

## Interstitial void structure in Cu–Sn liquid alloy as revealed from reverse Monte Carlo modelling

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2005 J. Phys.: Condens. Matter 17 S31

(<http://iopscience.iop.org/0953-8984/17/5/004>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 20:18

Please note that [terms and conditions apply](#).

# Interstitial void structure in Cu–Sn liquid alloy as revealed from reverse Monte Carlo modelling

W Hoyer<sup>1</sup>, R Kleinhempel<sup>1</sup>, A Lőrinczi<sup>2</sup>, A Pohlers<sup>1</sup>, M Popescu<sup>2</sup> and F Sava<sup>2</sup>

<sup>1</sup> Technische Universität Chemnitz, Institut für Physik, D-09107 Chemnitz, Germany

<sup>2</sup> National Institute of Materials Physics, Bucharest-Magurele, PO Box MG 7, Romania

Received 7 January 2005

Published 21 January 2005

Online at [stacks.iop.org/JPhysCM/17/S31](http://stacks.iop.org/JPhysCM/17/S31)

## Abstract

A model for the structure of copper–tin liquid alloy has been developed using the standard reverse Monte Carlo method. The interstitial void structure (size distribution) was analysed. The effects of various kinds of voids (small size and large size) on the interference function and radial distribution function were investigated. Predictions related to the formation of some ternary alloys by filling the interstices of the basic alloy were advanced.

## 1. Introduction

Information regarding the structure and properties of amorphous solid and molten metallic alloys is important from both fundamental and practical points of view. The fundamentals are related to the understanding of the material at the atomic scale including the structure–properties relation. The applications are related to the discovery of new soldering alloys, with low melting temperatures, without the classical lead component. New interest has emerged in the structure and properties of liquid alkali metals [1], alkaline-earth metals [2], rare-earth metals [3], liquid transition metals [4] and various alloys in the molten state [5].

The atomic scale structure in disordered solids and in liquids is still challenging, although the structural features are essential in controlling the properties of the materials. Several investigations have shown that for concentrations corresponding to the ordered intermetallic phase, the properties do not depend linearly on the concentration of a particular atom type. For example, the electrical resistance shows higher values for Cu–Sn and Ag–Sn alloys in the range of intermetallic phase formation [6]. Moreover, the viscosity [7, 8], the molar volume, the heat of formation, the magnetic susceptibility and the surface tension [9] show important deviations from linear behaviour. Information on the structure in solid and liquid phases over a large concentration range is therefore necessary for understanding the systems. This information can be obtained by means of x-ray diffraction.

On the other hand, the structural information on disordered solids and on molten alloys cannot be complete and unequivocal. That is why the developing of structural models is of vital importance for revealing the atomic scale structure of disordered materials.

There are several methods used to simulate the atomic scale structure of a given material: molecular dynamics, direct Monte Carlo modelling and reverse Monte Carlo modelling. Each method has its advantages and shortcomings.

If a good model is obtained for a given material, as confirmed by the fit of the structural partial factors, radial distribution functions and density, then it is possible to make a realistic analysis of the interstitial void size distribution in the material. The information on the voids is of great interest because the void size and distribution influence the diffusion properties of the material, the mechanical behaviour and the possibility of homogeneous alloying with other chemical elements. In the case of defects induced by gamma irradiation, the problem of void characterization is of outstanding importance [10, 11]. Fortunately, the development of positron annihilation lifetime spectroscopy (PALS) has allowed us to probe the free volume (voids) in the materials. In the last few decades the method has been used to examine crystalline semiconductors such as Si, Ge, SiC, as well as III–V compounds (GaP, GaAs, InP, GaN) and II–VI compounds (CdTe, CdHgTe). Jensen *et al* [12] have shown that the different values of the positron lifetimes are a linear function of the vacancy volume and these should correspond to the proper void distribution in an atomic network. Shpotyuk *et al* [13] have recently shown that the PALS method can be used to tag radiation induced open volume defects in glasses.

The aim of this paper is to model the atomic scale structure of the liquid alloy  $\text{Cu}_{27}\text{Sn}_{73}$  and to investigate the void size distribution in order to predict the possible formation of some useful ternary alloys by filling the voids in the basic structure of molten Cu–Sn.

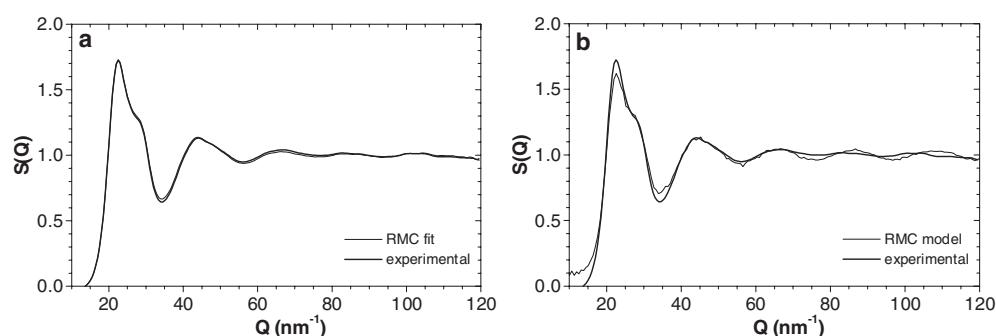
## 2. Experimental details

The x-ray diffraction pattern of the molten Cu–Sn alloy at  $540^\circ\text{C}$  has been taken on a theta–theta diffractometer provided with a molybdenum target tube ( $\lambda_{\text{K}\alpha 1} = 0.070926\text{ nm}$ ). The angular range for the recording of the scattered x-ray radiation was  $\theta = 3.23^\circ\text{--}42.4^\circ$  corresponding to the maximum wavevector  $Q$  of  $119.5\text{ nm}^{-1}$  (with  $Q = (4\pi \sin \theta)/\lambda$ ). Corrections for background, polarization and Compton scattering were carried out. The corrected diffracted intensity curve has been normalized with the Krogh-Moe–Norman method [14, 15] and Fourier transformed in order to get the radial distribution function  $g(r)$ .

## 3. Reverse Monte Carlo modelling

The simulation of the structure of the alloy Cu–Sn was performed using RMC modelling [16]. The input parameters were the experimental structure factor, the density (number density) and the weight factors, as well as the minimum distance accepted for Cu–Cu, Cu–Sn and Sn–Sn, corresponding to the atomic radii. Finally, the length of the side of the simulation box has been calculated. The number of the atoms in the box was 5000: 1350 Cu atoms and 3650 Sn atoms. The box side was 4.9872 nm. The copper radius was taken as 0.128 nm while the Sn radius was taken as 0.162 nm. The fitting parameter  $\sigma$  was pre-established in the first stage of simulation: 0.1, while for the sixth (last) stage of the simulation  $\sigma$  was reduced to 0.001. The measured density,  $8.86\text{ g cm}^{-3}$ , was considered.

The computer program calculates for every simulation step the pair distribution function and then the differential function  $g(r)$ . These functions are compared to the experimental ones. After imposing small aleatory movements on the atoms of the model, at every step, one calculates  $g(r)$  and, if the fit to the experimental  $g(r)$  is improved, then the movements are retained. The process is continued until a satisfactory fit is obtained.



**Figure 1.** The comparison between the experimental structure factor and that calculated from the model using RMC modelling.

#### 4. The interstitial void size distribution

In order to investigate the void size distribution in the model of Cu–Sn alloy, we calculated by a Monte Carlo procedure the void size for every interstice of the model.

The void size is defined as the diameter of the sphere of maximum size that can be introduced in an interstice without intersecting any surrounding atom defined by its radius. The position of the centre of a void is obtained by moving the starting position inside an interstice in small aleatory steps and retaining only those movements that increase the radius of the sphere that can be introduced in the interstice. The distribution of the void size, the spatial configuration of the void centres, the structure factor corresponding to the scattering of x-rays on the void centres and the pair correlation function of the void centres have been calculated on PC Pentium high power computers. The calculation time of the model was several days, while the void calculation was carried out in several hours.

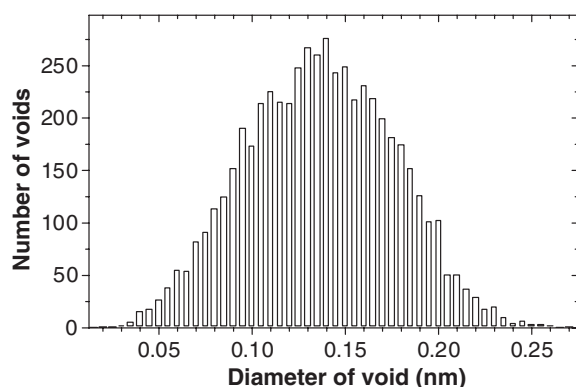
#### 5. Results and discussion

Figure 1(a) shows the fit of the RMC model for liquid Cu<sub>27</sub>Sn<sub>73</sub> alloy at 540 °C. The structure factor reveals a first large maximum with a shoulder on the right-hand side of the peak. The next maxima are satisfactorily reproduced by the curve calculated from the model. The introduction of the temperature factor in the calculation of the structure factor considerably improves the agreement between the experimental and model structure factors. In the RMC calculation the temperature factor corresponding to the Cu–Sn alloy at 540 °C is taken into account in the form  $\exp(-BQ^2)$  where  $B$  is a constant dependent on temperature and  $Q$  is the scattering vector.

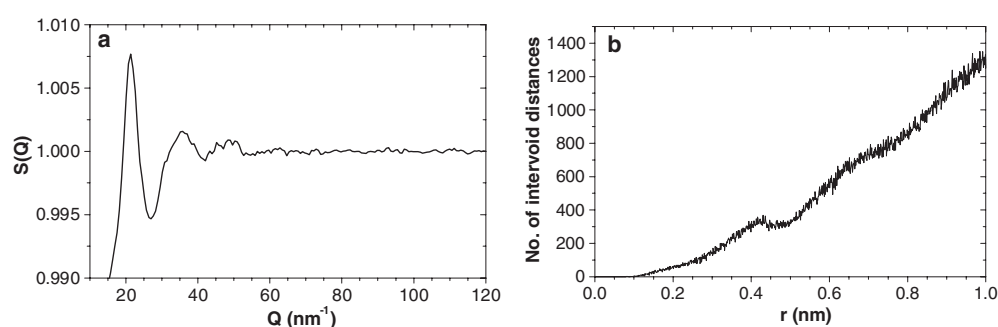
Figure 1(b) shows the structure factor calculated from the static RMC model (without considering the temperature factor) compared to the experimental structure factor. As expected, the agreement is worse.

The void size distribution in the model is represented in figure 2. A maximum number of 5527 voids have been revealed in the 5000-atom model.

We have calculated the structure factor and the pair distribution function for a hypothetical network of atoms having as positions those of the voids and neglecting the influence of the atoms of the model. Figure 3 shows the results. It is quite surprising that the detailed structure of both curves proves that the disposal of the interstices in the model is not at random but some regularity exists. Because short range ordering and long range ordering are excluded, the only possibility for explaining the details of the curves is the presence of medium range order. It is



**Figure 2.** The interstitial void size distribution in the RMC model of amorphous Cu–Sn alloy.

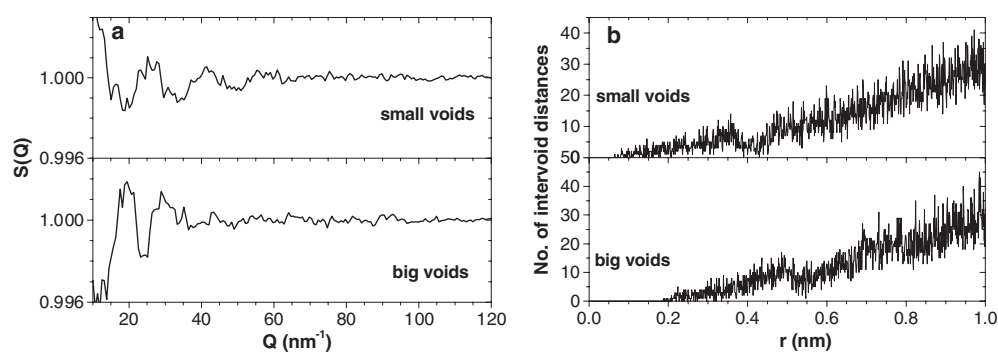


**Figure 3.** The structure factor (a) and the radial distribution function (b) of the void system in the RMC model of disordered Cu–Sn alloy.

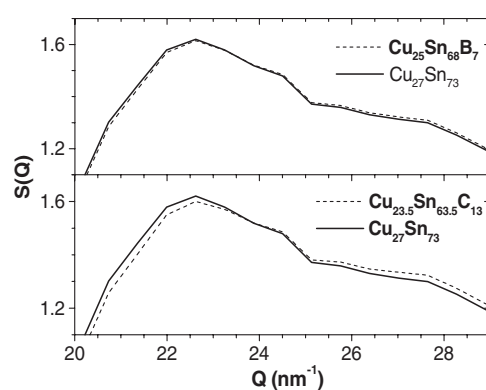
interesting to observe that the first peak in  $g(r)$  is large, slightly asymmetrical and situated at the average distance of 0.42 nm. This distance corresponds roughly to triple the diameter of the mean size of the voids, and that means that it represents the position of the second-order neighbours of a void.

The structure factor and the pair correlation function for the voids corresponding to the maximum diameter of 0.0938 nm of the voids (842 voids) and the same functions for the large voids (starting from 0.179 nm, 843 voids) are represented in figure 4. The pair correlation functions clearly show that the disposal of the small voids corresponds to a medium range order with the first neighbours situated at 0.35 nm (around 2.5 times the average diameter of the voids in the model), while the disposal of the large voids corresponds to the first coordination sphere situated at 0.49 nm (around 3.5 times the average diameter of the voids in the model).

Taking into account the possibility of filling the interstitial voids with some kinds of atoms, thus designing new ternary alloys, we calculated the maximum number of boron and carbon atoms that could be introduced into the alloy while preserving the basic structure of the binary alloy. The maximum number of boron atoms that could be introduced in the interstices of the Cu–Sn alloy model is 377. This corresponds to a composition  $\text{Cu}_{1350}\text{Sn}_{3650}\text{B}_{377}$  or  $\text{Cu}_{25}\text{Sn}_{68}\text{B}_7$ . Above this composition a clustering of boron is expected. For the case of carbon introduced in Cu–Sn alloy, the composition that ensures a homogeneous distribution of carbon (without clustering) is  $\text{Cu}_{1350}\text{Sn}_{3650}\text{C}_{748}$  or  $\text{Cu}_{23.5}\text{Sn}_{63.5}\text{C}_{13}$ .



**Figure 4.** The structure factors (a) and the pair correlation functions (b) for small and large interstitial voids in the model.



**Figure 5.** The first part of the structure factor (including the first maximum and its shoulder) for the simulated ternary disordered alloys Cu–Sn–B and Cu–Sn–C with the maximum number of boron and carbon atoms that can be introduced into the interstices in the RMC model of the binary alloy Cu–Sn. The structure factors of the ternary alloys are compared with those of the liquid binary Cu–Sn alloy.

When boron or carbon is introduced into the atomic network of the Cu–Sn alloy, the structure factor of the material is changed accordingly. Figure 5 shows the main changes expected in the structure of Cu–Sn alloy when boron and carbon are added. The modifications are the largest in the position of the first maximum, with its shoulder. The first maximum decreases while its shoulder increases with the addition of boron or carbon. At the same time, the maximum with its shoulder shifts a little toward higher  $Q_s$ . The modifications are larger for Cu–Sn–C, and smaller for Cu–Sn–B. The remaining parts of the structure factors are less affected and not represented in figure 5.

The investigation of the interstitial void structure in the model revealed a non-random arrangement of the voids with characteristic coordination at medium range distance. The filling of the voids with small size, light atoms determines the particular modification of the first large maximum of the structure factor. The diminishing of the intensity of the maximum and the growth of the right-hand side shoulder can be related probably to the specific configuration of the atoms that defines the largest interstices in the model. The full explanation is still challenging. Up to the maximum number of light atoms that could be introduced into the interstitial voids the physical properties of the ternary alloy are expected to vary linearly.

Thereafter, for a larger amount of light atoms a strong change is expected to occur. Popescu [17] has shown that in the structural model of Ge–Fe amorphous alloy the limit of  $\sim 19$  at. % Fe in Ge corresponds to complete filling of the germanium network by iron atoms and correlates well with the abrupt change from semiconductor to metallic electrical conductivity of the material. The modelling and the investigation of the void structure of the models can throw new light on the structure and properties of the non-crystalline materials and must be used in designing new materials.

Recently, Sava [18] has shown how the void size distribution in a model of crystalline silicon is changed when an increased number of defects are introduced into a crystalline cluster until the formation of an amorphous structure occurs.

It is expected to be possible to relate various kinds and sizes of voids to the detailed features of the x-ray diffraction pattern. As a consequence, the general aspects of the void structure in the material can be guessed by analysing the structure factor.

## 6. Conclusions

The reverse Monte Carlo method is a versatile method for creation of realistic models for complex non-crystalline materials. In the case of liquid binary metallic alloy based on copper and tin, the main characteristics of the structure factor have been satisfactorily reproduced.

New insight into the structure and properties of non-crystalline solids and liquids can be acquired by analysing the interstitial void structure of the atomic scale models.

The knowledge of the void size distribution can be used for predicting the property changes in a series of compositions and for designing new alloys.

## References

- [1] Dubinin N E 2003 *J. Optoelectron. Adv. Mater.* **5** 1259
- [2] Kes H, Dalgıç S S, Dalgıç S and Tezgor G 2003 *J. Optoelectron. Adv. Mater.* **5** 1281
- [3] Dalgıç S S, Dalgıç S, Celtek M and Sengul S 2003 *J. Optoelectron. Adv. Mater.* **5** 1271
- [4] Dalgıç S S, Dalgıç S and Domekeli U 2003 *J. Optoelectron. Adv. Mater.* **5** 1263
- [5] Hoyer W, Kaban I and Merkwitz M 2003 *J. Optoelectron. Adv. Mater.* **5** 1069
- [6] Roll A and Motz H 1957 *Z. Metallk.* **48** 435
- [7] Gebhardt E, Becker B and Schaefer S 1952 *Z. Metallk.* **43** 292
- [8] Gebhardt E, Becker B and Traegner E 1953 *Z. Metallk.* **44** 379
- [9] Lauermann I, Metzger G and Sauerwald F 1961 *Z. Phys. Chem.* **216** 42
- [10] Shpotyuk O, Kovalskiy A, Kavetskiy T and Golovchak R 2003 *J. Optoelectron. Adv. Mater.* **5** 1169
- [11] Shpotyuk O, Kovalskiy A, Kavetskiy T, Golovchak R and Popescu M 2003 *J. Optoelectron. Adv. Mater.* **5** 1181
- [12] Jensen K O, Salmon P S, Penfold I T and Colemans P G 1994 *J. Non-Cryst. Solids* **170** 57
- [13] Shpotyuk O I, Filipecki J, Hyla M, Kovalskiy A S P and Golovchak R Ya 2001 *Physica B* **308–310** 1011
- [14] Krogh-Moe J 1956 *Acta Crystallogr.* **951–953** 9
- [15] Norman N 1957 *Acta Crystallogr.* **370–373** 10
- [16] McGreevy R L and Pusztai L 1988 *Mol. Simul.* **359** 1
- [17] Popescu M 1983 *J. Non-Cryst. Solids* **56** 273
- [18] Sava F 2003 *J. Optoelectron. Adv. Mater.* **5** 1075