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Eutectic reaction between copper oxide and titanium dioxide

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Abstract

Eutectic reaction between copper oxide (CuO) and titanium dioxide (TiO_2) was investigated by using directly Cu and TiO_2 samples and by employing optical microscopy, X-ray diffraction (XRD), scanning electron microscopy, and electron probe for microanalysis (EPMA). Different types of samples including Cu plate/TiO_2 pellet samples and TiO_2/Cu/TiO_2 sandwiched samples were prepared. The samples would react with each other at as considerably low as about 900°C in air, which is due to a eutectic reaction. The reaction diagram was generated, in which different reaction categories were denoted at various temperatures (300–1070°C) and times. After annealing, the weight changes normalized to the original Cu samples were also analyzed to verify the eutectic reaction. The eutectic was identified to be the CuO–TiO_2 system characterized from XRD and EPMA analyses. Annealing in $N_2/O_2=9$ at the same temperature as in air resulted in similar but not so drastic eutectic melting phenomena. The eutectic reaction would enhance significantly the grain growth of TiO_2 and the oxidation of Cu. The changes in the microstructures and the morphologies of the samples were also investigated. The eutectic temperatures of CuO and other oxide systems were compared and discussed. The eutectic points as well as the phase diagram of the CuO–TiO_2 system were calculated and analyzed. Several potential applications of the reactions were also proposed.

Keywords: Cu; CuO; Eutectic reaction; Microstructure-final; TiO_2

1. Introduction

The metal–ceramic reactions at high temperature under controlled atmosphere are of technological importance. Cu is a widely used material in industry and an important material for future interconnects in ICs. Moreover TiO_2 is also a widely used material for its excellent optical, chemical, and many other properties. Hence the Cu–TiO_2 system was chosen for the study. Nevertheless very few studies concerning the reactions of Cu and TiO_2 at high temperature under controlled oxygen partial pressures have been systematically investigated before. This part of the research focuses on the reactions mainly in air and partly in $N_2/O_2=9$ where eutectic reactions would occur. It is worth noting that little information on the eutectic reactions between CuO and TiO_2 is available in the literature.

The objective of this research is to investigate the eutectic reaction of the CuO–TiO_2 system mostly in air. The changes in the appearance, the weight, the crystal structure, and the microstructure after annealing have been analyzed to study the eutectic reaction. Another gas with different oxygen partial pressure such as $N_2/O_2=9$ has also been used for comparing the microstructural changes. For the ease of sample preparation and the increase of reaction areas, two types of samples: Cu plates were directly placed on the top of TiO_2 pellets and TiO_2/Cu/TiO_2 sandwiched samples were prepared. The eutectic temperatures of copper oxides and other oxide systems available in the literature have been compared and discussed. The CuO–TiO_2 phase diagram including the eutectic points has been calculated assuming that the quasi-binary system exhibits complete miscibility in the liquid state and virtually complete immiscibility in the solid state. The applicability of the eutectic reactions has also been discussed.

2. Experiments

The eutectic reactions of CuO and TiO_2 were investigated mainly by using directly Cu and TiO_2 samples for

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the ease of sample preparation. For comparison, CuO samples were also prepared from the oxidation of Cu plates in air at 1020°C for at least 3 h. Surface CuO phase was confirmed by X-ray diffraction. The copper (JIS H 3100 C1201R-1/4H, 99.9%+ purity) plates was first mechanically ground and polished. Then the plates were electrolytically polished by using H_3PO_4:H_2O (7:3) as the electrolyte. To avoid pitting occurring on the substrates, the operation voltage was maintained at 2.0 V and the polishing time was about 5 min. After that the copper plates (10×10×0.5 mm) were embedded in the TiO_2 powders (Showa Denko, 99.9%, ~0.3 μm) and then cold pressed into the disks with the size of about 17 mm in diameter and 5 mm in thickness. The main advantage of this type of simple sample preparation is to increase the reaction area between Cu and TiO_2. Another type of sample was also prepared, i.e. Cu plates with the same size were placed directly on the top of the TiO_2 pellets (17 mm in diameter and 2 mm in thickness), which were prepared from pressing the TiO_2 powders. The measured green density of the TiO_2 pellets was about 60% of the theoretical density.

Annealing in air was performed in a muffle furnace. For comparison, three samples including a Cu/TiO_2 sample, a single Cu plate, and a single TiO_2 pellet were placed in the furnace during each annealing run. The ramping rates were about 6°C/min. The temperatures were monitored by an R-type thermocouple and were calibrated to the melting point of Au (99.99%), i.e. 1064°C. Annealing in $N_2/O_2=9$ was done in a tube furnace equipped with an oxygen sensor (15%CaO–doped ZrO_2). After annealing, the changes in the appearance of the samples were examined by using both a stereo microscope and an optical microscope. The weight changes were also recorded. The changes in the crystal structure were determined by the MacScience MXP3 X-ray diffractometer. The microstructure and the morphology were examined by the JEOL JSM-5400 scanning electron microscope (SEM) equipped with the LINK ISIS energy dispersive spectrometer (EDS). When necessary, a JEOL 8900R Electron Probe Micro-analyzer (EPMA) with 20 kV accelerating voltage was also used to identify the change in the composition.

3. Results and discussion

3.1. Changes in the appearance and weight

The Cu plate/TiO_2 pellet (a Cu plate was placed directly on the top of a TiO_2 pellet) samples were annealed in air for 10 min and 1 h at temperatures varying from 300 to 1070°C. After the anneal samples were first examined by using a stereo microscope and an optical microscope. The reaction results concerning the appearance of the samples are given in Fig. 1. In the figure, the notation "partly reaction" refers to that the Cu plates are oxidized and the resulted oxides react with the adjacent TiO_2, then the melts diffuse into part of the TiO_2 pellets. Since the occurring diffusion is so fast (the calculated diffusion coefficient, by using $x^2 \sim D{\cdot}t$, would be larger than 10^{-5} cm^2/s) that only liquid state diffusion would be possible. Furthermore the reaction temperatures are much lower then the melting points of Cu (1083°C [1]) and TiO_2 (1825°C [1]) as well as the eutectic point of Cu–Cu_2O (1066°C [2]) and Cu_2O–CuO (1091°C [2]). Hence the melts that turn black in appearance are most possibly the eutectic melts. The melting denoted in the figure then refers to a eutectic melting. The boundary temperature between no apparent reaction and apparent reactions (including partly reaction and melting) is about 900°C which may be considered as the eutectic temperature.

Fig. 2 shows the normalized weight changes of the Cu/TiO_2 samples and the Cu plates alone after annealing at above various temperatures for 10 min. The weight changes are normalized to the original Cu sample for comparison. Since the weight changes of the Cu/TiO_2

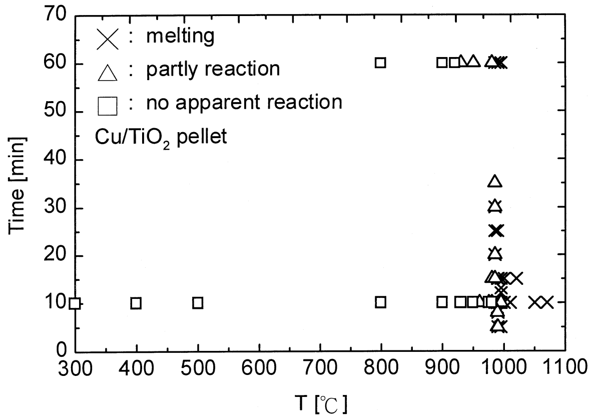

Fig. 1. The reaction diagram in which the resulted appearance of Cu/TiO_2 samples after annealing at various temperatures and times was denoted.

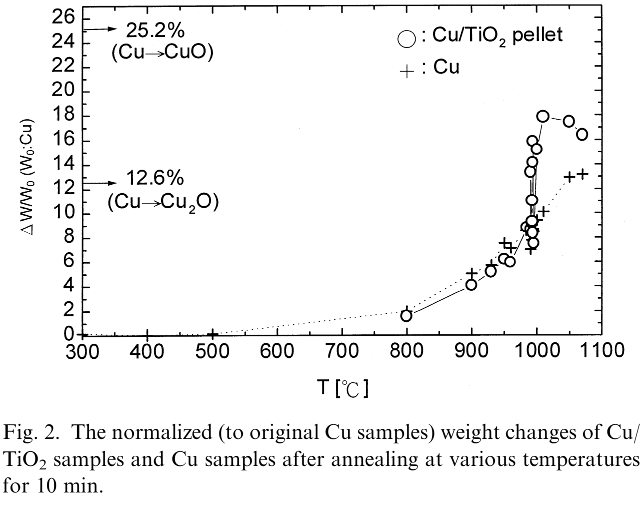

Fig. 2. The normalized (to original Cu samples) weight changes of Cu/TiO_2 samples and Cu samples after annealing at various temperatures for 10 min.

samples are mainly due to both the oxidation of Cu and the Cu_xO (Cu_2O or CuO)–TiO_2 eutectic reaction (the weight changes of TiO_2 after annealing are minimal), the difference in the normalized weight changes between the Cu/TiO_2 sample and the single Cu plate at corresponding conditions would mainly attribute to the eutectic reaction. In the figure, it is shown that the major difference in the weight changes of the two samples occurs at 990°C. The temperature is near but lower than the boundary temperature as described earlier. Since the difference in the normalized weight change would not be so obvious when the eutectic melting starts to occur and is not so drastic, it is reasonable that the difference temperature concerning the normalized weight change would be lower than the boundary temperature concerning the resulted appearance. Nevertheless the major difference of the normalized weight changes is also another clear evidence of the eutectic reaction in the system. Very similar results concerning the resulted appearance and the normalized weight change at above temperatures were also obtained for the TiO_2/Cu/TiO_2 sandwiched samples.

It is worth noting that the calculated weight change is 12.6% when pure Cu is completely oxidized into Cu_2O (25.2% for CuO). As shown in the figure the weight change for pure Cu samples would be only slightly larger than 12.6% even the annealing temperature reaches 1070°C. But the normalized weight change of the Cu (in contact with TiO_2) samples could reach about 18% (about 50% weight increase) at similar temperatures. That also indicates the only a small amount of CuO exists in the single Cu sample but a large amount of CuO is present in the Cu/TiO_2 sample at corresponding conditions.

After annealing in air at 1020°C for 30 min, Cu plates alone could only be partially oxidized into both Cu_2O and CuO phases as revealed by XRD. It has been reported in the literature that it would take about 30 days at 1000°C in oxygen to completely oxidize Cu foils with the thickness about 0.1 mm into CuO.[3] It is reported that the oxidation of Cu to Cu_2O in air or oxygen occurs much faster compared to that of Cu_2O to CuO. Since mostly the CuO phase beside TiO_2 is present in the annealed Cu/TiO_2 samples, the eutectic reaction apparently enhances the oxidation of Cu. This may be due to the quick exposure of Cu plates to air after the repetitive consumption of the plates during the eutectic reaction.

3.2. *Changes in the crystal structures and microstructures*

Since the eutectic reaction could be possibly due to either Cu_2O–TiO_2 or CuO–TiO_2, the samples were examined by X-ray diffraction. Both types of the samples (Cu placed on TiO_2 pellets and Cu/TiO_2/Cu sandwiched samples) were checked. The diffraction results at the TiO_2 sides show that only CuO and TiO_2 (rutile) phases are present as revealed in Fig. 3. Moreover as described earlier, the color turns black which also indicates the presence of CuO. Hence the eutectic refers to the CuO–TiO_2 system.

The cross-sectional view (backscattered electron image, BEI/SEM) of the sample in which copper plates were embedded in the TiO_2 powders, then cold pressed, and annealed in air at 1020°C for 30 min is shown in Fig. 4(a). As shown in the figure, a large void is present inside the sandwiched sample. This is because that the original Cu plate was oxidized, then the resulted oxide reacted with the adjacent TiO_2, and finally the eutectic melts diffused away from the original Cu plate region into the TiO_2 region. Meanwhile, the original TiO_2 region can be distinguished into two phases: dark and light phases as given in the figure. An enlarged backscattered electron image of Fig. 4(a) at the original Cu/TiO_2 interface is given in Fig. 4(b). Combining the information obtained from BEI and XRD as well as EPMA, it is known that large TiO_2 grains (dark phase) are dispersed in the CuO–TiO_2 eutectic (light phase) matrix. To verify the eutectic structure, the above samples were further annealed in a very reducing $N_2/H_2 = 9$ atmosphere at 1000°C for 2 h. After the reduction, the samples turned from black (CuO color) into red (Cu color). In the samples only Cu and TiO_2 phases are present confirmed by XRD, which indicates a complete reduction of CuO into Cu. The crosssectional view (BEI) of the samples after the reduction is shown in Fig. 4(c). The dark phase is TiO_2 and the eutectic structure could be then observed in the previous light region of Fig. 4(b). Similar melting phenomena and microstructure changes could also be observed in the reactions of the samples in which Cu plates with and without the prior oxidation were placed directly on the top of TiO_2 pellets.

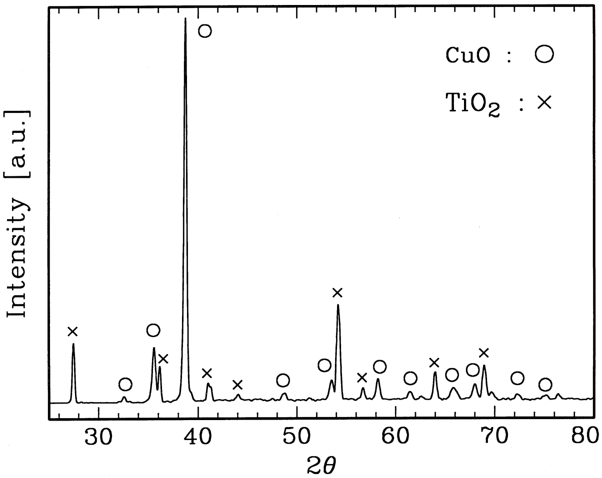

Fig. 3. XRD results of the TiO_2 side in the TiO_2/Cu/TiO_2 sandwiched samples after annealing at 1020°C for 30 min in air.

In the melted samples the grain size of the TiO_2 ranges from a few microns to 50 μm, which is much larger than that of TiO_2 samples without being in contact with Cu at corresponding conditions. The averaged grain size of the TiO_2 samples is about 0.3 μm before sintering and remains about the same size after annealing. Hence the eutectic reaction could aide drastically the grain growth of TiO_2. Moreover as seen in Fig. 4(b) almost no porosity could be observed in the Cu/TiO_2 samples. This is quite interesting since there still exists about 10–20% porosity in the pure TiO_2 samples alone after sintering at 1000–1300°C.

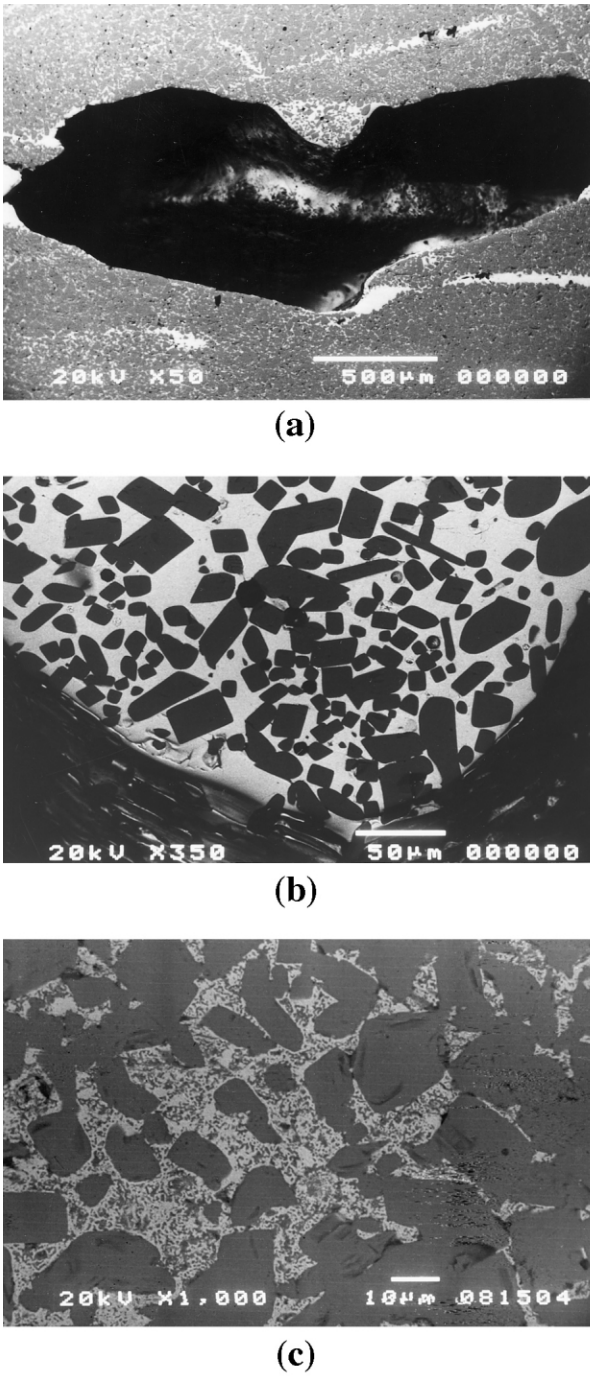

Fig. 4. Cross-sectional view (SEM/BEI) of the TiO_2/Cu/TiO_2 sandwiched samples after annealing in air at 1020°C for 30 min. (a) A large void is present inside the sandwiched sample; (b) Enlarged image of (a) at the original Cu/TiO_2 interface. The dark phase is the TiO_2 and the light phase is the CuO-TiO_2 eutectic; (c) The sample was further reduced in $N_2/H_2=9$ at 1000°C for 2 h. The dark phase is TiO_2 and the eutectic structure could be observed in the previous light region.

In addition to air, another gas mixture $N_2/O_2=9$ was also used for comparison. The oxygen partial pressure in the gas mixture is 0.1 atm confirmed by the oxygen sensor. The oxygen partial pressure is slightly smaller than that in air (=0.21 atm). After annealing at 1020°C in the gas mixture for more than 3 h, no drastic melting could be observed in the sandwiched TiO_2/Cu/TiO_2 samples although the whole samples also turn black. Only CuO and rutile TiO_2 phases could be identified at the TiO_2 sides of the samples by XRD. The cross-sectional view of the samples in the SEM/BEI mode is given in Fig. 5. The light phase in the original TiO_2 region is the CuO–TiO_2 eutectic and the dark phase is TiO_2 similar to that described earlier. As shown in the figure, the original embedded Cu plates do not disappear unlike those annealed in air although the annealing time is much longer. As shown in the figure, the eutectic melts diffuse apparently in liquid state through cracks, which might be resulted from thermal mismatch between TiO_2 and the copper sample. This less drastic melting phenomenon could be possibly due to a higher eutectic temperature since the oxygen partial pressure is lower compared to that in air.

3.3. Calculation of the eutectic points

The phase diagram of the Cu–Ti–O system is rather scarce. Only a few phase diagrams are available concerning the existence of several intermediate phases, e.g. in Refs. 4,5. The intermediate phases in the Cu–Ti–O system contain Cu_3TiO_4,[4] Cu_2Ti_4O, Cu_3Ti_3O,[5] etc. The

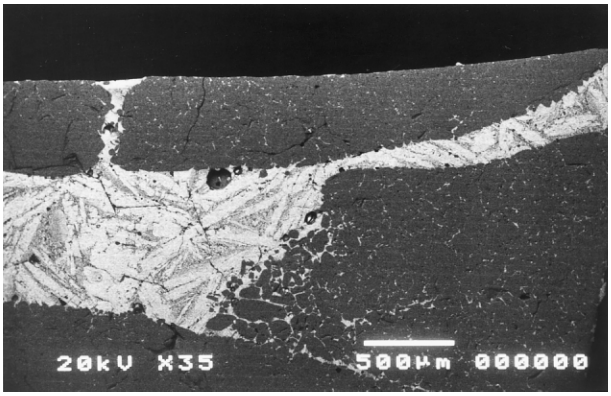

Fig. 5. Cross-sectional view (SEM/BEI mode) of the TiO_2/Cu/TiO_2 sandwiched samples after annealing in $N_2/O_2=9$ gas mixture at 1020°C for 3 h. No void is present and the trace of the diffusion of eutectic melts through cracks could be observed.

Cu_3TiO_4 phase, which is only stable in a narrow range of temperatures and oxygen partial pressures, can only be prepared from quenching the CuO, Cu_2O and TiO_2 samples. Cu_2Ti_4O, Cu_3Ti_3O compounds observed as products of reactions at Ag–Cu–Ti/Al_2O_3 interface also exhibit a narrow phase stability range.[5]

The eutectic points of the copper oxides and titanium dioxides are not available in the literature. Hence it is interesting to compare the eutectic temperatures in the copper oxides and other simple oxide systems. The eutectic temperatures for CuO, Cu_2O and other oxide (M_xO_y) system at $pO_2 = 1$ atm and 0.21 atm were compiled in Table 1. The melting temperatures of the oxide M_xO_y are also given. The simple oxide systems, denoted as a terminal oxide in the table, include Al_2O_3,[6] B_2O_3,[7] CaO,[6] Cr_2O_3,[7] Fe_2O_3,[8] NiO,[9] PbO,[10] SiO_2,[10] TeO_2,[7] ZrO_2,[8] etc. As given in the table, the eutectic temperatures are higher than 1010°C when the melting points of M_xO_y are larger than 1000°C. It is worth noting that CuO decomposes into Cu_2O at about 1031°C in air.[2] Consider the Cu_xO and simple oxide system like PbO, SiO_2, TeO_2 and ZrO_2 where no intermediate phases occur; the eutectic temperature tends to increase when the melting point of the simple oxide is higher. Since no intermediate phases have been observed in air for the CuO–TiO_2 system, the eutectic temperature in the system as previously observed from the microstructural changes is considerably low concerning the high melting point of TiO_2 ($T_m = 1825$°C).

Table 1
The eutectic temperatures (T_{EU}) in the Cu_xO and other oxide (M_xO_y) system at mainly $pO_2 = 1$ and 0.21 atm. The melting temperatures of the oxide (M_xO_y), $T_m(M_xO_y)$ are also given

Cu_xO	M_xO_y/terminal oxide	T_{EU} (°C)	pO_2 (atm)	$T_m(M_xO_y)$ (°C)	Ref.
Cu_2O	$Cu_2O{\cdot}Al_2O_3/Al_2O_3$	1130	0.21	1238	6
CuO	$CuO{\cdot}Al_2O_3/Al_2O_3$	1108	1	1240	
CuO	$3CuO{\cdot}B_2O_3/B_2O_3$	950	0.21	1000	7
CuO	$CuO{\cdot}2CaO/CaO$	1013	0.21	1030	6
CuO	$CuO{\cdot}2CaO/CaO$	1052	1	1080	
Cu_2O	$CuCrO_2/Cr_2O_3$	1130	0.21	–	7
CuO	$CuFe_2O_4/Fe_2O_3$	1070	1	–	8
Cu_2O	(Cu,Ni)O/NiO	1090	0.21	–	9
Cu_2O	PbO/PbO	680	–	850	10
Cu_2O	SiO_2/SiO_2	1060	–	1713	10
Cu_2O	TeO_2/TeO_2	610	(Ar)	733	7
Cu_2O	ZrO_2/ZrO_2	1130	0.21	2715	8
CuO	ZrO_2/ZrO_2	1097	1	2710	

Assume the quasi-binary system exhibits complete miscibility in the liquid state and virtually complete immiscibility in the solid state, the liquidus curves and the eutectic points can be calculated providing the eutectic reactions occur.[11] Consider the CuO–TiO_2 system exhibits this type of phase diagram. If the liquid solutions are Raoultian, when pure CuO is in equilibrium with the liquid solution of the liquidus composition, the standard Gibbs free energy change can be expressed as

$$\begin{aligned}\Delta G^{\circ}_{m(CuO)} &= G^{\circ}_{CuO(l)} - G^{\circ}_{CuO(s)} \\ &= -RT\ln X_{CuO}(\text{liquidus}) = \Delta H^{\circ}_{m(CuO),Tm} \\ &+ \int_{T_m}^{T} \Delta C_{p,CuO} dT \\ &- T\left(\Delta S^{\circ}_{m(CuO),Tm} + \int_{T_m}^{T} \frac{\Delta C_{p,CuO}}{T} dT\right)\end{aligned}$$

where $X_{CuO(liquidus)}$ is the compostion of the CuO liquidus at T, $\Delta C_p = C_{p(l)} - C_{p(s)}$, T_m is the melting point. Using the thermodynamic data available in the literature[1] as given in Table 2, the liquidus curves could be calculated.

$$\begin{aligned}\Delta G'_{m(CuO)} &= -RT \ln X_{CuO(liquidus)} = -1834 + 52.45T \\ &+ 3.1 \times 10^{-3}\ T^2 - 7.66\ T\ln T\end{aligned}$$

Similar to CuO, the TiO_2 liquidus could be calculated

$$\begin{aligned}\Delta G^{\circ}_{m(TiO_2)} &= \Delta H^{\circ}_{m(TiO_2),T_m} + \int_{T_m}^{T} \Delta C_{p,TiO_2}\ dT \\ &- T\left(\Delta S^{-}_{m(TiO_2),T_m} - + \int_{T_m}^{T} \frac{\Delta C_{p,TiO_2}}{T} dT\right) \\ &= 5027 +\ 23.59T + 1.4 \times 10^{-4} T^2 - 2.18 \times 10^5 \frac{1}{T} \\ &- 3.43\ T\ln T = -RT\ \ln X_{TiO_2(liquidus)}\end{aligned}$$

Table 2
Thermodynamic data of CuO and TiO_2 [1] for the calculation of the phase diagram. T_m is the melting point, $\Delta H_{m,T_m}$ represents the heat of fusion, and C_p denotes the heat capacity

	CuO	TiO_2
T_m (°C)	1121 (1394 K) ($pO_2 = 1$ atm)	1825 (2098 K)
$\Delta H_{m,T_m}$ (cal/g-mol)	2,820	11,400
$C_{p(s)}$ (cal/g-mol)	$14.34 + 6.2\times10^{-3}T$	$17.97 + 0.28 \times 10^{-3}T - \frac{4.35 \times 10^5}{T^2}$
$C_{p(l)}$ (cal/g-mol)	22	21.4

Hence the CuO and TiO_2 liquidus curves can be rewritten as

$$\ln X_{\mathrm{CuO(liquidus)}} = \frac{926}{T} - 26.5 - 1.57 \times 10^{-3} T + 3.87\ T$$

$$\ln X_{\mathrm{TiO_2(liquidus)}} = \frac{1.10 \times 10^5}{T^2} - \frac{2539}{T} - 11.91 - 7.07 \times 10^{-5} T + 1.73 \ln T$$

The liquidus curves are plotted in Fig. 6. The calculated eutectic point is at $T = 919$°C and $X_{\mathrm{TiO2}} = 16.7$ mol%. The eutectic temperature is rather low compared to that in other CuO-oxide systems. It is worth noting that the obtained phase diagram was calculated at $pO_2 = 1$ atm where CuO, the only stable oxide phase of Cu in pure oxygen, melts at 1121°C. Since CuO may melt congruently or incongruently at quite different temperatures when pO_2 changes,[2] the phase diagram apparently would be varied accordingly. In air CuO would not melt but decomposes at 1031°C into Cu_2O which in turn melts incongruently at 1134°C.[2] Hence the diagram in air would be quite different. This is worth being further investigated.

3.4. Potential applications

Several potential applications of the eutectic reactions in the system have been proposed. As described earlier the CuO–TiO_2 eutectic reaction could aide significantly the grain growth of TiO_2. Large-grained TiO_2 samples could be easily prepared by adding a small amount of Cu or CuO into TiO_2 during sintering. The grain size could increase more than 100 times (from 0.3 to 50 μm) comparing to that prepared from the normal sintering process. Since the eutectic reaction could also enhance the oxidation of Cu. A small amount of TiO_2 could be added to Cu to prepare a large CuO crystal that is almost not possible when prepared directly from the oxidation of Cu.

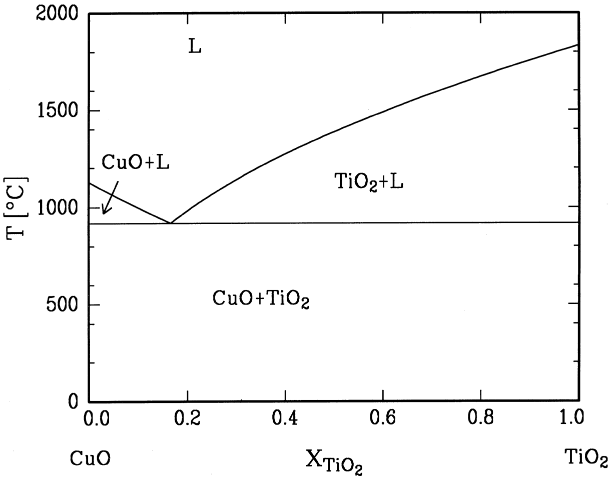

Fig. 6. The calculated CuO–TiO_2 phase diagram at $pO_2 = 1$ atm. Eutectic point is at $T = 919$°C and $X_{\mathrm{TiO2}} = 16.7$ mol%.

When annealing the Cu/TiO_2 samples at 900°C for 10 min, CuO resulted from the reactions would diffuse into TiO_2 at the contact area to form a thin layer. After the CuO-diffused TiO_2 samples were annealed in a reducing gas such as $N_2/H_2 = 9$ at the same temperature for about 30 min, CuO was completely reduced to Cu and Cu films then remained on the top of TiO_2 surface. The conductive films are continuous, which was verified by a resistance meter. This could provide another way to prepare Cu films on oxides by employing the reactions. Like many other systems, eutectic bonding of the Cu and TiO_2 is the nature candidate for the application of the reaction. Hence it is important to investigate systematically the reactions between Cu and TiO_2 under different oxygen partial pressures including the eutectic reactions in the CuO–TiO_2 and Cu_2O–TiO_2 systems.

4. Summary

After annealing at various temperatures ranging from 300 to 1070°C, the changes in the appearance, the normalized (to original Cu) weight, the crystal structure, and the microstructure of the Cu/TiO_2 samples have been analyzed to investigate the eutectic reaction. The reaction diagram concerning the resulted appearance of the samples have been generated. The CuO–TiO_2 eutectic reaction could be observed at as low as 900°C which is considerably low compared to copper oxides and other high melting point oxides eutectic systems. Annealing in gases possessing lower oxygen partial pressures at corresponding conditions as in air would cause less drastic melting, which may attribute to a higher eutectic temperature. The CuO–TiO_2 eutectic reaction could enhance significantly the oxidation of Cu and the grain growth of TiO_2. The eutectic point of the CuO and TiO_2 has been successfully calculated to be at $T = 919$°C and $X_{\mathrm{TiO2}} = 16.7$ mol% in $pO_2 = 1$ atm. Several applications of the eutectic reactions have been proposed and demonstrated.

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