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SYNTHESIS, STRUCTURE AND THERMAL REDUCTION BEHAVIOUR OF DELAFOSSITE-TYPE $CuRh_xAl_{1-x}O_2$*

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Summary

Delafossite-type oxides $CuRh_xAl_{1-x}O_2$ with $0 \leqslant x \leqslant 1$ have been synthesized and structurally characterized. The temperature range and the mechanistic course of the thermal reduction have been found to be strongly dependent on the composition of the initial materials. As products, elemental copper, thermally metastable Cu–Rh alloys and Al_2O_3 are formed. These products represent not only interesting metallic materials but also potential bimetallic catalysts.

1. Introduction

The class of delafossite-type metal oxides ABO_2 is characterized by its highly anisotropic, layered structure, which is made up of linearly coordinated A(I) metals interlinking sheets of face-sharing $B(III)O_6$ octahedra. The fact that a number of different metal combinations can be stabilized in this structure renders these phases interesting with respect to their physical and chemical properties [1 - 3]. There are, however, only scarce data available on the possible existence of quaternary $A_xA'_{1-x}BO_2$ or $AB_xB'_{1-x}O_2$. Moreover, the chemical reactivity, and in particular, the thermal reduction behaviour of such compounds is not known. The present study focuses on the preparation of $CuAlO_2$, $CuRhO_2$ and the respective mixed phases $CuRh_xAl_{1-x}O_2$. Emphasis is given to the role of the B cations aluminium and rhodium, *i.e.* two metals with very different properties, which influence the structure as well as the thermal reduction behaviour in a hydrogen atmosphere and thus the formation of the solid products.

2. Experimental details

$CuAlO_2$ and $CuRhO_2$ were prepared by solid state reactions of the respective binary oxides CuO, Al_2O_3 and Rh_2O_3 at a temperature of 1350 K.

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*Dedicated to Professor Harald Schäfer on the occasion of his 75th Birthday.

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Single crystals of the pure and mixed phases were obtained by recrystallization of powder samples in a Cu_2O melt in the temperature range 1450 - 1320 K [4]. Structural investigations were performed using a Siemens Kristalloflex diffractometer with monochromatized Cu Kα radiation. The composition of the mixed Cu–Rh–Al phases was checked by conventional chemical analyses. The thermal reduction behaviour in a hydrogen atmosphere was monitored by means of thermogravimetric measurements using a Perkin–Elmer TGS-2 microbalance. Morphological studies were carried out by scanning electron microscopy (SEM) using a Cambridge Instruments Stereoscan III. For the detailed characterization of the microstructure of the reduced samples, high resolution electron microscopy (HREM) studies were performed on a JEOL 200CX microscope equipped with a top entry stage.

3. Results

The pure and mixed oxide phases $CuAlO_2$, $CuRhO_2$ and $CuRh_xAl_{1-x}O_2$ are isostructural. The X-ray powder diffraction patterns for all compositions in the range of $0 \leqslant x \leqslant 1$ could be indexed on the basis of the hexagonal unit cell (space group R$\bar{3}$m) found for $CuAlO_2$ [5]. Depending on the value of x, *i.e.* the rhodium content, an enlargement of the unit cell is observed. By means of least-squares fitting procedures the cell parameters a and c were determined as functions of the rhodium content. Figure 1 represents the observed changes in the axes. Whereas for the short axis a the rule of Vegard [6] is perfectly valid, slight discontinuities are registered for the metric changes in the c-axis. A detailed analysis of selected X-ray reflections provided evidence that this $CuRh_xAl_{1-x}O_2$ system is monophasic in the full range $0 \leqslant x \leqslant 1$. Selected-area electron diffraction patterns confirmed these results, *i.e.* no extra reflections or streaking caused by the possible presence of superstructures could be observed. In addition, HREM carried out on

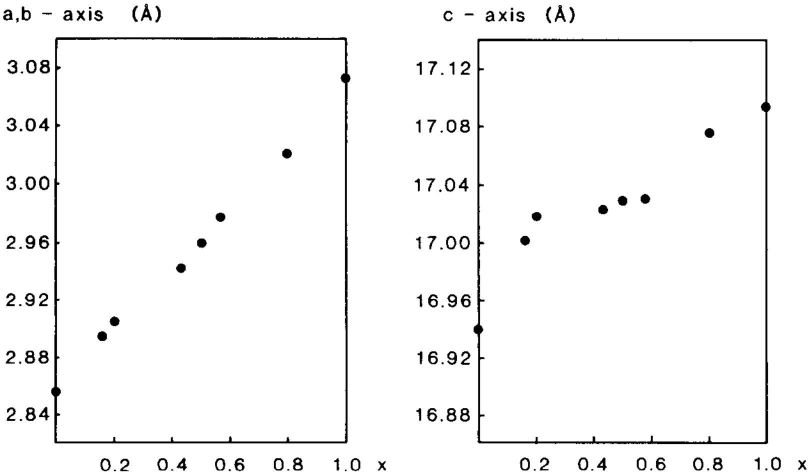

Fig. 1. Measured changes in the a-axis and c-axis respectively of the hexagonal unit cell of $CuRh_xAl_{1-x}O_2$ as a function of x.

samples with various rhodium contents supported these findings. In summary, the structural investigations provide evidence for a statistical Rh–Al distribution on the B positions of all the phases studied.

The thermal reactivity of $CuRh_xAl_{1-x}O_2$ is determined by the gas atmosphere under which the degradation and reduction processes are initiated. In inert or oxidizing gas atmospheres, all compounds prove to be stable up to temperatures of 1300 K. In a hydrogen atmosphere, however, the Cu(I) as well as the Rh(III) metal ions are reduced to the respective elemental metals. For Al(III) no reduction processes could be detected under the experimental conditions described. Thus, the possible reduction schemes in hydrogen can be summarized by the following stoichiometric equations:

$$CuRh_xAl_{1-x}O_2 + \frac{1+3x}{2}H_2 \longrightarrow Cu^0 + xRh^0 + \frac{1-x}{2}Al_2O_3 + \frac{1+3x}{2}H_2O$$

$$CuRh_xAl_{1-x}O_2 + \frac{1+3x}{2}H_2 \longrightarrow Cu^0Rh^0{}_x + \frac{1-x}{2}Al_2O_3 + \frac{1+3x}{2}H_2O$$

$$CuRh_xAl_{1-x}O_2 + \frac{1+3x}{2}H_2 \longrightarrow (1-y)Cu^0 + Cu^0{}_yRh^0{}_x + \frac{1-x}{2}Al_2O_3 + \frac{1+3x}{2}H_2O$$

$$CuRhAl_{1-x}O_2 + \frac{1+3x}{2}H_2 \longrightarrow Cu^0{}_yRh^0{}_z + Cu^0{}_{y-1}Rh^0{}_{x-z} + \frac{1-x}{2}Al_2O_3 + \frac{1+3x}{2}H_2O$$

The composition of the initial materials and the temperature range of the reduction process determine the product formation. In turn, the reduction temperatures strongly depend on the actual compositions of the initial materials. As displayed in Fig. 2, the temperature range varies from about 1000 K (for pure $CuAlO_2$) to about 450 K (for pure $CuRhO_2$). The thermogravimetric curves further reveal that all compounds are reduced in a single-step process. This is also confirmed by heating the materials with very low heating rates. Again, the compounds are reduced in a single-step degradation. These facts provide evidence that both metals, *i.e.* Cu(I) and Rh(III), are reduced simultaneously; in other words, the reductive degradation of these delafossite-type metal oxides is not selective with respect to the transition metals present. The measured weight losses are in very good agreement with the theoretical values and indicate the formation of pure products.

The properties of the solid products formed are strongly influenced by the experimental conditions, in particular the temperatures, under which the initial samples were reduced. As has been stated by the above-mentioned equations, $CuAlO_2$ decomposes to Cu^0 and Al_2O_3. As a consequence of the

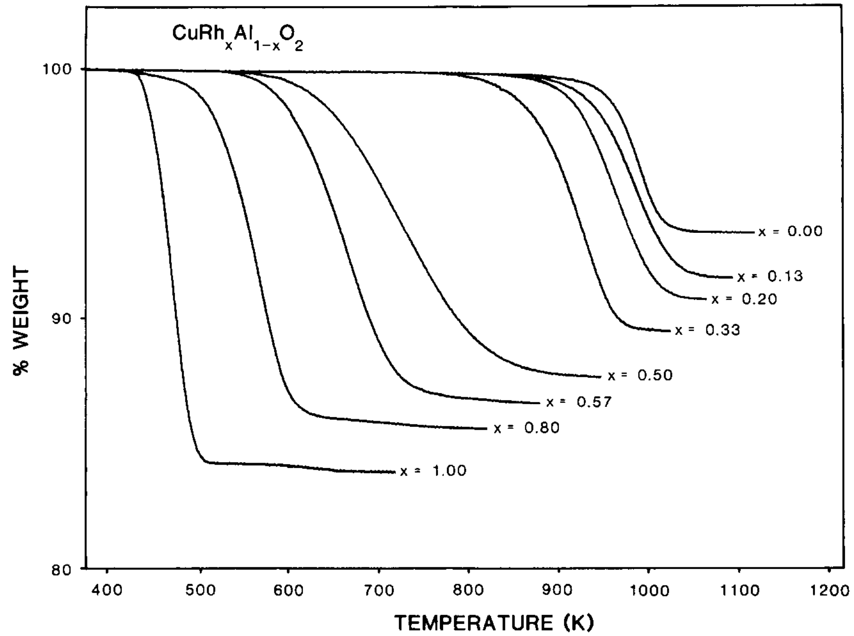

Fig. 2. Thermogravimetric measurements of the thermal reduction of $CuRh_xAl_{1-x}O_2$ in pure hydrogen (10^5 Pa) as a function of x. Experimental conditions: heating rate, 20 K min^{-1}; hydrogen flow, 70 ml min^{-1}.

relatively high reduction temperature, the copper particles undergo sintering and thus comparatively large particles are formed. By slowly reducing $CuAlO_2$ at 950 K, Al_2O_3 is formed as X-ray amorphous material. This is also confirmed by the absence of any crystalline domains on investigation by HREM. At reduction temperatures around 1150 K, microcrystalline Al_2O_3 is formed. The evaluation of X-ray diffraction and electron diffraction patterns indicates the presence of Θ-Al_2O_3, which is a metastable phase formed during the thermal decomposition of the AlOOH phases hydrargillite, bayerite, boehmite or diaspore [7, 8]. The Θ-Al_2O_3 transforms to the thermodynamically stable phase α-Al_2O_3 at elevated temperatures. The reduction of $CuAlO_2$ single crystals under isothermal conditions at 1050 K proceeds with the formation of Cu^0 drop-like particles disposed on Al_2O_3 as seen in Figs. 3(a) and 3(b). The morphology of the initial crystals is roughly conserved. By dissolving the Cu^0 particles with dilute HNO_3, highly orientated pseudocrystals are obtained. These are identified by X-ray diffraction using a Gandolfi camera as Θ-Al_2O_3.

The reduction of $CuRhO_2$ is registered at remarkably low temperatures (450 K) and yields a monophasic, thermally metastable intermetallic phase $Cu_{0.5}Rh_{0.5}$. The evaluation of the linewidths of selected X-ray reflections using the equation of Scherrer [9] as well as the inspection of high resolution electron micrographs (Fig. 4) yielded extents in the range of 10 nm for the perfectly crystalline domains. The metastability of this intermetallic phase was proven by stepwise heating procedures in the temperature range

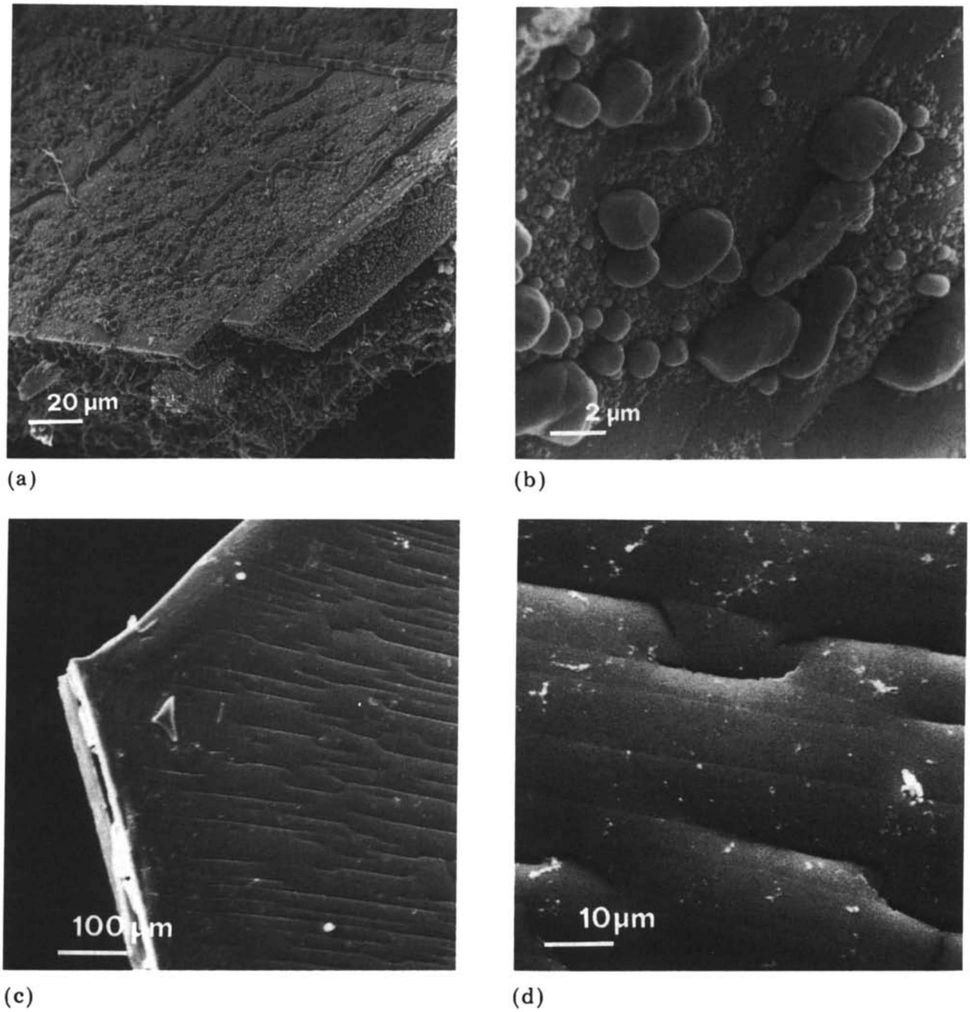

Fig. 3. Scanning electron micrographs of Cu^0/Al_2O_3 ((a) and (b)) and of the alloy $Cu_{0.5}Rh_{0.5}$ ((c) and (d)) obtained by the isothermal reduction of the respective oxides $CuAlO_2$ (reduction temperature, 1050 K) and $CuRhO_2$ (reduction temperature, 450 K).

450 - 1300 K in a pure nitrogen atmosphere. Starting with a stoichiometrically well-defined sample of $Cu_{0.5}Rh_{0.5}$, X-ray diffraction patterns were taken at each 50 K step. In Fig. 5, the temperature dependence of the X-ray diffractograms of the (111) (Fig. 5(a)) and the (200) (Fig. 5(b)) reflections is displayed. They provide evidence that the segregation of the metastable phase begins above 700 K. The defined new reflections registered starting from about 950 K were compared with the crystallographic data of known stable Cu–Rh alloys [10]. The evaluation indicated the formation of a copper-rich phase Cu_yRh_{1-y} with $y = 0.80 \pm 0.02$ and of a respective rhodium-rich phase with $y = 0.18 \pm 0.02$. The diameters of the stable alloy domains increase above 900 K and reach 40 - 50 nm at 1300 K. The

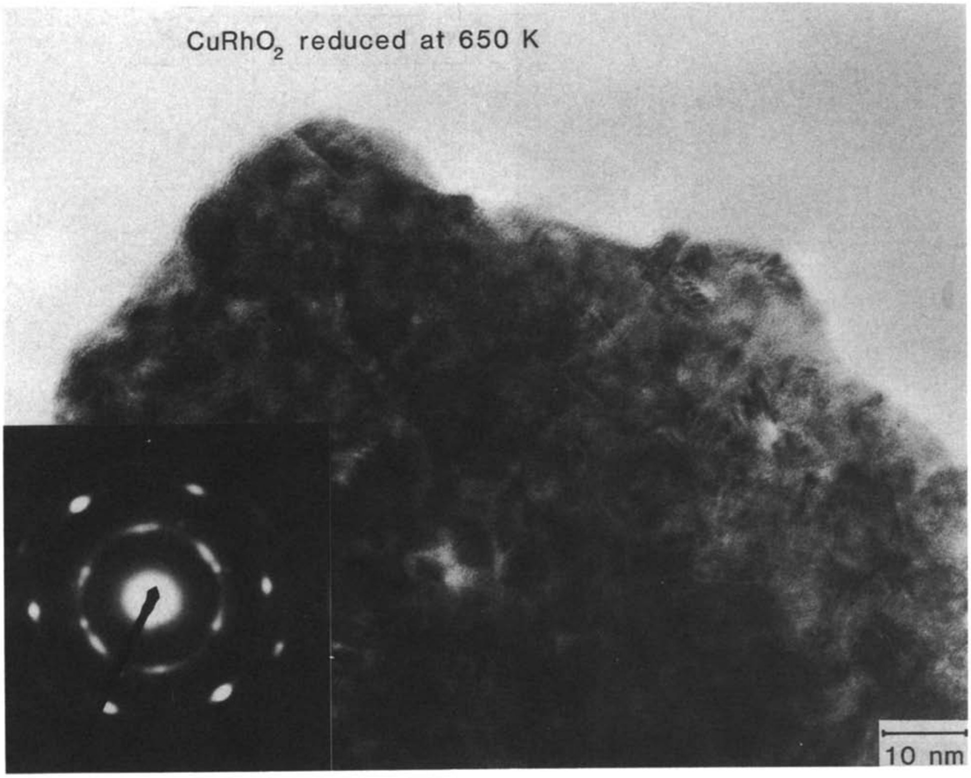

Fig. 4. High resolution electron micrograph showing the microcrystalline metastable $Cu_{0.5}Rh_{0.5}$ alloy obtained by the reduction of $CuRhO_2$ (reduction temperature, 650 K).

reduction of $CuRhO_2$ single crystals at 450 K is characterized by the formation of pseudomorphous products with a metallic lustre. Scanning electron micrographs reveal the presence of orientated cracks owing to the volume contraction caused by the loss of oxygen (Figs. 3(c) and 3(d)).

The thermal reduction of the mixed $CuRh_xAl_{1-x}O_2$ phases proves to be complicated, inasmuch as the formation of the solid products depends not only on the experimental conditions but also on the actual composition of the initial material. By reducing the mixed oxides at heating rates of 20 K min^{-1} (see Fig. 2) in the temperature range 370 - 1170 K, two crystalline metallic Cu_yRh_{1-y} phases and an X-ray amorphous Al_2O_3 phase are obtained. Depending on the value of x in the initial material, different metallic phases Cu_yRh_{1-y} were detected by X-ray diffraction. For $0 \leqslant x \leqslant 0.2$, two copper-rich alloys with $y = 0.9$ and $y = 0.8$ were identified, whereas for $0.35 \leqslant x \leqslant 1$, a copper-rich phase with $y \approx 0.9$ and a rhodium-rich phase with $y \approx 0.1$ were found. Moreover, $CuRh_{0.57}Al_{0.43}O_2$ was reduced at 570 K, a temperature at which the full degradation is only reached after 20 h. As products, a pure copper phase with relatively large particles and a microcrystalline Cu–Rh alloy with $y = 0.5$ are formed, for which the evaluation of the linewidth of the X-ray reflections indicates particle sizes with diameters

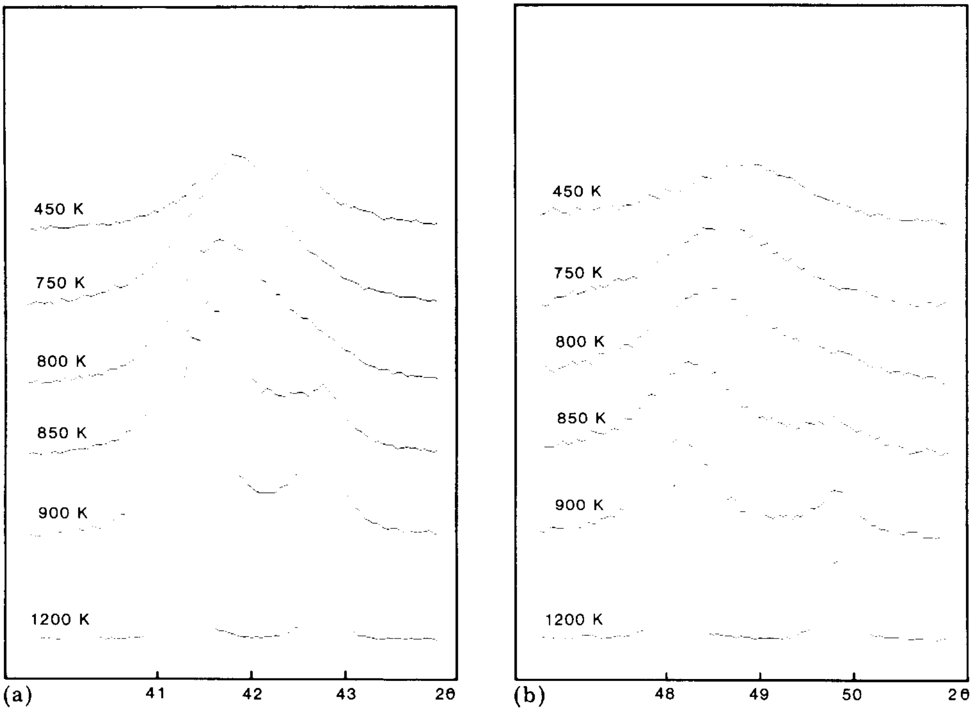

Fig. 5. X-ray powder diffraction measurements of the (111) (a) and (220) (b) reflections of the bimetallic Cu–Rh phases obtained by the thermal treatment of the metastable $Cu_{0.5}Rh_{0.5}$ in a nitrogen atmosphere (temperature range, 450 - 1200 K).

below 5 nm. HREM and electron diffraction (Fig. 6) confirm these findings. The diffraction patterns can be interpreted using the crystallographic data of the above-mentioned alloy and the data of a new metastable Al_2O_3 phase. On dissolving the elemental copper phase with dilute HNO_3, the Cu–Rh alloy and the new alumina phase persist. Again, HREM studies (Fig. 7) show the very small domains making up these product phases.

4. Discussion

The above-mentioned experimental results indicate several remarkable aspects of the structural properties as well as of the thermal reactivity of the quaternary delafossite-type oxide $CuRh_xAl_{1-x}O_2$. Considering the differences in the radii of Rh^{3+} (0.068 nm) and Al^{3+} (0.051 nm), the possibility of substituting one metal ion by the other in the full range $0 \leqslant x \leqslant 1$ is surprising. As a condition for isomorphous miscibility, Vegard's rule [6] allows deviations in the different radii only up to 15%. In the present case the deviation is 30%. This fact accounts well for a high stabilization potential of the delafossite structure. The thermal reduction behaviour in hydrogen of these investigated mixed phases is strongly influenced by the actual compositions, *i.e.* by the Cu:Rh ratio. In other words, increasing the aluminium

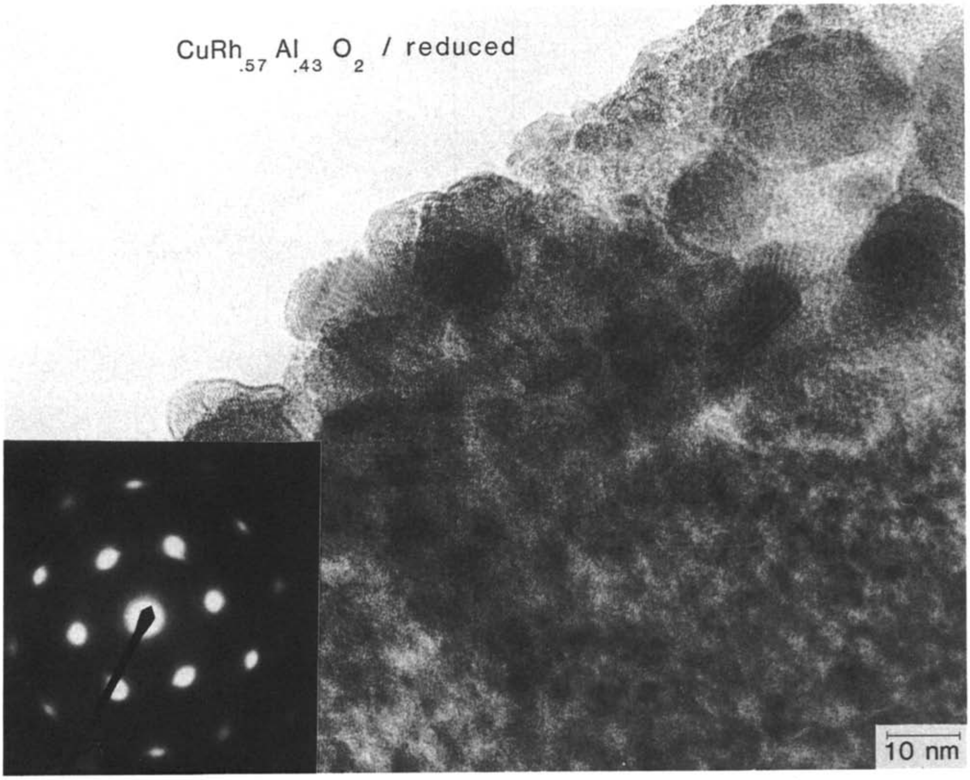

Fig. 6. High resolution electron micrograph and electron diffraction pattern of Cu^0/Cu–Rh alloy and alumina obtained by isothermal reduction of $CuRh_{0.57}Al_{0.43}O_2$ at 570 K.

content stabilizes the two reducible metal ions, copper and rhodium within the delafossite structure. The enormous temperature range of more than 600 K, within which these phases undergo reduction processes, is of importance for the product formation. This is confirmed by the production of thermally metastable Cu–Rh alloys. By conventional preparative techniques, only a few monophasic Cu_yRh_{1-y} alloys could be obtained, *i.e.* phases with $0 \leqslant y \leqslant 0.1$ and $0.8 \leqslant y = 1$. For alloys with compositions in the range $0.1 \leqslant y \leqslant 0.8$, only rapid-quenching techniques yielded monophasic products [11]. Thus, the thermal reduction of ternary or quaternary metal oxides represents an elegant alternative for the production of metastable intermetallic phases. In addition, such products are of potential importance as highly active catalysts [12]. The system described is particularly interesting inasmuch as the thermal reduction of the starting material $CuRh_xAl_{1-x}O_2$ yields not only the highly dispersed catalytically active species copper and/or the respective intermetallic phases, but also metastable alumina as an adequate support phase. Thus, the initial material represents an integrated precursor system for a supported bimetallic catalyst. The activity of such a catalyst prepared by thermal reduction of $CuRh_{0.04}Al_{0.96}O_2$ and subsequent removal of elemental copper was measured for the reduction of CO_2 in a hydrogen

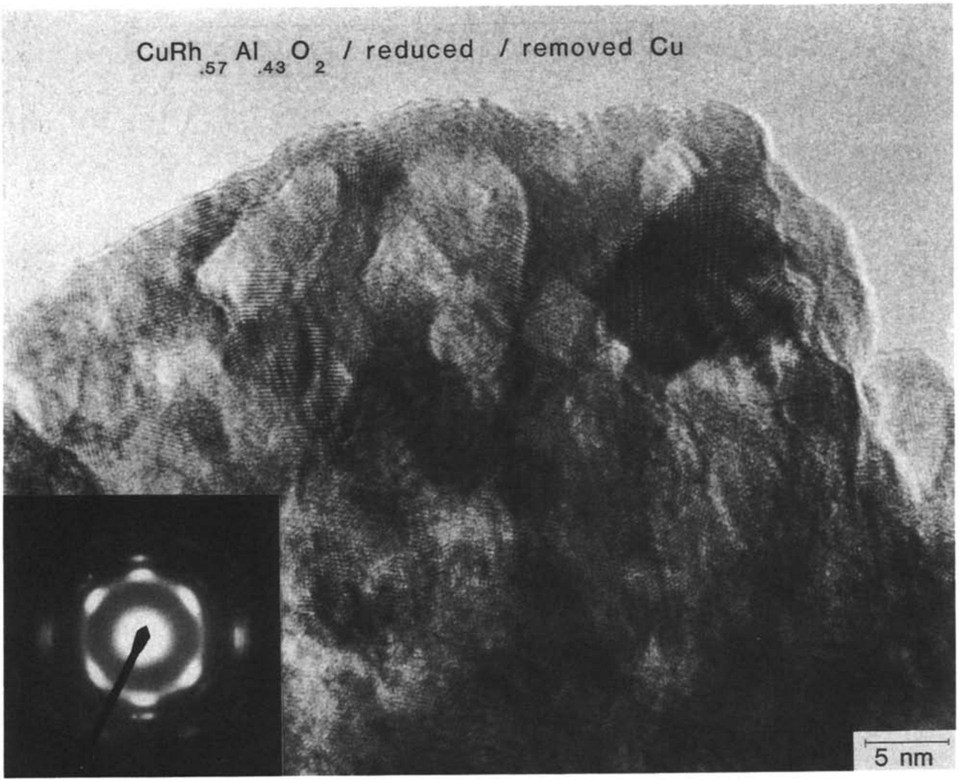

Fig. 7. High resolution electron micrograph and electron diffraction pattern of Cu–Rh alloy on alumina obtained by the thermal reduction of $CuRh_{0.57}Al_{0.43}O_2$ and subsequent removal of the elemental copper with dilute HNO_3.

atmosphere (10^5 Pa). At 600 K the catalyst selectively produces methane [13].

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