JOURNAL OF SOLID STATE CHEMISTRY 31, 275–279 (1980)

Phase Equilibria and Thermodynamics of the Double Oxide Phase Cu_3TiO_4

D. HENNINGS

Philips GmbH Forschungslaboratorium Aachen, 5100 Aachen, Federal Republic of Germany

Received December 12, 1978; in revised form April 10, 1979

Phase equilibria in the system CuO–Cu_2O–TiO_2 were investigated in the temperature range of 1160–1270 K by means of thermogravimetry and measurements of the oxygen partial pressure. The tie lines on the isothermal phase diagram run from the phase Cu_3TiO_4 to CuO, Cu_2O, and TiO_2. The existence of Cu_3TiO_5 and Cu_2TiO_3 could not be confirmed in this temperature range. The phase "Cu_3TiO_4" is only stable above about 1140 K and its composition fluctuates between about $Cu_3TiO_{4.3}$ and $Cu_3TiO_{3.9}$. The formation of $Cu_3TiO_{4.3}$ according to the reaction $1.6\,CuO + 0.7\,Cu_2O + TiO_2 = Cu_3TiO_{4.3}$ is endothermic: $(1160 < T < 1270\text{ K})$ $\Delta H° = (7600 \pm 450\text{ J-mole}^{-1}$; $\Delta S° = (6.7 \pm 0.4)\text{ J}\cdot\text{K}^{-1}\cdot\text{mole}^{-1}$. The standard Gibbs free energy, enthalpy, and entropy of formation of $Cu_3TiO_{4.3}$ at 1200 K are $\Delta G_f^\circ = -101.39$ kJ, $\Delta H_f^\circ = -1115.84$ kJ, and $S_f^\circ = 466.76\text{ J}\cdot\text{K}^{-1}$. Rather similar values were found for $Cu_3TiO_{3.9}$.

Introduction

The existence of double oxides in the system Cu–Ti–O was for a long time a matter of uncertainty. While Schmahl and Müller (*1, 2*) considered phases of the composition Cu_2TiO_3 and Cu_3TiO_4 to be possible, other authors (*3, 4*) reported also the existence of a phase with the composition Cu_3TiO_5.

A precise characterization of the crystallographic and electric properties of monocrystalline Cu_3TiO_4 was undertaken by Hayashi and Kato (*5*) and by Range and Ketter (*8*). The preparation of Cu_3TiO_4 encounters difficulties because the phase exists only in a narrow range of temperatures and of partial pressures of oxygen.

The above difficulties were quite probably one of the reasons why the existence of the phase Cu_3TiO_4 was disputed for so long. If the phase Cu_3TiO_4 is to be prepared at the lowest possible temperatures, in order to avoid undesirable grain growth of CuO and TiO_2, a knowledge of the thermodynamic conditions governing the formation of Cu_3TiO_4 is necessary.

Experimental

The impurities of the initial materials CuO (p.A., Merck, Darmstadt) and TiO_2 (Kronos R 1053, Dtsch. Titangesellschaft, Leverkusen) were less than 0.02% by weight. CuO and TiO_2 were mixed under ethanol in an agate ball mill and then pressed isostatically to about 60% of the theoretical density.

The phase equilibria of the ternary system Cu–Ti–O were investigated in a closed gas volume by means of the isothermal decomposition of various mixtures of CuO and TiO_2 at Cu : Ti ratios of from 9 : 1 to 1 : 1 in a thermobalance (Sartorius, Type 4201) at 1160–1270 K. The change of free energy could be derived from measurements of the

0022-4596/80/020275-05$02.00/0

Printed in Great Britain

oxygen pressure occurring after restoration of equilibrium which were followed directly with an absolute pressure gauge (Wallace & Tiernan—Chlorator GmbH, Günzburg, Model 129). Reaction temperatures of more than 1275 K had to be avoided because of the occurrence of molten phases.

Depending on the temperature and the composition of the specimen, the restoration of equilibrium from one measuring point to another required between 5 and 24 hr. The mixtures were furthermore examined in different stages of the reaction both by X-ray diffraction and microscopically.

Results and Discussion

During the isothermal decomposition of mixtures of CuO and TiO_2 into mixtures of Cu_2O and TiO_2 (Fig. 1), several clearly separate regions of the partial pressure of oxygen can be observed. Depending on the ratio of copper to titanium in the mixtures, these regions in the individual experiments occur at different oxygen contents of the copper (measured as atoms O/atoms Cu in the mixture, neglecting the TiO_2 component, since this is unchanged under the experimental conditions). The results of all the isothermal decompositions allowed the construction of a uniform isothermal phase triangle (Fig. 2), in which the individual regions having the same partial pressure of oxygen are bounded by tie lines.

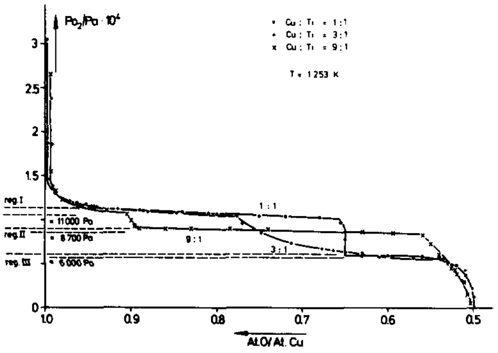

FIG. 1. Isothermal decompositions of CuO/TiO_2 mixtures at 1253 K.

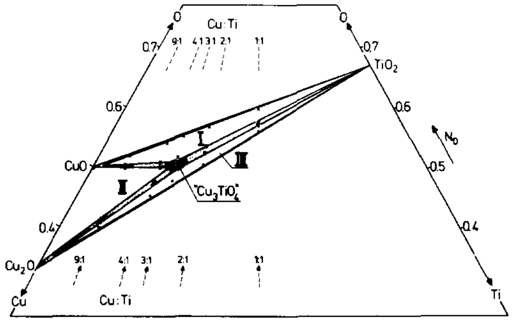

FIG. 2. Isothermal phase triangle of the system Cu–Ti–O at 1253 K. Detail of CuO–Cu_2O–TiO_2. The homogeneity ranges of Cu_3TiO_4, Cu_2O, and CuO are sketched, TiO_2 as fixed composition. Region I: univariant phase equilibrium CuO–TiO_2–$Cu_3TiO_{4,3}$–O_2, $p_{O_2} = (11000 \pm 400)$ Pa. Region II: univariant phase equilibrium CuO–Cu_2O–$Cu_3TiO_{4,3}$–O_2, $p_{O_2} = (8700 \pm 200)$ Pa. Region III: univariant phase equilibrium Cu_2O–TiO_2–$Cu_3TiO_{3,9}$–O_2, $p_{O_2} = (6000 \pm 150)$ Pa.

The examples of decomposition curves of the system Cu–Ti–O at 1253 K represented in Fig. 1 show three characteristic regions in which the oxygen partial pressure of the specimens does not vary substantially even during changes in the composition (reduction, oxidation). These plateau regions, designated as regions I, II, and III, are attributed to univariant phase equilibria in the system Cu–Ti–O. The decomposition curves of the CuO : TiO_2 mixtures agree well with those measured by Müller (*1*), apart from a shift of the univariant pressures which is due to the temperature.

As can be seen from Fig. 1 and from the isothermal phase triangle (Fig. 2), region I, with a univariant pressure of (11000 ± 400) Pa, corresponds to the equilibrium of the three solid phases CuO–TiO_2–"Cu_3TiO_4"; region II, with an oxygen partial pressure of (8700 ± 200) Pa, to the univariant equilibrium between the three solid phases CuO–Cu_2O–"Cu_3TiO_4"; and region III, with an oxygen partial pressure of (6000 ± 150) Pa, to the univariant equilibrium Cu_2O–TiO_2–"Cu_3TiO_4." While TiO_2 under the given experimental conditions can be regarded as a fixed phase, CuO and Cu_2O show distinct regions of homogeneity (*6*). Also "Cu_3TiO_4" exhibits a rather wide region of homogeneity in terms of the oxygen content and most probably also of the TiO_2 content. Among the fields of univariant phase equilibrium, there are therefore several fields which correspond to bivariant or even trivariant phase equilibria (shaded areas in Fig. 2).

The boundary compositions of "Cu_3TiO_4" could be approximately determined from the tie line of region I to $Cu_3TiO_{4.3}$ and from the tie line of region III to $Cu_3TiO_{3.9}$. Because of the rather high thermal instability of "Cu_3TiO_4," a determination of the homogeneity range in terms of the TiO_2 content by means of X-ray examination of quenched samples was not possible.

X-Ray powder diffraction of quenched mixtures of CuO and TiO_2 showed, besides reflections of CuO or Cu_2O and TiO_2, several additional reflections which could be attributed to a hexagonal phase with the lattice constants $a = 3.05$ Å and $c = 11.5$ Å. in good agreement with the single crystal data of Cu_3TiO_4 reported by Hayashi and Kato (*5*). Scanning electron microscopic examination of a sample with the Cu:Ti ratio of 3:1, quenched from 1270 K and $p_{O_2} = 13{,}000$ Pa (region I) to room temperature, yielded the existence of three phases which were determined by the electron microprobe as CuO, TiO_2, and a phase having a Cu:Ti ratio of about 3:1 (Fig. 3). From the thermogravimetric measurements, however, the existence of a phase of composition Cu_3TiO_5 at 1253 K can be unambiguously excluded. The tie lines in the isothermal phase triangle (Fig. 2) do not support any conclusions concerning other double oxide phases such as Cu_2TiO_3, etc.

The phase relations and reactions occurring in regions I–III are specified in Table I. Comparison of ΔG_1° and ΔG_2°, the free energies of formation of $Cu_3TiO_{4.3}$ and $Cu_3TiO_{3.9}$, respectively, from the oxides CuO, Cu_2O, and TiO_2, reveals no great difference. Accordingly, one can estimate the free energy of formation of the stoichiometric phase Cu_3TiO_4 at 1253 K, in accordance with the equation

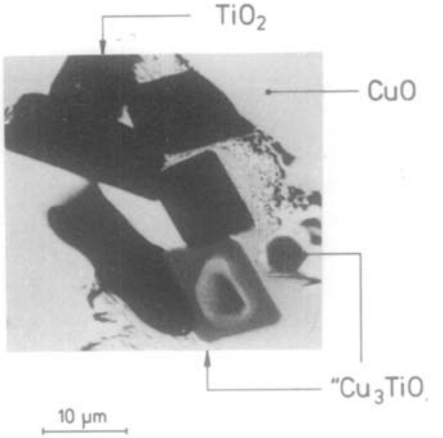

FIG. 3. SEM micrograph of a mixture (3 CuO · 1 TiO_2) quenched from region I (1270 K, $p_{O_2} = 13000$ Pa). Light phase = CuO; grayish phase = "Cu_3TiO_4"; dark phase = TiO_2.

$$CuO + Cu_2O + TiO_2 = Cu_3TiO_4,$$

to be not far away from a mean value of $\Delta G^\circ \approx -800$ J/mole.

The temperature dependence of ΔG_1° was determined from the temperature dependence of the oxygen pressure in regions I and II in the range of 1160–1270 K and by use of the equation $\log p_{O_2} = -13{,}157.89/T + 12.3189$ (atm), derived by Schmahl and Müller (*2*) for the reaction $4\,CuO = 2\,Cu_2O + O_2$ (region II).

The corresponding values are found in Table II. The determination of the temperature dependence of ΔG_2° ($Cu_3TiO_{3.9}$) was omitted because of the hesitant restoration of equilibrium in region III.

From the temperature dependence of ΔG_1° in the range of 1160–1270 K, the enthalpy and entropy of formation of the phase $Cu_3TiO_{4.3}$ from the oxides, according to

TABLE I

PHASE RELATIONS AND REACTIONS IN THE SYSTEM Cu_2O–CuO–Cu_3TiO_4–TiO_2 AT 1253 K

Region	Reaction proposed	p_{O_2} (Pa)	ΔG° (J/mole, related to the reaction of 1 mole O_2)
I	$3\,CuO + TiO_2 = Cu_3TiO_{4.3} + 0.35\,O_2$	11,000 ± 400	$\Delta G^\circ_I = (23{,}130 \pm 380)$
II	$4\,CuO = 2\,Cu_2O + O_2$	8,700 ± 200	$\Delta G^\circ_{II} = (25{,}574 \pm 240)$
III	$2\,Cu_3TiO_{3.9} = 3\,Cu_2O + 2\,TiO_2 + 0.4\,O_2$	6,000 ± 150	$\Delta G^\circ_{III} = (29{,}444 \pm 260)$
	$1.6\,CuO + 0.7\,Cu_2O + TiO_2 = Cu_3TiO_{4.3}$		$\Delta G^\circ_1 = 0.35(\Delta G^\circ_I - \Delta G^\circ_{II}) = -(855 \pm 220)$
	$0.8\,CuO + 1.1\,Cu_2O + TiO_2 = Cu_3TiO_{3.9}$		$\Delta G^\circ_2 = 0.20(\Delta G^\circ_{II} - \Delta G^\circ_{III}) = -(774 \pm 100)$

Table II, were derived by a least-squares fit as, respectively, $\Delta H^\circ_1 = (7600 \pm 450)\ J \cdot mole^{-1}$ and $\Delta S^\circ_1 = (6.7 \pm 0.4)\ J \cdot K^{-1} \cdot mole^{-1}$. The positive sign of ΔH°_1 indicates that the formation of the phase "Cu_3TiO_4" is endothermic. It becomes stable only at temperatures above 1130 to 1140 K.

The standard Gibbs free energy of formation of $Cu_3TiO_{4.3}$ at 1200 K could be determined by use of ΔG°_1 and the thermodynamic data of CuO, Cu_2O, and TiO_2 (*7*).

$$\Delta G^\circ_f(Cu_3TiO_{4.3}) = 1.6 \times \Delta G^\circ_f(CuO) + 0.7 \times \Delta G^\circ_f(Cu_2O) + \Delta G^\circ_f(TiO_2) + \Delta G^\circ_1.$$

In the same way, ΔH°_f and S°_f of $Cu_3TiO_{4.3}$ at 1200 K were determined using ΔH°_1, ΔS°_1, and the data listed in Ref. (*7*). The thermodynamic data of $Cu_3TiO_{4.3}$ at 1200 K thus determined are:

$$\Delta G^\circ_f = -101{,}39\ kJ,$$

$$\Delta H^\circ_f = -1115.84\ kJ,$$

$$S^\circ_f = 466{,}76\ J \cdot K^{-1} \qquad (T = 1200\ K).$$

The quantity ΔG°_1 was also used for calculating the region of p_{O_2} and T in which the phase "Cu_3TiO_4" is thermodynamically stable within its range of homogeneity. Figure 4 shows, in the range of temperature from 1100 to 1270 K, the calculated and measured values of oxygen pressures in which the phase "Cu_3TiO_4" can exist. The measured points in Fig. 4 are oxygen pressures determined in the plateau (univariant) regions I, II, and III.

From Fig. 4 it becomes evident that "Cu_3TiO_4" dissociates at too low partial pressures of oxygen into Cu_2O and TiO_2, while at too high partial pressures of oxygen it decomposes just as readily into CuO and TiO_2.

The thermogravimetric measurements indicate unambiguously that Cu_3TiO_5 does not not appear to be stable at 1160–1270 K.

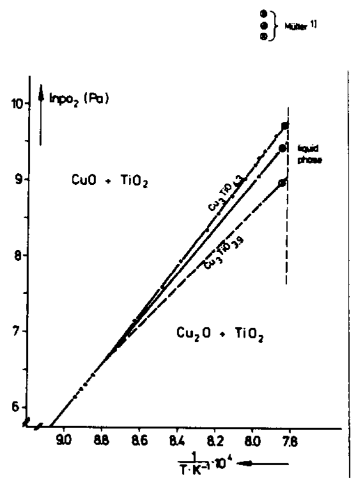

FIG. 4. Stability region of the solid double oxide phase "Cu_3TiO_4."

TABLE II

T (K)	p_{O_2}I (Pa)	ΔG°_I [a] (J·mole^{-1})	p_{O_2}II[b] (Pa)	ΔG°_{II} (J·mole^{-1})	ΔG°_I [c] (J·mole^{-1})
1,275	17,140	18,795	13,290	21,500	−947
1,268	14,900	20,181	11,660	22,765	−904
1,258	12,220	22,098	9,640	24,572	−866
1,253	11,030	23,067	8,760	25,475	−855
1,250	10,230	23,792	8,760	26,020	−780
1,242	8,520	25,547	7,070	27,462	−670
1,231	6,770	27,644	5,680	29,450	−632
1,221	5,310	29,883	4,650	31,257	−481
1,212	4,250	31,916	3,860	32,883	−338
1,192	2,830	35,422	2,540	36,497	−376
1,178	1,990	38,440	1,880	39,026	−205
1,158	1,290	41,985	1,200	42,640	−229

[a] Related to the formation of 1 mole O_2.

[b] Related to the formation of 1 mole $Cu_3TiO_{4.3}$.

[c] Calculated by the equation of Schmahl and Müller (*2*).

Furthermore, the results do not support any conclusions concerning other double oxide phases in the system CuO–Cu_2O–TiO_2 between 1160 and 1270 K.

Acknowledgments

The author wishes to thank Mr. J. v. d. Boomgaard, Philips Research Laboratories, Eindhoven, and Prof. Dr. G. H. Jonker, Techn. University Twente, for valuable discussions.

References

1. F. Müller, Thesis, RWTH, Aachen (1960).

2. N. G. Schmahl and F. Müller, *Z. Anorg. Allg. Chem.* **332**, 12–24 (1964).

3. A. A. Slobodyanyuk, Yu. D. Tret'yakov, and A. F. Bessonov, *Russ. J. Inorg. Chem.* **17**, 922–923 (1972).

4. Amin, Rajnikant Babubhai, German patent 2 333 318 (1974).

5. K. Hayashi and M. Kato, *Nippon Kagaku Kaishi* 1112–1114 (1975); *Chem. Abstr.* **83**, No. 9/10 (1975), 8926 (Sept. 1976).

6. C. Wagner and H. Hammen, *Z. Phys. Chem. Abt. B* **40**, 167 (1938).

7. J. Bahrin and O. Knacke, "Thermochemical Properties of Inorganic Substances," Springer-Verlag, Berlin; Verlag Stahleisen, Düsseldorf (1973).

8. K. Range and F. Ketter, *Z. Naturforsch.* **32b**, 1356–1357 (1977).