Materials Chemistry and Physics 166 (2015) 16–19

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Materials science communication

Inoculator dependent induced growth of α-Sn

Agata Skwarek*, Piotr Zachariasz, Jan Kulawik, Krzysztof Witek

Institute of Electron Technology, Krakow Division, Zablocie 39, 30-701 Kraków, Poland

HIGHLIGHTS

- Deformation, surface treatment and inoculation induce β → α Sn transformation.
- Inoculator type influence on β → α incubation phase.
- Inoculator type influence on β → α transformation rate, as well.
- Incubation phase is the shortest for sample inoculated with α-Sn stored at −30 °C.
- Transformation rate is the highest for sample inoculated with α-Sn stored at −30 °C.

ARTICLE INFO

Article history:
Received 1 April 2015
Received in revised form
31 August 2015
Accepted 12 September 2015

Keywords:
Alloys
Electronic materials
Crystallisation
Optical microscopy
Phase transitions

ABSTRACT

Tin pest is the allotropic transformation of white, metal β-Sn into grey, semiconductor α-Sn at temperatures under 13.2 °C. The transformation changes the mechanical and electrical properties of tin. A long time is needed for spontaneous nucleation. So, for a better understanding of the nature of the transformation, an induction of the transformation is carried out.

It is proved that harsh deformation, surface treatment with HCl solution and inoculation, applied together, induce the transformation within less than 24 h. The inoculator type, among other factors, is the one with a strong influence on the transformation rate. The transformation rate is dependent on inoculator type, as well as the temperature.

1. Introduction

Tin is an excellent example of the fact that, under certain thermodynamic conditions, the phase of a metal is much more important than its composition. The unique solid-state transformation of metallic material to a semiconductor powder changes its electrical properties [1]. White tin (β-Sn) with a stable *bct* (body-centred tetragonal) structure crystallises in the space-group symmetry $I4_1/amd$ (No. 141) with lattice parameters $a = 5.8316(2)$ Å and $c = 3.1815(2)$ Å at a temperature above 13.2 °C [2]. The phase transformation into grey tin (α-Sn) demands the overcooling of the β-Sn solid solution to tens of degrees below 13.2 °C. This phenomenon intensifies with decreasing temperature. A displacive-type transformation concurrently rearranging the whole groups of Sn atoms leads to the formation of a diamond structure with cubic symmetry *Fd*-3*m* (No. 227), lattice parameter $a = 6.4892(1)$ Å and a much larger volume (26.3%) with respect to β-Sn structure [2].

Normally, although only small-range atomic movement takes place during lattice-distortive transformations, structural rebuilding into a new α-Sn phase induces catastrophic changes in the physical properties of grey tin. sp^3 orbital hybridization with 4 unpaired electrons induces a tetrahedral symmetry with a reduction of the coordination number from 6 to 4 for Sn atoms. The covalent character of atomic bonds effectively changes the electronic band structure of grey tin so that valence and conduction bands do no longer overlap. The increase in volume during the transformation and the very low ductility of α-Sn lead to the material blistering and cracking [3], which causes a deterioration in mechanical properties or even the complete disintegration of tin material. β-Sn is a metal, while α-Sn is a semiconductor grey powder with an energy gap of 0.08 eV. That is why, the process kinetics and factors affecting the transformation of white tin into its grey analogue is of great practical interest due to it being a common

* Corresponding author.
E-mail address: askwarek@ite.waw.pl (A. Skwarek).

http://dx.doi.org/10.1016/j.matchemphys.2015.09.017

element widely used for engineering and industrial applications.

The transformation is a process nucleation and growth. The transformation of β-Sn to α-Sn is very sluggish because of the long time needed for nucleation, and so the kinetics of the transformation remains poorly understood [3]. Once nucleation is under way, the growth is fast. That is why it is important to develop a method for the induction of the β → α transformation to simulate the susceptibility of different tin materials to tin pest. There are several methods for the induction of α crystals [4].

Certain authors believe that mechanical treatment is a driving force of the transformation because of increases in internal compressive stress [5]. Others think that any factor that leads to increased strength in the Sn matrix, e.g. cold rolling, should be able to inhibit tin pest [6,7].

Previous tests on the β → α transformation have shown that the onset of tin pest after strong mechanical compression takes place after 14 days of temperature storage at −30 °C [8].

As proposed by certain authors [1,9,10] the inoculation can also be an effective way to induce the transformation. Inoculation should involve inoculators that have the same crystal structure as α-Sn and similar lattice parameters [1]. However, inoculation alone is not enough to induce the transformation within hours. By combining of two or more methods of tin pest induction it is possible to accelerate the transformation within less than 24 h.

There are several methods for identifying α-Sn growth including electrical measurements [1], XRD study [10], SEM with EDS analysis [11] and others. However the easiest way to monitor growth is optical observation. When the transformation is so fast that identification is possible with the naked eye after several hours, there is no need for sophisticated equipment.

This work examines the influence of the inoculator type on α-Sn growth. The procedure described here involves the inoculation, surface treatment with HCl solution and compressing of the samples and leads to a speedy induction of the β → α transformation.

2. Experimental

The samples were prepared with the method developed earlier [12] (Fig. 1). Bulk samples (n = 30) of Sn99Cu1 wt. % (purity of 99.9 wt. %) were cast in the form of roller-shaped ingots with a diameter of 1.0 cm and a height of 0.7 cm. This alloy was chosen, on the basis of a previous report, as the most prone to tin pest formation [8]. The upper surface of the ingots was drilled using a drill with a diameter of 1.5 mm to make a hole of the same depth in all samples (2 mm). Before inoculation, the samples were dipped in a HCl solution to remove the oxide layer which may prevent the transformation [9]. The samples were divided into three groups. Each of them consisted of 10 samples. In the first group, the drilled holes were filled with α-Sn powder. The concentration of α phase in the α-Sn powder was at a level of 30%. The second and third groups were inoculated with InSn and CdTe, respectively. The purity of inoculation agents were at the level of 99.99.%.

These inoculation agents were chosen because of their similarity in structure to α-Sn and, as known from the literature, agents with the same or similar structure can promote transformation [9]. Additionally, CdTe as well as InSb are used in electronics, so they are a possible source of infection in electronic devices.

The formation of the binary crystalline structure of a metal or alloy requires several factors. Firstly, solid solubility occurs when the solvent and solute have the same number of valence electrons in their atoms. Secondly, related atomic radii with a difference of less than 15% and similar electronegativities of both constituents are essential. Thirdly, there must be structural isomorphism of the crystal structures of solute and solvent. Hence, in a common inoculation method based on nucleation from foreign seeds, the elements that are next to each other in the periodic table are embedded into the β-Sn. Thus, powder crystals of α-Sn, InSb and CdTe are mechanically pressed into white tin specimens in order to accelerate the incubation stage and facilitate the nucleation of a new phase.

The solubility of the alloying elements has the influence on α-Sn nucleation. The elements which are soluble in Sn (such as Pb, Bi, Sb) help pin dislocations and hinder the lattice expansion. The hindering of the lattice expansion leads to the lowering of the β → α transformation temperature. From the point of kinetics, the transformation can not be possible [11]. Oppositely, the elements with limited solubility in Sn (Zn, Al, Mg, Mn) accelerate the transformation [13].

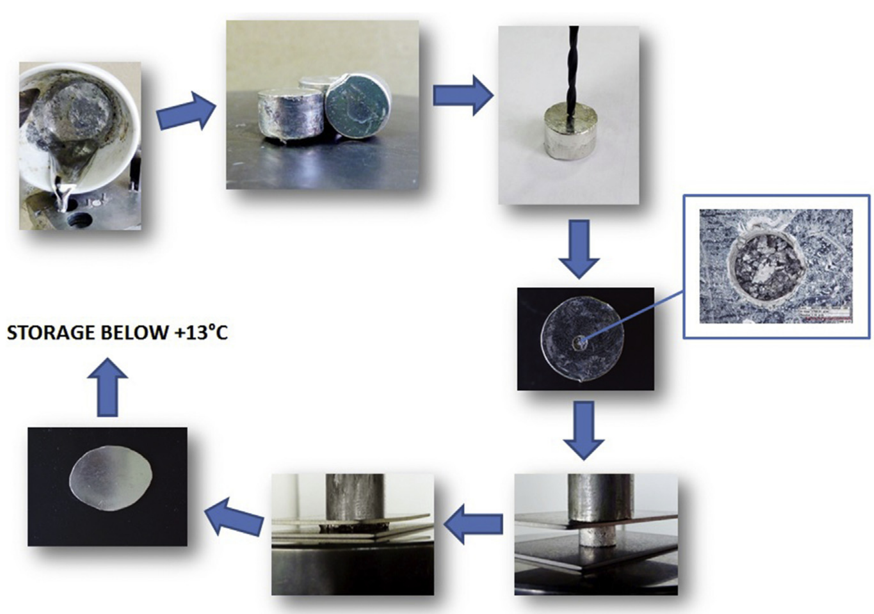

Fig. 1. Preparation scheme for the inoculated, compressed samples [12].