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ARTICLE

Study of Phase Equilibria in the Cu-Co-Zn Ternary System

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Abstract: The phase equilibria of the Cu-Co-Zn ternary system at 800 °C and 1000 °C were investigated by electron probe microanalysis and X-ray diffraction. Results show that no ternary compound was found. At 800 °C, the solubility of Co in the β-CuZn, and Cu in the β1-CoZn at 800 °C are 32.36 at% and 5.28 at%, respectively. The γ-Co_5Zn_{21} and γ-Cu_5Zn_8 show that the same crystal structure, and thus an infinite region of mutual solubility is observed in the Cu-Co-Zn ternary system. It is confirmed that as the temperature rises from 800 °C to 1000 °C, the liquid-phase region is further expanded. The isothermal section of 1000 °C is simple. The phases of β-CuZn, β1-CoZn, γ-Co_5Zn_{21} and γ-Cu_5Zn_8 disappear. The region of liquid phase is very large.

Key words: Cu-Co-Zn ternary system; phase equilibria; electron probe microanalysis

In the design and development of lead-free solder, Cu is often used as the preferred element for solder alloys. For example, the common SAC305, SAC105, Sn-0.7Cu, etc. contain Cu element. Meanwhile, the appearance of Cu interconnection technology in the electronic packaging field made Cu become the main interconnection material in the integrated circuit[1]. Therefore, the study of Cu-containing phase diagrams is very important for the development of lead-free solders and the interface reaction of soldering. Zn has also attracted wide attention due to its low price and ability to form eutectic structure with Sn[2,3]. In recent years, Co has also become an important alloying element for lead-free solder systems. Related studies have shown that the addition of trace amounts of Co can improve the wettability of solder, while the addition of Co can make the interfacial layer of intermetallic compound (IMC). The layer structure is more compact and plays a crucial role in improving the mechanical properties[3]. Although the above alloying elements have achieved a great deal of research results, the experimental research on the Cu-Co-Zn ternary system is still very scarce, and the experimental determination of Cu-Co-Zn ternary phase diagram is important to improve the lead-free solder database. Therefore, it is necessary to conduct in-depth experimental research on the phase equilibrium information of the Cu-Co-Zn ternary system.

Three binary subsystems and stable solid phases of Cu-Co[4], Co-Zn[5] and Cu-Zn[6] constitute the Cu-Co-Zn ternary system, as shown in Fig.1 and Table 1. The Cu-Co phase diagram is a very simple system without any intermetallic compounds which has been reported by Nishizawa and Ishida[4]. Pattanaik[7] et al investigated the structure of Cu-Co alloy and Kubišta[8] et al determined the molar excess Gibbs energy, enthalpy and entropy of mixing, as well as the thermodynamic activities of components in the liquid Cu-Co system. Cao[9] et al investigated the phase separation in the metastable miscibility gap of undercooled Cu-Co alloys by electromagnetic levitation and differential thermal analysis. For Co-Zn system, Straumal[10] et al determined the partial phase boundaries in the Co-Zn system. Cu-Zn phase diagram was reported by Okamoto[5] which demonstrates five stable compounds β(CoZn), β1(CoZn), γ(Co_5Zn_{21}), γ($CoZn_7$) and γ($CoZn_{13}$). Cu-Zn is an important brass alloy system, and Spencer[11] et al performed the first thermodynamic calculation of the Cu-Zn system in 1986. Kowalski[12] et al and

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David[13] et al re-assessed the Cu-Zn binary system. In addition, Chen[14], Wang[15], Du[16], Liang[17] et al have successively evaluated and optimized the Cu-Zn system. Cu-Zn phase diagram was reported by Effenberg[6] which demonstrated five stable compounds β(CuZn), β'(CuZn), γ(Cu_5Zn_8), $\delta$$CuZn_3$ and $\varepsilon$$CuZn_5$. In 2004, Vassiley[18] et al according to the research of Cu-Co-Zn ternary system by Xie[19], found that there is an extensive region of mutual solubility existing between γ-Co_5Zn_{21} phase and γ-Cu_5Zn_8 phase. However, the phase equilibria information of the Cu-Co-Zn ternary system has still been incompleted. In this study, the phase equilibria information of the Cu-Co-Zn ternary system at 800 °C and 1000 °C will be determined.

1 Experiment

In this work, high purity metals were used: Copper (99.99%), Cobalt (99.99%), Zinc (99.99%). Each Cu-Co-Zn ternary alloy weighed around 20 g was prepared in sealed transparent quartz capsules with an argon atmosphere. To achieve compositional homogeneity, the ingots were remelted at least 4 times and the mass losses were less than 0.5 wt%.

Afterwards, the ternary Cu-Co-Zn alloys were cut into small pieces and resealed in quartz tubes with argon for further annealing treatment. The specimens in the quartz capsules were annealed at 800 and 1000 ºC for various durations from several days to almost one month, depending on the alloy composition and annealing temperature. After the end of heat treatment, the specimens were re-quenched into ice water.

After standard metallographic preparation, microstructure observations and chemical analysis of the equilibrium phases were carried out on electron-probe-microanalyzer (EPMA, JXA-8100, JEOL, Japan). High purity metals were used as standard metallographic and the measurements were carried out at a voltage of 20 kV and a current of 1.0×10^{-8} A. The crystal structure analysis was conducted by X-ray diffraction (XRD) on a Philips Panalytical X-pert diffractometer (Cu Kα radiation at 40 kV and 40 mA). The data were collected in the range of 2θ from 20° to 100° at a step size of 0.01°. Corresponding XRD evaluations were carried out using the Jade software, version 6.5.

2 Results and Discussion

2.1 Phase equilibrium at 800 and 1000 °C

In the present study, 26 samples with different compositions were prepared in order to determine the phase equilibria at 800 and 1000 °C in the Cu-Co-Zn ternary system. Alloys with different compositions were marked with different numbers for reading convenience. The related equilibrium compositions of the Cu-Co-Zn ternary system at 800 and 1000 ºC were summarized in Table 2. Back-scattered electron (BSE) images and X-ray diffraction (XRD) patterns for most of the Cu-Co-Zn ternary specimens are shown in Fig.2 and Fig.3, respectively.

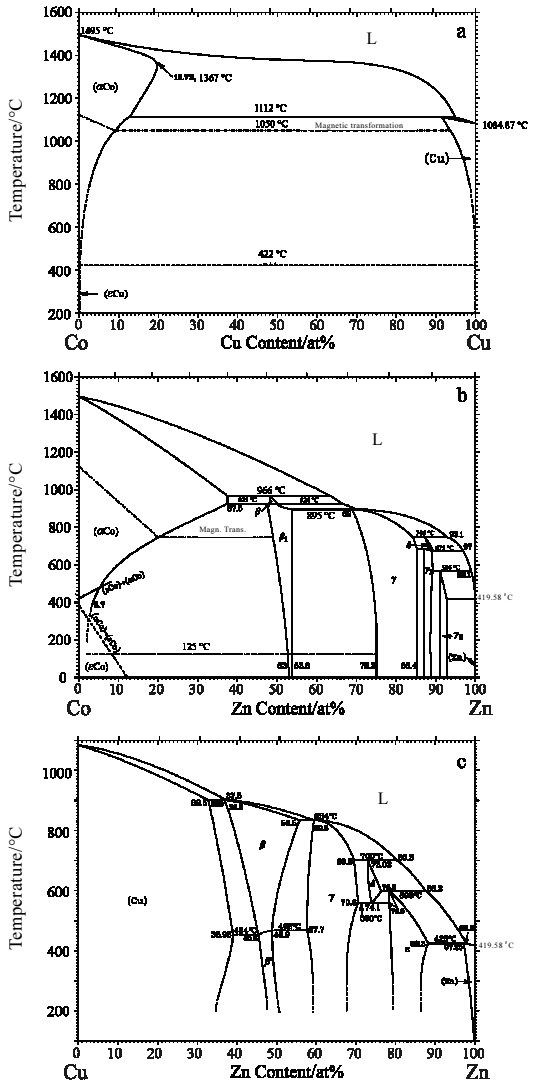

Fig.1 Binary phase diagrams that constitute the Cu-Co-Zn ternary system: (a) Co-Cu[4] binary system, (b) Co-Zn[5] binary system, and (c) Cu-Zn[6] binary system

Table 1 Stable solid phases in the three binary systems[4-6]

Published phase label	Phase prototype	Pearson symbol	Struk-tur-bericht	Space group	Ref.
(αCo)	Cu	cF4	A1	Fm-3m	[5]
(εCo)	Mg	hP2	A3	P63/mmc	[5]
(Cu)	Cu	cF4	A1	Fm-3m	[5]
β(CuZn)	W	cI2	A2	Im-3m	[6]
β'(CuZn)	CsCl	cP2	B2	Pm-3m	[6]
$\gamma$$Cu_5Zn_8$	Cu_5Zn_8	cI52	D82	I-43m	[6]
$\delta$$CuZn_3$	-	hP3	-	P-6	[6]
$\varepsilon$$CuZn_5$	Mg	hP2	A3	P63/mmc	[6]
(Zn)	Mg	hP2	A3	P63/mmc	[6]
β(CoZn)	W	cI2 or cP2	A2	Im-3m	[7]
β1(CoZn)	βMn	cP20	A13	$P4_132$	[7]
γ(Co_5Zn_{21})	Cu_5Zn_8	cI52	D81-3	I-43m	[7]
γ($CoZn_7$)	γ-brass related	-	-	Cubic	[7]
γ($CoZn_{13}$)	$CoZn_{13}$	mC28	-	C2/m	[7]

Table 2 Equilibrium composition of the Cu-Co-Zn ternary system at 800 and 1000 °C determined in the present work

No.	*T*/°C	Alloy(at%)	Annealing time/ d	Phase equilibria	Composition/at%					
				Phase 1/ Phase 2/ Phase 3	Phase 1		Phase 2		Phase 3	
					Cu	Co	Cu	Co	Cu	Co
1	800	$Cu_{15}Co_{10}Zn_{75}$	1	γ / L	18.7	12.9	4.5	6.5	-	-
2	800	$Cu_{15}Co_{20}Zn_{65}$	20	γ	15.3	21.3	-	-	-	-
3	800	$Cu_{15}Co_{45}Zn_{40}$	20	(αCo)/β-CuZn	7.1	63.0	19.0	30.8	-	-
4	800	$Cu_{20}Co_{10}Zn_{70}$	20	β-CuZn	38.6	10.0	-	-	-	-
5	800	$Cu_{24}Co_{20}Zn_{56}$	20	β-CuZn	27.7	22.8	-	-	-	-
6	800	$Cu_{32}Co_{16}Zn_{52}$	20	β-CuZn	32.7	16.1	-	-	-	-
7	800	$Cu_{10}Co_{45}Zn_{45}$	20	(αCo)/β1-CoZn/β-CuZn	5.0	62.1	5.1	47.6	16.44	32.26
8	800	$Cu_{20}Co_{25}Zn_{55}$	20	β-CuZn	21.5	27.0	-	-	-	-
9	800	$Cu_{70}Co_{13}Zn_{17}$	20	(αCo)/(Cu)	7.3	89.9	76.6	3.4	-	-
10	800	$Cu_{20}Co_{40}Zn_{40}$	20	(αCo)/β-CuZn	6.3	67.7	31.5	20.4	-	-
11	800	$Cu_{10}Co_{50}Zn_{40}$	20	(αCo)/β-CuZn	5.8	60.8	17.5	32.4	-	-
12	800	$Cu_{30}Co_{28}Zn_{42}$	20	(αCo)/β-CuZn	6.04	70.3	35.5	17.7	-	-
13	800	$Cu_{25}Co_{9}Zn_{66}$	20	γ	25.2	9.5	-	-	-	-
14	800	$Cu_{15}Co_{30}Zn_{55}$	20	β1-CoZn/β-CuZn/γ	5.3	44.9	18.4	27.7	17.83	19.32
15	800	$Cu_{14}Co_{41}Zn_{45}$	20	(αCo)/β-CuZn	6.4	62.1	17.9	32.2	-	-
16	800	$Cu_{29}Co_{28}Zn_{43}$	20	β-CuZn	33.5	18.4	-	-	-	-
17	1000	$Cu_{40}Co_{30}Zn_{30}$	1	(αCo)/L	6.2	82.7	57.0	6.0	-	-
18	800	$Cu_{24}Co_{12}Zn_{64}$	20	γ	23.92	11.9	-	-	-	-
19	800	$Cu_{30}Co_{20}Zn_{50}$	20	β-CuZn	31.7	19.6	-	-	-	-
20	1000	$Cu_{63}Co_{20}Zn_{17}$	7	(αCo)/(Cu)	8.2	88.5	72.2	8.9	-	-
21	1000	$Cu_{60}Co_{18}Zn_{22}$	1	(αCo)/L	7.2	86.1	3.1	72.3	-	-
22	800	$Cu_{56}Co_{16}Zn_{28}$	20	(αCo)/(Cu)	7.52	86.0	63.5	6.4	-	-
23	800	$Cu_{39}Co_{20}Zn_{41}$	20	(αCo)/β-CuZn	7.7	78.8	43.8	12.7	-	-
24	800	$Cu_{60}Co_{20}Zn_{20}$	20	(αCo)/(Cu)	7.6	87.5	72.8	3.8	-	-
25	1000	$Cu_{10}Co_{47}Zn_{43}$	1	(αCo)/L	4.0	66.0	17.0	26.0	-	-
26	800	$Cu_{50}Co_{15}Zn_{35}$	20	(αCo)/(Cu)/β-CuZn	7.2	82.3	55.9	9.5	54.06	6.1

All the mentioned chemical compositions in this work were given in the form of an atomic ratio (at%). All observed phases were identified via two methods: the equilibrium composition measured by EPMA, and the crystal structure analysis by XRD. Most of the identification of equilibrium phases could be confirmed by taking advantage of the available composition ranges and crystal structure information of the intermetallic compounds in the binary and ternary systems.

A BSE image of the alloy $Cu_{10}Co_{45}Zn_{45}$ annealed at 800 °C is presented in Fig.2a, showing three-phase coexistence of β-CuZn (white), β1-CoZn (gray) and (αCo) (black). The corresponding XRD pattern is shown in Fig.3a. The two results are highly consistent. In the alloy $Cu_{60}Co_{20}Zn_{20}$ annealed at 800 °C, a two-phase equilibrium of (αCo) + (Cu) is found, as shown in Fig.2b. And Fig.2c shows a typical two-phase microstructure from the annealed alloy $Cu_{20}Co_{40}Zn_{40}$. The EPMA analysis indicates that the dark grey phase is (αCo), while the light grey phase is β-CuZn. Fig.2d shows the BSE image of annealed $Cu_{15}Co_{30}Zn_{55}$ alloy, in which three-phase microstructure of (β1-CoZn+β-CuZn+γ) was identified by EPMA analysis. And the XRD analysis (Fig.3b) was further matched up with them. In addition, Fig.2e and Fig.2f present the BSE images of the alloys $Cu_{40}Co_{30}Zn_{30}$ and $Cu_{63}Co_{20}Zn_{17}$, annealed at 1000 °C for 1 and 7 d, respectively. The EPMA results indicate that these microstructures are composed of (αCo) + Liquid and (αCo) + (Cu).

2.2 Isothermal section at 800 and 1000℃

Based on the above experimental data, the 800 and 1000 ºC isothermal section diagram were established. Fig.4 shows the 800 ºC isothermal section. In total, three three-phase regions of [(αCo) + β1-CoZn + β-CuZn],

[β1-CoZn+β-CuZn+γ] and [(αCo)+(Cu)+β-CuZn] and one liquid region were experimentally confirmed at 800 ºC and they were marked with different symbols. As we can see in Fig.4, the solubility of Co in the β-CuZn phase is measured to be about 32.3 at%. The solubility of Cu in the β1-CoZn phase is about 5.3 at%. According to the research of Cu-Co-Zn ternary system by Xie[19], there is an extensive region of mutual solubility existing between γ-Co_5Zn_{21} phase and γ-Cu_5Zn_8 phase. For the validation of the existence of a continuous solid solution between γ-Co_5Zn_{21} phase and γ-Cu_5Zn_8 phase, two different alloys ($Cu_{15}Co_{20}Zn_{65}$/$Cu_{25}Co_9Zn_{66}$) in this single-phase region were prepared. Their BSE micrographs show the appearance of a single phase and their compositions determined with EPMA approach the values anticipated for the preparation of alloys.

The γ-Co_5Zn_{21} and γ-Cu_5Zn_8 have the same crystal structure, and their XRD results are the same as shown in Fig.5a~5b, where the characteristic peaks of the γ-Co_5Zn_{21} and γ-Cu_5Zn_8 phase are only confirmed and well marked by star symbols. Based on the analyses of EPMA and XRD, an extensive region of mutual solubility existing between

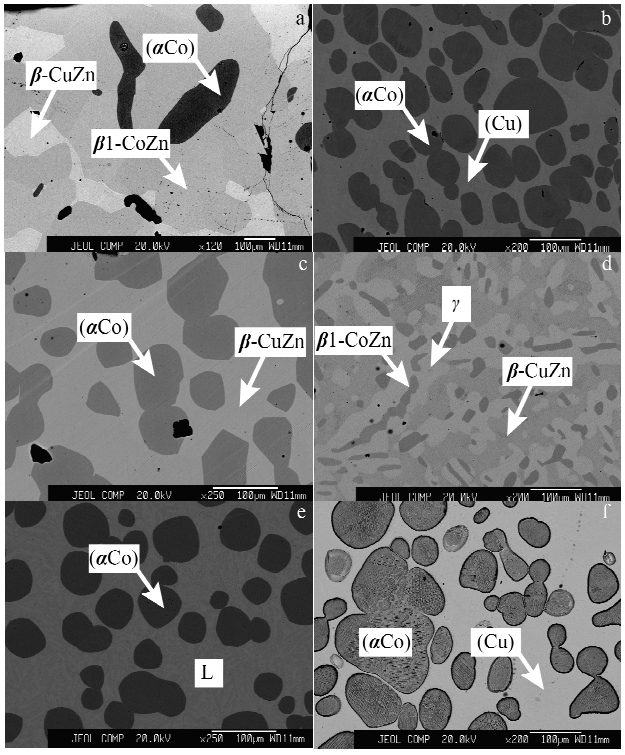

Fig.2 Typical ternary BSE images obtained from Cu-Co-Zn ternary alloys: (a) $Cu_{10}Co_{45}Zn_{45}$ alloy annealed at 800 °C for 20 d; (b) $Cu_{60}Co_{20}Zn_{20}$ alloy annealed at 800 °C for 20 d; (c) $Cu_{20}Co_{40}Zn_{40}$ alloy annealed at 800 °C for 20 d; (d) $Cu_{15}Co_{30}Zn_{55}$ alloy annealed at 800 °C for 20 d; (e) $Cu_{40}Co_{30}Zn_{30}$ alloy annealed at 1000 °C for 1 d; (f) $Cu_{63}Co_{20}Zn_{17}$ alloy annealed at 1000 °C for 7 d

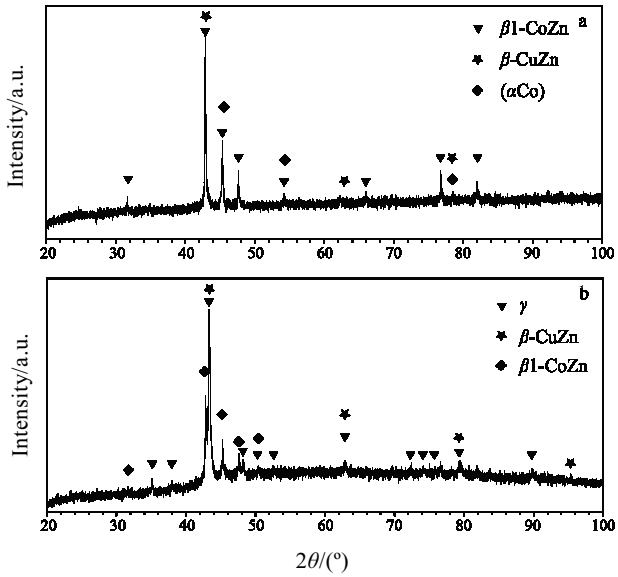

Fig.3 XRD patterns of $Cu_{10}Co_{45}Zn_{45}$ (a) and $Cu_{15}Co_{30}Zn_{55}$ (b) alloy annealed at 800 °C for 20 d

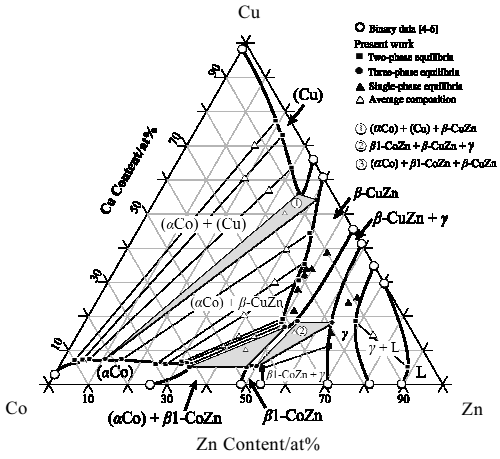

Fig.4 Experimentally determined isothermal section diagram of Cu-Co-Zn ternary system at 800 °C

γ-Co_5Zn_{21} and γ-Cu_5Zn_8 was confirmed and labeled as γ. XRD pattern of β-CuZn phase is shown in Fig.5c, where the characteristic peaks of the β-CuZn phase are well confirmed.

Fig.6 shows the isothermal section of Cu-Co-Zn ternary system at 1000 ºC. There is only one three-phase region of [(αCo)+(Cu)+Liquid], but this three-phase zone is too small to be determined. As the temperature raised, the liquid-phase region was further expanded.

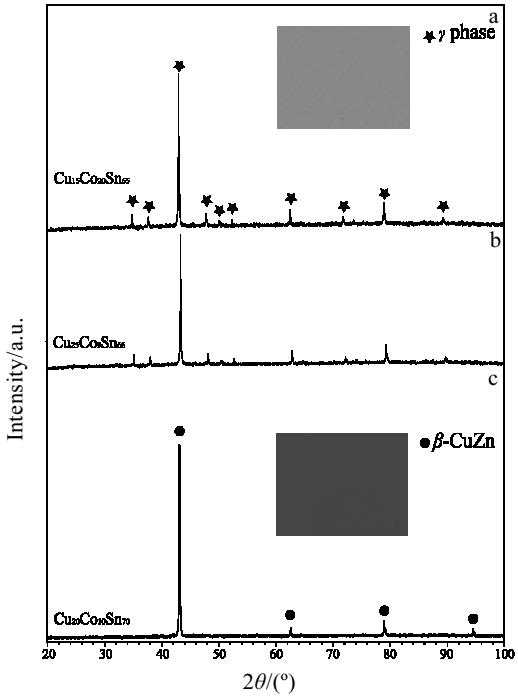

Fig.5 XRD patterns of partial Cu-Co-Zn ternary alloys annealed at 800 °C for 30 d

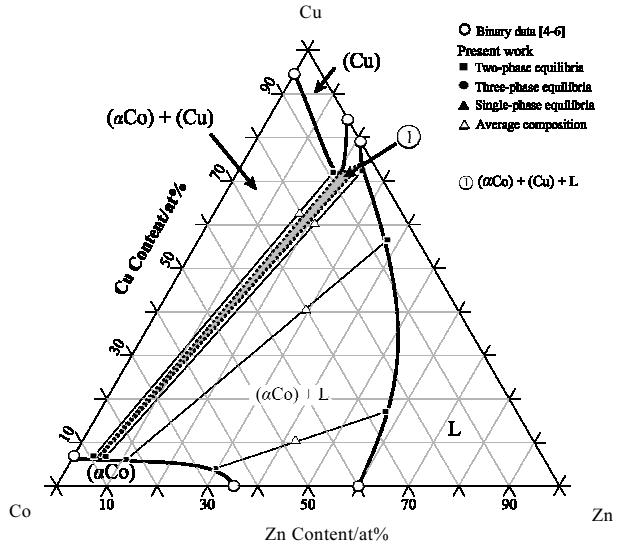

Fig.6 Experimentally determined isothermal section diagram of Cu-Co-Zn ternary system at 1000 °C

3 Conclusions

1) The isothermal sections of the Cu-Co-Zn ternary system at 800 °C and 1000 °C were experimentally investigated. No any ternary compound is found.

2) The solubility of Co in the β-CuZn, and Cu in the β1-CoZn at 800 °C are 32.4 at% and 5.3 at%, respectively.

3) The γ-Co_5Zn_{21} and γ-Cu_5Zn_8 have the same crystal structure. Therefore, an extensive region of mutual solubility is observed in the Cu-Co-Zn ternary system.

4) As the temperature rises from 800 °C to 1000 °C, the liquid-phase region is further expanded.

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Co-Cu-Zn 三元系相平衡的实验研究

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摘 要：采用电子探针显微分析和X射线衍射分析方法研究了Co-Cu-Zn三元体系在800和1000 ℃时的相平衡。在这2个等温截面中均未发现三元化合物。在800 ℃等温截面，Co在β-CuZn相中的固溶度为32.36%，Cu在β1-CoZn相中的固溶度为5.28%。除此之外，γ-Co_5Zn_{21}和γ-Cu_5Zn_8具有相同的晶体结构，因此，它们之间形成了一个贯穿连续固溶体相。1000 ℃的等温截面中，β-CuZn相、β1-CoZn相、γ-Co_5Zn_{21}相、γ-Cu_5Zn_8相都消失了。随着温度从800 ℃上升到1000 ℃，液相区域增大。

关键词：Co-Cu-Zn三元系；相平衡；电子探针

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