

Cu₉Ni₆Sn: Determination of Phase Transformation at High Temperature

A. Deraisme, C. Servant, D. Pachoutinsky, Y. Bienvenu, J.-D. Bartout, L.-T. Mingault, P. Bertrand, and R. Bailly

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The copper rich corner of the CuNiSn system is frequently studied for the high tensile strength and good electrical conductivity of the alloys. In this study, we focus on the phase transformations at high temperature. The incipient melting is studied in some detail just below 1000 °C since the presence of an unexpected peak at 985 °C on the DTA's thermograms is detected.

Keywords CuNiSn, Differential Thermal Analysis, high temperature, precipitates, γ -phase

1. Introduction

Studies about the CuNiSn system are generally limited to temperatures above 400 °C and below 800 °C. This alloy is generally homogenized around 800 °C, since at higher temperatures, porosities appear.^[1] The CuNiSn ternary diagram in the Cu rich corner shows that Ni limits the Sn solubility in Cu and the ($\alpha + \gamma$) equilibrium domain width increases.^[2]

The solidification process is seldom studied in the case of the CuNiSn system. The Cu₉Ni₆Sn (in wt.%) alloy is the limit at present time for conventional processing: continuous casting and cold rolling. This grade could be rolled without defect^[1] while more alloyed CuNiSn grades like Cu₁₅Ni₈Sn₈ have to be processed along the powder metallurgy routes.

The interest in the CuNiSn alloy is motivated by the search for properties equivalent to those of the CuBe alloy used in the electric and electronic applications, in the automotive and aeronautical fields. The Cu-Be alloys are known for a high tensile strength (around 1000 MPa) and good electrical conductivity (>80% IACS). The fundamental studies in the CuNiSn alloys were essentially concerned with the hardening mechanisms, starting with a spinodal decomposition around 400 °C.^[3,4] Microstructural observations suggested that tin segregation in the former interdendritic space^[5] promotes the spinodal decomposition and explains the hardness of the alloy when it is not fully homogenized.

A. Deraisme, D. Pachoutinsky, Y. Bienvenu, J.-D. Bartout, and L.-T. Mingault, MinesParisTech, Centre des Matériaux P.M. Fourt, CNRS UMR 7633, BP 87 F-91003 Evry Cedex, France; C. Servant, Laboratoire de Physicochimie de l'Etat Solide, Bât 410-415, Université de Paris-Sud, 91405 Orsay Cedex, France; and P. Bertrand and R. Bailly, Griset SA, Rue du Grand Pré, F-60870 Villers Saint-Paul, France. Contact e-mail: aurelie.deraisme@orange.fr.

In this report, the Cu₉Ni₆Sn alloy transformations are studied with Differential Thermal Analysis (DTA) combined with metallographical observations to determine the phase transformation sequence. To understand the puzzling presence of a DTA peak at 985 °C during the melting process, it is necessary to investigate the effect of isothermal heat treatments just below this temperature. The experimental results are compared with the equilibrium ones calculated from the optimized thermodynamic database by Miettinen.^[6]

2. Experimental

Differential Thermal Analysis has been performed with a Setaram TGD TA 16-18 analyser. The samples of the Cu₉Ni₆Sn alloy (actually 9.6% Ni, 5.3% Sn, and 85.1% Cu (in wt.%) were removed to an ingot of Cu₉Ni₆Sn, made by the Griset French society. They were heated in an alumina crucible (7 mm high and 3 mm inner diameter) until 850 °C with a 5 °C/min heating rate, held at 850 °C during 1 h to homogenize the alloy, then heated until 1200 °C with a 5 °C/min rate and finally cooled with the same rate. The atmosphere was argon (with around 10 ppm O₂). To determine the eventual influence of the holding, another DTA experiment has been performed, therefore without the homogenization stage at 850 °C, with a heating until to 1200 °C with a 10 °C/min rate (followed by a cooling at the same rate). Furthermore, in order to show the influence of the cooling rate on the microstructure of the Cu₉Ni₆Sn alloy, thermal treatments were made in a furnace under air to perform a quench.

Polished sections are observed with a Zeiss Axiovert 450 M optical microscope, then the backscattered electron imaging mode of a LEO 1450 VP Scanning Electron Microscope (SEM) was used and combined with an Energy Dispersive Spectroscopy x-ray microanalysis from Thermo-Electron. More precise microanalyses were also possible with the CAMECA SX 100 Electro Probe Micro Analyser (EPMA) (using Wavelength Dispersive x-ray spectrometry). The analyses of composition of phases were complemented by x-ray diffraction (XRD) using a D500 Siemens Brucker θ - 2θ diffractometer. The diffractometer is equipped with a

Co anticathode ($\lambda_{K\alpha} = 0.1789$ nm), operating under 40 kV with a current of 25 mA. The selection of this anticathode may be justified by a better separation of the peaks with a Cu anticathode. The diffracted rays are detected by a Positional Sensitive Detector by EPHYSE.

For the sake of understanding and comparison with the experimental results, it is necessary to give some details on the thermodynamic modeling of the different phases considered in the Cu-Ni-Sn Miettinen's database as well as on their crystal structures. Four ternary phases were modeled with the sub-lattice formalism^[7]:

- the face centered cubic solid solution noted (fcc) modeled with the three substitutional elements Cu, Ni, Sn in one sub-lattice (Cu%, Ni, Sn). The element marked with the % is the major element. The (fcc) space group is $225 Fm\bar{3}m$ and its crystal parameters are $a = b = c = 0.364$ nm;
- the ordered face centered cubic gamma phase noted as γ -phase modeled as (fcc) as a substitutional (Cu%, Ni, Sn) solid solution in one sub-lattice, but with different excess optimized parameters. Its space group is $Fm\bar{3}m$ and its crystal parameters are $a = b = c = 0.66$ nm. In the binary Cu-Sn, the γ -phase noted as Cu_3Sn has a smaller parameter $a = b = c = 0.6116$ nm;
- the $(CuNi\%)_3Sn$ phase noted as γ_1 -phase with two sub-lattices $(Cu,Ni)_{0.75}Sn_{0.25}$; therefore with a Cu-Ni substitution in the first sub-lattice;
- the stoichiometric $Cu_3Ni_{27}Sn_{10}$ phase noted as $\Gamma 1$ -phase modeled with three sub-lattices $(Cu)_{0.075}(Ni)_{0.675}(Sn)_{0.25}$.

As for the $Cu_{41}Sn_{11}$ phase, noted as δ -phase, it was only thermodynamically modeled in the case of the low-order Cu-Sn binary system with two sub-lattices as $(Cu)_{0.788}(Sn)_{0.212}$. Its space group is $216 F43m$ and its crystal parameters are $a = b = c = 1.798$ nm. In the present work, as we will see below the δ -phase is in fact a ternary one containing Cu, Sn and Ni, similar to $Cu_9Ni_3Sn_3$ or $(Cu,Ni)_3Sn$. So, new ternary thermodynamic modeling will be required in the future for that phase.

The calculation of the phase transformations was performed with the Thermocalc[®] software,^[7] R version.

3. Results and Discussion

DTA can be used as a fingerprint for identification purpose in the search for the phase transformation from the solidification range to 600 °C. The thermogram also displays peaks between 400 and 600 °C due to the formation of different phases but rather far from equilibrium. The *solidus* of the Cu9Ni6Sn alloy is between 890 and 930 °C on the heating leg of the DTA cycle, but it is difficult to determine exactly the beginning of the melting process. The *liquidus* is easier to locate at 1096 °C. During the cooling, an apparent *solidus* is observed at 880 °C. The cooling procedure of our ternary alloy was calculated at equilibrium with Miettinen's database. The different stages of phase transformations are the following: the *solidus* temperature is calculated at

996 °C, so somewhat higher than the experimental one, while the *liquidus* is calculated at 1108 °C, in good agreement with the experiment. At room temperature, the simulation calculates two-phase in the alloy: (fcc) + γ_1 .

During the melting process, an unusual peak is detected on the DTA heating thermogram at 985 °C, see Fig. 1 where two thermograms are compared: the first with the hold at 850 °C to homogenize the alloy (continuous line) and the second without hold (dashed line). It appears that this event in the thermogram is smaller without the homogenizing stage, thus the homogenization process promotes this event of the phase transformation. On a thermogram of the Cu15Ni8Sn alloy with a 20 °C/min heating rate and without homogenizing stage, Lebreton^[8] observed the same peak around 985 °C but with a weaker amplitude. The cooling simulation of this alloy is similar to the one of our alloy (*liquidus* at 1116 °C and *solidus* at 968 °C). Without homogenization, at room temperature, our alloy is two phase: the matrix is the γ -phase with tin rich precipitates having a composition range 34-38 wt.% Sn, 13-15 wt.% Ni, and 45-50 wt.% Cu. If we compare with the heating simulation performed with the Miettinen's database, this unexpected DTA peak appears just before the calculated melting process. The thermogram shows that the melting process has just begun. The endothermic peak is probably due to a phase transformation just above the *solidus*.

To understand the nature of this phase transformation a thermal treatment was performed on a sample of our alloy in a furnace under air thus allowing a cooling rate faster than the ones used in DTA experiments; the alloy is reasonably immune to hot corrosion (which only affects a thin layer at the surface of the sample). As with the DTA, the sample was homogenized at 850 °C for 1 h. Then, it was maintained at 985 °C for 2 min and quenched in water. A thermocouple was inserted in the sample, for controlling the temperature. The quench of the sample allowed freezing the microstructure of the alloy at 985 °C. In order to determine the presence of different phases, this sample was then polished for optical and SEM metallographic observations.

The polished section of the sample observed in the SEM (backscattered electron mode) shows white precipitates between 5 and 2 μ m in size with a homogenous distribution inside the grains (Fig. 2a) and at their boundaries; these precipitations have an elongated morphology and are around 2 μ m in length (Fig. 2b).

The quenched sample when observed with a high magnification shows liquid pockets of this phase. The liquid phase, in equilibrium with a solid matrix, solidifies in the first instant of the quench with enough segregation to form the intermetallics. Similar observations of incipient melting of a powder metallurgy nickel based superalloy were made by Jeandin et al.^[9]: intragranular pockets of molten alloys do not contain intermetallics but some pores and incipient melting also decorates grain boundaries. In our case, porosity is the result of the shrinkage of the liquid phase during solidification. In the sample, pores are observed inside the grains and at the grain boundaries. It is possible to distinguish the beginning of a dendritic structure (Fig. 2b). The composition of the intermetallics is the same whatever their localization. EPMA gives the composition of the phase

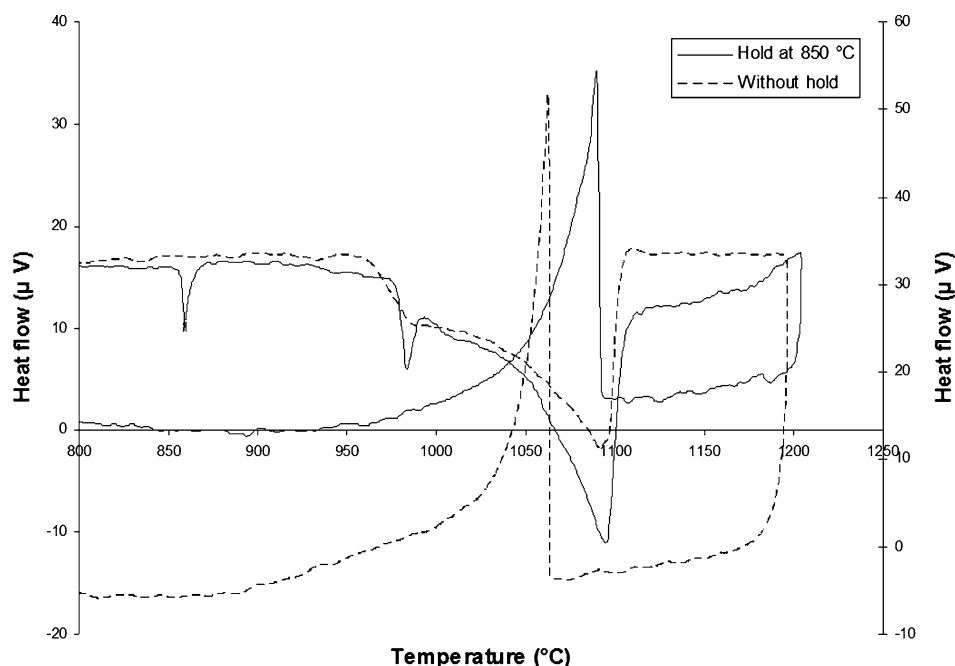


Fig. 1 Thermograms of the Cu₉Ni₆Sn alloy. Firstly, in *continuous line*, 5 °C/min rate heating, with a 1 h hold at 850 °C and 5 °C/min rate heating until 1200 °C, then 5 °C/min rate cooling. On this curve, the peak at 850 °C is due to the homogenization. Secondly, in *dashed line*, 10 °C/min rate heating and cooling without homogenizing stage

appearing in white with backscattered electrons (Table 1). The white contrast compared to the gray one of the matrix indicates a richer Sn composition; this contrast is due to the Sn atomic number higher than the ones of Cu and Ni. It is difficult to decide between the γ and the δ ternary intermetallic phases. In the Cu-Sn binary diagram, these phases have the same composition (around 35 wt.% Sn) and a similar structure (fcc symmetry). In the case of a diffusionless transformation, it is not possible to distinguish the two phases. Thus, the XRD experiments show that the white phase observed at room temperature is a δ -phase, but the γ -phase is probably present at the beginning of the quench from 985 °C. On the Ni-Sn binary diagram,^[10] the formation of the γ -phase is at 1175 °C. The presence of Cu decreases its melting point, thus the peak at 985 °C could indicate the melting point of this phase with this (Ni,Cu)₃Sn = γ_1 composition. If the experimental observations are compared with the calculation of the phase equilibria in the Cu rich corner of the Cu-Ni-Sn system using the thermodynamic database by Miettinen,^[6] at 985 °C the γ -phase must be metastable. Furthermore it is also not predicted as a stable phase at 900 °C (Fig. 3a, b). Moreover, the isothermal section calculated at 985 °C shows that the composition of our alloy is situated just at the limit of the two-phase (Liquid + (fcc)) and (fcc) single-phase domains. Taking into account the small uncertainty on the composition of the alloy, it is possible for this alloy to be inside the two-phase domain (Liquid + (fcc)). The metallographic observations indicate that a tin enriched area (14 wt.% Sn) extends 1 μ m away from the precipitate (Fig. 2b, 4).

Using XRD, the lattice parameters of the phases are determined. The sample shows a texture linked to large

grains as confirmed by metallographic observation. The grains are around 500 μ m in size. The matrix is a face centered cubic phase noted as (fcc) with a cell parameter: $a = b = c = 0.364$ nm. The white intermetallic phases also have the face centered cubic structure but with a larger cell parameter: $a = b = c = 1.798$ nm.

If we compare with the data given in the *Pearson's Crystallographic Data*,^[11] this white phase is similar to Cu₉NiSn₃, but the tin content is only half that corresponding to the stoichiometry given by Villars. This could be explained by the presence of vacancies in the atomic structure. Only 50% of the atomic sites of tin seem to be occupied. It must be recalled that the crystal parameter ($a = b = c = 1.79807$ nm) of the δ -phase in the Cu-Sn binary system is slightly smaller than three times the one ($a = b = c = 0.6116$ nm) of the γ -phase. The volume ratio is 25.40. The δ -phase contains $416 - 4 = 412$ atoms per cell (because one site 16e of Cu has only a 0.75 occupancy) whereas the γ -phase contains 16 atoms per cell, the atom ratio is 25.75. The atom sites are noted with the Wyckoff symbol.^[11] By introducing vacancies on the Sn sites of the δ -phase, it is possible to give account of its composition determined by EPMA in the ternary system. The simulation of 50% vacancies on the Sn sites of Cu₉NiSn₃ gives $412 - (0.5 \times [16e + 24g + 48h]) = 368$ atoms per cell and $16 - (0.5 \times 4a) = 14$ atoms per cell, thus a 26.28 ratio. The atom ratios are in very good agreement with the volume ratio. With the Rietveld simulation, by using the Fullprof software,^[12] it can be observed that the calculated XRD diagram is the same whatever the occupancy of the Sn sites (either 1 or 0.5), only the intensities change, that is visible on the main two peaks situated at $2\theta = 49.49^\circ$ and 92.95°

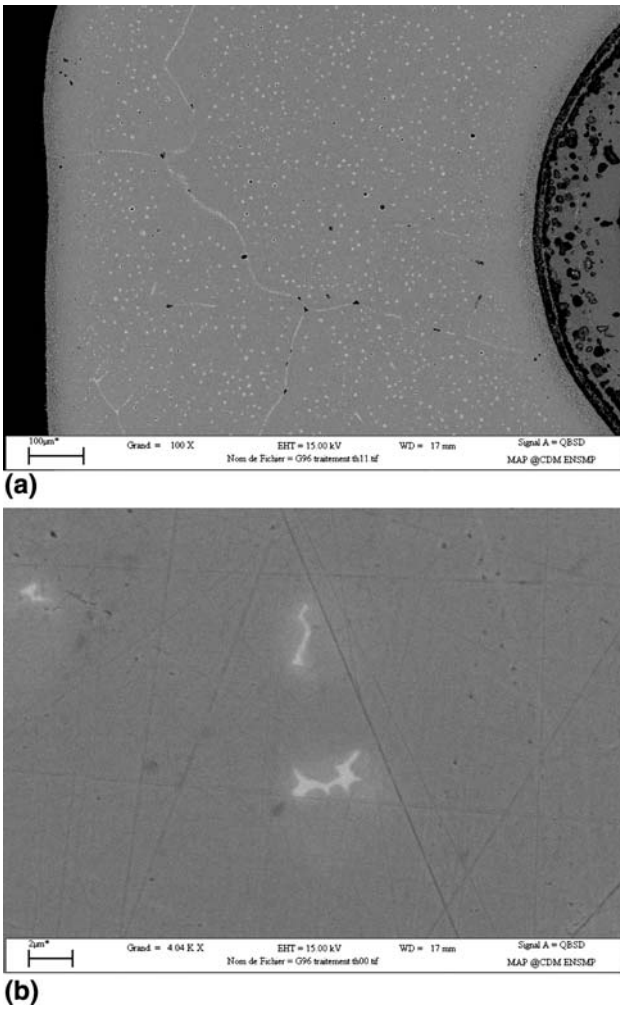
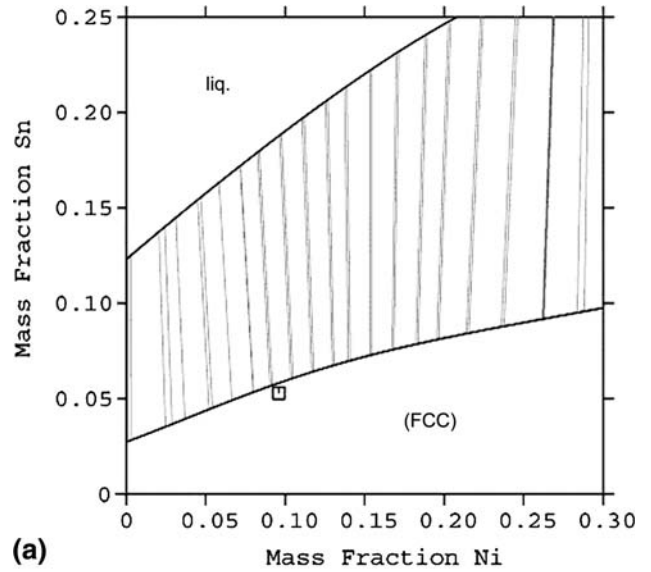


Fig. 2 SEM micrographs (a) X 100—15 kV-backscattered electrons—precipitates in the core of the alloy and on the grains boundaries (b) X 4.04 K—15 kV-backscattered electrons—intragranular precipitates

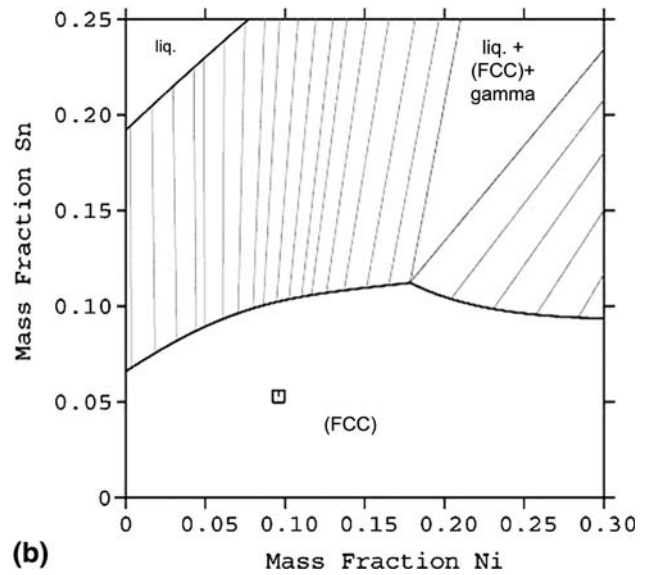
Table 1 Composition of the white precipitate in Fig. 2 analyzed with EPMA

	Ni	Sn	Cu	O
wt. %	10	22	66	2
at. %	11.5	12	69	7.5

(Table 2, Fig. 4a, b). Our experimental XRD diagram shows that the intensity of such peaks is low (Fig. 5), so in agreement with the hypothesis of vacancies on the Sn sites of the Cu_9NiSn_3 , and at a slightly higher temperature on the Sn sites of $(\text{Cu,Ni})_3\text{Sn}$ (γ -phase). The Miettinen's calculations indicate that the melting point of the δ -phase is around 920 °C, but with a lower tin content, the melting point of the phase increases. Thus the occupation of only 50% of the Sn site could promote the increase of the melting point up to about 985 °C. Hence, it appears that the δ -phase, namely



(a)



(b)

Fig. 3 Calculated isothermal sections in the copper rich part of the CuNiSn system at (a) 985 °C, (b) 900 °C

Cu_9NiSn_3 , may be a super cell of the γ -phase allowing easy $\gamma \leftrightarrow \delta$ transformation.

4. Conclusion

The study of the core of the $\text{Cu}_9\text{Ni}_6\text{Sn}$ alloy quenched after an isothermal hold at 985 °C, about the temperature of an unexpected DTA event in the heating sequence allows determining the presence of phase formed after the quench at 985 °C. This phase is not predicted in the equilibrium ternary phase diagrams. This phase is Cu_9NiSn_3 (δ -phase) with a cubic face centered crystallographic structure, but it is due probably to the diffusionless transformation from the

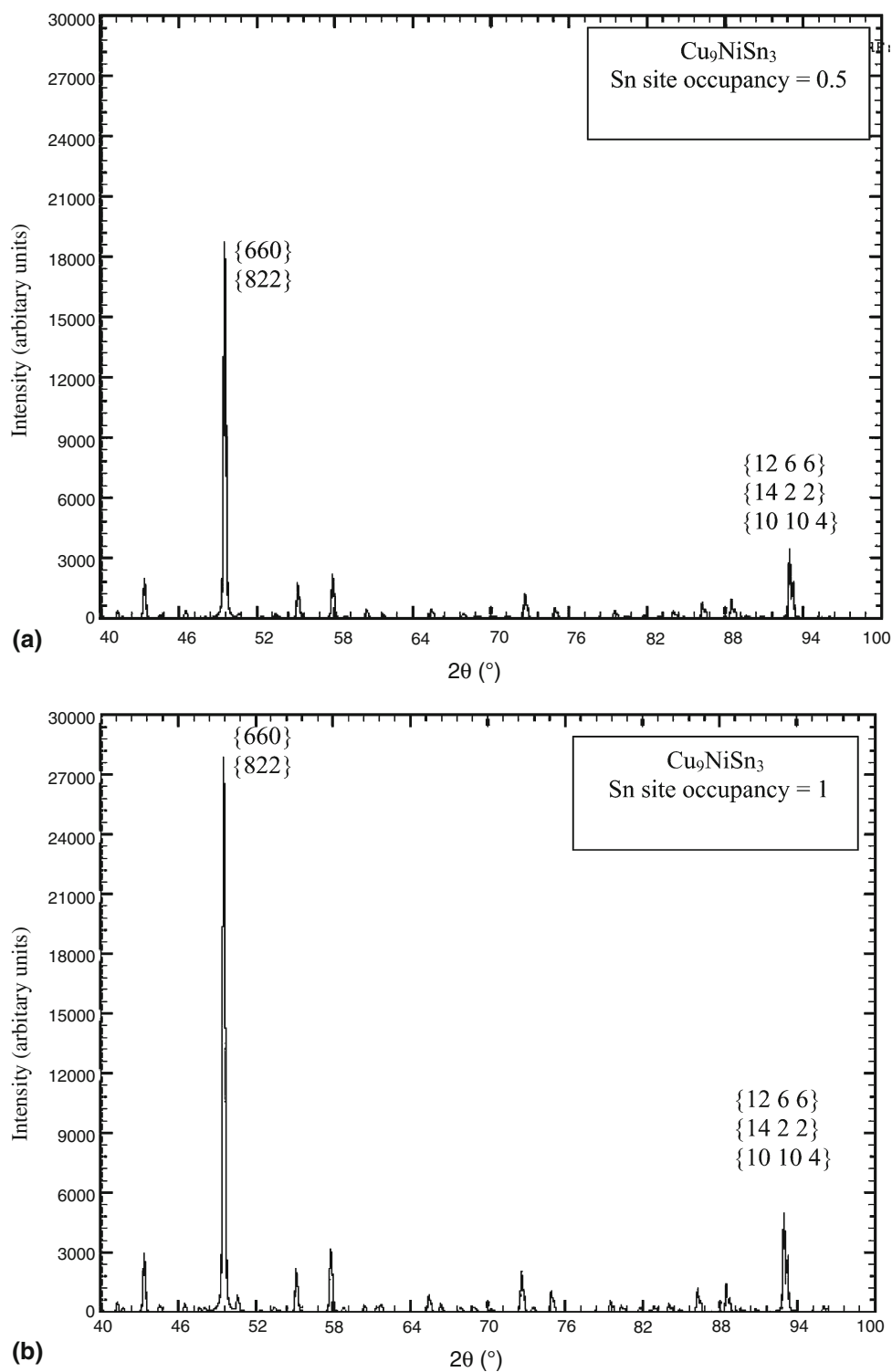


Fig. 4 XRD diagrams of the Cu_9NiSn_3 phase calculated with the Fullprof software with an occupancy for the Sn sites of (a) 0.5 and (b) 1

gamma γ -phase and is formed at 985°C . The Miettinen's calculated isothermal sections show that the γ -phase is metastable at 985°C . This difference could be explained by the presence of vacancies in the crystal structure of the

Cu_9NiSn_3 phase. The lower tin content makes that phase more stable, thus the phase equilibria are different from presented in the paper by Miettinen.^[6] In addition, some oxygen detected by EPMA in this phase can modify slightly

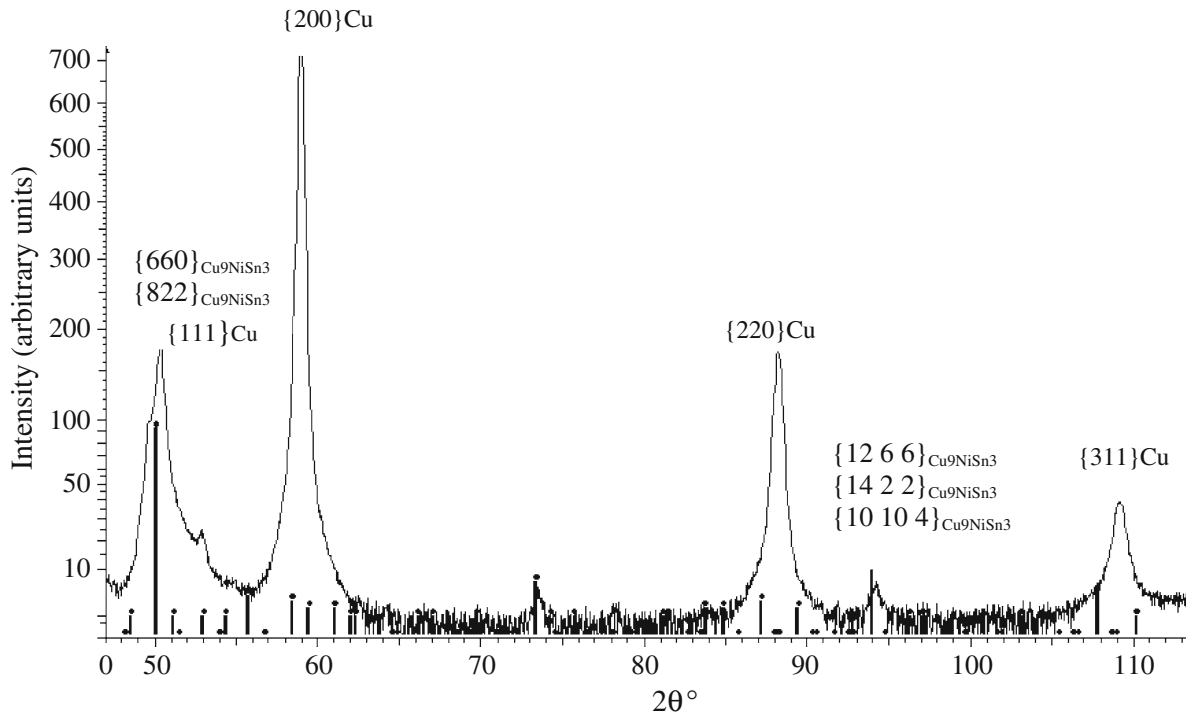


Fig. 5 XRD diagram of the Cu₉Ni₆Sn alloy with Co anticathode. The diagram shows Cu peaks and peaks of the Cu₉NiSn₃ phase. The intensity expected appears with the black draft. The intensity at 92.95° is bigger than this observed experimentally

Table 2 Comparison of the intensities of two main peaks of the Cu₉NiSn₃ phase, when the occupancy of the Sn sites is 1 and 0.5

2θ° {hkl}	49.49 {660}-{822}	92.95 {12 6 6}- {14 4 2}-{10 10 4}
Intensity (cps)		
100% occupied Sn sites	28039	5294
50% occupied Sn sites	18920	3416

the temperatures of the invariant equilibria compared to the ones calculated at equilibrium in the Cu-Ni-Sn ternary system optimized by Miettinen.

In conclusion, the peak observed at 985 °C by DTA on heating is probably due to the formation of the ternary γ -phase with about 50% vacancies in the tin sites of its atomic structure, which is transformed in a δ -phase when cooled or quenched. A practical significance is that the Cu₉Ni₆Sn alloy may become fragile when exposed to excessive homogenization temperatures (>900 °C)

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