Solid-State Displacement Reaction between Chromium and Cuprous Oxide

By Hitoshi Taimatsu*, Shinji Hirama** and Hiroyuki Kaneko*

The solid-state displacement reaction between Cr and Cu2O was carried out in argon at 1173 K and 1273 K. The product zone consisted of three layers of Cr2O3, Cu+CuCrO2 two-phase product and Cu. The Cu and Cu+CuCrO2 two-phase layer grew as one aggregate layer. The Cr2O3 layer once formed became thinner during the reaction and correspondingly the Cu+CuCrO2 layer became thicker. The consumption of Cr2O3 is considered to be due to the side reaction 2Cu + O + Cr2O3 = 2CuCrO2. The stability of the reaction products is discussed on the basis of the phase diagram of the Cu–Cr–O system.

(Received May 24, 1988)

Keywords: displacement reaction, metal-oxide reaction, solid-state reaction, chromium, Cu2O, CuCrO2, chromium-copper-oxygen system

I. Introduction

When a metal is in contact with the oxide of a less base metal at elevated temperatures, displacement reaction occurs, that is, the metal is oxidized to metal oxide by reducing the coupled oxide to lower oxide or to metal. Consequently, the layer sequence of reaction products is expected to be formed in the reaction couple.

The solid-state displacement reactions between metals and oxides were investigated in the couples Ni/Cu2O(1)-(4), Co/Cu2O(1)-(4), Fe/Cu2O(1)(3)(6), Fe/NiO(1)(3)(7) and Cr or Cr-Fe alloy/FeO or FeCr2O4(8). Similar reactions between metals and non-metallic compounds were investigated in metal-halide systems(9) metal-sulfide systems(3)(10)-(12) and a metal-carbide system(13). Observed morphologies of displacement reaction products with the layer sequence of A|A2O|B|B2O are classified into two groups: a layered type and an aggregate type as schematically shown in Fig. 1. On the basis of the Wagner’s theory(14) for the stability of an alloy-oxide interface during alloy oxidation, Rapp et al.(1) presented a criterion to predict whether reaction products for a given displacement reaction couple would grow to a layered type or to an aggregate type. According to the model, reaction products will have an aggregate morphology when the migration of neutral oxygen across a newly-formed metal layer (B in Fig. 1) is rate-controlling, and they will have a layered morphology when cation migration across a newly-formed oxide layer (A2O in Fig. 1) is rate-controlling. This model on the development of the layer sequence of A|A2O|B|B2O was successful in explaining the morphologies observed in the metal-oxide systems. In the metal-sulphide systems, however, the layer sequence of A|B|A2S|B2S

* Department of Metallurgy, Mining College, Akita University, Akita 010, Japan.
** Graduate Student, Akita University, Akita 010, Japan.
has been found\(^\text{(12)}\). In order to make the solid-state displacement reaction mechanism clearer, much more reaction couples should be investigated.

In this study, the Cr/Cu\(_2\)O displacement reaction with an interesting aggregate product layer is investigated morphologically, thermodynamically and kinetically.

II. Experimental

Specimens of Cr were made by grinding Cr flakes (Rare Metallic, 99.99% purity) to discs 5 mm in diameter and 2 mm thick. Specimens of cuprous oxide, Cu\(_2\)O, were obtained by oxidizing Cu as described by Rapp et al.\(^\text{(1)}\). A Cu rod of 5 mm in diameter (Johnson Matthey Chemicals, 99.999% purity) was cut into slices 2 mm thick. The Cu was transformed into Cu\(_2\)O by heating in an Ar-1%O\(_2\) stream at 1273 K for 360 ks. After oxidation, the Cu\(_2\)O was ground to discs with dimensions similar to those of the Cr specimen. The specimens thus prepared were mounted in stainless steel holders with sealing wax and were polished with SiC paper and diamond paste until their surfaces became flat and smooth.

The reaction couple formed by batting together the discs of Cr and Cu\(_2\)O was sandwiched between two fused-quartz pedestals to be evenly compressed, and was then placed into the fused-quartz cylinder, as shown in Fig. 2. It was enclosed with a Ni sheet to be uniformly heated and to be maintained at a constant low oxygen partial pressure of Ni/NiO equilibrium. The pressure applied to the reaction couple was 90 kPa, since higher pressures did not affect the product morphology and the reaction kinetics.

The experimental setup is shown in Fig. 3. The reaction couple thus constructed was placed in the center of the hot zone (140 mm) of the infrared image furnace (Shinkuriko, RHL-E45P) which can rapidly heat and cool the specimen to avoid an excessive reaction. The reaction chamber was evacuated at about 400 K for 3.6 ks at 0.1 Pa, and then purified Ar gas was introduced.

Reactions were carried out at 1173 K and 1273 K within ±0.5 K. The time necessary to
raise the couple to the reaction temperature
and to lower it to 473 K was within 180 s.

After the reaction, the couple was sectioned
and polished. The reaction zone was examined
by metallographic observation and electron
probe microanalyzer (JEOL, JXA-733) sur-
vey. The thickness of the reaction product
layers was measured with a screw micrometer
eyepiece attached to a microscope. To identify
reaction products, the powder X-ray diffrac-
tion analysis was performed on reaction pro-
donth product surfaces which were obtained by pro-
gressively grinding off product layers parallel
to the product/Cr interface.

III. Results and Discussion

1. Reaction products and product
   morphology

The growth rates of the products formed in
the Cr/Cu₂O displacement reactions at 1173 K
and 1273 K were different as described later,
but the observed product morphologies were
fundamentally the same.

Figure 4 shows the product morphology and
the distributions of Cr, Cu and O in the couple
reacted at 1273 K for 90 ks. The product zone
consisted of three layers of chromium oxide,
two-phase product and Cu. Large Cu particles
were locally precipitated in the chromium
oxide layer near the chromium oxide/Cr inter-
face. The two-phase product consisted of
chromium-copper oxide and Cu. X-ray diffraction studies indicated that the chromium oxide
and the chromium-copper oxide were Cr₂O₃
and CuCrO₂, respectively. No other oxides
could be detected in the product zone. The Cu
phases in and close to the Cu + CuCrO₂ layer
contained a very small amount of Cr. The Cr
phase close to the Cr₂O₃ layer was free from
Cu. This fact is consistent with the Cr–Cu
phase diagram.

As shown in Fig. 5, the Cu chips like turn-
ings entangled themselves in the CuCrO₂
matrix. The tentacles of Cu elongated from the
Cu layer into the Cu + CuCrO₂ layer. Obvi-
ously, the Cu phases in the CuCrO₂ matrix are not
precipitates formed during cooling the couple.
Thus, the Cu and Cu + CuCrO₂ layers can be re-

Fig. 4 Electron probe microanalyzer survey for displacement reaction products at 1273 K for
90 ks: (a) backscattered electron image, (b) distribution of Cr, (b) distribution of Cu and
(c) distribution of O.
garded morphologically as one aggregate product layer.

Aggregate product morphologies were classified into two sub-groups: a lamellar (rod like) aggregate product observed in the Fe/Cu$_2$O couple and an interwoven aggregate product observed in the Fe/NiO couple\(^{(1)}\). The aggregate morphology in the Cr/Cu$_2$O couple in this study resembles that in the Fe/Cu$_2$O couple in respect of accompanying the apparent Cu layer. The morphology of Cu phase in the Cu + CuCrO$_2$ layer resembles that of the metallic phase in the aggregate layer in the Fe/NiO couple. However, the morphology of the whole product zone differs from those in both the Fe/Cu$_2$O and Fe/NiO couples, because the product zone in Cr/Cu$_2$O couple contained the non-aggregate Cr$_2$O$_3$ layer while the product zones in the Fe/Cu$_2$O and Fe/NiO couples did not contain a single iron oxide layer.

2. Thermodynamic stability of reaction products

During the Cr/Cu$_2$O displacement reaction, the products Cu, CuCrO$_2$ and Cr$_2$O$_3$ were present in the reaction zone of the couple. Thermodynamic equilibrium would be established at both the Cu/Cu$_2$O and Cr$_2$O$_3$/Cr interfaces in the course of the reaction, though oxygen is transported from the Cu$_2$O side to the Cr side in the reaction couple. Therefore, the substances thermodynamically stable in the range of Cu/Cu$_2$O equilibrium oxygen pressure to Cr/Cr$_2$O$_3$ equilibrium oxygen pressure are expected to exist as reaction products.

Figure 6 shows the oxygen partial pressure-composition phase diagram for the Cr-Cu-O system at 1173 K and 1273 K. This type of phase diagram developed by Pelton and Schmalzried\(^{(16)}\) is a useful aid in understanding the phase stability in a ternary system A-B-O. The equilibrium oxygen partial pressures of Cu$_2$O/CuO, Cu/Cu$_2$O and Cr/Cr$_2$O$_3$ were calculated from the Gibb's energy changes of their equilibrating reactions\(^{(17)}\). The equilibrium oxygen partial pressures of CuCr$_2$O$_4$/CuCrO$_2$ and Cu/CuCrO$_2$/Cr$_2$O$_3$ were calculated from the reported values by Jacob \textit{et al.}\(^{(18)}\) for their three-phase equilibrating reactions, since the reported values by Schmahl \textit{et al.}\(^{(19)}\), Rosén\(^{(20)}\), Jacob \textit{et al.}\(^{(18)}\) and Vlach \textit{et al.}\(^{(21)}\) are in agreement with one another. It is assumed in this analysis that CuCr$_2$O$_4$ and CuCrO$_2$ are stoichiometric compounds. In addition, the mutual solubility of Cr and Cu is ignored because it is very small\(^{(15)}\).

It is clear from the figure that CuCrO$_2$ is stable between the oxygen pressure range for the Cu/Cu$_2$O equilibrium and that for the Cr/Cr$_2$O$_3$ equilibrium. Furthermore, Cu can co-exist thermodynamically with both the CuCrO$_2$ and Cr$_2$O$_3$ phases. All the phases thermodynamically possible to exist in this displacement reaction were observed in the product zone as shown in Fig. 4. However, thermodynamic analysis can not predict the arrangement of the reaction products.

3. Reaction kinetics

Figure 7 shows the change in the sequence of the product layers in the couple at 1273 K with time. In the early stage of the reaction, the Cu
and Cr₂O₃ layers were formed in the product zone, while the Cu+CuCrO₂ two-phase layer was scarcely observed. However, as the reaction proceeded, the Cu+CuCrO₂ layer became thicker than the Cr₂O₃ layer, and the Cu layer and the Cu+CuCrO₂ layer grew as main reaction products.

The relations between the thickness of product layers and the reaction time at 1173 K and 1273 K are shown in Figs. 8 and 9, respectively. At both temperatures the growth rate of the Cu+CuCrO₂ layer was increased with time. On the other hand, the Cr₂O₃ layer ceased to grow after about 15 ks at 1173 K and about 44 ks at 1273 K and then it became thinner.

As for the metal-oxide displacement reactions investigated so far, it has been found that the growth kinetics of the product layers obeys
the parabolic rate law, irrespective of formations of layered products or aggregate products\(^{(1)(2)(7)}\). In the Cr/Cu\(_2\)O couple, the thickness of every product layer did not increase linearly with the square root of the reaction time in the early stage of the reaction. After the Cr\(_2\)O\(_3\) layer became thinner considerably, the growth of the total layer obeyed the parabolic rate law.

The formation of CuCrO\(_2\) followed the formation of Cu and Cr\(_2\)O\(_3\). The CuCrO\(_2\) is considered to be formed by a side reaction concomitant with the main reaction to form Cu and Cr\(_2\)O\(_3\). The overall side reaction is considered to be

\[
2\text{Cu} + \text{O} + \text{Cr}_2\text{O}_3 = 2\text{CuCrO}_2
\]

because oxygen dissolves atomically and migrates in the Cu layer. Although this is not an oxide-oxide reaction, it is analogous to the spinel formation reaction MO+Me\(_2\)O\(_3\)= MMe\(_2\)O\(_4\) in respect of forming a double oxide. As for the spinel formation, it is widely known that the spinel layer grows by the counter-diffusion of M\(^{2+}\) and Me\(^{3+}\) through the layer, since oxygen ion transport can be neglected in comparison with cation transport\(^{(22)-(24)}\) Taimatsu et al.\(^{(25)}\) studied the NiAl\(_2\)O\(_4\) formation reaction between Al\(_2\)O\(_3\) and liquid Ni containing oxygen. They showed that NiAl\(_2\)O\(_4\) was formed by the reaction of Ni, O and Al\(_2\)O\(_3\) with counter-diffused Al\(^{3+}\) and Ni\(^{2+}\). Also in the CuCrO\(_2\) formation reaction oxygen ion transport will not participate, because the delafossite structure compounds, CuFeO\(_2\) isotypic with CuCrO\(_2\) do not exhibit oxygen ion conduction\(^{(26)}\). Therefore, it can be considered that the above side reaction proceeds by the counter-diffusion of Cu\(^{+}\) and Cr\(^{3+}\) through CuCrO\(_2\) and by the diffusion of O through Cu as shown below:

at the Cu/CuCrO\(_2\) interface

\[
4\text{Cu} + 2\text{O} + \text{Cr}^{3+} = \text{CuCrO}_2 + 3\text{Cu}^{+}
\]

at the CuCrO\(_2\)/Cr\(_2\)O\(_3\) interface

\[
3\text{Cu}^{+} + 2\text{Cr}_2\text{O}_3 = 3\text{CuCrO}_2 + \text{Cr}^{3+}
\]

After the Cr\(_2\)O\(_3\) layer is perfectly consumed by this side reaction, consequently, the apparent displacement reaction 2Cu\(_2\)O + Cr = CuCrO\(_2\) + 3Cu proceeds, although this direct reaction is not caused thermodynamically.

As described above, the product zone of this displacement reaction had the aggregate product layer. The criterion for the development of layered or aggregate products by Rapp et al.\(^{(1)}\) was successful in explaining the experimental results for the reported reaction couples Ni/Cu\(_2\)O\(^{(1)(2)}\), Co/Cu\(_2\)O\(^{(1)(2)}\), Fe/Cu\(_2\)O\(^{(1)}\) and Fe/NiO\(^{(1)(7)}\). As predicted by the model, growth rates for layered products were consequently much lower than those for aggregate products. However, the parabolic rate constant for the total product layer in the Cr/Cu\(_2\)O couple is about the same as that for the total product layer in the Co/Cu\(_2\)O couple with a layered morphology. Therefore, this model is probably not applicable to the Cr/Cu\(_2\)O displacement reaction. To elucidate the fundamental mechanism of the displacement reaction, experiments on several other metal-oxide reaction couples are in progress in our laboratory.

**IV. Conclusions**

The solid-state displacement reaction between Cr and Cu\(_2\)O was carried out in argon at 1173 K and 1273 K. The reaction zone was examined by metallographic observation, electron probe microanalyzer survey and X-ray diffraction analysis.

The product zone consisted of three layers of Cr\(_2\)O\(_3\), Cu+CuCrO\(_2\) two-phase product and Cu. The Cu and Cu+CuCrO\(_2\) layers were morphologically one aggregate layer. All the phases thermodynamically possible to exist in this displacement reaction were observed in the product zone. The thickness of the Cu layer and the Cu+CuCrO\(_2\) layer increased with time. The Cr\(_2\)O\(_3\) layer ceased to grow after about 15 ks at 1173 K and 44 ks at 1273 K, and then it became thinner gradually. The consumption of Cr\(_2\)O\(_3\) can be explained by the side reaction: Cr\(_2\)O\(_3\) once formed reacts again with Cu and diffused O through Cu to produce CuCrO\(_2\).

**REFERENCES**

(1) R. A. Rapp, A. Ezis and G. J. Yurek: Met. Trans., 4
Solid-State Displacement Reaction between Chromium and Cuprous Oxide (1973), 1283.

(2) P. J. C. Vosters, M. A. J. Th. Laheij, F. J. J. van Loo and R. Metselaar: Oxid. Met., 20 (1983), 147.

(3) F. J. J. van Loo, J. A. van Beek, G. F. Bastin and R. Metselaar: Oxid. Met., 22 (1984), 161.

(4) F. J. J. van Loo, J. A. van Beek and G. F. Bastin: Solid State Ionics, 16 (1985), 131.

(5) G. Y. Yurek, R. A. Rapp and J. P. Hirth: Met. Trans., 4 (1973), 1293.

(6) G. Y. Yurek, R. A. Rapp and J. P. Hirth: Met. Trans. A, 10A (1979), 1473.

(7) C. Tangchitvittaya, J. P. Hirth and R. A. Rapp: Met. Trans. A, 13A (1982), 585.

(8) M. A. J. Th. Laheij, F. J. J. van Loo and R. Metselaar: Oxid. Met., 14 (1980), 207.

(9) C. Wagner: Z. Anorg. Allg. Chem., 236 (1938), 320.

(10) C. Wagner: J. Metals, 4 (1952), 214.

(11) S. R. Shatynski, J. P. Hirth and R. A. Rapp: Mat. Trans. A, 10A (1979), 591.

(12) J. A. van Beek, P. M. T. de Kok and F. J. J. van Loo: Oxid. Met., 22 (1984), 147.

(13) C. J. Quinn and D. L. Kohlstedt: J. Amer. Ceram. Soc., 67 (1984), 305.

(14) C. Wagner: J. Electrochem. Soc., 103 (1956), 571.

(15) M. Hansen and K. Anderko: Constitution of Binary Alloys, 2nd Ed., McGraw-Hill Book Co. Inc., New York, (1958), p. 524.

(16) A. D. Pelton and H. Schmalzried: Met. Trans., 4 (1973), 1395.

(17) O. Kubaschewski and C. B. Alcock: Metallurgical Thermochemistry, 5th Ed., Pergamon Press, New York, (1979).

(18) K. T. Jacob, G. M. Kale and G. N. K. Iyengar: J. Mater. Sci., 21 (1986), 2753.

(19) N. G. Schmahl and E. Minzl: Z. Phsik. Chem. Neue Folge, 47 (1965), 358.

(20) E. Rosén: Chemica Scripta, 8 (1975), 43.

(21) K. C. Vlanch, Y. You and Y. A. Chang: Thermochemica Acta, 103 (1986), 361.

(22) J. B. Holt: UCRL-12396, (1965).

(23) M. Nakano, G. Yamaguchi and K. Saito: Yogyo-Kyokai-Shi, 79 (1971), 92.

(24) H. Schmalzried: Treatise on Solid State Chemistry, Vol. 4, Ed. by N. B. Hannay, Plenum Press, New York, (1976), p. 233.

(25) H. Taimatsu, Y. Undo, F. Nakatani and K. Ogino: J. Japan Inst. Metals, 50 (1986), 568.

(26) D. B. Rogers, R. D. Shannon, C. T. Previtt and J. L. Gillson: Inorgan. Chem., 10 (1971), 723.