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The Reduction Mechanism of Powdered Copper–Nickel Oxides

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The mechanism of the formation of copper–nickel alloys from copper and nickel nitrates by calcination and by reduction with hydrogen was investigated by means of X-ray diffraction and measurement of the rate of the reduction. X-ray diffraction showed that the unreduced copper–nickel oxides were composed of cupric oxide and miscible oxide of nickel and copper. Cuprous oxide and free nickel did not appear in the process of reduction. The completely reduced copper–nickel was composed of nickel-rich alloy and extremely copper-rich alloy. The rate of reduction of copper–nickel oxide was practically the same as that of cupric oxide. From these results and the change in the BET areas, it was concluded that the alloys are formed by the interdiffusion of nickel into a copper phase which forms earlier than nickel.

INTRODUCTION

The catalytic activities of alloys are affected not only by alloy composition but also by the preparation of the alloy. In our earlier studies (*1–5*) on powdered copper–nickel alloy catalysts we concluded that they were composed of nonuniform alloy phases. Since then, details of the nonuniformity of the surfaces of alloys have been investigated in various ways (*6–11*). Modern methods such as Auger electron spectroscopy are advantageous for the observation of the details of such compositions. These methods are especially favorable for evaporated films or sheets which have flat surfaces.

Since the steps involved in the preparation of powdered copper–nickel alloys are co-precipitation, calcination, and reduction with hydrogen, the occurrence of nonuniformity in powdered alloys prepared from a mixed solution of copper and nickel salts differs from that of films or sheets. Since reduction with hydrogen is the last process which is conducted at high temperature, it is probably most responsible for nonuniformity. The recent study by Robertson *et al.* (*12*) has proved that the surface of silica-supported copper–nickel is formed of nonuniform alloys and that the composition is changed by the repetition of reduction and oxidation. The rates of reduction of metal oxides are influenced by impurities and by the supporting substance (*13, 14*). It was reported (*15*) by one of the authors that the surface area of the copper–nickel oxide increased markedly during the first half of the reduction and then decreased. A similar result was also reported by Frety *et al.* (*16, 17*). These results show that the relationship between reduction and the nonuniformity of the powdered alloy is complicated.

The present work deals with the mechanism of the formation of powdered copper–nickel alloys from the copper–nickel oxides by reduction with hydrogen. The changes in bulk composition during the process of reduction with hydrogen were observed by

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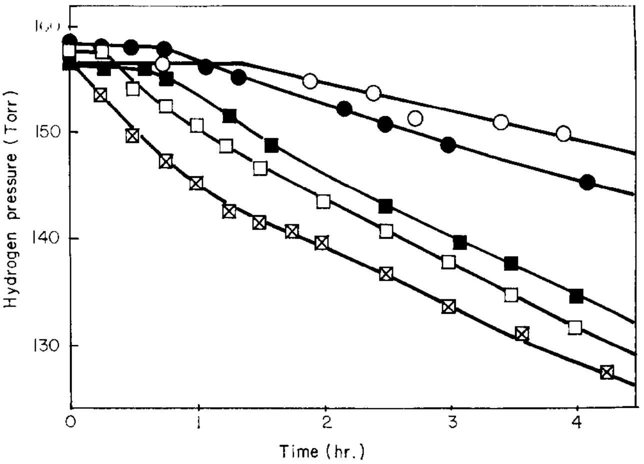

FIG. 1. The decrease in the pressure of hydrogen due to reduction (200°C). ○, NiO; ●, CuO; ■, Cu-Ni-O(20:80); ☒, Cu-Ni-O(41:59); □, Cu-Ni-O(75:25).

means of X-ray diffraction, because the nonuniformity of the surface is directly or indirectly related to bulk composition. In addition, the rates of reduction and the change in the BET areas of cupric oxide, cuprous oxide, and nickel oxide in the process of reduction were measured to elucidate the mechanism of the reduction.

EXPERIMENTAL

The single component oxides, copper oxides (CuO, Cu_2O) and nickel oxide, were used in this study for comparison with copper–nickel oxides. Cuprous oxide was obtained from the Katayama Chemical Co. Cupric oxide, nickel oxide, and copper–nickel oxides of various compositions were prepared from nitrates of copper and nickel, which were obtained from the Kanto Chemical Co. The purity of these nitrates was 99.9%. The temperature of calcination was 500°C, and reduction was carried out using the static method. One-half gram of each oxide was placed in a reaction vessel of ca. 500 ml in volume, including the McLeod gauge. The hydrogen used was purified by diffusion through a palladium thimble. The initial pressure of the hydrogen was ca. 160 Torr. The decrease in the pressure during reduction was measured by a U-type manometer. The samples were reduced at a temperature of 200 or 280°C.

The relationship between the BET area of each single oxide and the percentage of

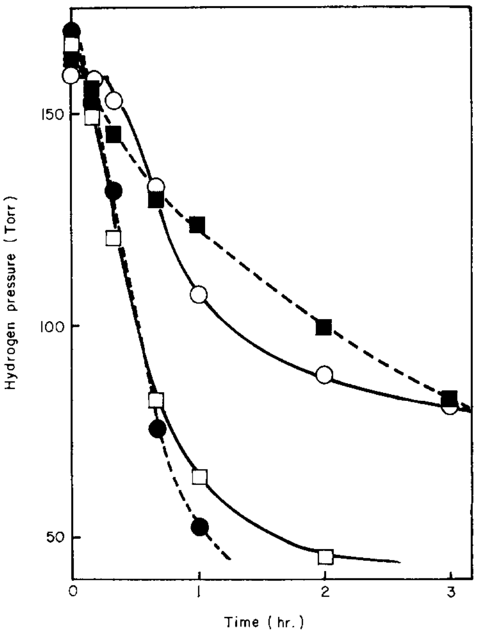

FIG. 2. The decrease in the pressure of hydrogen due to reduction (280°C). ○, NiO; □, CuO; ■, Cu_2O; ●, Cu-Ni-O (41:59).

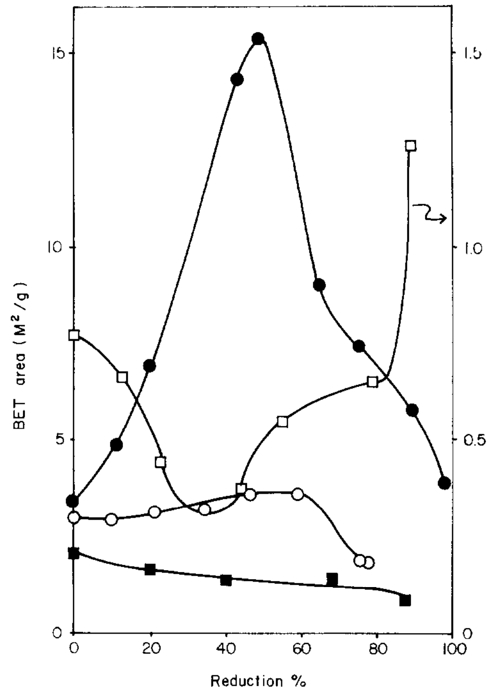

FIG. 3. The changes in BET areas during the process of reduction (280°C). ○, NiO; □, CuO; ■, Cu_2O; ●, Cu-Ni-O (41:59).

reduction for comparison with that of copper–nickel oxide (*15*) was obtained by periodically stopping the reduction. A trap cooled with liquid nitrogen was connected to the reaction vessel to quickly condense the water produced by reduction. The percentage of reduction was expressed by the atomic ratio of the removed oxygen to that of the remaining oxygen, assuming that the atomic ratio of metal to oxygen was 1:1 at the beginning of the reduction.

The diffraction patterns of the oxides in the course of the reduction were obtained by X-ray diffractometer using CuKα radiation. The samples were covered with gaseous ammonia to avoid oxidation before they were subjected to analysis. The alloy compositions were obtained from the spacing *d* which was determined from the X-ray diffraction peaks of (111) and (220) by referring to data published elsewhere (*18*).

RESULTS

The change in the pressure of hydrogen due to the reduction of each oxide is shown in Figs. 1 and 2. The reduction of nickel oxide showed a long induction period at

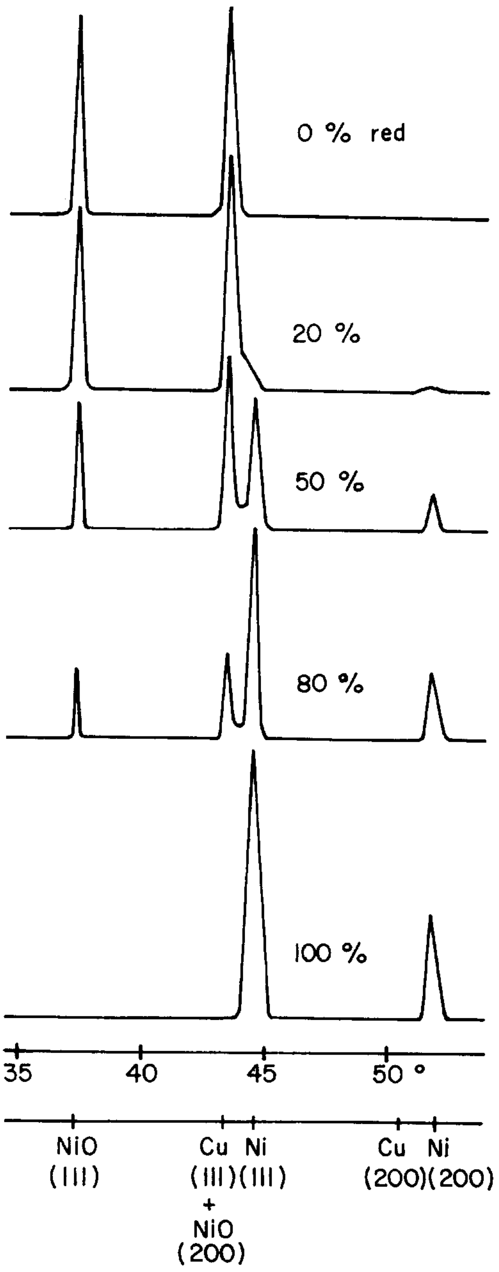

FIG. 4. The changes in the diffraction patterns of Cu-Ni-O (20:80) during the process of reduction.

200°C, as had been reported elsewhere (*19, 20*). However, it became shorter with the elevation of temperature or the addition of copper oxide. The induction period of cupric oxide was shorter than that of nickel oxide and disappeared with the elevation of the temperature. The induction period for the reduction of cuprous oxide was shorter, ca. $\frac{1}{10}$ that of cupric oxide. It was interesting that the rates of reduction of copper–nickel oxides were approximately the same as that of cupric oxide. Figure 3 shows the change in the BET area of each oxide due to reduction. The results for a copper–nickel oxide of (41:59) are from a previous paper (*15*). The area of cupric oxide decreased during the first half of the reduction, then increased drastically. However, the area of cuprous oxide was quite different from that of cupric oxide. It decreased constantly until the oxide was completely reduced. The area of nickel oxide slightly increased in the initial stage, then decreased. It was of particular interest that the change in each single oxide was quite different from that of copper–nickel oxide.

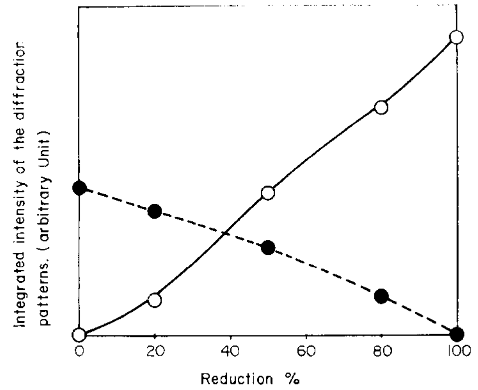

FIG. 5. The change in the integrated intensity of the diffraction patterns of Cu–Ni–O (20:80) during the process of reduction. ●, NiO; ○, Cu–Ni.

X-ray diffraction indicated that the incompletely reduced nickel is composed of two phases of free nickel and nickel oxide, and no intermediate oxides of nickel were found. In the case of cupric oxide, the oxide changed to its metallic form, passing through cuprous oxide. The unreduced copper–nickel oxides were composed of two phases of cupric oxide and nickel oxide whose diffraction patterns shifted slightly to the smaller value of glancing angle, suggesting that the miscible

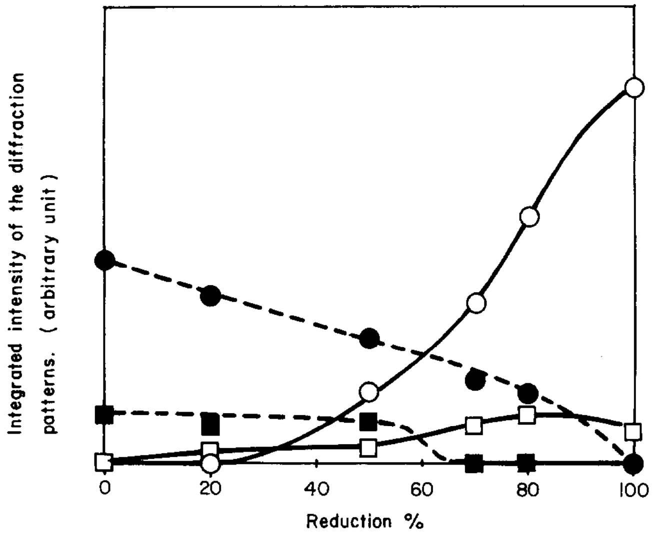

FIG. 6. The change in the integrated intensity of the diffraction patterns of Cu–Ni–O(41:59) during the process of reduction. ●, NiO; ■, CuO; □, Cu; ○, Cu–Ni.

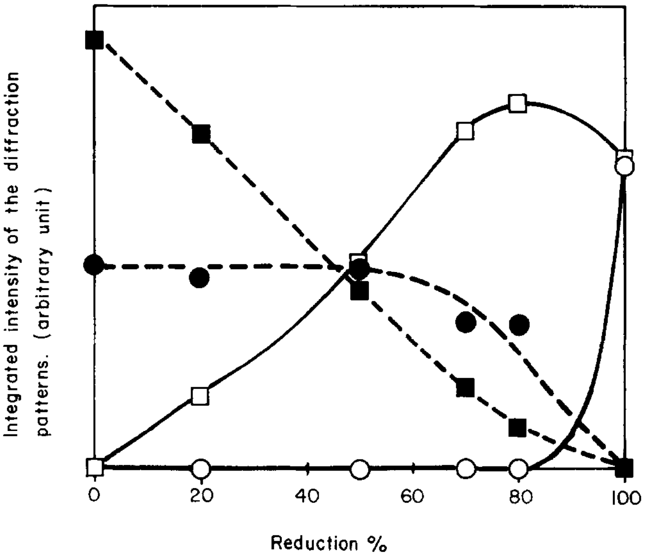

FIG. 7. The change in the integrated intensity of the diffraction patterns of Cu-Ni-O(75:25) during the process of reduction. ●, NiO; ■, CuO; □, Cu; ○, Cu-Ni.

TABLE 1

The Change in Composition in the Process of Reduction of Each Oxide[a]

	Percentage reduced						
	0	10	20	50	70	80	100
CuO	CuO		CuO Cu_2O Cu	CuO Cu_2O Cu			Cu
NiO	NiO		NiO Ni	NiO Ni			Ni Ni
Cu-Ni-O (8:92)	NiO*						Cu-Ni
Cu-Ni-O (20:80)	NiO*		NiO* Cu-Ni	NiO* Cu-Ni	NiO* Cu-Ni		Cu-Ni
Cu-Ni-O (41:59)	CuO NiO*	CuO NiO*	Cu NiO*	Cu NiO* Cu-Ni	Cu NiO* Cu-Ni	Cu NiO* Cu-Ni	Cu* Cu-Ni
Cu-Ni-O (66:34)	CuO NiO*		Cu CuO NiO*	Cu CuO NiO* Cu-Ni	Cu NiO* Cu-Ni	Cu NiO* Cu-Ni	Cu* Cu-Ni
Cu-Ni-O (75:25)	CuO NiO		Cu CuO NiO*	Cu CuO NiO*	Cu CuO NiO*	Cu CuO NiO*	Cu* Cu-Ni

[a] Cu*, extremely copper-rich alloy; NiO*, miscible oxide of CuO and NiO.

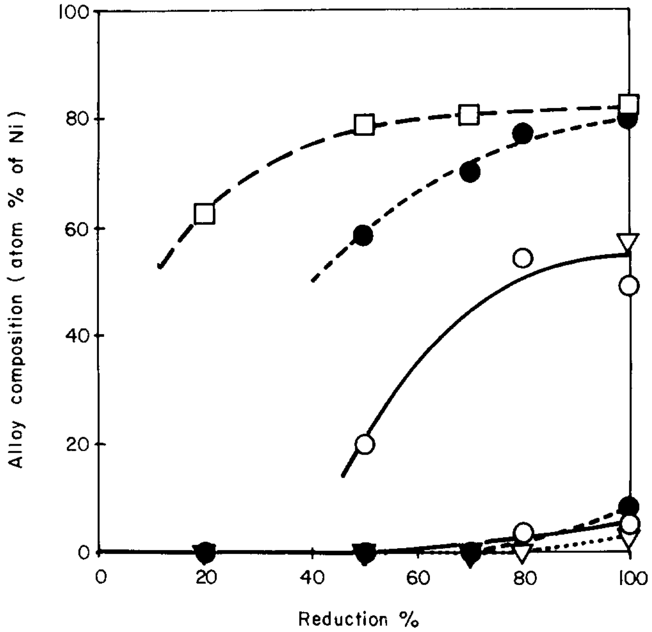

FIG. 8. The change in the alloy composition during the process of reduction. □, Cu-Ni (20:80); ●, (41:59); ○, (66:34); ▽, (75:25).

oxide was partly formed. However, this deviation was not found in the patterns of cupric oxide. The widths of the diffraction patterns of cupric oxide were less than those of nickel oxide. In the case of the copper–nickel oxides of (8:92) and (20:80), the diffraction patterns were simple, as had been reported by Hall and Alexander (*21*). The pattern of cupric oxide did not appear, though it did appear in more copper-rich oxides, and the patterns of nickel oxide shifted to the smaller value of glancing angle. It is notable that no free nickel appeared in the reduction of copper–nickel oxides; nickel always appeared in the form of an alloy with copper. During the reduction process of cupric oxide to copper, the cuprous oxide was obtained as an intermediate product, but in the case of copper–nickel oxides, no such intermediate product was obtained.

Figure 4 shows an example of the diffraction pattern of copper–nickel oxide during the process of reduction. Figures 5, 6, and 7 show the change in the integrated intensity obtained from the diffraction patterns. These results are summarized in Table 1. Each alloy composition is given by the position of its X-ray diffraction peak. If the diffraction pattern has no distinctly separated peak and has one peak with a shoulder, it indicates that the mixture is of free copper and alloy. The composition of the alloy was obtained by eliminating the symmetrical area of free copper which overlaps the area of the alloy. In most cases, the pattern of the alloy obtained in this way was nonsymmetrical and broad. Therefore, the composition of each alloy in these figures is the most probable value. These figures indicate that the completely reduced copper–nickel oxides of (8:92) and (20:80) were composed of nickel-rich alloy, and free copper was not detected. The reduced oxides of (41:59), (66:34), and (75:25) were composed of two different alloy phases. One is a nickel-rich alloy, and the other is pure copper or an extremely copper-rich alloy. The composition of these phases changed with the

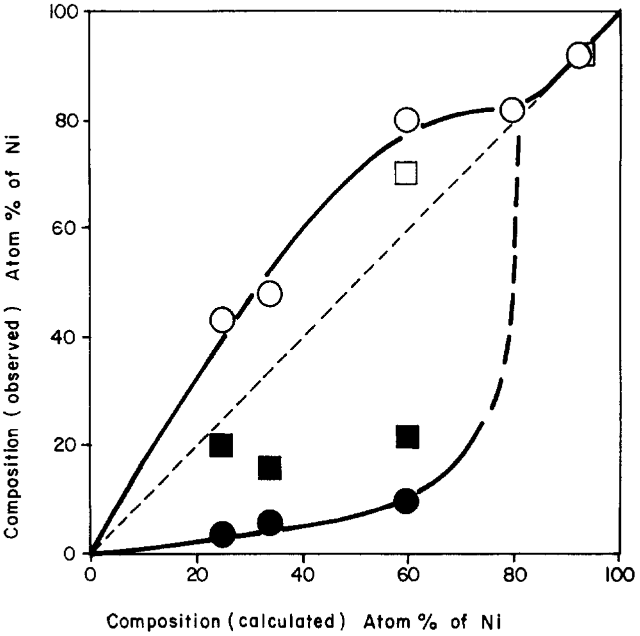

FIG. 9. The observed concentration of nickel for each alloy. ○, ●, soon after reduction is finished; □, ■, 10 days after reduction is finished.

progression of the reduction as shown in Fig. 8. The pure copper became slightly alloyed copper, ca. 95% Cu, and the copper-rich alloy became a copper-poor alloy. The nickel-rich alloy became more nickel-rich. The relationship between the composition obtained by the X-ray diffraction and that obtained overall is shown in Fig. 9.

DISCUSSION

We may estimate the crystal growth of the particles produced by the reduction from the BET area as well as from the width of the diffraction patterns of the products, because the area is related to the particle size. Table 1 showed that cuprous oxide is formed as an intermediate substance between cupric oxide and copper. It can be said that the decrease in the BET area in the first half of the reduction of cupric oxide is mainly attributable to the formation of cuprous oxide, and the increase in the area during the latter half is attributable to the formation of copper from cuprous oxide. The decrease in area by the formation of cuprous oxide can be explained in terms of the crystal growth of cuprous oxide. The rate of reduction of cuprous oxide is less than that of cupric oxide; therefore, the concentration of cuprous oxide becomes excessive for a time. The increase in the BET area in the latter half is probably caused by the separation of the copper phase from the oxide phase.

The increase in the BET area of nickel oxide in the initial stage of the reduction would be due to the separation of free nickel from the oxide phase, and the gradual decrease in the area at the end of the reduction would be due to the sintering of the nickel phase.

It is notable that the rates of reduction of copper–nickel oxides were very similar to the rate of cupric oxide, and also that the induction period disappeared or became brief. These findings suggest that the formation of copper accelerates the reduction of nickel oxide. There is much evidence that the addition of a foreign metal to nickel oxide hastens the rate of the reduction and lowers the activation energy (*22–24*). Spillover of chemisorbed hydrogen onto the "d-metals" is especially efficient in the lowering of the activation energy of the reduction (*25*). Recent studies (*26–28*) have proved that hydrogen chemisorbs on copper, though it is not a "d-metal." We may expect the spillover of chemisorbed hydrogen from copper onto the nickel oxide at a high temperature as the oxide is reduced. The marked increase in the surface area of copper–nickel oxide due to reduction suggests that the separation of the mixture of free copper and the unreduced oxides takes place during the reduction. The increase in the surface area would accelerate reduction, while the decrease in surface area suggests that sintering of metal is taking place with the reduction of oxide.

The miscibility of nickel oxide for copper oxide and that of copper oxide for nickel oxide are ca. 5 and ca. 35%, respectively (*29*). As was pointed out in the recent study made by a Dutch group (*30*), such poor mutual miscibility of these oxides would be responsible to the formation of a nonuniform alloy. The absence of cupric oxide in copper-poor oxides (8 and 20% Cu) had been explained by Hall and Alexander (*21*) in terms of the dissolution of copper into the phase of nickel oxide which is assumed to be highly defective. The difference in the temperatures of decomposition of copper nitrate and nickel nitrate seems to depend upon the difficulty in formation of the complete solid solution of both oxides. The temperature of decomposition for copper nitrate is 170°C and that of nickel nitrate is more than 190°C. The difference in the crystal structures of the two oxides is also responsible for the separation of the oxides; nickel oxide has a cubic lattice and cupric oxide has a monoclinic lattice.

The absence of a free nickel in the process of reduction of copper–nickel oxides can be explained in terms of the difference in the surface energies of copper and nickel, and in terms of the diffusion of nickel atoms into copper phase, which is produced more readily than nickel. The absence of free nickel suggests that the crystal growth or the segregation of nickel atoms is very poor. The surface energy of the nickel particles must be smaller than that of the copper particles, because the diameter of the nickel particles is smaller than the diameter of copper particles. For this reason, the particles of nickel would be merged into those of copper.

The activation energy of the self-diffusion of copper, 47 kcal, is smaller than that of nickel, 70 kcal; however, the activation energy of the diffusion of copper into nickel, 61 kcal, is greater than that of nickel into copper, 56 kcal, and the frequency factor of the former is 0.72 cm^2/sec and that of the latter is 1.7 cm^2/sec (*31*). The rate of the diffusion in the former case is 10^{-2} times smaller than that of the latter. Such a conclusion is also understandable from the difference in the lattice constant of both metals. The occurrence of the following reaction should be taken into consideration from the evidence that the cuprous oxide and free nickel were not found and from the free energy change in the reaction:

$$\mathrm{Cu_2O + Ni = 2Cu + NiO}$$
$$\Delta F = -22\ \mathrm{kcal}$$

The oxygen of cuprous oxide transfers to the nickel.

The mechanism of alloy formation from copper–nickel oxides can be that proposed in Fig. 10 by considering the change in concentration of each constituent in the process of reduction, along with the activation energies of the mutual diffusion, and the change in free energy of the reaction. This mechanism is different from the proposal made by other authors (*7*), who established their mechanism on the basis

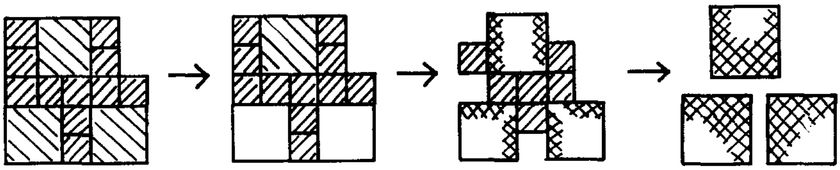

FIG. 10. Schematic representation of mechanism for the reduction of one particle of Cu–Ni oxide. ▧, CuO; ▨, NiO; □, Cu; ▩, Cu–Ni.

of the contact of metal particles of copper and nickel and the activation energies of self-diffusion of copper and nickel. The squares in Fig. 10 represent the crystals of each constituent. The predominance of cupric oxide in the reduction followed by the interdiffusion of nickel into copper at the interface of the free copper and nickel oxide would destroy the arrangement of the oxides and enlarge the surface area. The concentration of nickel in the copper on the side of nickel oxide becomes greater with the reduction of nickel oxide. As a result two metal phases, extremely copper-rich and nickel-rich alloys, will appear here. When the concentration of nickel oxide is high, the formation of nickel predominates over the copper. The diffusion of copper into nickel phase must be taken into consideration, and as a result no copper phase appears. The decrease in the BET area in the latter half of the reduction is attributable to the sintering of metal phase. "Hot-spots" (*32*) would develop during reduction, because reduction is exothermic and very fast. Unfortunately, we could not monitor them.

There is much evidence (*9*, *11*, *33*) that nickel is enveloped by copper, because of the surface diffusion of copper, which is more volatile constituent. For this reason, the nickel-rich alloy would finally be enveloped in a similar way by the copper which had remained from the interdiffusion of nickel. A subsequent interdiffusion of the metals in the nickel-rich alloy core and copper shell would take place, as has been proved by the change in concentration of copper–nickel alloy and the purity of copper (Fig. 9). We may obtain a copper–nickel whose composition in bulk is uniform, if the samples have been standing for very long time. However, the surface of the composition of the particle would not be similar to that of the bulk, because of the difference in the volatility of copper and nickel as was concluded by Burton *et al.* (*34*).

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