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MÖSSBAUER STUDY OF INTERNALLY OXIDIZED SILVER–TIN ALLOYS

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A Mössbauer study of internally formed oxides as a function of oxidation temperatures between 200 °C and 850 °C was performed on previously annealed 1 at% *Ag*Sn alloys. The oxide formed at high temperatures ($t \geqslant 500$ °C) consists in agglomerates of tin dioxide ($\delta_{CaSnO_3}/RT = 0.00 \pm 0.01$ mm/s, $\Delta Q = 0.50 \pm 0.03$ mm/s). The low temperature oxide ($t \leqslant 300$ °C) is characterized by $\delta_{CaSnO_3}/RT = 0.29 \pm 0.02$ mm/s and $\Delta Q = 0.32 \pm 0.03$ mm/s, and could be in the form of one-Sn-atom oxide complexes in the silver matrix. From the measured isomer shifts in the range $400 \leqslant t \leqslant 550$ °C, the maximum contribution of the silver matrix to the effective number of electrons per Sn atom in oxide agglomerates has been estimated to have a value of about 0.06. The effect of the cold work on the hyperfine parameters of the oxidized tin has also been investigated. 'As rolled' samples were found to attain the same values of isomer shifts and quadrupole splittings as annealed specimens, but at lower temperatures.

1. Introduction

It is well-known that the size of oxide agglomerates formed by internal oxidation [1] in diluted binary alloys depends on the oxidation temperature as well as on the solute concentration and oxygen pressure [2,3].

Time-differential perturbed angular correlation (TDPAC) measurements performed on *Ag*In alloys internally oxidized at different temperatures have given indirect evidence of the dependence of the internal structure of the formed oxides on the size of the solute aggregates [4]. Moreover, in recent TDPAC studies on the electron relaxation following electron capture decay in ^{111}Cd embedded in oxidized *Ag*In alloys, it was possible to show the influence of the metal matrix on the electron availability at the oxide precipitates. This influence was found to be high when the concentration and other oxidation conditions favoured the formation of small precipitates [5].

In a chemical and diffusional study of interstitial oxygen in the *Ag*Sn system, Huffman and Podgurski [6] found that the Mössbauer isomer shift of internally oxidized tin in an alloy 0.33 at% oxidized at 300 °C was slightly larger than that obtained in an 6.1 at% alloy oxidized at 400 °C. Based on enriched oxygen absorption experiments, the authors explained this difference through the production of big precipitates of SnO_2 in the concentrated oxidized alloy, and isolated complexes with four oxygens per tin atom in the 0.33 at% alloy. These results have recently been used in the discussion of implantation experiments of ^{119m}Sn radioactive precursors into a silver matrix [7].

In this work we present a detailed Mössbauer study of the dependence on the oxidation temperature of the hyperfine parameters of Sn internally oxidized in *Ag*Sn alloys. An estimation of the maximum silver matrix contribution to the effective number of electrons per tin atom in the oxide aggregates was made. Besides, the effect of the cold work on the type of oxide internally produced is investigated. The consideration of this effect could be useful in the interpretation of investigations associated with internal oxidation of samples with a high density of defects like the implantation experiments mentioned above.

2. Sample preparation

Alloys with 1.0 ± 0.1 at% of Sn were made by fusion in quartz tubes under Ar atmosphere in an electric oven using Ag and Sn with natural isotopic abundances with purities of 99.99 and 99.5% supplied by Vega y Camji S.A. (Argentina) and BDH Chemicals Ltd. (England), respectively.

The ingots were rolled down to proper thickness for the Mössbauer measurements between 30 and 125 μm and were annealed in an Ar atmosphere in order to get rid of the damage produced by the cold work and to assure composition homogeneity, using carbon as a reducing agent. Typical annealing treatments were performed for about one hour at 750 °C. The oxidations were done by heating each sample in air ($P = 1$ atm) at one specified temperature, between 200 and 850 °C.

3. Instrumental

The Mössbauer data, obtained with transmission geometry in a constant acceleration mode, were accumulated simultaneously in two halves of 256 channels each, in a multiscaler and waveform generator developed and built at this Physics Department [8]. The $Ca^{119m}SnO_3$ source of 5 mCi activity was moved via a 'Wissenschaftliche Elektronik' MVT 1000 transducer. A 50 μm Pd filter was used and the detector was an NaI(Tl) crystal of 2 mm thickness. Room temperature was kept constant within ± 1 °C at 20 °C. The two halves of the spectra were fitted independently with lorentzian curves on a parabolic baseline with a non-linear least-squares program with constraints. Peak areas were normalized with respect to the off-resonance background. The velocity calibration was obtained by means of a 10 mCi ^{57}FeRh source and a 6 μm thick natural Fe foil as absorber. The zero of velocity was also checked against a $CaSnO_3$ absorber. Velocity non-linearity was fitted to a 3rd degree polynomial.

4. Results

Typical Mössbauer spectra obtained for two samples oxidized at difference temperatures (300 and 550 °C) are shown in fig. 1. One unsplit line and one unresolved quadrupole doublet were used to fit the signals coming from the Sn in silver solution (Sn_s) and oxidized (Sn_o), respectively. Both components of the doublet were assumed to have equal heights and widths. Isomer shifts δ, referred to $CaSnO_3$ at room temperature, quadrupole splittings ΔQ, and relative recoil-free fractions f_R, of Sn_o to Sn_s are shown in fig. 2 as a function of oxidizing temperatures for annealed and 'as rolled' samples. The above mentioned results for the 0.33 at% alloy of Huffman and Podgurski reduced to $CaSnO_3$ standard [9,10] have also been included. It should be mentioned that results obtained for a 6.3 at% alloy oxidized at 400 °C yielded $\delta = 0.03 \pm 0.01$ mm/s and $\Delta Q = 0.52 \pm 0.03$ mm/s coincident, within experimental errors, with the values reported by Huffman and Podgurski for the 6.1 at% alloy. The values of f_R were obtained by comparison, following both the increase of the Sn_o and the decrease of the Sn_s peak areas with the oxidation progress. A linewidth of 0.83 ± 0.03 mm/s was obtained for the lorentzian fitted to the unsplit signal belonging to the Sn_s peak. Fittings never yielded linewidths greater than 0.95 mm/s for the components of the Sn_o unresolved doublet. No linewidth dependence on the oxidation temperature was found within experimental errors (± 0.03 mm/s).

All the measured isomer shifts are in the range belonging to stannic compounds. For the annealed samples, an apparent change in the ΔQ values can be seen between 300 and 400 °C, while the variation in δ and f_R spreads from 300 to 550 °C. It can be noted that the values of the isomer shifts and quadrupole splittings for the samples oxidized at higher temperatures are very close to those of SnO_2. These parameters, obtained for a sample of pure SnO_2 prepared by oxidation in air at 900 °C, are shown in the vertical axis of this same figure. The 'as rolled' samples exhibit lower isomer shifts and higher quadrupole splittings than the annealed samples oxidized at the same temperatures.

5. Discussion

Oxide agglomerates are mainly created by diffusion and further association of Sn atoms to already formed molecules of oxide. This process, highly dependent on temperature, has favourable conditions of occurring at the zone of the oxidizing front,

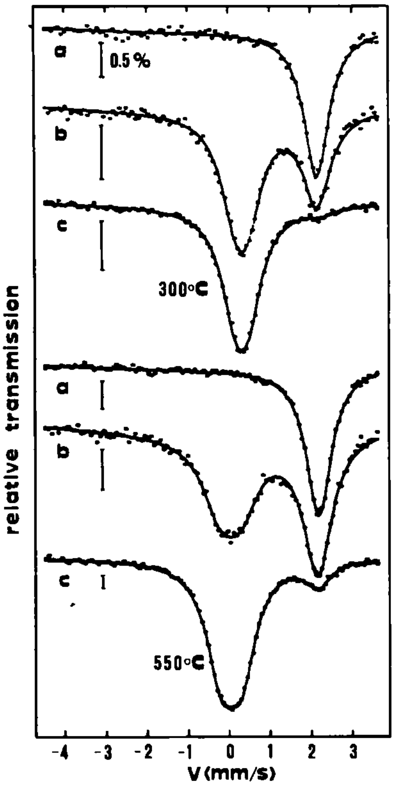

Fig. 1. Mössbauer spectra of two 1 at% *Ag*Sn samples oxidized at 300 °C and 550 °C. (a) unoxidized, (b) partially oxidized, (c) almost fully oxidized. Spectra (b) were obtained after annealings of 1375 min at 300 °C and 7 min at 550 °C, respectively. For spectra (c) annealing lengths were 2640 min at 300 °C and 30.5 min at 550 °C, respectively.

where oxidized and non-oxidized Sn atoms are found at the same time and the free oxygen concentration is low. $N(T)$, the mean number of Sn atoms per oxide agglomerate, will then be governed by the balance between the average distance that a diffusing Sn atom can travel at the oxidation front and the distance that the front can move forward in the same time.

After a study of the dynamics of internal oxidation of impurities in Ag and size effects by Ehrlich [3], it is possible to estimate the relative mean number of Sn atoms per oxide agglomerate at two different temperatures for alloys of the same composition through

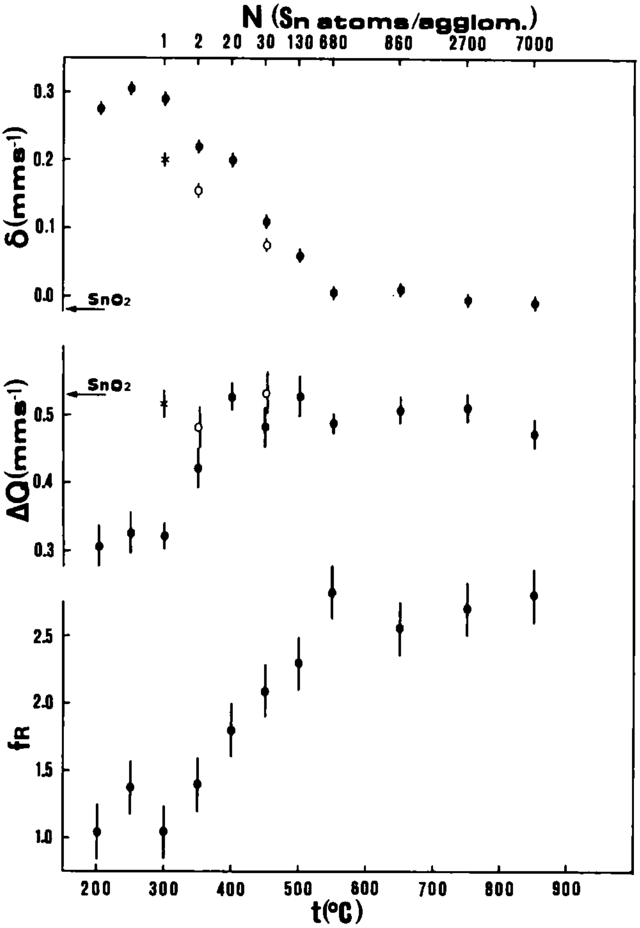

Fig. 2. Tin oxide isomer shifts (δ) referred to $CaSnO_3$, quadrupole splittings (ΔQ) and relative recoil-free fractions versus oxidizing temperatures for annealed (full circles) and 'as rolled' (open circles) samples. $N(T)$ values calculated from eq. (1) are shown in the upper horizontal axis. Isomer shifts and quadrupole splittings for a 0.33 at% AgSn [6] (crosses) and SnO_2 prepared by oxidation at 900 °C in air are included for comparison. The errors quoted are the statistical deviations after averages over several measurements.

$$\frac{N(T_1)}{N(T_2)} = \left[\frac{C_1(T_2)D_1(T_2)D_2(T_1)\xi_1}{C_1(T_1)D_1(T_1)D_2(T_2)\xi_2}\right]^{3/2} , \tag{1}$$

where: $C_1(T) = C_1 \exp(-(E/RT))$ is the oxygen concentration at the sample surface; $D_1(T) = D_1 \exp(-(E_1/RT))$ and $D_2(T) = D_2 \exp(-(E_2/RT))$ are the oxygen and tin diffusion coefficients in the alloy, respectively; ξ_1 and ξ_2 are the depths of the oxidation front at temperatures T_1 and T_2, respectively.

The validity of eq. (1) requires that a freely diffusing oxygen atom must meet an impurity in a time t short compared to the time t_p necessary for the oxidation front to move a distance equal to its own thickness. We then have $(t/t_p) = aC_1/48\,\xi C_2^{3/2}$ (a is the lattice constant). Taking solubility and diffusivity values for oxygen and tin from refs. [11,12], the condition is fulfilled in our case, since t/t_p at 300 and 850 °C yielded 8.8×10^{-11} and 1.44×10^{-8}, respectively.

In order to have an idea of the expected agglomerate sizes at different temperatures for previously annealed samples, $N(T)$ was calculated from eq. (1) taking $N(T) = 1$ for 300 °C. This arbitrary choice was made after an examination of fig. 2, where the isomer shifts, quadrupole splittings and relative recoil-free fractions remain constant up to 300 °C. The onset of the agglomeration process at some temperature between 300 and 350 °C has been assumed responsible for the changes observed in the hyperfine parameters. This picture is coherent with the calculation of the mean tin diffusion length ΔX_{Sn} during t_p. Indeed, at 300 °C $\Delta X_{Sn} = (2D_2 t_p)^{1/2}$ gives a value of $1.92a$, which is not enough for tin solutes to form clusters, while at 400 °C ΔX_{Sn} is already about $6a$. The values of $N(T)$ belonging to the thicknesses and temperatures of each sample are shown in the upper horizontal axis of fig. 2.

Three different zones can be seen in the temperature behaviour of the Mössbauer parameters. A high temperature region ($t \geqslant 550$ °C, $N \geqslant 700$) where the hyperfine parameters are those of the pure SnO_2, a low temperature zone ($t \leqslant 300$ °C) where a one-Sn-atom oxide complex is very likely formed, and an intermediate range (300 °C $\leqslant t \leqslant$ 550 °C) where several changes take place. Since for the samples oxidized at 350 and 450 °C the parameters reported in this paper are close to those measured by Huffman and Podgurski [6] that were associated to a complex with four oxygens per tin atom, we believe that the transition from the one-Sn-atom oxide complex to this four-oxygen complex may occur at some temperature between 300 and 400 °C ($N \leqslant 20$). On the other hand, being the quadrupole splittings of this last complex [6] and SnO_2 almost the same, it is not possible based only on Mössbauer measurements to decide at what temperature the transition to SnO_2 takes place. Furthermore, because the oxide complexes are formed embedded in a metal matrix, it is also not possible to assign the isomer shift changes solely to the structural changes occurring around tin. The silver conduction electrons could also cause an increase of the measured isomer shift when the oxide agglomerates are small enough.

The hyperfine parameters obtained after oxidation of 'as rolled' samples at 350 and 450 °C are similar to those of previously annealed samples oxidized at higher temperatures (fig. 2). This behaviour could have been anticipated, since the 'as rolled' samples are expected to have a less homogeneous distribution of solute caused, among other things, by its segregation during oxidation due to the high number of defects and grain boundaries present in the non-annealed material [13]. On these accounts, at the same oxidation temperatures, bigger agglomerates of oxide can be foreseen to be formed in 'as rolled' specimens. This temperature shift is also consistent with the value obtained for the 'as rolled' 0.33 at% Sn sample measured by Huffman and Podgurski. Probably, in this case the measured isomer shift and quadrupole splitting do not correspond to a one-Sn-atom oxide complex, but to very small agglomerates containing only a few oxidized tin atoms. However, their measurements of the oxygen uptake show that at this incipient state of aggregation of the oxidized phase, a complex with four oxygens per tin atom is produced.. According to our results, the one-Sn-atom oxide complexes are characterized by $\delta_{\mathrm{CaSnO_3}/RT} = 0.29 \pm 0.02$ mm/s and $\Delta Q = 0.32 \pm 0.03$ mm/s. It might prove interesting to investigate through oxygen absorption measurements the oxygen-to-tin atomic ratio in these complexes.

It can be observed that there seems to be a correlation between δ and f_R (fig. 3) of the type observed by Bryukhanov [14] for ^{119}Sn embedded in different metals. Its origin is not clear, although it could be linked to the size of the oxide particles.

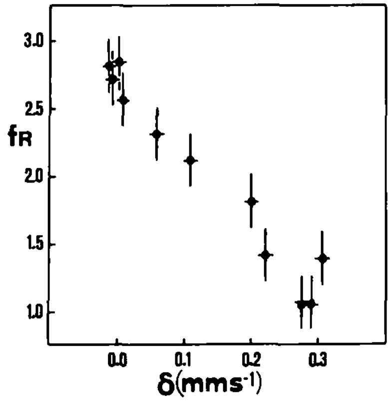

Fig. 3. Recoil-free fractions of Sn_O relative to Sn_S against the corresponding Sn_O isomer shifts for annealed samples oxidized at temperatures between 200 and 850 °C.

In what follows we shall make an estimation of the maximum contribution, Δn_s, of the silver matrix to the effective number of electrons per tin atom in oxide agglomerates. Although the calculated value of Δn_s will depend on the role assigned to the conduction electrons in the observed changes of the isomer shift between 400 and 550 °C, its maximum value can be estimated attributing the full change in δ to that origin. At least two isomer shift calibration scales, which connect its value to the effective number of electrons per tin atom, have been deduced, one by Lees and Flinn [15] and the other by Parish [16]. In these scales, apart from a shift constant, the dominant term is linear with the effective number of s-type electrons n_s. Hence, when small increments in δ are considered (such as the ones we measured), the following simple relationship can be used:

$$\Delta\delta = A\,\Delta n_s\,.$$

In order to obtain Δn_s we have used both values of 3.10 and 4.08 mm/s per electron of the linear coefficients in the Lees and Flinn and Parish scales, respectively. From the variation in δ of about 0.2 mm/s in the range $400\ ^\circ\mathrm{C} \leqslant t \leqslant 550\ ^\circ\mathrm{C}$ we have estimated that Δn_s would have maximum values of 0.06 and 0.05 electrons, respectively, for the smallest oxide agglomerates.

6. Conclusions

(1) The low temperature oxide ($t \leqslant 300$ °C) is characterized by the parameters:

$$\delta_{\mathrm{CaSnO_3}/RT} = 0.29 \pm 0.02\ \mathrm{mm/s} \qquad \Delta Q = 0.32 \pm 0.03\ \mathrm{mm/s}$$

$$\Gamma = 0.90 \pm 0.04\ \mathrm{mm/s} \qquad f_R = 1.2 \pm 0.2\,.$$

(2) At these temperatures of oxidation, tin seems to be oxidized in the form of one-Sn-atom oxide complexes isolated in the silver matrix.

(3) The hyperfine parameters obtained after oxidations at 350 and 400 °C are close to the values reported by Huffman and Podgurski [6] for an oxide complex with four oxygen atoms per tin atom.

(4) For oxidation temperatures from 550 °C upwards, SnO_2 is formed.

(5) The silver matrix contribution to the effective number of electrons per tin atom in the internally produced oxide is at most 0.06 electrons for the smallest oxide agglomerates.

(6) The cold work prior to oxidation favours the agglomeration of the internally formed oxide.

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