Mössbauer and X-Ray Studies on Splat Cooled SnGeCu Alloy

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Solid samples of $(Sn_xGe_{1-x})_{36}Cu_{64}$ with different tin concentrations were produced by the Splat Cooling technique. The melted material was cooled down from different initial temperatures (T_0). These samples were analyzed by Mössbauer spectroscopy and X-ray diffraction. The results are compared with those obtained in similar measurements on the annealed samples and on the slowly cooled material. The fast quenched samples were all polycrystallines. The resultant phases are analized and a memory effect of the liquid state in the solid material is discussed.

Introduction

This work is the continuation of studies performed on several systems (SnPb [1], SnTe [2], SnInTe [3], and SnGeTe [4]). Our aim is to analize the influence of the initial melting temperature on the properties of the solid samples obtained by fast cooling from the melt and the existence of memory effects of the liquid state in these samples as a consequence of the production technique employed.

Experimental

Whang [5] points out that the CuGe alloy becomes amorphous in a concentration range around 36 at.% Ge using fast cooling methods from the melt, so it was chosen as a base alloy to form the $(Sn_xGe_{1-x})_{36}Cu_{64}$ ternary system. The different tin concentrations with which this system was prepared were 2, 5, 8, 11 and 14 at.%. In all cases the material was heated in a previously evacuated furnace under Ar pressure. The fast cooled samples, with thicknesses between 50 and 80 µm, were obtained by means of a splat-cooling device [6] using Cu pistons at room temperature. The cooling rate is estimated in 10^5-10^6 K/s and the initial melt temperatures from which the material was cooled down ranged from 600 to 1060 °C. The quenched alloys were analized by Mössbauer spectroscopy (absorber and source of SnO_3Ba at room temperature) and X-ray diffraction (Debye chamber with Cu target).

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Results and Discussion

The samples obtained by splat cooling were all policrystallines. The phases observed by X-ray diffraction were: Cu_6Sn_5 (phase η), Cu_3Sn (phase ε), Cu_3Ge (phase ε) and Ge. On the other hand, the best fit of the experimental data obtained by Mössbauer spectroscopy was achieved superposing three single lines. The slowly cooled material showed Mössbauer spectra (Figure 1) similar to those belonging to the rapidly quenched samples. The first line, with an Isomer Shift about $IS_1 = 1.73$ mm/s, corresponds to Cu_3Sn [7] and the third one (IS_3) corresponds to Sn_β [8]. The second line (IS_2), with an Isomer Shift about 2.05 mm/s, corresponds to

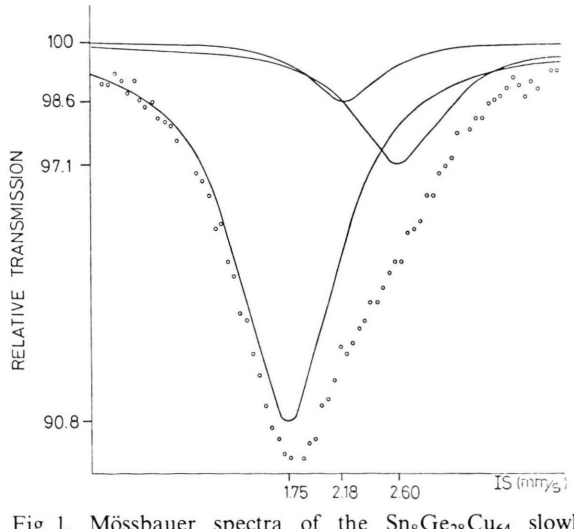

Fig. 1. Mössbauer spectra of the $Sn_8Ge_{28}Cu_{64}$ slowly cooled material.

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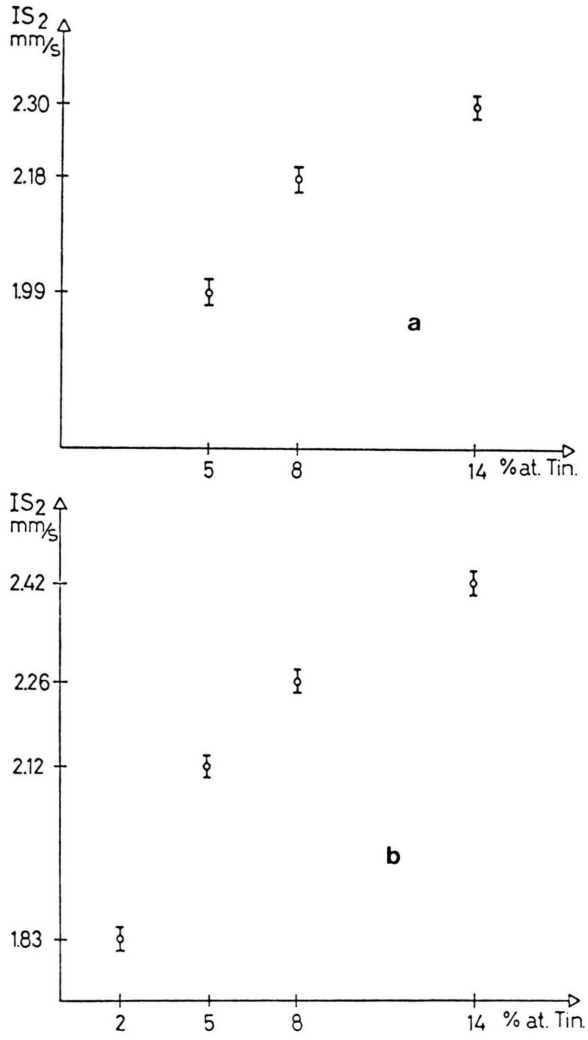

Fig. 2. Relationship between the Isomer Shift of the second line (IS_2) and tin concentration; a) slowly cooled material, b) fast cooled samples.

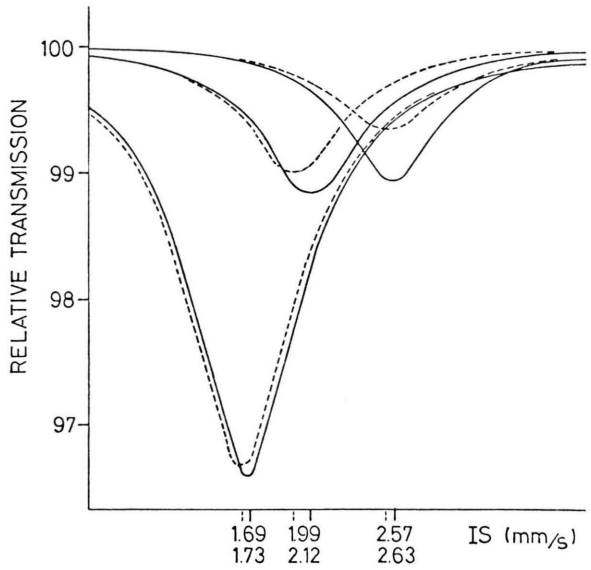

Fig. 3. Mössbauer spectra of $Sn_5Ge_{31}Cu_{64}$ alloy; – – – slowly cooled, —— fast cooled.

Cu_6Sn_5 [7]. However there are strong reasons to think that tin also contributes to this line as a substitutional impurity in the Ge lattice. Supporting this, X-ray measurements showed that this lattice was expanded related to the Ge net. This fact is attributed to the existence of tin in the Ge lattice ($r_{Sn} > r_{Ge}$). In this crystalline distribution, the tin atoms have a smaller atomic volume than in the Sn lattice. Therefore the shielding effect produced by the 5 p electrons over the 5 s ones becomes more important and as a consequence the Isomer Shift value decreases related to the Sn_β one. Furthermore, higher IS_2 values were found with increasing tin concentration (Figure 2). This fact is explained by the growth in the effective s electron number on the tin atoms as a consequence of the growth of their atomic volume produced by the Ge lattice expansion.

The Isomer Shift of this line, according to Lees and Flinn [9], allows us to compute the effective number of s electrons (n_s) relate to neutral tin which goes from $n_s = 1$ for 2 at.% tin alloy to $n_s = 1.20$ for 14 at.% tin alloy, while the Sn_β has a $n_s = 1.31$ value.

The same phases were observed by X-ray diffraction in the slowly cooled material and in the rapidly quenched samples. However, these ones had a smaller amount of Ge phase than the former. This fact is explained assuming that the fact cooling method freezes the Cu_3Ge ε_2 phase, which does not exist at room temperature. This phase contains more Ge than the ε_1 one, which exists at this temperature. Both phases are solid solutions with concentrations that correspond approximately to Cu_3Ge and have similar diffraction patterns. Supporting this assumption the above mentioned effect was reversed when the quenched samples were annealed.

In the rapidly cooled material a systematic correlation between the Isomer Shift and the initial temperature of the melt from which the alloy was

cooled down could not be observed, as it happened with other systems [1–3]. This fact can be related with the smooth change in the electronic structure of the liquid state over the considered temperature range. This has been shown by the metallic nature of the electrical conductivity of Ge in the melt [10] as well as the rather metallic character of CuGe and CuSn at these temperatures [11].

The Isomer Shift of all phases in the fast quenched samples were greater that the ones which correspond to the slowly cooled material. Figure 3 shows this behaviour for the $Sn_5Ge_{31}Cu_{64}$ alloy. This is attributed to a memory effect of the situation in the liquid state: the fast cooling preserves in the solid samples a greater atomic volume than in the slowly cooled material, which therefore means an increasing of the Isomer Shift.

Finally, the Cu_3Sn alloy was prepared at the stoichiometrical composition because the Mössbauer line corresponding to this phase in the rapidly cooled samples showed a rather large width. The Mössbauer spectra of this alloy and the best fit when a Quadrupole Splitting with $Q = 0.24 \pm 0.02$ m/s and an Isomer Shift of 1.76 ± 0.02 mm/s were proposed. This result is in disagreement with published data [7] which described it as a single line.

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