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# The 473 K isothermal section of the Cu–Ti–Sn ternary system

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ABSTRACT

The phase relationships of the Cu–Ti–Sn ternary system at 473 K have been investigated mainly by means of X-ray powder diffraction (XRD), scanning electron microscopy (SEM), optical microscopy (OM) and differential thermal analysis (DTA). The isothermal section consists of 17 single-phase regions, 33 two-phase regions and 17 three-phase regions. The existence of 12 binary compounds and 2 ternary compounds, namely $Cu_4Ti$, $Cu_3Ti_2$, $Cu_4Ti_3$, CuTi, $CuTi_2$, $Cu_3Sn$, $Cu_6Sn_5$, $Ti_3Sn$, $Ti_2Sn$, $Ti_5Sn_3$, $Ti_6Sn_5$, $Ti_2Sn_3$, $CuTi_5Sn_3$ and CuTiSn, are confirmed in the Cu–Ti–Sn ternary system at 473 K. No new ternary compound is found. The maximum solid solubility of Cu in $Ti_6Sn_5$ was approximately 10 at.% Cu.


## 1. Introduction

It is well known that Cu–Ti alloys are susceptible to age-hardening. This type of alloys is considered to be a possible substitute for expensive and toxic age-hardenable Cu–Be alloys. Besides, Cu–Ti alloys have also shown to be ultra-high strength conductive materials for applications such as conductive springs, interconnections, etc. [1]. In order to improve the combination properties of Cu–Ti alloys and step up their practical applications, complex alloying method is considered to be an important researching direction. As a conventional alloying addition for Cu–Ti alloys, Sn can significantly increase strength and corrosion resistance. Suiter [2,3] and Kornilov and Nartova [4] investigated the effect of Sn additives on the mechanical properties of pure titanium and found that significant increase in strength occurred by alloying Ti to 3–6 at.% Sn. Thus, it is necessary to investigate the phase relationships in the Cu–Ti–Sn ternary system.

According to Kumar et al. [5], the phase diagram shows five intermediate phases in the Cu–Ti system, i.e. $Cu_4Ti$, $Cu_3Ti_2$, $Cu_4Ti_3$, CuTi and $CuTi_2$. Although Canale and Servant [6] recently suggested that $CuTi_3$ is a stable phase on the basis of their experimental results, it should be a metastable phase in light of the works carried out subsequently by the other groups [7–9]. In the Ti–Sn phase diagram, four binary compounds, namely $Ti_3Sn$, $Ti_2Sn$, $Ti_5Sn_3$ and $Ti_6Sn_5$, were reported in Ref. [10]. A formerly unknown stable phase $Ti_2Sn_3$ was revealed by Kuper et al. [11]. Later, its crystal structure has been identified by Künnen et al. [12]. The Cu–Sn phase diagram [13] shows two intermediate phases, i.e. $Cu_3Sn$ and $Cu_6Sn_5$. Structural data for the reported intermetallic compounds in the three binary systems are given in Table 1. To our knowledge, two ternary compounds CuTiSn [14] and $CuTi_5Sn_3$ [15] in the Cu–Ti–Sn systems have been reported, and their structural data are given in Table 2.

Up to now, the isothermal section of the Cu–Ti–Sn system at 670 K have been constructed by Koblyuk et al. [14] through X-ray powder diffraction (XRD) analysis. However, a few of the phase relationships were presented uncertainly. Moreover, the ternary compound $CuTi_5Sn_3$ is described as solid solution of $Ti_5Sn_3$ in their work. According to Hamar-Thibault et al. [15], $CuTi_5Sn_3$ is a stable ternary compound and its crystal structure has also been identified. Summarily, phase equilibria in the Cu–Ti–Sn ternary system are far from completion, and more work is needed for this ternary system. In the present work, the main purpose is to investigate experimentally the isothermal section of Cu–Ti–Sn ternary system at 473 K for constructing the phase equilibria in detail and developing the new-type Cu–Ti alloys.

### 2. Experimental procedures

The 2 g alloy samples were prepared in an arc melting on a water-cooled copper cast with a non-consumable tungsten electrode under pure argon atmosphere. The starting materials for the synthesis of these alloys were from commercially available metals of high purity (Cu 99.99%, Ti 99.99%, Sn 99.99%). Each arc-cast button had been melted three times and turned around after melting for better homogeneity. In all, 129 samples (all weighting 2 g) were prepared. The weight loss of each sample is less than 1% after melting.

The as-cast alloy samples were sealed in evacuated quartz tubes. Then the quartz tubes were placed in a furnace and annealed at different temperatures for best homogenization. The homogenization temperatures of the samples were determined according to the phase diagrams of the Cu–Ti, Ti–Sn and Cu–Sn systems and the results of differential thermal analysis (DTA) of some typical ternary alloys. The Sn-rich alloys containing more than 40 at.% Sn were homogenized at 873 K for 480 h.

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**Table 1**
Crystal structure data of the binary compounds in the Cu–Ti–Sn system.

| Compound | Space group | Lattice parameters (nm) | | | Reference |
|---|---|---|---|---|---|
| | | *a* | *b* | *c* | |
| $Cu_4Ti$ | Pnma | 0.4530 | 0.4342 | 0.1293 | [16] |
| $Cu_3Ti_2$ | P4/nmm | 0.3130 | – | 1.395 | [16] |
| $Cu_4Ti_3$ | I4/mmm | 0.3130 | – | 1.994 | [16] |
| CuTi | P4/nmm | 0.3118 | – | 0.5921 | [16] |
| $CuTi_2$ | I4/mmm | 0.2994 | – | 1.0786 | [16] |
| $Cu_3Sn$ | Cmcm | 0.5529(8) | 4.775(6) | 0.4323(5) | [13] |
| $Cu_6Sn_5$ | $P6_3/mmc$ | 0.4192(2) | – | 0.5037(2) | [13] |
| $Ti_3Sn$ | $P6_3/mmc$ | 0.5916 | – | 0.4764 | [17] |
| $Ti_2Sn$ | $P6_3/mmc$ | 0.4653 | – | 0.569 | [17] |
| $Ti_5Sn_3$ | $P6_3/mcm$ | 0.8049(2) | – | 0.5454(2) | [17] |
| $Ti_6Sn_5$ | $P6_3/mmc$ | 0.922 | – | 0.569 | [17] |
| $Ti_2Sn_3$ | Cmca | 0.596 | 1.994 | 0.702 | [12] |

The other alloy samples were homogenized at 1073 K for 480 h. Subsequently, the furnace was cooled down to 473 K and kept at this temperature for 240 h. Then, the samples were removed and quenched in liquid nitrogen.

All the sample buttons were powdered and performed on a Rigaku D/Max 2500 V diffractometer with Cu Kα radiation and graphite monochromator operated at 40 kV, 250 mA ($20^\circ \leq 2\theta \leq 60^\circ$). The Materials Data software Jade 5.0 [18] and Powder Diffraction File (PDF release 2002) were used for phase analysis. The three phase regions were established mainly by investigating the XRD results of at least three alloys for each region. Optical microscopy (OM) and scanning electron microscopy (SEM) were used for microstructural analysis. By all these means, the phase relationships of the Cu–Ti–Sn ternary system at 473 K were determined.

## 3. Results and discussion

### *3.1. Binary system*

#### *3.1.1. Cu–Ti system*

In the Cu–Ti system, the phase diagram [5] shows five intermediate phases, i.e. $Cu_4Ti$, $Cu_3Ti_2$, $Cu_4Ti_3$, CuTi and $CuTi_2$. It is confirmed in this work that these binary compounds all exist at 473 K.

#### *3.1.2. Cu–Sn system*

In the Cu–Sn system, two compounds $Cu_3Sn$ and $Cu_6Sn_5$ were reported in Ref. [13], which is in well agreement with the present work.

#### *3.1.3. Ti–Sn system*

The Ti–Sn phase diagram [10] shows four intermediate phases, i.e. $Ti_3Sn$, $Ti_2Sn$, $Ti_5Sn_3$ and $Ti_6Sn_5$. A formerly unknown stable phase $Ti_2Sn_3$ and its crystal structure have been reported [11,12,17]. According to our previous work on the phase relationships of the La–Ti–Sn ternary system [19], the existence of a single phase $Ti_2Sn_3$ has been clearly conformed at 473 K. In this work, the XRD pattern of #56 sample with (10 at.% Cu, 20 at.% Ti, 70 at.% Sn) also clearly indicates the existence of $Ti_2Sn_3$ phase besides $Cu_3Sn$ and $Cu_6Sn_5$ phases, as illustrated in Fig. 1. In addition, the XRD pattern of the equilibrated sample (26 at.% Cu, 32 at.% Ti and 42 at.% Sn) clearly indicates the existence of three phases, i.e. $Ti_2Sn_3$, $Cu_2Sn$ and $Ti_6Sn_5$ in Fig. 2. The microstructure of #56 sample examined by both SEM and OM clearly observed the existence of the above three phases. EDX result indicated that the black phase was $Cu_6Sn_5$, the gray one was $Ti_2Sn_3$ while the white phase was Sn, as is shown in Fig. 3. Therefore, it is clearly indicated that the binary compound $Ti_2Sn_3$ exists in the present isothermal section.

**Table 2**
Crystal structure data of the ternary compounds in the Cu–Ti–Sn system.

| Phase | Space group | Lattice parameters (nm) | | | Reference |
|---|---|---|---|---|---|
| | | *a* | *b* | *c* | |
| CuTiSn | $P6_3mc$ | 0.43972(1) | – | 0.60168(2) | [14] |
| $CuTi_5Sn_3$ | $P6_3/mcm$ | 0.816 | – | 0.558 | [15] |

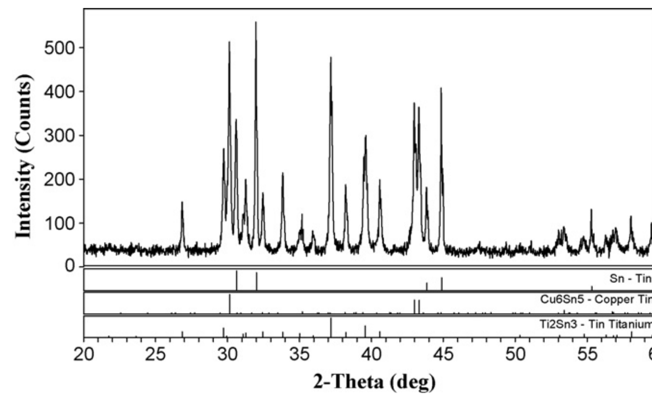


**Fig. 1.** The XRD pattern of #56 sample (10 at.% Cu, 20 at.% Ti and 70 at.% Sn) indicating the existence of $Ti_2Sn_3$, $Cu_6Sn_5$ and Sn.

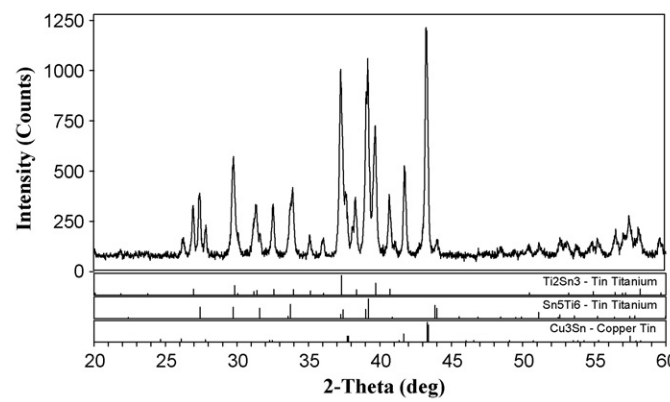


**Fig. 2.** The XRD pattern of the equilibrated sample (26 at.% Cu, 32 at.% Ti and 42 at.% Sn) containing $Ti_2Sn_3$, $Ti_6Sn_5$ and $Cu_3Sn$.

### *3.2. Ternary compounds*

To our knowledge, two ternary compounds (i.e. $CuTi_5Sn_3$ and CuTiSn) and their crystal structural data have been reported [14,15].

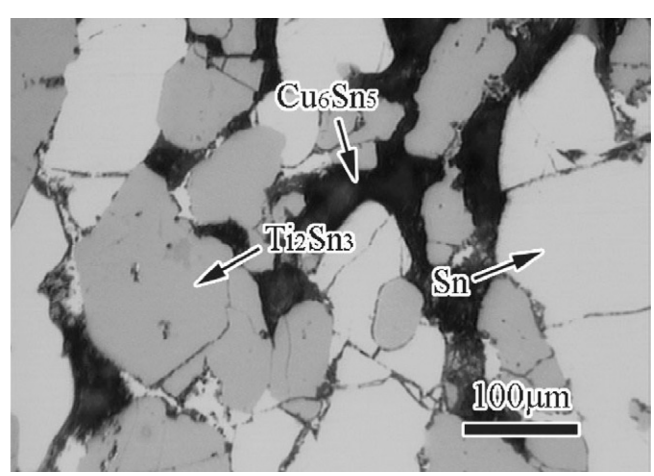


**Fig. 3.** The micrograph of #56 sample containing 10 at.% Cu, 20 at.% Ti and 70 at.% Sn.

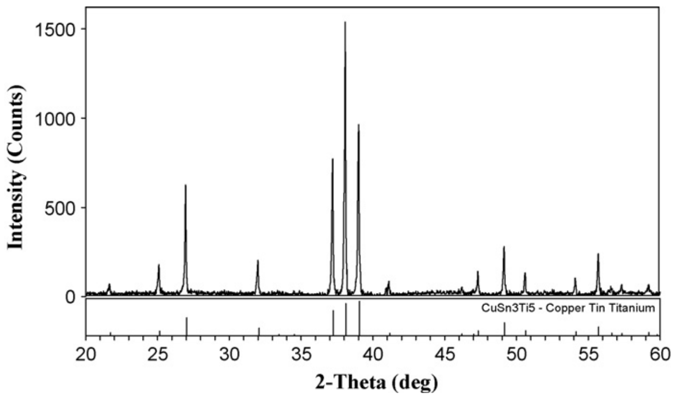


**Fig. 4.** The XRD pattern of the equilibrated sample (11.11 at.% Cu, 55.56 at.% Ti and 33.33 at.% Sn) indicating the existence of $CuTi_5Sn_3$.

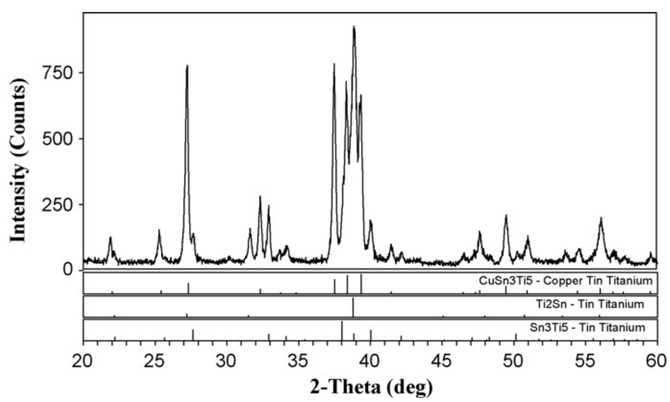


**Fig. 5.** The XRD pattern of the equilibrated sample (3 at.% Cu, 62 at.% Ti and 35 at.% Sn) containing $CuTi_5Sn_3$, $Ti_2Sn$ and $Ti_5Sn_3$.

In this work, the XRD pattern of the equilibrated sample which contains 11.11 at.% Cu, 55.56 at.% Ti and 33.33 at.% Sn clearly indicates the existence of the $CuTi_5Sn_3$ single phase, as illustrated in Fig. 4. From Fig. 5, it can be observed that, at 473 K, there are three phases in the sample with 3 at.% Cu, 62 at.% Ti and 35 at.% Sn, i.e. $CuTi_5Sn_3$, $Ti_2Sn$ and $Ti_5Sn_3$. In addition, it also clearly indicates that three phases exist in the sample with (20 at.% Cu, 44 at.% Ti and 36 at.% Sn), i.e. $CuTi_5Sn_3$, CuTiSn and $Ti_6Sn_5$ as is shown in Fig. 6. At the same time, the CuTiSn phase is observed in Fig. 6. Moreover, from the XRD pattern of the equilibrated sample (33.34 at.% Cu, 33.33 at.% Ti and 33.33 at.% Sn) in Fig. 7, the existence of the single phase CuTiSn is indicated. Combined with the above results, the ternary compounds $CuTi_5Sn_3$ and CuTiSn were confirmed in the present isothermal section.

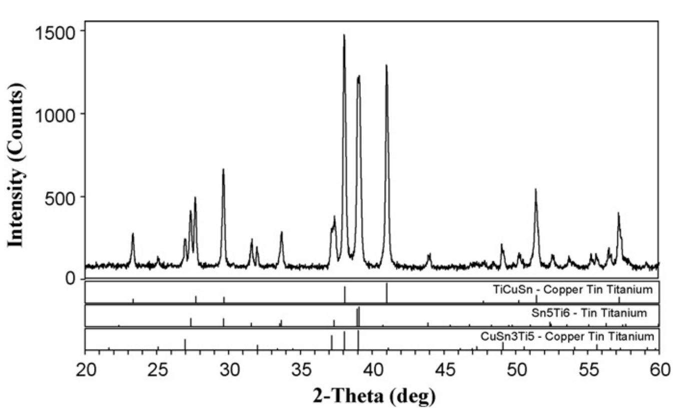


**Fig. 6.** The XRD pattern of the equilibrated sample (20 at.% Cu, 44 at.% Ti and 36 at.% Sn) containing CuTiSn, $CuTi_5Sn_3$, and $Ti_6Sn_5$.

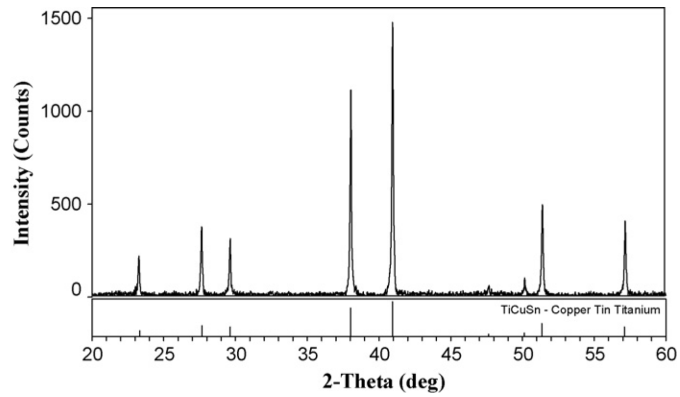


**Fig. 7.** The XRD pattern of the equilibrated sample (33.34 at.% Cu, 33.33 at.% Ti and 33.33 at.% Sn) indicating the existence of CuTiSn single phase.

### 3.3. Solid solubility

The solid solubility ranges in this isothermal section were determined using the phase-disappearing method and comparing the shift of the XRD pattern of the samples near the compositions of the binary phases. The results indicate that the solubility of Cu in $Ti_6Sn_5$ were about 10 at.% Cu. No remarkable solid solubility was found in the other compounds of the Cu–Ti–Sn ternary system at 473 K.

### 3.4. Isothermal section

The isothermal section of the Cu–Ti–Sn ternary system at 473 K has been determined on the basis of XRD, SEM and OM, as is shown in Fig. 8. This isothermal section consists of 17 three-phase regions, 33 two-phase regions and 17 single phase regions. Constitutions of the three-phase regions and compositions of the typical alloys are listed in Table 3. The XRD results confirm that 12 binary compounds and 2 ternary compounds, namely $Cu_4Ti$, $Cu_3Ti_2$, $Cu_4Ti_3$, CuTi, $CuTi_2$, $Cu_3Sn$, $Cu_6Sn_5$, $Ti_3Sn$, $Ti_2Sn$, $Ti_5Sn_3$, $Ti_6Sn_5$, $Ti_2Sn_3$, $CuTi_5Sn_3$ and CuTiSn exist in this system at 473 K.

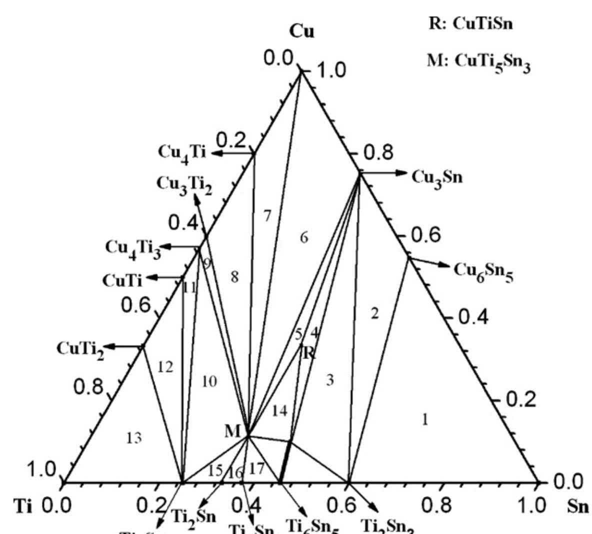


**Fig. 8.** The experimental isothermal section of the Cu–Ti–Sn ternary system at 473 K.

**Table 3**
Details of the three-phase regions and compositions of the typical alloys of the Cu–Ti–Sn system at 473 K.

| Phase regions | Alloy composition (at.%) | | | Phase composition |
|---|---|---|---|---|
| | Cu | Ti | Sn | |
| 1 | 10 | 20 | 70 | $Ti_2Sn_3 + Cu_6Sn_5 + Sn$ |
| 2 | 30 | 20 | 50 | $Ti_2Sn_3 + Cu_6Sn_5 + Cu_3Sn$ |
| 3 | 26 | 32 | 42 | $Ti_2Sn_3 + Ti_6Sn_5 + Cu_3Sn$ |
| 4 | 42 | 25 | 33 | $Ti_6Sn_5 + Cu_3Sn + TiCuSn$ |
| 5 | 34 | 34 | 32 | $TiCuSn + CuTi_5Sn_3 + Cu_3Sn$ |
| 6 | 56 | 24 | 20 | $CuTi_5Sn_3 + Cu_3Sn + Cu$ |
| 7 | 50 | 34 | 16 | $CuTi_5Sn_3 + Cu_4Ti + Cu$ |
| 8 | 56 | 36 | 8 | $CuTi_5Sn_3 + Cu_4Ti + Cu_3Ti_2$ |
| 9 | 50 | 44 | 6 | $CuTi_5Sn_3 + Cu_3Ti_2 + Cu_4Ti_3$ |
| 10 | 20 | 60 | 20 | $CuTi_5Sn_3 + Ti_3Sn + Cu_4Ti_3$ |
| 11 | 36 | 56 | 8 | $Ti_3Sn + TiCu + Cu_4Ti_3$ |
| 12 | 24 | 66 | 10 | $Ti_3Sn + TiCu + CuTi_2$ |
| 13 | 17 | 73 | 10 | $Ti_3Sn + Ti + CuTi_2$ |
| 14 | 20 | 44 | 36 | $CuTiSn + CuTi_5Sn_3 + Ti_6Sn_5$ |
| 15 | 4 | 64 | 32 | $CuTi_5Sn_3 + Ti_3Sn + Ti_2Sn$ |
| 16 | 3 | 62 | 35 | $CuTi_5Sn_3 + Ti_2Sn + Ti_5Sn_3$ |
| 17 | 4 | 58 | 38 | $CuTi_5Sn_3 + Ti_6Sn_5 + Ti_5Sn_3$ |

## 4. Conclusion

The phase relationships of the Cu–Ti–Sn ternary system at 473 K have been determined. The isothermal section consists of 17 single phase regions, 33 binary phase regions and 17 ternary phase regions. It has been confirmed that the binary compound $Ti_2Sn_3$ exist in the isothermal section. The solubility of Cu in $Ti_6Sn_5$ were determined to be about 10 at.% Cu. The ternary compounds CuTiSn and $CuTi_5Sn_3$ are confirmed in the ternary system at 473 K.


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