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New phases in the ternary Cu–Ti–Sn system

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Abstract

Cu–Sn–Ti alloys are used as binders for diamond tools processed by liquid phase sintering. The design of the processing requires data on the phase constitution of the alloy. Little information is available on the ternary Cu–Ti–Sn phase diagram. Some data reported the possible existence of two ternary phases: a ternary Ti–Sn rich phase and the compound Cu_2SnTi with a cubic structure. The present work was the experimental determination of the phase constitution in the composition range between the lines Cu–Ti_3Sn and Cu–Ti_6Sn_5. One new ternary phase — characterised by electron probe microanalysis and by X-ray diffraction — has the stoichiometry Ti_5Sn_3Cu. Its crystallographic structure has an hexagonal symmetry and is related to those of the binary phases Ti_5Sn_3 and Ti_6Sn_5 that belong to the Mn_5Si_3 family. The compound Ti_5Sn_3Cu is present in all the multiphase fields identified in the composition range under investigation.

Keywords: Ti_5Sn_3Cu; Composition; Crystal structure

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1. Introduction

Diamond cutting segments can be manufactured by liquid phase sintering using Cu–Sn–Ti as binder [1,2]. The homogeneous distribution of the diamond particles, their adhesion to the binder and full density is the major requirements for good properties of the material. They could be achieved through the strict control of the liquid phase sintering conditions used for the material processing. The Cu–Sn–Ti phase diagram is one of the main guidelines for the design of the process.

No literature data were found concerning the Cu–Ti–Sn system but the possible existence of the two ternary phases Cu_2SnTi [3] and Ti_5Sn_3Cu [2] was reported. The three binary systems are complex and contain several compounds. The Cu–Sn [4] and Cu–Ti [5] phase diagrams are characterised by a series of peritectic reactions and by a number of stable and unstable intermetallic phases. The Ti–Sn phase diagram [6] shows four intermediate phases Ti_3Sn, Ti_2Sn, Ti_5Sn_3 and Ti_6Sn_5 with high temperature melting points and tight homogeneity ranges. Recently a new phase ($TiSn_x$ with $x \approx 1.5$) was reported but its crystallographic structure was not identified [7].

The purpose of the present work is the investigation of the ternary phases formed at 900°C in the composition range between the lines Cu–Ti_3Sn and Cu–Ti_6Sn_5.

2. Experimental methods

Alloys were prepared either from an initial prealloyed powder (0) used as binder for diamond tools, from Cu–Sn binary powders or from pure elements. Ternary alloys with different compositions were prepared from pure Ti, high purity Sn granules and Cu as reported in Table 1. The initial prealloyed powder contains some amount of Zr (1 at.%).

To obtain the equilibrium state, the alloys were annealed for 10 h in static argon atmosphere at 600–1000°C. Due to the oxygen affinity of the alloys, a strict control of the atmosphere was observed. The cooling rate is about 5 K/min.

The samples were sectioned, polished and examined by optical microscopy and scanning electron microscopy (SEM) in backscattered electron mode (BSE). Energy dispersive spectrometer (EDX) analysis gives the magnitude range in composition of the small phases.

The phase compositions were determined by electron probe microanalysis (EPMA) on a CAMECA-SX50 using

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Table 1
Phase compositions in alloys (at.%) after heat treatment at 900°C for 10 h

Alloy		Nominal composition	State	Cu-rich phase	Ti_5Sn_3Cu	CuTiSn	Ti_3Sn
0	Cu	78.0	L	97.0	11.7	34.7	
	Sn	7.6		2.6	33.3	33.7	
	Ti	13.5		0.4	52.2	19.5	
	Zr	0.9		0.0	2.5	12.1	
4	Cu	50.7	Ti_3Sn	92.8	12.4		2.5
	Sn	14.8	+	0.6	34.2		26.0
	Ti	33.9	L	6.6	52.4		71.5
	Zr	0.5		0.0	0.8		0.0
5	Cu	68.7	Ti_5Sn_3Cu	92.2	12.2	34.1	
	Sn	18.6	+	7.7	34.8	32.8	
	Ti	12.1	L	0.1	52.2	33.1	
	Zr	0.6		0.0	0.8	0.0	
10	Cu	53.6	Ti_5Sn_3Cu	98.2	12.8		
	Sn	17.4	+	0.9	33.3		
	Ti	28.6	L	0.9	53.0		
	Zr	0.4		0.0	0.9		
11	Cu	40.4	Ti_5Sn_3Cu	92.4	13.1	34.0	
	Sn	26.2	+	7.5	34.9	33.9	
	Ti	33.4	L	0.1	52.0	32.0	
	Zr	–		–	–	–	

as standards Cu, Ti, Sn and Zr. Atomic number, absorption and fluorescence effects were corrected with a computer program according to the PAP model [8]. The crystallographic structure of the phases was systematically checked by X-ray diffraction (Cu Kα=1.542 Å) on powdered alloys.

3. Results and discussion

3.1. Microstructure and phase constitution in alloys solidified from 900°C

The phase constitution of the studied specimens, deduced from their microstructure features and the phase compositions, after cooling, are reported in Table 1. At 900°C, the samples consist of pure liquid (0) or of solid–liquid mixtures. After cooling, the liquid phase, rich in Cu, exhibits some segregations of solidification and only approximate compositions are given. The other phases correspond to stoichiometric ratio Ti_5Sn_3Cu, CuSnTi and Ti_3Sn.

Alloy 0 (Fig. 1a) presents a typical solidification microstructure. On cooling, a small amount of primary white phase with hexagonal shape (about 50 μm in size) appears in the Cu-rich liquid. Then, a binary eutectic solidifies: it consists of Cu-rich matrix and white needles with the same contrast as the hexagonal phase. The white phase is a ternary compound with constant amounts of Ti (≈52 at.%), Sn (≈33 at.%) and 11–13 at.% of Cu. A small amount of Zr is always present (≈2–3 at.%) in this phase. The composition of the ternary phase, close to $(Ti,Zr)_5Sn_3Cu_1$ is in agreement with the results [1] obtained from the solidification of ternary alloys with similar compositions.

In alloy 11 (Fig. 2a), large hexagonal crystals of ternary compound Ti_5Sn_3Cu are evidenced: at 900°C, Ti_5Sn_3Cu is in equilibrium with a liquid, which evolves during cooling. The BSE images show a second intermediate phase surrounding the white Ti_5Sn_3Cu compound, with a composition near CuSnTi. The location of this phase should be consistent with its formation by peritectic reaction from Ti_5Sn_3Cu. According to the microstructure, alloy 4 consists of solid round particles of binary Ti_3Sn in equilibrium with the liquid. After solidification, long needles of Ti_5Sn_3Cu are observed.

The X-ray diffraction pattern (Fig. 1b) of the alloy 0 in the initial state identifies without ambiguity the fcc Cu matrix with the three largest peaks corresponding to a face centred cubic cell of 3.63 Å, close to the theoretical cell of pure Cu (3.615 Å). Some other weaker peaks are detected with a characteristic group of three peaks at 2.41, 2.36 and 2.30 Å.

The solidified alloys 4, 10, and 11, very brittle, exhibit X-ray diffraction patterns with the same reflections, but more intense (Fig. 2b). The peaks cannot be indexed by spacings characteristic of any of the compounds of the binary systems Cu–Ti [5], Cu–Sn [4] and Ti–Sn [3]. These peaks are related to the ternary compound (Ti_5Sn_3Cu): the corresponding (d_m) spacings and intensities (I_m/I_0) are reported in Table 2. Only weak reflections are due to the Cu phase.

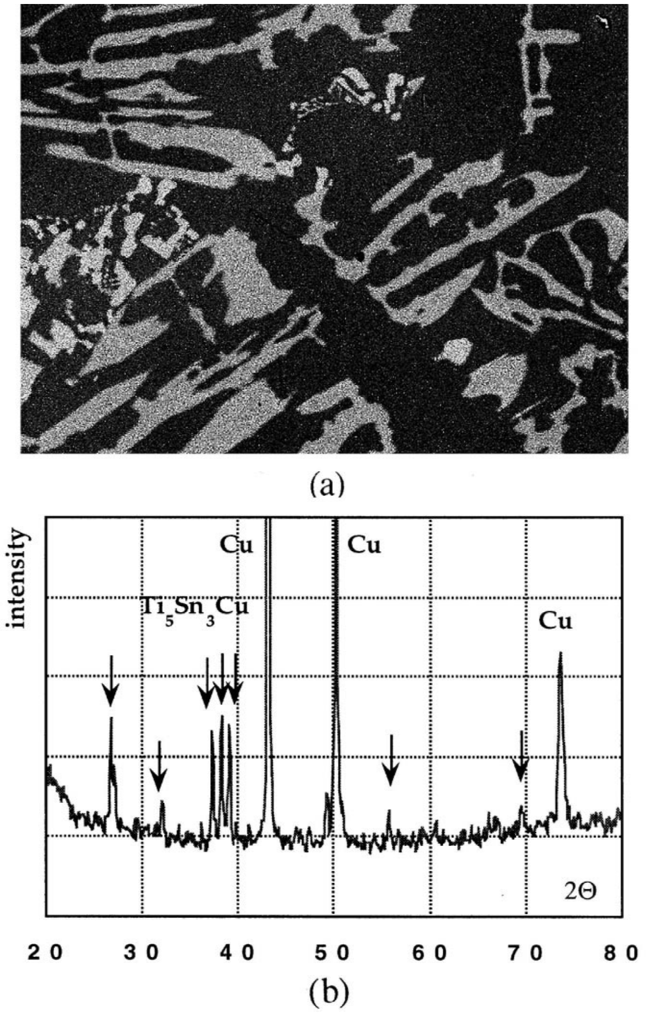

Fig. 1. (a) Microstructure of alloy 0 showing needles of the Ti_5Sn_3Cu in a Cu-rich matrix. (b) X-ray diffraction pattern showing the peaks attributed to Ti_5Sn_3Cu (arrows).

3.2. Phase constitution in the solid state

The evolution of the phase constitution of alloy 0 is examined by comparison of the solidified and heat-treated state. Until 600°C, the diffraction patterns of alloy 0 do not change significantly. Above 700°C, two peaks, which neither belong to the Cu cell or Ti_5Sn_3Cu cells nor to any binary compounds are observed at 2.22 and 2.04 Å. The intensity ratio between the peaks at 2.22 and 2.04 Å increases with treatment temperature and is maximum at 840°C for 10 h. Simultaneously, the intensity of peaks related to Ti_5Sn_3Cu decreases, indicating unambiguously the growth of a second ternary phase at the expense of Ti_5Sn_3Cu. It is noticed that a third peak at 2.36 Å increases with temperature: as it belongs to Ti_5Sn_3Cu, it must also be included in the pattern of the second ternary phase. These three peaks cannot be indexed with the Cu_2SnTi compound (a=2.91 Å) reported by Heine and Zwicker [3].

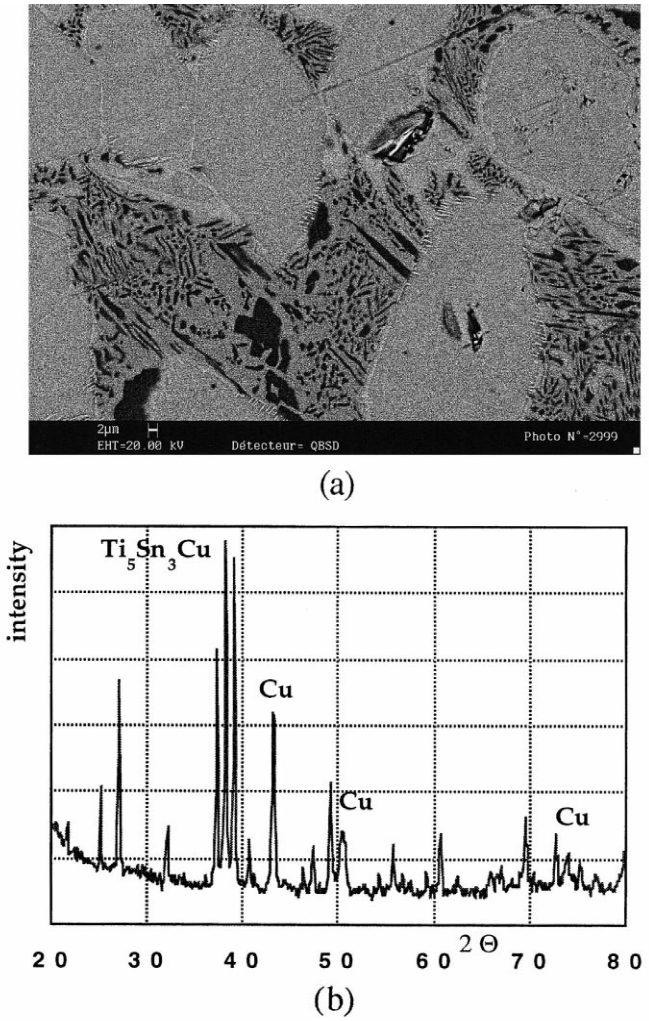

Fig. 2. (a) Microstructure of alloy 11 heated for 10 h at 900°C (BSE image). The Ti_5Sn_3Cu compound appears with an hexagonal shape surrounded with small amount of a second ternary phase with a white contrast. (b) X-ray diffraction pattern showing the peaks attributed to Ti_5Sn_3Cu. Very small amount of Cu is present.

The results clearly display two ternary phases in the studied concentration range of the Cu–Ti–Sn ternary system: the Ti_5Sn_3Cu compound and another phase with stoichiometry close to CuTiSn. Due to its small size, this phase is difficult to analyse with precision. The small number of X-ray diffraction peaks, which can be attributed unambiguously to CuTiSn, does not enable to characterise its crystallographic structure. No indication could be obtained from similar systems CuSnNi [9] or CuTiNi [10,11].

3.3. Crystallographic structure of Ti_5Sn_3Cu

The structures of the binary compounds formed by Sn with Ti, Zr, Hf belong to the hexagonal Mn_5Si_3 family. Ti_5Sn_3 (a=8.049 Å and c=5.405 Å [6]), Zr_5Sn_3, Hf_5Sn_3

Table 2
X-ray diffraction pattern of Ti_5Sn_3Cu: measured in alloy 10 (m) and calculated (c)[a]

d_m (Å)	d_c (Å)	I_m/I_0	I_c/I_0	*hkl*
4.077	4.09	5	6	11.0
3.541	3.53	20	14	20.0
3.293	3.294	50	46	11.1
2.793	2.790	15	20	00.2
2.412	2.409	60	40	21.1
2.359	2.356	100	100	30.0
2.305	2.303	80	95	11.2
2.190	2.190	5	3	20.2
1.963	1.965	5	3	31.0
1.918	1.916	15	7	22.1
1.853	1.849	30	30	31.1
1.802	1.800	20	14	30.2
1.694	1.692	5	7	11.3
1.649	1.647	10	22	22.2
1.528	1.526	20	11	41.0
1.416	1.413	5	6	50.0
1.396	1.395	7	2	00.4
1.351	1.350	25	19	41.2–31.3
1.301	1.299	15	19	42.1
1.201	1.205	10	5	42.2

[a] Interplanar spacings (d) and peak intensities (I/I_0) based on a hexagonal cell with $a=8.16$ Å and $c=5.58$ Å.

have the $D8_8$ type. Ti_6Sn_5 is of (D_{3d}^2) type ($a=9.24$ Å and $c=5.69$ Å [12]). Zr_5Sn_4 and Hf_5Sn_4 are of Ti_5Ga_4 type which derives also from the Mn_5Si_3 family. Rieger et al. [13] reported the existence of the ternary compounds Hf_5Sn_3Cu and Zr_5Sn_3Cu with structure of Ti_5Ga_4 type. Consequently, it can be expected that the structures of Ti_5Sn_3Cu and of the phases with Hf and Zr with same stoichiometry are related. The diffraction pattern of Ti_5Sn_3Cu can be indexed from the hexagonal structure of Hf_5Sn_3Cu related to the Ti_5Ga_4 type. The lattice parameters calculated for Ti_5Sn_3Cu are: $a=8.16$ Å and $c=5.58$ Å with $c/a=0.684$, with a hexagonal cell of the Ti_5Ga_4 type and a space group $P6_3/mcm$.

As reported in Table 2, the calculated interplanar spacings (d_c) are in good agreement with the values (d_m) deduced from the XDR spectrum of alloy 10. The group of three peaks observed at 2.41, 2.36 and 2.30 Å corresponds to the strong reflections on the (21.1), (30.3) and (11.2) planes. The rough estimation of the intensities of the peaks (I_c/I_0) is consistent with the measured intensity (I_m/I_0). These results agree with results published recently [14].

4. Conclusion

Our results show the existence of the ternary compound Ti_5Sn_3Cu, which crystal structure is related to related to the Ti_5Ga_4 type. In the composition field investigated, this compound — with a homogeneity range which is very tight — is present in all the two- or three-phase domains identified. Another ternary phase, with composition around CuTiSn, was found but its structure remains unidentified.

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