

Determination of the crystal structure of CuSnTi by full profile Rietveld analysis

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The crystal structure of the new ternary phase CuSnTi is determined by full profile Rietveld analysis of the powder diffractogram. 104 reflections were refined to a final R_{Bragg} value of 5.60%. CuSnTi crystallizes with the spacegroup $P6_3/mmc$ and is isostructural to InNi_2 . The lattice parameters are $a = 0.439\,555(5)$ nm and $c = 0.601\,505(9)$ nm. © 2000 International Centre for Diffraction Data. [S0885-7156(90)00301-3]

INTRODUCTION

In the course of investigating phases occurring in Cu–Sn–Ti solder alloys (Uray *et al.*, 1998) the structure of ternary phase CuSn_3Ti_5 was recently characterized (Schuster *et al.*, 1999). This phase is a major constituent in Cu–Sn–Ti alloys having a wide range of compositions including alloys quite rich in Cu such as $\text{Cu}_{45}\text{Sn}_{25}\text{Ti}_{30}$ (Naka *et al.*, 1999). However, in the neighboring alloy $\text{Cu}_{45}\text{Sn}_{30}\text{Ti}_{25}$ only traces of CuSn_3Ti_5 are observed and a new diffraction pattern occurs, which was not identifiable with any phase listed in the book of Villars and Calvert (1991). The present paper reports on the composition and crystal structure of this phase as determined by full profile analysis (Rietveld, 1969) of the X-ray diffractogram.

EXPERIMENT

An alloy of composition $\text{Cu}_{45}\text{Sn}_{30}\text{Ti}_{25}$ was arc melted from Ti sponge (purity: 99.8mass%, from Sumitomo Sitix, Amagasaki, Japan), Cu and Sn ingots (purity: 99.9mass%, from Osaka Asahi, Osaka, Japan) sealed in evacuated quartz tubes, and heat treated at 800 °C for 115 h. No mass loss was observed during these steps. The alloy was pulverized manually in a tungsten carbide mortar and spread on a thin polymer foil. Powder photographs were taken in transmission using a Guinier–Huber chamber, $\text{CuK}\alpha_1$ -radiation, and Ge standard (pulverized from lump, metal purity 99.9999%, from Johnson Matthey GmbH, Karlsruhe, Germany) assuming a lattice parameter of $a = 0.565\,790\,6$ nm. The powder diffraction profile was recorded on a Philips PW 1051/81 diffractometer in the range of $2\theta = 5$ to 140° in steps of 0.02° using $\text{CuK}\alpha$ -radiation ($\lambda K\alpha_1 = 0.154\,056$ nm, $\lambda K\alpha_2 = 0.154\,440$ nm). The width of the receiving slit was 0.1 mm. Total measuring time was 48 h, equivalent to 25.4 s per scan step.

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REFINEMENT

Refinement was done using the ‘FullProf’ software (Rodriguez-Carjaval, 1997). Diffraction peaks were indexed based on lattice parameters derived from the Guinier powder photographs. Beginning with the phases where the crystal structure and approximate composition was known, each phase was refined separately to convergence by employing the following sequence of steps: (1) refinement of global parameters such as lattice parameters and peak profile parameters for the peak profile function identified suitable (Pseudo-Voigt), (2) atom position parameters, (3) occupation factors, peak asymmetry, and preferred orientation. The total number of parameters refined was 56.

RESULTS

Three phases were present in the alloy investigated (Figure 1): A dominant phase indexed using a hexagonal unit cell [$a = 0.439\,39(4)$ nm, $c = 0.6012(5)$ nm] and two minority phases, identified to be $\text{Cu}_{10}\text{Sn}_3$ (spacegroup $P6_3/m$, Lenz and Schubert, 1971) and CuSn_3Ti_5 (Schuster *et al.*, 1999), respectively. Reducing the symmetry of $\text{Cu}_{10}\text{Sn}_3$ to space group $P6_3$ (Brandon *et al.*, 1975) did not result in comparable R_{Bragg} factors unless the Sn content was allowed to decrease by about one-third of the starting value, which is unacceptable in view of the Cu–Sn phase diagram.

Initial attempts to refine the majority phase in spacegroup $P6_3/mmc$ with CaIn_2 structure type did not yield R_{Bragg} values below 18%. Starting with the NiAs-type crystal structure of Cu_6Sn_5 (Gangulee *et al.*, 1973), however, opened the door to successful refinement. Assuming the space group $P6_3/mmc$, the atomic positions (2d) for Cu, (2c) for Sn, and (2a) for Ti, and allowing for some mutual site exchange between Cu and Ti, refinement to convergence resulted in a final R_{Bragg} value of 5.60% (Table I). For the minority phases R_{Bragg} values of 8.34% (for $\text{Cu}_{10}\text{Sn}_3$) and 10.30% (for CuSn_3Ti_5) were obtained. Thus the new ternary phase is labeled CuSnTi. This composition is corroborated by EPMA (Naka *et al.*, 1999). It is isostructural to InNi_2 . In

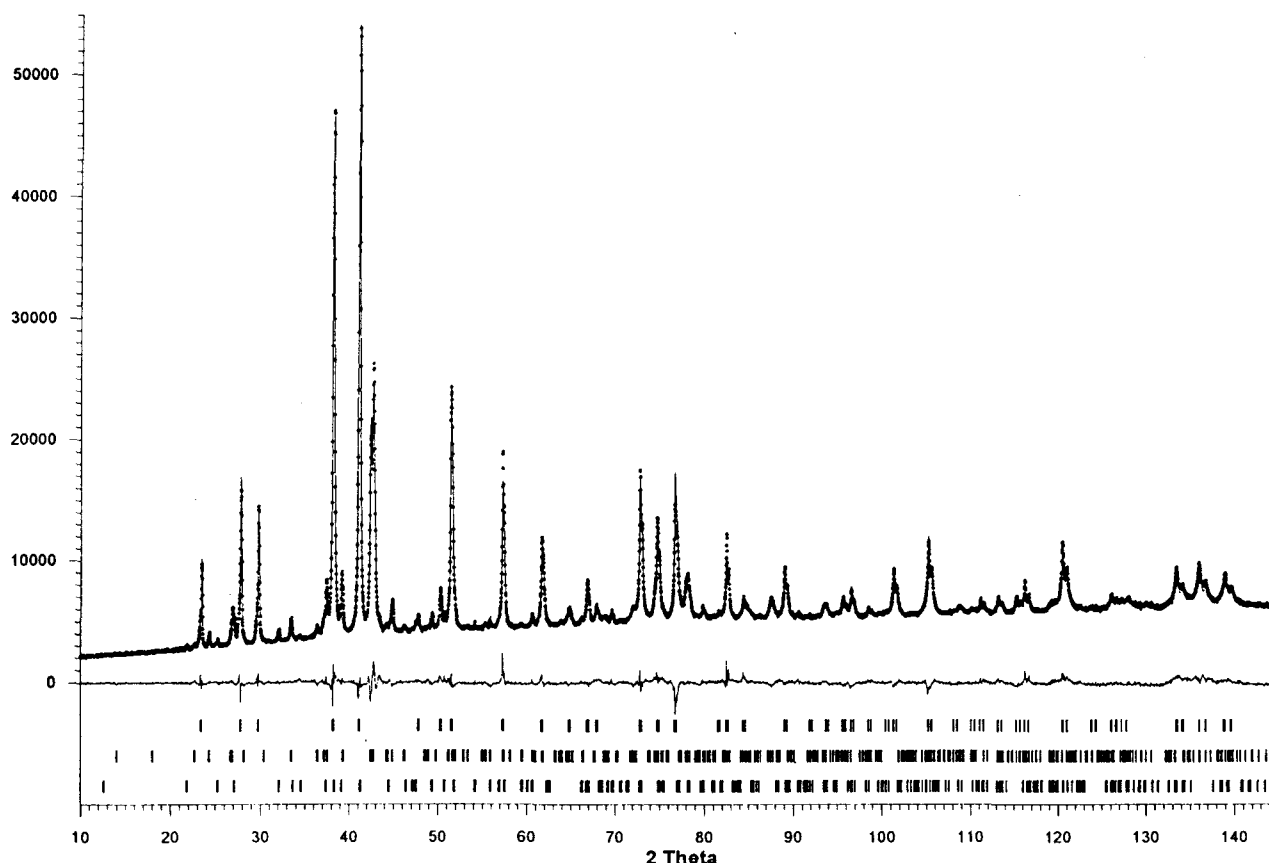


Figure 1. Diffraction profile of alloy $\text{Cu}_{45}\text{Sn}_{30}\text{Ti}_{25}$ (arc melted and annealed at 800°C) using $\text{CuK}\alpha$ -radiation. Top: dots=data points observed (I_{obs}); line=calculated profile (I_{calc}). Below: line=difference $I_{\text{obs}} - I_{\text{calc}}$. Bottom: Bragg peak positions for CuSnTi (highest line), $\text{Cu}_{10}\text{Sn}_3$ (center line), and CuSn_3Ti_5 (lowest line) calculated using the lattice parameters given in Table I.

TABLE I. Crystallographic data obtained from refinement (final $\chi^2 = 5.58$).

Space group: $P6_3/mmc$, $hP6$, InNi_2 -type, $a = 0.439\,555(5)\text{ nm}$, $c = 0.601\,505(9)\text{ nm}$; 104 reflections refined; $R_{\text{Bragg}} = 5.60\%$, $R_f = 4.11\%$					
Main phase: CuSnTi					
	x	y	z	B	occup.
Cu_1 in $(2d)$	$1/3$	$2/3$	$3/4$	0.4	1.81
Ti_1 in $(2d)$	$1/3$	$2/3$	$3/4$	0.4	0.190(6)
Sn_1 in $(2c)$	$1/3$	$2/3$	$1/4$	0.2	2.00
Cu_2 in $(2a)$	0	0	0	0.4	0.16
Ti_2 in $(2a)$	0	0	0	0.4	1.803(6)
Space group: $P6_3/m$, $hP26$, $\text{Cu}_{10}\text{Sn}_3$ -type $a = 0.733\,14(2)\text{ nm}$, $c = 0.786\,40(3)\text{ nm}$; 638 reflections refined; $R_{\text{Bragg}} = 8.34\%$, $R_f = 7.01\%$					
Second phase: $\text{Cu}_{10}\text{Sn}_3$					
	x	y	z	B	occup.
Cu_1 in $(12i)$	0.6701(8)	0.0239(8)	0.0792(6)	0.4	12.00
Sn_1 in $(6h)$	0.2958(7)	0.9763(8)	$1/4$	0.2	4.74(6)
Ti_1 in $(6h)$	0.2958(7)	0.9763(8)	$1/4$	0.3	1.30
Cu_2 in $(4f)$	$1/3$	$2/3$	0.0709(12)	0.4	4.00
Cu_3 in $(2d)$	$2/3$	$1/3$	$1/4$	0.2	2.00
Cu_4 in $(2b)$	0	0	0	0.4	2.00
Space group: $P6_3/mcm$, $hP18$, Ti_5Ga_4 -type $a = 0.815\,07(7)\text{ nm}$, $c = 0.558\,95(6)\text{ nm}$; 269 reflections refined; $R_{\text{Bragg}} = 10.3\%$, $R_f = 6.85\%$					
Third phase: CuSn_3Ti_5					
	x	y	z	B	occup.
Sn_1 in $(6g)$	0.6163(6)	0	$1/4$	0.2	6.00
Ti_1 in $(6g)$	0.2720(16)	0	$1/4$	0.2	6.00
Ti_2 in $(4d)$	$1/3$	$2/3$	0	0.2	4.00
Cu_1 in $(2b)$	0	0	0	0.2	1.04(4)

TABLE II. Powder diffraction pattern of CuSnTi calculated from the parameters given in Table I for Guinier chamber geometry and CuK α_1 radiation (x marks the reflections observed on the Guinier film).

<i>h k l</i>	<i>d</i> -value in Å	$\sin^2 \vartheta$	Relative intensity	
1 0 0	3.8066	0.04095	143.1	x
1 0 1	3.2166	0.05735	207.9	x
0 0 2	3.0075	0.06560	267.5	x
1 0 2	2.3598	0.10654	897.2	x
1 1 0	2.1978	0.12284	1000.0	x
2 0 0	1.9033	0.16379	24.2	x
2 0 1	1.8146	0.18019	45.9	x
1 1 2	1.7745	0.18844	372.4	x
1 0 3	1.7740	0.18854	43.3	x
2 0 2	1.6083	0.22938	285.7	x
0 0 4	1.5037	0.26239	108.6	x
2 1 0	1.4388	0.28663	23.4	
2 1 1	1.3993	0.30303	49.5	x
1 0 4	1.3986	0.30334	21.9	x
2 0 3	1.3804	0.31138	24.1	x
2 1 2	1.2979	0.35222	319.5	c Ge (331)
3 0 0	1.2689	0.36852	212.9	x
3 0 1	1.2415	0.38492	0.0	
1 1 4	1.2410	0.38523	408.5	x
2 0 4	1.1799	0.42618	16.5	
3 0 2	1.1691	0.43412	140.9	x
2 1 3	1.1689	0.43422	39.5	x
1 0 5	1.1471	0.45093	19.8	x
2 2 0	1.0989	0.49136	185.1	x
3 0 3	1.0722	0.51611	0.0	
3 1 0	1.0558	0.53231	17.5	
3 1 1	1.0399	0.54871	46.4	x
2 1 4	1.0396	0.54902	36.3	x
2 2 2	1.0321	0.55696	156.3	x

Table II the powder diffraction pattern calculated for CuSnTi using the parameters in Table I is given. Powder diffractograms calculated from these data for Cu₁₀Sn₃ and CuSn₃Ti₅ match excellently the patterns published by Lenz and Schu-

bert (1971) and Schuster *et al.* (1999), respectively.

It is interesting to note that other ternary Cu–Sn–Me alloys of 1:1:1 composition are reported to have CaIn₂-type crystal structure for Me=Sc, Y, and RE metal, but InNi₂-type structure for Me=Dy (Villars and Calvert, 1991). On the other hand, the phase CuSiTi crystallizes with Co₂Si-type structure (Villars and Calvert, 1991).

Due to the small amounts of the minority phases present in the sample investigated the accuracy of parameter determination as well as the reliability factors obtained for Cu₁₀Sn₃ and CuSn₃Ti₅ are considerably inferior than the data regarding CuSnTi (Table I). Nevertheless, the data clearly show that Cu₁₀Sn₃ crystallizes in spacegroup *P6₃/m* rather than *P6₃*. Furthermore, Cu₁₀Sn₃ is found to dissolve (about 5 at%) Ti on the Sn sites. The phase CuSn₃Ti₅ is found to be stoichiometric confirming the proposed structure (Schuster *et al.*, 1999).

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