MORPHOLOGY OF THE METALLIC TIN ALLOTROPIC TRANSFORMATION AND IMPURITIES ROLE IN STRUCTURAL STABILITY ASSURANCE

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A fost studiată prin microscopie electronică morfologia transformării alotropice şi modul concret în care temperatura şi conţinutul de impurităţi existente în mărcile comerciale de staniu metalic influenţează procesul de germinare şi creştere a fazei α. Staniul face parte din categoria metalelor care prezintă fenomenul de alotropie, structura sa cristalină fiind diferită în funcţie de cele două stări alotropice β şi α. Transformarea polimorfică a staniului se desfăşoară prin procese de germinare şi creştere a grăunţilor cristalini asigurate de difuzia atomilor, însoţite de creşterea volumului metalului şi apariţia unor tensiuni interne foarte mari care distrug coeziunea dintre grăunţi, materialul metalic devenind o pulbere cenuşie.

The present paper presents the results concerning the morphology by electron microscopy and the way in which temperature and impurities contents may influence the nucleation and growth of the α Sn. Tin is a metal with polymorphic phenomenon, with great difference between two allotropic structure β and α.. The polymorphic transformation of tin is developed between nucleation and grains growth processes assured by atoms diffusion. The transformation is accompanied by metal volume increase and very high internal stresses, which may destroy the grains cohesion. Finally, the metallic material turns in a gray powder.

Keywords: tin, polymorphic transformation, crystalline structure

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1. Introduction

Usually, polymorphic transformations are heterogeneous transformations, which are determined by heterogeneous fluctuation developed through nucleation and growth. Considering the temperature at which this transformation may take place, polymorphic transformation can be with diffusion, if under cooling is low, intermediary or massive at relative high sub cooling, and/or without diffusion if under cooling is very high [2, 3]. Tin polymorphic transformation is developed through nucleation and grain growth processes provided by atoms diffusion, accompanied by an increase in volume and appearance of very high internal stresses, which destroy the cohesion between grains. This transformation process is known as “tin plague” because nucleation occurs always at metal surface and once started on a small area it expands rapidly in all the metallic mass.

Tin polymorphic transformation involves the existence of a driving force due to the difference between free energies of the two phases with identical chemical composition, which is temperature dependent [1,3]. In impure tin, the polymorphic transformation is also influenced by accompanying elements (Fe, Cu, Sb, Bi, Pb, As, Zn, Co, Ni, Mg, Al, Ag), amount and their solubility level in solid phase in one of the allotropic phase of the base metal [4, 5]. In this case the influence of the accompanying elements results in a displacement of the critical points depending on the nature and concentration of the accompanying element, in a change of the temperature range for transformation and slowing down of the process of the polymorphic transformation. So, a start value and an end value of transformation must be defined. On the other hand, a large number of transition metals, used as accompanying elements in tin, dissolves great amounts hydrogen during elaboration. Stable hydrides may be formed at certain temperature and pressure ranges with positive effect (Ni, Au, Ag) or negative effect (Zn, Cu, Co) on the polymorphic transformation of this metal. At the time being metallic tin is commercialized as ingots or bars, whose minimum content of tin is between 96 % and 99.999 %. These semi finished products are deposited on long or medium term for further processing. In order to prevent $Sn\beta$ – $Sn\alpha$ transformation process, some rules and international standards require the temperature in storage space to be of minimum +12 ^{0}C. In this connection, the polymorphic transformation of metallic tin presents a great economic importance indeed the assurance of this minimum temperature requires storage time during the consumption of energy and serious financial efforts depending on particularities of constructive warehouse, the annual minimum temperatures, which characterizes geographic area of location of this, and the stock size of tin.

2. Results and Discussion

Four type of tin, with different purity: 99.995 %; 99.95 %; 99.85 %; 99.75 % were used for the experimental works. The samples were analyzed from the point of view of chemical composition, as well as macro and micro structural investigations. The chemical composition of the samples is presented in Table 1.

Table 1

Chemical composition of investigated metallic tin

Sn	Impurities max. %								
min. %	As	Fe	Cu	Pb	Bi	Sb	Zn	Al	S
99.995	$1x10^{-4}$	$1x10^{-4}$	$1x10^{-5}$	$5x10^{-5}$	$5x10^{-5}$	$5x10^{-5}$	$3x10^{-5}$	$3x10^{-4}$	-
99.95	0.01	0.01	0.01	0.02	0.002	0.02	0.002	0.002	-
99.85	0.04	0.01	0.02	0.05	0.01	0.02	0.002	0.002	-
99.75	0.05	0.015	0.05	0.10	0.10	0.05	0.002	0.002	0.01

The micro structural analysis performed at the optical microscope of *Carl Zeiss* type show in the case of Sn 99.85 % sample a compact structure without discontinuities that is a feature of a poured material in horizontal ingots, with oriented crystals according to the heat flow during cooling at solidifications, (Fig. 1).

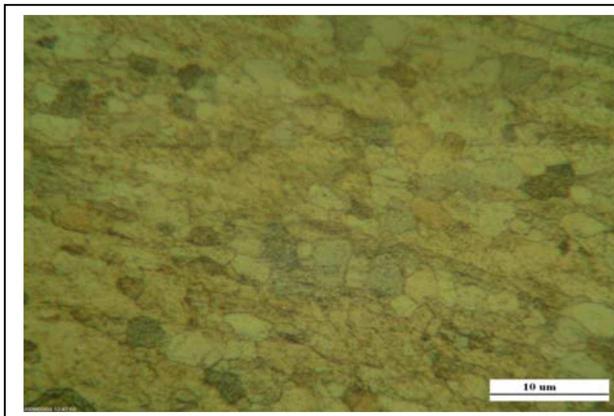

Fig. 1. Optical micrograph of Sn99,85% from Table 1, x 200

The micro structural analysis performed at the electron microscope of XL30SEM Philips type provided with EDX equipment reveals in the case of Sn 99.85 % sample the presence of the phase β. The crystalline structure is of tetragonal body centered type, with lattice parameters: $a_0 = 5.8191$ Å, $c_0 = 0.5457$ Å as computrd from the X-ray diffraction in Fig. 2. The electron microsgraphs obtained through transmission (TEM) reveal the existence of the β phase with crystalline structure (electron diffraction in spots), Fig. 3b, with equiaxed aspect, Fig. 3a, which contain only tin as revealed by the EDX spectrum.

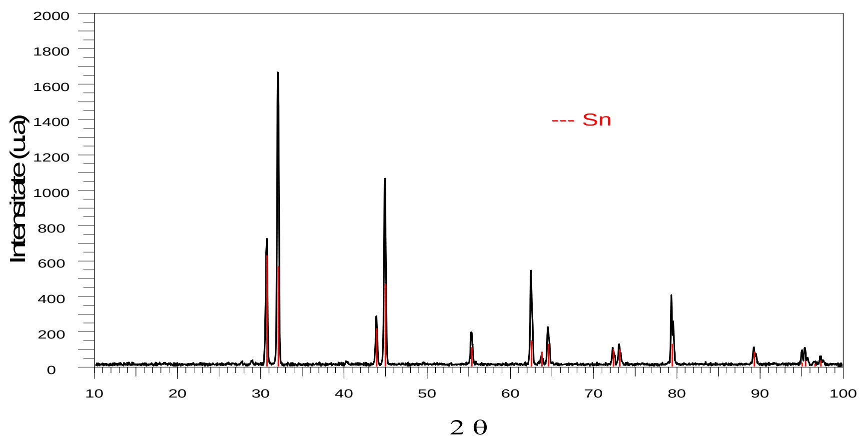

Fig. 2. X-Ray diffraction patterns of Sn 99.85%

Table 2

Crystalline lattice parameters of Sn99.85%

Angle 2θ (grd.)	Interplane distance, Å	β phase, Miller index
30.7	2.915	200
32	2.794	101
43.9	2.061	220
44.3	2.017	241
55.4	1.660	301
63.25	1.487	112
64.6	1.441	321
72.45	1.304	420
73.2	1.292	411

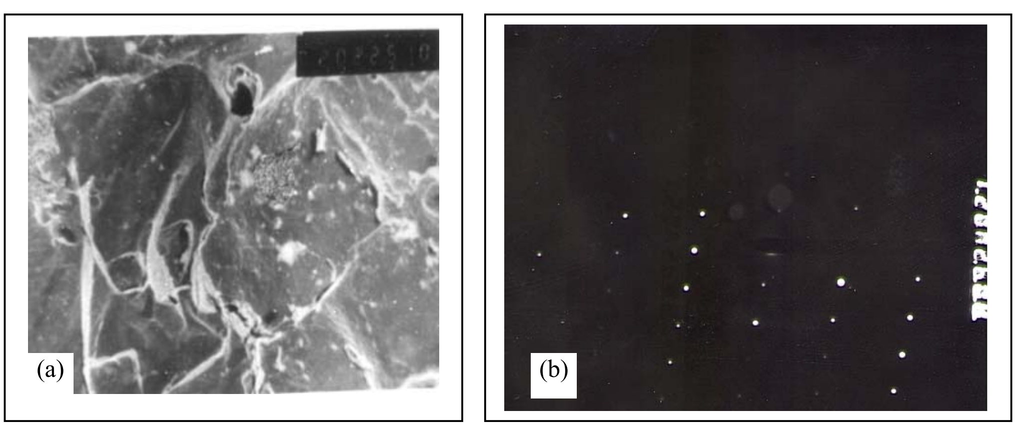

Fig. 3. (a) SEM image x9000, (b) TEM image, x 42000 of the analyzed surface of Sn 99.85%

In the crystallites of β phase, often contain linear defects represented by crystalline imperfections existent in planes as a result of constraints exercised on crystal during the metal solidification process, in special because of differences in temperature and concentration (Fig. 5).

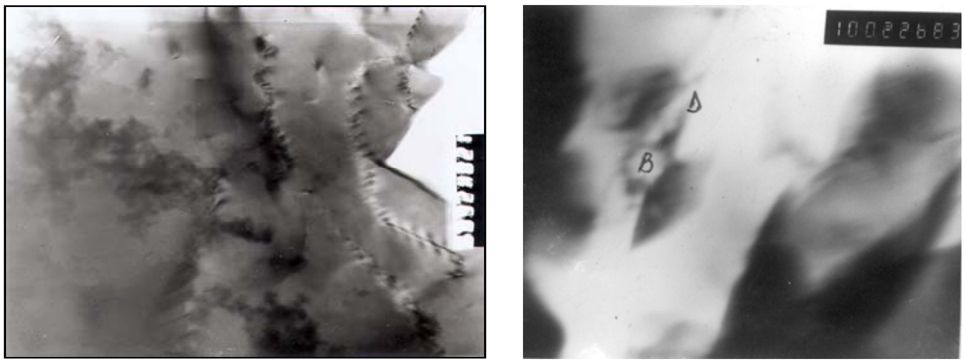

Fig. 5. TEM images of Sn 99.85 %; x 120000

Accompanying elements present in tin, which constitutes the inclusionary state of metal, consist of nanometric particles, with crystalline structure that show concentric circles frame outlined in images of electron diffraction (Fig. 6 a, b).

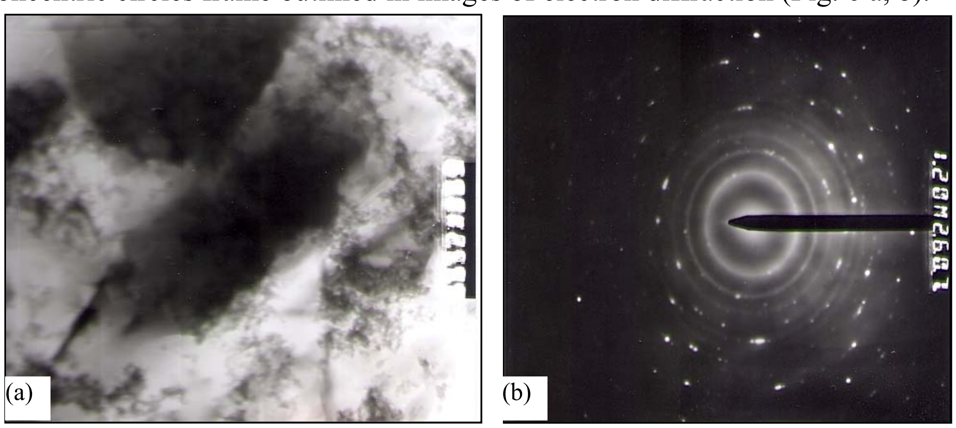

Fig. 6. (a) TEM image of Sn 99.85 %, x 69000, (b) electron diffraction image

The tin samples, with chemical compositions presented in Table 1, were kept at temperatures between -5 ^{0}C ± 3 ^{0}C and -65 ^{0}C ± 3 ^{0}C, with sudden and slow application of temperature, for time periods between 4 and 96 hours. After time consuming, the aspect of samples surface is not changed in comparison with the witness samples. As a result of this finding, the experiments were extended for temperatures below -65 ^{0}C ± 3 ^{0}C. Also, at the temperature of -70 ^{0}C, the tin sample 99.995 % occurred, after 48 hours, a partial process of transformation

(Fig. 7 (a)), compared with the others samples whose surface left unchanged. On the sample surface it is observed the appearance of gray spots and a strong cracking of the processed portion. Also, it is shown the increasing of specific volume at phase α, which has as a result the grinding of metallic material (Fig. 7 (b), (c), (d)). The micro structural analyses reveal the presence of some smooth areas corresponding to phase β and some areas with sandy aspects, corresponding to phase α (Fig. 8). There are observed sliding lines in Sn β (E), islands of Sn α (A) and cracks (B, C, D). The volume increase that accompanies this transformation causes the appearance of cracks. There are observed cracks at the intersection of two islands in growing (B), big cracks in islands (C) and also fine cracks at Sn β/Sn α junction (D). For identification of phase α, it was analyzed through electronic diffraction a surface of the sample where the transformation is in an advanced transformation state, emphasizing the aspect of polycrystalline material, small crystallites that are crystallographic non-orientated and the modification of the crystalline network parameters, Fig. 9.

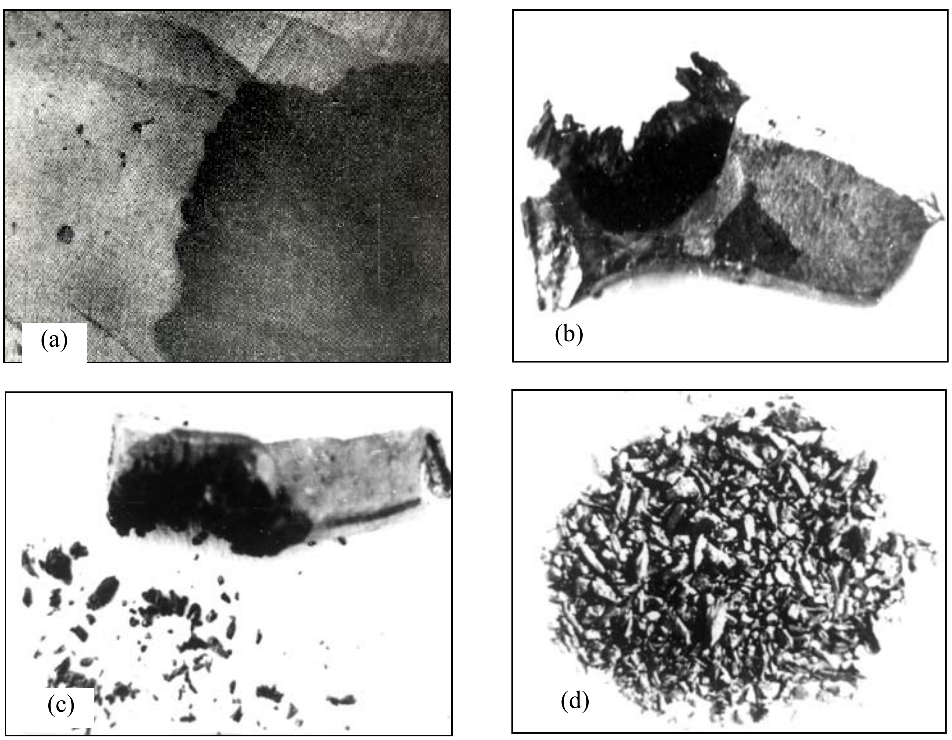

Fig. 7. Images of Sn 99.995 % sample kept at –70 ^{0}C, for: (a) optic microscopy for a sample after 48 hours, (b), (c) macroscopic images for sample after 96 hours; (d) macroscopic aspects for sample after 96 hours at -70 ^{0}C and 350 days at –15 ± 5 ^{0}C, X 50

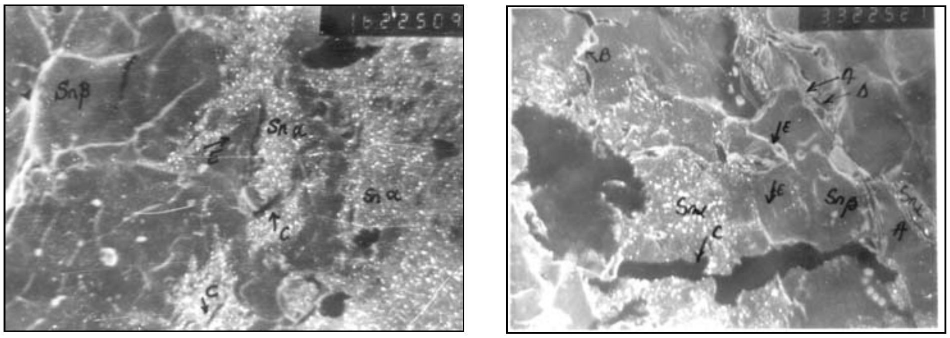

Fig. 8. SEM images of Sn 99.9995 % kept 96 hours at -70^{0}C and 350 days at –15 ± 5 ^{0}C, x 5000

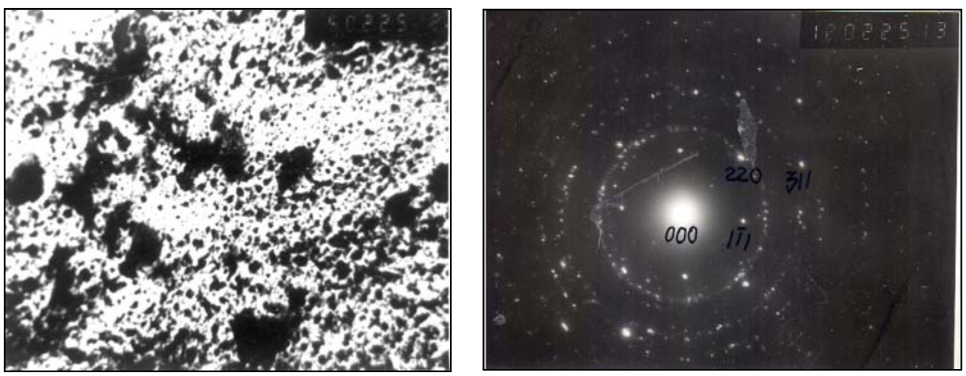

Fig. 9. (a) TEM image of Sn 99.9995 % kept 96 hours at -70 ^{0}C and 350 days at –15 ± 5 ^{0}C, (b) image of Sn α electron diffraction x 5000

3. Conclusions

Our experiments have put in evidence the effect of impurity content on the transformation temperature of tin and morphology of the phases involved in the allotropic transformation

1. Determinant factors that are involved in this process are: material purity and environment temperature of exposure, less than + 13.2 ^{0}C.
2. At the same purity, the allotropic transformation of tin is accelerated by less temperature and at the same temperature the transformation process is faster as the tin purity is higher.

R E F E R E N C E S

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