FIZIKA 2 Suppl. 2 (1970) 46.1

MICROSEGREGATION IN TIN-LEAD ALLOYS AS A FUNCTION OF COMPOSITION AND COOLING RATE

Dj. Milosavljević, B. Djurić, B. Lukić

"Boris Kidrič", Institute of Nuclear Sciences, Beograd-Vinča

Introduction

Microsegregation, formed during solidification of metals, has been studied by a number of research workers (1-3). However, solidification in these works was performed mainly in idealized conditions (constant solidification parameters, unidirectional growth). Nevertheless, their contribution to explanation of microsegregation mechanisms and resulting structural characteristics was tremendous. They elucidate, to a great extent, the phenomena taking place at the solid-liquid interface, and the role which different solidification parameters and factors play in formation of various types of substructure.

On the other hand, during solidification in real conditions, (similar to those existing in a foundry), the phenomena at the solid-liquid interface are much more complex. They are now a function of unsteady, time dependent solidification parameters which change not only in the main direction of growth but also in the other directions, That was the reason that relation real conditions of solidification - microsegregation has been studied very little. This work is an attempt to obtain some new data concerning microsegregation in unsteady state solidification.

Experimental

Technique.- Solidification has been carried out in simulated real conditions where heat extraction through the bottom of the casting was dominant comparing to the lateral directions (directional solidification).

The apparatus used in this work is presented schematically in Fig. 1. The quartz tube /1/ with metal charge is immersed in the bath of the Sn-Pb eutectic /2/. After the charge is melted and superheated (up to 50° above the liquidus temperature), the quartz tube was taken out of the bath, tilted for 90° in clock-wise direction to cast molten metal into a glass mould /3/, placed in the lateral tube extension. Both of them are closed by a water cooled copper chill /4/. Melting and casting were performed in vacuum of 5×10^{-2} mm Hg. Cast specimens (12 mm diameter, 70 mm length) were cut to obtain cross sections at 10,20 and 40 mm respectively (levels "1", "2" and "4") from the bottom (level "0"). The preparation of these surfaces for metallography and electron microanalysis has been done in a usual manner.

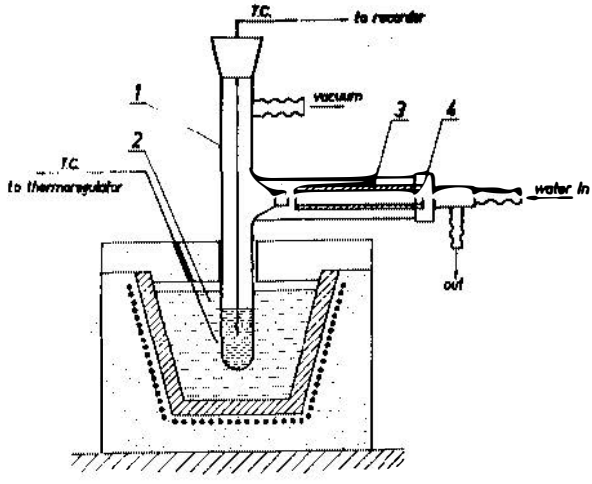

FIG. 1.

Apparatus for melting and casting of metals: 1-quartztube, 2-bath, 3-glass mould, 4-mould bottom (copper chill)

Materials.- To obtain Sn-Pb alloys, solidified in this work, tin and lead of 99.999 w/o and 99.998 w/o purity respectively were used. These alloys, prepared formerly in a vacuum

resistance furnace, were:

A. Sn-0.005 a/o Pb	B. Sn-0.01 a/o Pb	C. Sn-0.05 a/o Pb
D. Sn-0.10 a/o Pb	E. Sn-0.50 a/o Pb	F. Sn-1.00 a/o Pb
G. Sn-2.00 a/o Pb	H. Sn-5.00 a/o Pb	I. Sn-10.0 a/o Pb
J. Sn-16.0 a/o Pb	K. Sn-26.07 a/o Pb (eutectic).	

Results and discussion

The basic characteristics of unsteady state directional solidification are:

- heat from a solidifying metal is conducted away in different directions, but one of them (usually through the bottom of the casting) is predominant, and

- rate of heat extraction is time dependent and decreases in the course of solidification of casting.

Such kind of solidification is able to induce very strong microsegregation all over the casting, and, as a consequence, different structural features either in the longitudinal or in the lateral direction. This used to happen to the specimens from this work.

If one compares the structures at the examined cross sections, the qualitative difference between the level "0" and the higher levels could be easily seen. However, between the levels "1", "2" and "4" there exists quantitative difference only, i.e. the structure is the same but becomes coarser going upward (from "1" to "4") (FIG. 2). Obviously, the reason for this is the abrupt decrease of the cooling rate between "0" and "1", and its slower change between "1" and "4".

Commencing with lead concentration of 0.05 a/o, the structure at the level "0" consists of the beta-phase (reach in Sn) in which are embedded the globules of the alpha-phase (reach in Pb), (FIG. 3).

Beneath this concentration exists the beta-phase only. It seems that room temperature solubility of Pb in Sn is lower than reported 0.17 a/o (4).

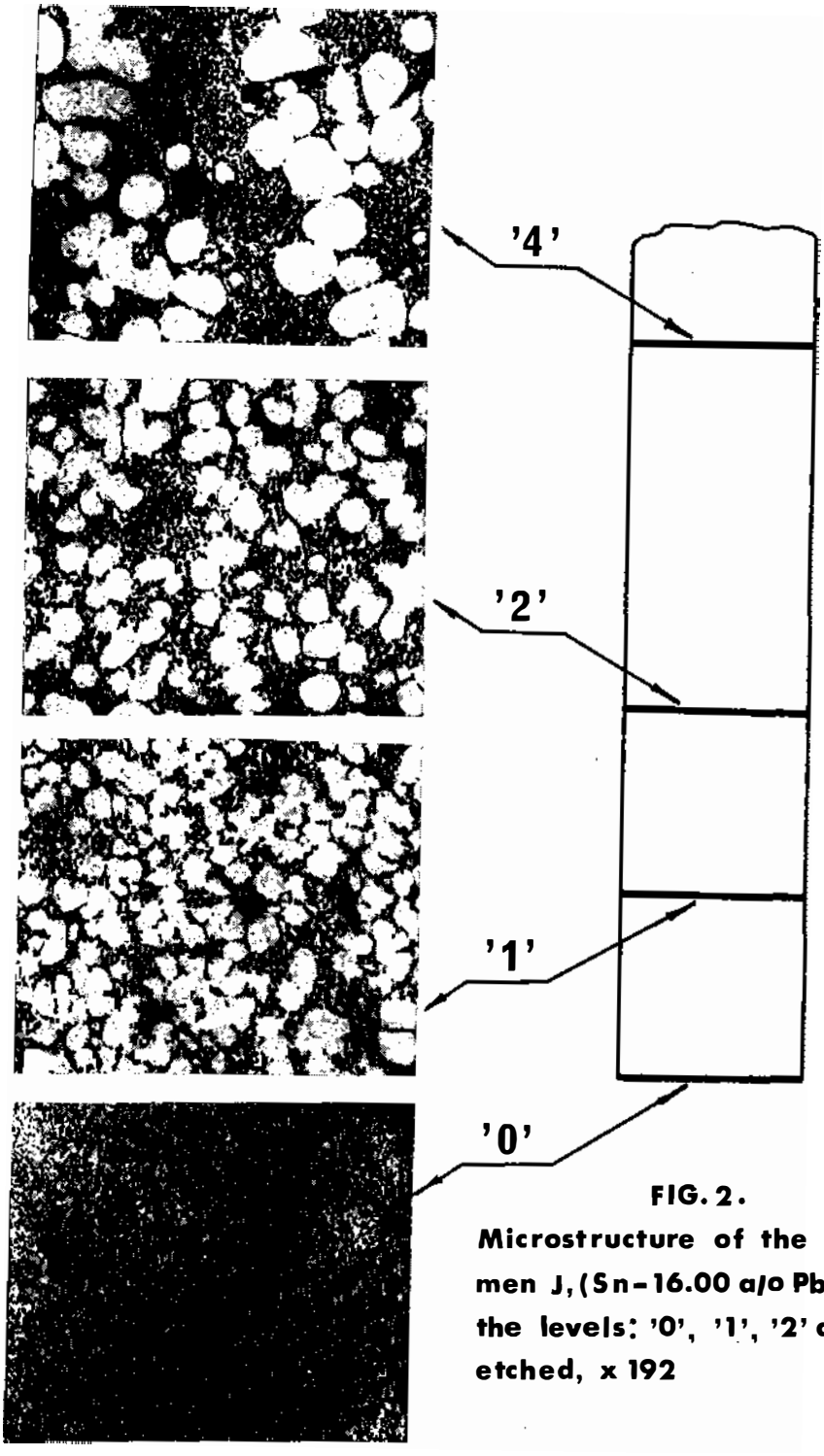

FIG. 2.
Microstructure of the specimen J, (Sn-16.00 a/o Pb), at the levels: '0', '1', '2' and '4', etched, x 192

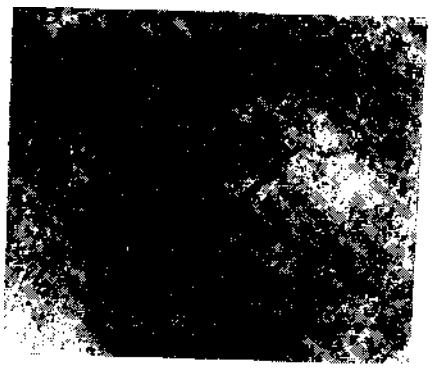

FIG. 3

Microstructure of the alloy C (Sn-0.05 a/o Pb) at the level "0", etched, x 192

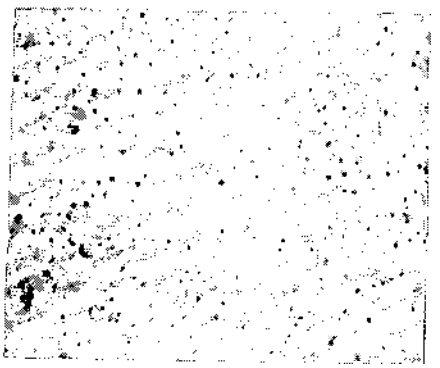

FIG. 4

Microstructure of the alloy F (Sn-1.00 a/o Pb)at the level "0", etched, x 192

Increase of lead concentration up to 1.00 a/o does not alter the structure of the level "0", besides size and number of the globules (FIG. 4).

Further augmentation of concentration makes that structure gradually adopt characteristics of a fine precipitated eutectic (FIG. 5).

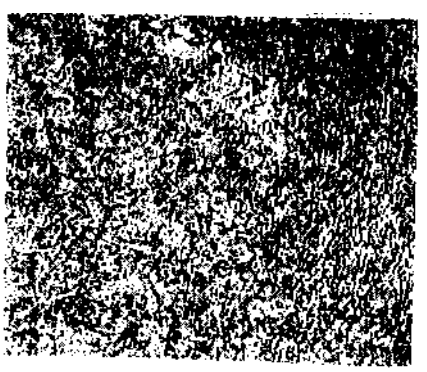

FIG. 5

Microstructure of the alloy I (Sn-10.00 a/o Pb) at the level "0", etched, x 192

Tin, superheated 50° above the melting point, solidifies on the water cooled copper chill with the rate of about 2000°/ /sec (5). Similar cooling rate existed probably at the specimen bottom in this work. According to this, supersaturated solid solution of Sn-Pb alloys having Pb > 0.05 a/o cannot be obtained in macroscopic dimensions at the cooling rates smaller than 2000°/sec. On the other hand, higher cooling

rates seem to favorize direct transition of substructureless to eutectic crystallization without intermediate substructures as, for instance, cellular or cellular dendritic ones which could be expected to take place due to the increase of lead concentration.

When lead concentration is ≥ 0.05 a/o, the cellular dendritic substructure appears permanently at the levels "1", "2" and "4", (FIG. 6). Further increase of lead concentration enlarges the size of dendrites and stimulates development of the globular eutectic in the dendrite branches, (FIG. 7). Furthermore, globular eutectic crystallization takes place in the dendrite branches of very dilute Sn-Pb alloys (FIG. 8).

Interdendritic area is not structureless, i.e. it is not a region of the solid solution, as stated before (6), but appears as intersected by a net of fine cells, (FIG. 7), whose walls have probably higher concentration of lead then the cells' centers, because the distribution coefficient of Pb in Sn is less then 1.

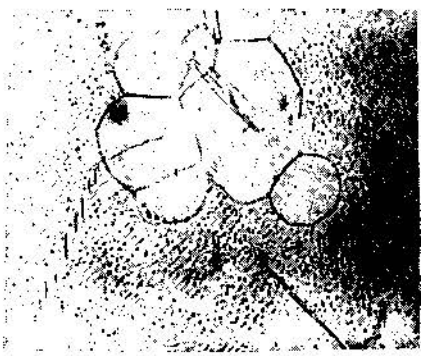

FIG. 6.
Microstructure of the alloy C (Sn-0.05 a/o Pb) at the level "1", etched, x 192

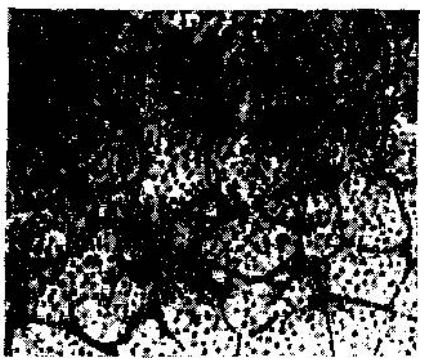

FIG. 7.
Microstructure of the alloy H (Sn-5.00 a/o Pb) at the level "4", etched, x 192

FIG. 8.
Microstructure of the alloy D (Sn-0.10 a/o Pb) at the level "4", etched, x 800

Maximal lead concentration in the dendrites (C_D) and minimal lead concentration in the interdentritic area (C_A), have been determined by a microanalyser. Their ratio is denoted in this work as the coefficient of microsegregation, $\eta = C_D/C_A$. The results obtained for alloys F, H and K are presented in Table 1. They could not be considered as quantitative values but only as approximative ones, because the electron beam was 1-2 /um in diameter, and it is practically impossible to determine the precise concentration of an area smaller then 5 /um (dendritic globules and interdendritic cells).

From Table 1 one could see that decrease of the cooling rate, v, increases η, while increase of the nominal concentration, C_o has an opposite effect. Quantitative determination of η, as a function of C_o and v, could be useful information for programmed solidification of a chosen alloy, particularly for obtaining supersaturated solid solutions ($\eta = 1$). In that case, other parameters and factors of solidification (temperature gradient at the solid-liquid interface, distribution coefficient, mixing, etc) should be taken into account as well, due to their effect on the type and intensity of microsegregation.

Tabl.1 The effect of cooling rate and concentration upon coefficient of microsegregation

Alloy		Concentration of Pb (w/o)		Coefficient of microsegregation
No and Concentrat	Level	Dendrites, C_D	Interdendritic area, C_A	C_D/C_A
F 1 a/o (1.73 w/o)	F_0	4.0[x]	0.8[xx]	5.0
	F_1	11.8	0.5	23.6
	F_2	10.8	0.2	54.0
	F_4	26.0	0.2	130
H 5 a/o (8.42 w/o)	H_0	8.7[x]	2.5[xx]	3.4
	H_1	24.8	1.2	20.5
	H_2	26.1	0.7	37.3
	H_4	29.5	0.4	73.5
K 26.07 a/o (38.1 w/o)	K_0	28.1[x]	19.7[xx]	1.4
	K_1	37.8	7.1	5.3
	K_2	54.3	4.6	11.8
	K_4	78.7	1.6	49.0

x-Globules of the α-phase. xx -matrix β-phase

Conclusion

Directional solidification of Sn-Pb alloys has been performed under conditions similar to those existing in a foundry. It has been shown that supersaturated solid solutions at room temperature could be obtained in submicroscopic dimensions only.

Room temperature solubility of Pb in Sn, as found in this work, is less then 0.05 a/o, i.e. three times lower comparing to the generally accepted value.

To analyse microsegregation as a function of cooling rate and concentration, it has been introduced the coefficient of microsegregation representing the ratio of the highest to the lowest Pb concentration, as found by a microanalyser.

Microsegregation is much more stronger in the alloys with the lower concentrations of Pb.

Cooling rates of the magnitude of 2000°/sec favourize a direct transition of the solid solution structure (Pb < 0.05 a/o) into the eutectic structure (Pb = 26.07 a/o) without intermediate types of substructure (cellular, cellular dendritic ones), which could be expected at higher concentrations of Pb.

Literature

1. B. Chalmers, Principles of Solidification, Chapt. 5, J. Wiley and Sons, Inc., New York (1964)

2. H.S. Peiser, Ed., Crystal Growth, Pergamon Press, Oxford (1966)

3. B.W. Berry, Ed., The Solidification of Metals, The Iron and Steel Institute Publication 110, (1968)

4. M. Hansen, Constitution of Binary Alloys, p. 1107, McGraw-Hill, New York (1958)

5. Dj. Milosavljević, Unpublished work

6. H. Biloni, in Ref. 3, p. 81.