer thickness d of Me_yO as a function of time t:

$$d^2 = 2k_p t \tag{1}$$

where the parabolic rate constant is given by

$$k_p = \frac{1}{2} \int_{P'_{O_2}}^{P''_{O_2}} \frac{z_{cat}}{|z_{an}|} D^*_{cat} d \ln P_{O_2} \tag{2}$$

Here, D^*_{cat} is the self-diffusion coefficient for cations in Me_yO, z_{cat} and z_{an} are the valencies of cations and anions in Me_yO, and P'_{O_2} and P''_{O_2} are the oxygen activities at the $Me-Me_yO$ and Me_yO-M interfaces, respectively.

Several years ago we started a study of phase relations and diffusion paths in ternary systems. Within this framework we also investigated the systems Cu–Ni–O and Cu–Co–O, using the diffusion couple technique. In a number of experiments we obtained results similar to those of Rapp *et al.*, with a layered morphology. However, in other experiments with the same components, we obtained a two-phase aggregate microstructure. The purpose of the present investigation is to show how the morphologies of reaction layers can be influenced.

EXPERIMENTAL PROCEDURE

The experimental technique of preparing diffusion couples differs from the method usually cited in the literature. Details were reported in earlier work[4]; therefore, only a brief summary will be given here. For couples of Ni–Cu_2O or Co–Cu_2O a sheet of Ni or Co was pressed against a sintered pellet or powder of Cu_2O in a metal cylinder (Fig. 2). We used Cu, Ni, or stainless steel for the cylinder. To avoid reaction of the oxide with the cylinder material, the starting materials were sometimes wrapped in Pt foil. Both sides of the metal sheets were ground and polished. After compaction with 300–400 MPa, the cylinder was annealed at 1000°C in an evacuated quartz glass capsule. After annealing and water quenching, the cylinders were sawed perpendicular to the sheet surface. Samples were impregnated with epoxy resin, ground, and polished before examination with a Reichert MeF2 microscope and a 733 JEOL Superprobe electron microprobe.

Ni sheets were prepared from a rod (M.R.C., purity 99.97%), Co sheets were bought as such (M.R.C., purity 99.9%). The Ni sheets were annealed for 60 hr at 1275°C in wet H_2 to remove traces of carbon and to promote recrystallization. Cu_2O powder was obtained from different suppliers: Cu_2O(I) (Merck, pure); Cu_2O(II) (Riedel de Haen, p.a.).
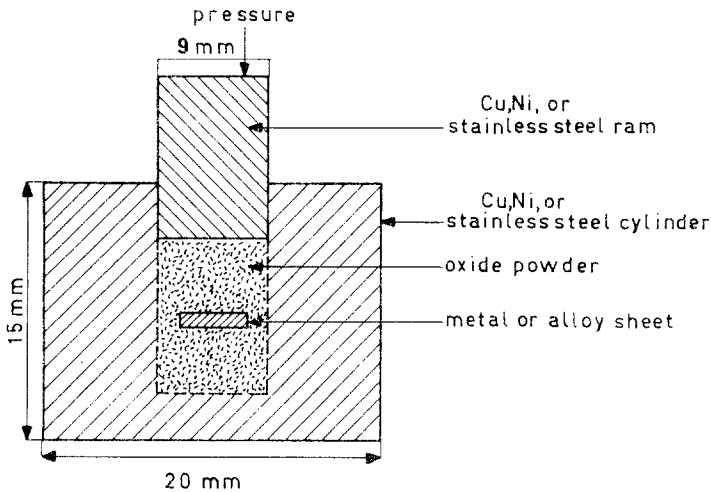
Fig. 2. Longitudinal section through the metal cylinder used for the displacement reaction.

Experiments were also performed with single-crystal Cu_2O and with Cu_2O grown on Cu sheet (Preussag, purity 99.98%) by annealing at 1000°C, for 64 hr in a partial oxygen pressure of 10^3 Pa. As discussed below, $Cu_2O(II)$ was suspected to contain Ca and Cl impurities. A Ca analysis was performed after dissolving the powder in HCl with the aid of ICP emission spectrometry; Cl was determined spectrophotometrically after dissolution in H_2SO_4.

EXPERIMENTAL RESULTS

As mentioned in the introduction, in some cases a layer structure was observed, and in other cases an aggregate structure was found. In couples with a layered structure the layer sequence is $Cu_2O–Cu–NiO–Ni$ or $Cu_2O–Cu–CoO–Co$, respectively. In couples with an aggregate structure the reaction layer consists of an oxide phase dispersed in a metal matrix, for example, NiO in Cu–Ni. Results are shown in Figs. 3 and 4. Though it is difficult to see on Fig. 4, there is a sharp boundary between the Co and the Cu matrix of the aggregate layer, whereas there is a gradual transition in the $Ni–Cu_2O$ couple. This is due to the limited miscibility between Co and Cu in contrast with the complete miscibility of Ni and Cu.

To obtain more insight into the factors influencing layer morphology, reaction conditions were varied systematically. It was soon found that couples with $Cu_2O(I)$ gave parallel reaction layers, while couples with $Cu_2O(II)$ gave variable results.
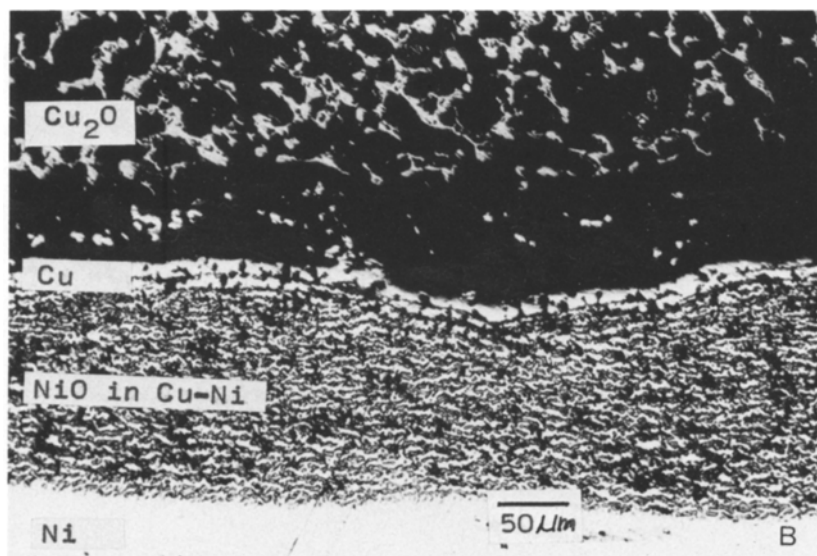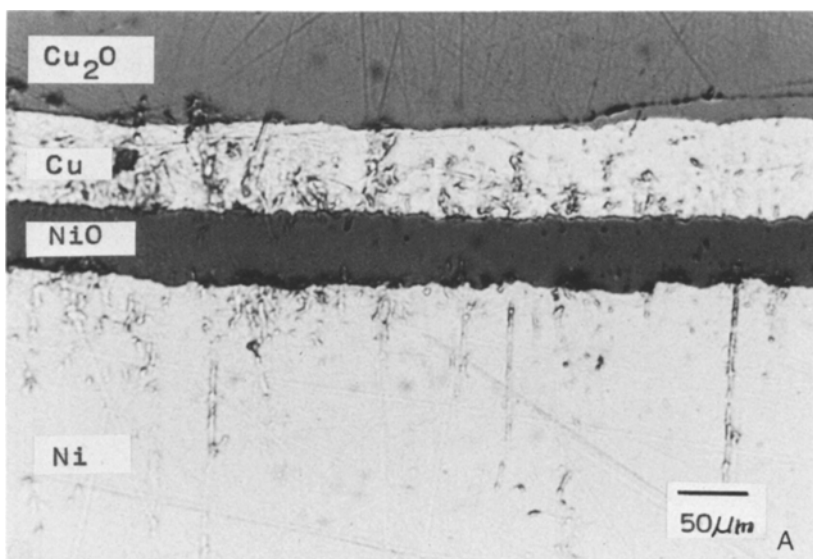
Fig. 3. Photomicrograph of Cu_2O–Ni couples. (a) Layered morphology; (b) aggregate morphology.
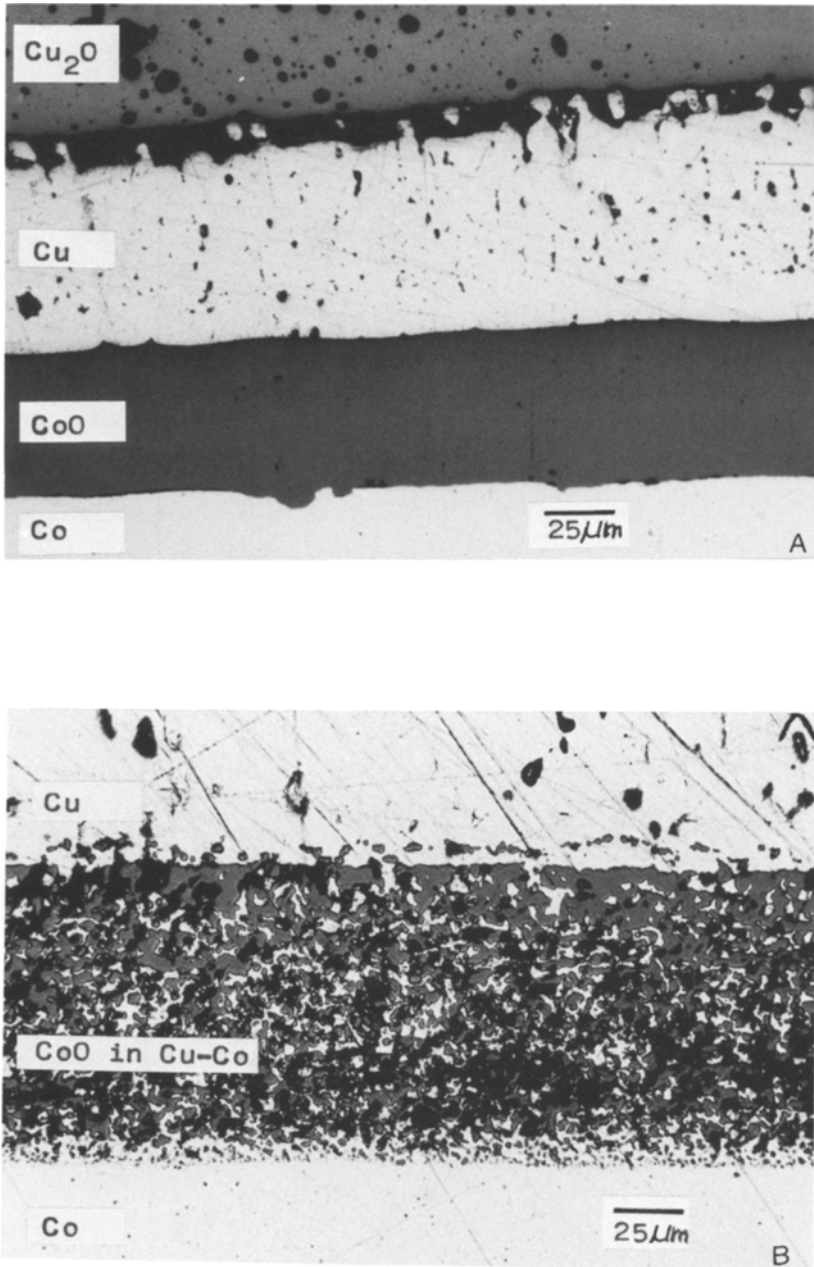
Fig. 4. Photomicrograph of Cu_2O–Co couples. (a) Layered morphology; (b) aggregate morphology.

Influence of the Cu_2O Stoichiometry and Density

According to thermodynamic data, at 1000°C the equilibrium oxygen pressure at the Cu–Cu_2O boundary is 4.9×10^{-2} Pa, and $1.2 \times 10^{+4}$ Pa at the boundary Cu_2O–CuO.[5] Therefore, the oxygen content is dependent on the pretreatment of the Cu_2O used.

Some experiments were performed with sintered $Cu_2O(II)$ pellets. By sintering under different oxygen activities, samples were obtained with densities ranging from 60% (3 hr at 1000°C in $P_{O_2} = 3 \times 10^3$ Pa) to 92% (3.5 hr at 1070°C in $P_{O_2} = 1$ Pa). The pellets were cooled rapidly by withdrawing them from the hot zone of the furnace. Some samples were cooled under the sintering ambient atmosphere; others were cooled under a flow of CO. Even under these circumstances, in some cases a surface layer containing CuO is formed, as shown by X-ray diffraction. Whether this surface layer is removed or not, parallel layers Ni–NiO–Cu–Cu_2O are observed in diffusion couples of Ni vs. sintered $Cu_2O(II)$.

Also, couples starting with single-crystal Cu_2O vs. Ni (or Co) invariably give parallel reaction layers. Finally, experiments were performed with 99.99% Cu sheets covered with a layer of Cu_2O, produced by heating for 64 hr at 1000°C in $P_{O_2} = 10^3$ Pa. Again, parallel layers were formed.

The conclusion is that neither the density nor the oxygen content of the Cu_2O starting material influences the layer morphology.

Influence of Impurities

When Cu_2O powder was used, a difference was observed between $Cu_2O(I)$ and (II). The Cu_2O from supplier II gave an aggregate morphology when used as such, and a layered morphology when the powder was annealed (or sintered) prior to the use in a diffusion couple. The Cu_2O from supplier I invariably gave parallel reaction layers. An electron microprobe analysis shows that Ca and Cl segregate near the Cu–Cu_2O interphase in a couple with aggregate morphology (Fig. 5). A chemical analysis of the oxide powders confirmed the presence of Ca and Cl impurities in $Cu_2O(II)$ (Table I). After annealing $Cu_2O(II)$ the chlorine has disappeared. Since the annealed powder also shows a normal behavior in a diffusion couple, we assume that Cl is responsible for the change in morphology.

To confirm this hypothesis, annealed Cu_2O powder was mixed with other compounds. The following results were obtained.

1. A couple of Ni–$(Cu_2O + 0.5$ wt.% $CaCl_2)$ gave an aggregate structure. NiO precipitates were found, dispersed in a metal matrix consisting of Cu enriched in Ni. X-ray microprobe pictures clearly showed the presence of Ca and Cl along the Cu_2O–Cu boundary (Figs. 6a, 6b). Analogous results were obtained with Co instead of Ni.
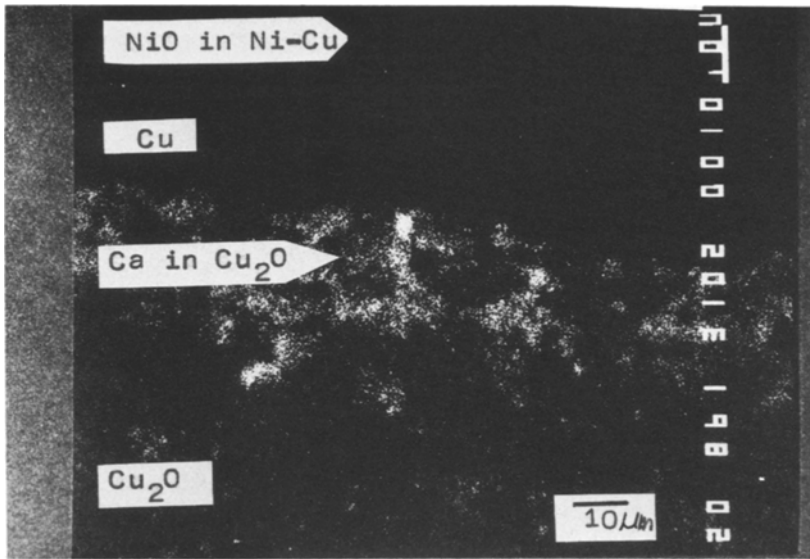
Fig. 5. Ca K_α X-ray area scan of a Cu_2O–Ni couple with aggregate morphology, showing Ca segregation near the Cu–Cu_2O interface.

2. Couples of Ni or Co vs. $Cu_2O + 0.5$ wt.% CuCl also gave aggregate morphologies with NiO (and CoO respectively) precipitates in a metal matrix of Cu(Ni) (and Cu(Co), respectively).
3. Couples of Ni or Co vs. $Cu_2O + 0.5$ wt.% CaO gave parallel, single-phase layers of Cu and NiO (or CoO).

From these experiments it is evident that Ca had no influence on the layer morphology, but that Cl impurities induced a change from the layered to the aggregate morphology. As to the mechanism of this change, we note that chlorides have low melting points. Therefore, it may well be that the Cl ions segregate at the phase boundary and form a liquid phase at the interphase.

Table I. Chemical Analysis of Cu_2O (ppm)

	Ca	Cl
$Cu_2O(I)$, untreated	25 ± 5	< 10
$Cu_2O(II)$, untreated	1700 ± 85	1200 ± 100
$Cu_2O(II)$, annealed 20 hr, 1000°C, 10^3 Pa O_2	1739 ± 85	< 60
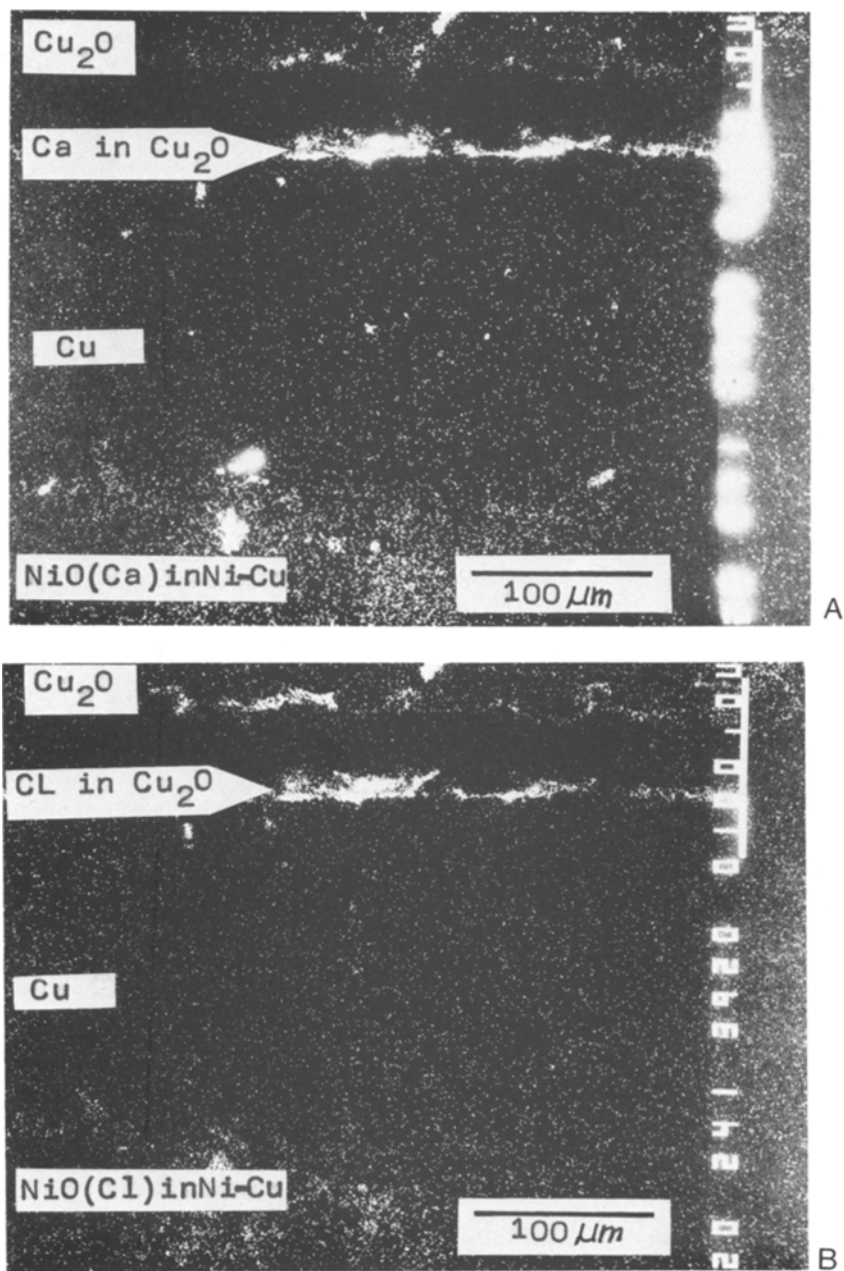
Fig. 6. X-ray area scans of a Ni–(Cu$_2$O + 0.5 wt.% CaCl$_2$) couple with aggregate morphology. (a) Ca K_α picture; (b) Cl K_α picture.

Influence of Grain Boundaries

In couples of pure Cu_2O vs. fine-grained Ni, much NiO was formed at the grain boundaries of the Ni substrate. Precipitates of Cu(Ni) were formed in the NiO layer near the grain boundaries of the Ni grains. When recrystallized, coarse-grained Ni substrates were used, a layered structure was obtained. In agreement with the observations of Rapp et al., we can say that the Wagner theory can be used to predict layer morphologies when the reaction proceeds via pure volume diffusion. Indeed, we have obtained ample evidence that this model can be applied generally in ternary systems.[6]

LAYER THICKNESS

Couples with Layered Morphologies

For the couples using pure Cu_2O as a starting material and showing a layered morphology, layer thicknesses were determined with the aid of an optical microscope. Figure 7 shows a plot of the layer thickness (d) of the formed oxides vs. the square root of the diffusion time (t) for Cu_2O–Ni and Cu_2O–Co couples. In both cases a parabolic growth was observed. From a least-squares fit the parabolic rate constant k_p was obtained [cf. Eq. (1)]. Results are given in Table II.
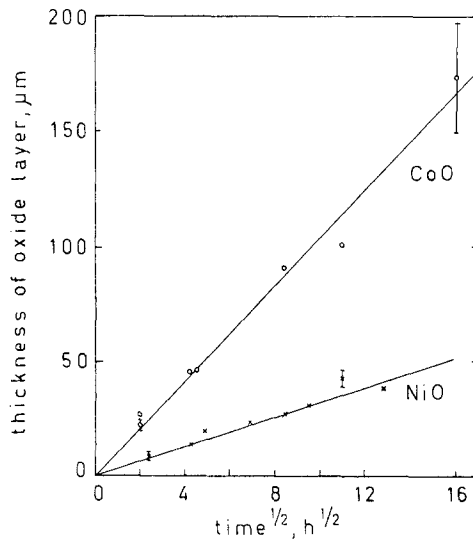

Fig. 7. Thickness of the oxide layers in Cu_2O–Ni and Cu_2O–Co couples with layered morphologies versus time$^{1/2}$.

Table II. Values of the Parabolic Rate Constant k_p (in cm^2/sec)

Couple	Layer	Calc.[a]	Exp.[a]	Exp.[b]
Ni–Cu$_2$O	NiO	7.7×10^{-13}	—	$(1.45 \pm 0.1) \times 10^{-11}$
	Cu	1.3×10^{-12}	1.7×10^{-11}	$(3.3 \pm 0.9) \times 10^{-11}$
Co–Cu$_2$O	CoO	3.1×10^{-11}	—	$(1.5 \pm 0.1) \times 10^{-10}$
	Cu	4.7×10^{-11}	1.4×10^{-10}	$(2.5 \pm 0.4) \times 10^{-10}$

[a]From Ref. 2.
[b]This work.

By use of Eq. (2) k_p values can be calculated if the oxygen pressures P'_{O_2} at the Ni–NiO and Co–CoO boundaries, respectively, and P''_{O_2} at the Cu–Cu$_2$O boundary are known. From a determination of the diffusion paths in the couples the equilibrium compositions at the phase boundaries were obtained. At 1000°C we found for the solubility of Cu in Ni only 1.5 at.% at the NiO–Ni interface and 0.5 at.% for the solubility of Ni in Cu at the Cu$_2$O–Cu interface.[7] Similar low solubilities were observed for the Cu$_2$O–Co couples. This means that the values of k_p calculated by Rapp et al.[2] should be good approximations (cf. Table II).

In both cases the experimental k_p values are too high. This is probably due to the contribution of grain-boundary diffusion in our couples. In the calculation of Rapp et al. the bulk diffusion coefficients were used. From the reaction equation

$$Cu_2O + Ni \rightarrow 2Cu + NiO$$
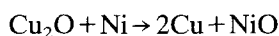
and the molar volumes one can predict the thickness ratio of the product layers. Theoretical values are $d(Cu)/d(NiO) = 1.27$ and $d(Cu)/d(CoO) = 1.22$; the experimentally observed ratios are 1.5 ± 0.2 and 1.3 ± 0.1, respectively. This close agreement between calculated and observed data shows that the experiments in the metal cylinders are indeed performed in a closed system.

Couples with Aggregate Morphologies

The occurrence of an aggregate structure has important consequences for the layer thickness. Since the Ni^{2+} (or Co^{2+}) diffusion through the oxide layer is no longer rate-determining, the growth may proceed faster. Figure 8 gives the resulting total thickness of the layer formed between the Ni (or Co) and Cu$_2$O. For comparison the total layer thickness Cu + NiO (or CoO) for couples with parallel layers is also displayed. It is difficult to measure the thickness of the aggregate layer accurately in the Cu$_2$O–Ni couples because
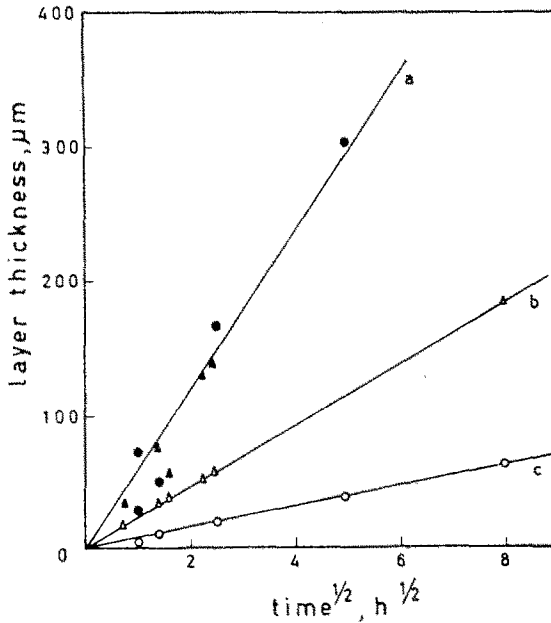
Fig. 8. Total thickness of the reaction layer formed between Cu_2O and Ni or between Cu_2O and Co plotted versus $time^{1/2}$. (a) Thickness of aggregate layer, circles indicating Cu_2O–Ni couples, triangles indicating Cu_2O–Co couples; (b) total thickness of $Cu + CoO$ layer in a Cu_2O–Co couple with layered structure; (c) total thickness of $Cu + NiO$ layer in a Cu_2O–Ni couple with layered structure.

of the mutual solubility of Cu and Ni. Yet, two conclusions can be drawn from the figure:

1. At a given annealing time, the resulting two-phase layer is considerably thicker than the single-phase layers in couples with parallel interfaces.

2. Within the accuracy of the measurement, the thicknesses of the aggregate layers are the same for the Cu_2O–Ni and Cu_2O–Co couples.

These results can be easily understood if it is assumed that the oxygen diffusion through the copper becomes rate-determining. In that case the thickness of the layer is determined by the k_p of Cu. From Ref. 2 we find k_p calc. (Cu, 1273 K) $= 1 \times 10^{-8}$ cm^2/sec. By use of Eq. (1), a least-squares plot through the data points in Fig. 8 yields a value of k_p for the aggregate layer; k_p (aggr. 1273 K) $= 0.97 \times 10^{-8}$ cm^2/sec, in excellent agreement with the calculated value.

In fact, this behavior is comparable to the phenomenon of internal oxidation in alloys. A similar example was mentioned by us in an earlier publication.[1] Namely, in the Cu–Ni–O system a transition is observed from a layered to an aggregate structure for couples of annealed Cu_2O vs. Cu–Ni alloys, with increasing Cu content. In a couple $Cu_2O/Ni_{0.75}Cu_{0.25}$ a layered morphology is observed. After 21 hr at 1273 K the thickness of the NiO layer is 10 μ, corresponding to a value of $k_p = 1.3 \times 10^{-11}$ cm^2/sec, in good agreement with the results given in Table II. In a couple $Cu_2O/Ni_{0.5}Cu_{0.5}$ a NiO layer is observed, together with some isolated NiO precipitates in the Cu layer. In a couple $Cu_2O–Ni_{0.25}Cu_{0.75}$ we obtain an aggregate structure consisting of NiO islands in a Cu-rich matrix. After 21 hr at 1273 K the thickness of the layer is about 250 μ, that is, $k_p = 0.83 \times 10^{-8}$ cm^2/sec, close to the k_p value of copper as expected if oxygen transport through the copper were rate-controlling. Due to the limited solubility of Co in Cu, similar experiments are not possible in the Cu–Co–O system.

CONCLUSIONS

For displacement reactions in the systems $Cu_2O–Ni$ and $Cu_2O–Co$ the Wagner theory predicts the formation of parallel diffusion layers. We have reconfirmed this theory. However, experiments with Cu_2O contaminated with chlorine show that the morphology can be changed completely in the presence of impurities that segregate at the reaction interface. The change of a layered to an aggregate morphology leads to a considerable increase in the thickness of the reaction layer. This is due to the fact that now the fast oxygen diffusion through the Cu matrix controls the reaction rate instead of Ni^{2+} (or Co^{2+}) diffusion through the oxide layer. The present study clearly shows the importance of impurities for diffusion behavior. In a separate paper[8] we will present another example, showing that this topic deserves attention.

ACKNOWLEDGMENTS

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