EXPERIMENTS CONCERNING THE ELIMINATION OF Cd AND As THROUGH VACUUM EVAPORATION FROM ANTIFRICTION Sn – BASED ALLOYS

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The chemical composition of antifriction Sn based alloys contains Cd and As as alloying elements which improve the mechanical and tribological properties of these alloys. Research conducted in the field of medicine and ecology have, however, highlighted the fact that Cd and As are harmful for the human health as they generate cancer. Therefore the aim of the present paper is to introduce a method that in the authors' opinion manages to eliminate these two elements successfully. Several methods of eliminating Cd and As have been tested by the authors and the best method has proven to be the vacuum elimination. This method is based on the fact that out of the elements that make up the antifriction alloys (Cu, Ni, Ca, Pb, Zn, Al, etc.), Cd and As have the lowest boiling and respectively sublimation temperatures. These low values lead implicitly to higher pressure values.

1. INTRODUCTION

The widely used Sn based antifriction alloys have been repeatedly enriched in their evolution by means of secondary alloying elements thus leading to an increase of their mechanical, tribological and processing properties. From these elements, cadmium and arsenic significantly improve these properties of the alloys. The addition of cadmium does not exceed 3% and that of arsenic 1.5 % in these antifriction alloys.

Research in the field of medicine and ecology have pointed to the fact that both these elements, however beneficial these may be for the properties they confer, they are nevertheless harmful for human health. Studies undertaken on groups of workers have suggested a straightforward connection between exposure to Cd, As and the occurrence of different forms of cancer, such as lung cancer, kidney or bladder cancer (according to the US Health Department Report , 2001)

Considering the harmful influence of these two elements upon human health, many countries no longer allow the use of these elements in the elaboration of antifriction alloys. This has brought about the existence of important stocks of *special or hazardous wastes* that have to be neutralized.

Following numerous experiments, the author has managed to establish a technology for the elimination of the two elements via melting and vacuum sublimation respectively.

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This technology is based on the fact that out of the elements that make up the Sn based antifriction alloys (Sn, Sb, Cu, Ni, Pb, Zn, Al, etc.), Cd and As have the lowest boiling (Cd) and respectively sublimation (As) temperatures. These low values lead implicitly to higher pressure values (Table 1).

Table 1

Melting and boiling temperatures of alloying elements

Element	Cd	As	Sn	Sb	Cu	Ni	Pb	Zn	Al
Melting temperature [°C]	320	817	231.9	630.5	1083	1453	327.4	419.5	660
Boiling temperature [°C]	765	Below 613	2270	1380	2595	2730	1725	907	2450

The possibility of eliminating Cd and As from the molten alloy using vacuum has been proven theoretically via the analysis of the thermodynamics and kinetics of the evaporation process of elements from a multi-component system. The elimination has been also practically demonstrated as the alloys have been elaborated in an installation linked to a vacuum generating system.

2. THE RESEARCH METHOD

In order to be able to determine whether the As and Cd contained in the melt evaporate at the standard pressure and at higher pressures as well, and in order to determine the evaporation speed, a vacuum smelting furnace was used having a preliminary vacuum of 10^{-2} torr.

The installation comprises: an electrical furnace with nitre bars for heating (0–1200ºC; a smelting furnace connected to the vacuum pump; a preliminary vacuum pump; a condenser, control and measurement equipment.

Two types of alloys were used for the experiments:

– a Romanian alloy – LgSnR, having the following chemical composition: Sb – 7.9%; Cu – 2.9%; **Cd – 1.02 %;** Ni- 0,6 %; Sn – 88% ; Pb – 0.1% and the following characteristics: HB 250/10/30 – 29 ÷ 33; R_{m} = 90 N/mm^2; $R_{\mathrm{p}0,2} = 75\mathrm{N/mm}^2$; A = 7%.

– a foreign alloy – RL 38.93, produced out of chips and having the following chemical composition: Sn – 81.10 %; Sb – 12.13 %; **As – 0.35 %;** Ni – 0,14%; Pb – 1.4 %; Bi < 0.02%; Cu – 4.79 % and the following characteristics: HB 250/10/60 – 26; R_{m} = 87 N/m^2; $R_{\mathrm{p}0,2} = 67\mathrm{N/mm}^2$; A = 4 % .

*Proceedings***.** The experiments were carried out on a quantity of 0.4 kg from each type of alloy.

Three determinations were made for each temperature and holding time. The Cd and As contents was taken to be the arithmetic average value of the three determinations.

The research method of the vacuum smelting is based on the fact that the boiling temperature of Cd is 765°C and the sublimation temperature of As is of 613°C, i.e they are much lower than the boiling temperatures of all the other elements in the composition of the respective alloys (Table 1).

By means of this research method, the author wanted to test the theoretical assumption according to which in vacuum smelting , the boiling and sublimation temperatures respectively decrease.

Another aspect that was studied using this procedure was the variation of the evaporation speed of As and Cd dependent on temperature and time, while the pressure (vacuum) remained constant.

Alloy LgSnR (containing Cd) was maintained in a 10^{-2} torr vacuum from a temperature of 450°C up to a temperature of 800°C for 15, 30 and 60 minutes respectively. The results obtained are shown in Table 2.

Alloy RL 38.93 was maintained in a 10^{-2} torr vacuum from a temperature of 450 ºC up to a temperature of 650 º C for 15, 30 and 60 minutes respectively (Table 2).

Table 2

Losses of Cd from alloy LgSnR and of As from alloy RL 38-93 at a pressure of $P = 10^{-2}$ torr

Nr. crt.	T° [C]/ t ‘	Initial amount of Cd %	Cd left %	Initial amount of As %	As left %
1	450/ 15	1.02	1.02	0.35	0.35
	30	1.02	1.02	0.35	0.35
	60	1.02	0.99	0.35	0.30
2	500/ 15	1.02	1.00	0.35	0.32
	/ 30	1.02	0.97	0.35	0.30
	/ 60	1.02	0.95	0.35	0.24
3	550/ 15	1.02	0.98	0.35	0.28
	/ 30	1.02	0.95	0.35	0.19
	/ 60	1.02	0.92	0.35	0.1
4	600/15	1.02	0.98	0.35	0.17
	/30	1.02	0.93	0.35	0091
	/60	1.02	0.89	0.35	traces
5	650/15	1.02	0.94	0.35	0.11
	/30	1.02	0.89	0.35	0.07
	/60	1.02	0.84	0.35	traces
6	700/15	1.02	0.94	0.35	–
	/30	1.02	0.88	0.35	–
	/60	1.02	0.81	0.35	–
7	750/15	1.02	0.68	0.35	–
	/30	1.02	0.41	0.35	–
	/60	1.02	0.21	0.35	–
8	800/15	1.02	0.59	0.35	–
	/30	1.02	0.34	0.35	–
	/60	1.02	0.09	0.35	–

Fit: concentration = 1.02 · exp (–time/*T*)

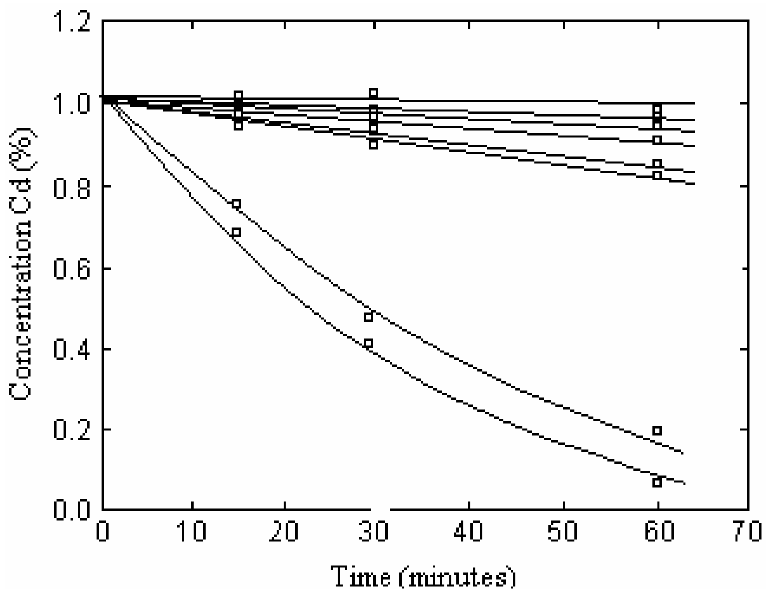

Fig. 1 – Losses of Cd dependent on time at $P = 10^{-2}$ torr
şi T = 450, 500,550, 600, 650, 700, 750, 800°C.

Analyses carried out. The following analyses were carried out for the two alloys:

1) the content of As and Cd left (according to Table 2);

2) the losses of Sn, Sb and Cu were determined at a temperature of 800°C and a holding time of 30 minutes, at a pressure of $P = 10^{-2}$ torr;

3) microstructures;

4) R_m, $R_{p0.2}$, A, Z, HB.

Results of analyses

1a) The elimination of Cd (Table2) – The alloy was vacuumed from a temperature of 450°C to 800°C for a holding time of 15, 30, 60 minutes. At the temperature of 800°C and a holding time of 6o minutes Cd is eliminated in a percentage of 1.02 % to 0,09% .

1b) The elimination of As (Table 2) – The alloy was vacuumed at temperatures of 450, 500, 550, 600, 650°C, for a holding time of 15, 30, 60 minutes. At the temperature of 650°C, after 60 de minute, As was completely eliminated.

2) The losses due to evaporation in vacuum were the following: Sn 4%, Sb 2%, Cu 1 %. These losses are smaller than the losses which would have occurred if the alloy had been elaborated in an ordinary atmosphere of 500°C (without the use of

this vacuum technology) (Sn 10%, Sb 10%, Cu 10%). 500ºC is the maximum elaboration temperature for the Sn based antifriction alloys.

3) After the evaporation the structures of the alloys no longer comply to the functional requirements.

4) The mechanical properties – For alloy LgSnR elaborated at 800°C and a holding time of 60 minutes 3 determinations were made and the following results obtained:

$R_m = 85\text{N/mm}^2$, $R_{p0.2} = 67\ \text{N/mm}^2$, A= 5 %, HB 250/10/60 = 27.

For alloy RL 38-93 e determinations were made on the alloy cast at 650° C and a holding time of 60 minutes and the following values were obtained:

$R_m = 84.3\text{N/mm}^2, R_{p0.2} = 64.1\text{N/mm}^2$, A = 3.6 %, HB 250/10/60 = 25.

3. CONCLUSIONS

The vacuum distillation technology has proven to be an ecological technology because the As and Cd could be recovered in a condenser.

The losses of elements such as Sn, Sb, and Cu through oxidation are smaller than in case of the elaboration in the ordinary atmosphere at 500°C (the elaboration temperature for these alloys), without using the proposed vacuum technology.

As is completely eliminated at a temperature of 650°C after 60 minute while Cd at a pressure of 10^{-2} torr and 800°C and a holding time of 60 minutes was eliminated in a percentage of 0.09 % .

The evaporation speed decreases as the amount of Cd decreases (according to Fig. 1).

A formula for the determination of element loss dependent on time could be determined based on the interpretation of the practical results (Fig.1).

After the elimination of As and Cd, the mechanical properties of the alloys became inferior even to the properties of Sn-Sb-Cu antifriction alloys.

The structures of these alloys no longer comply with their functional requirements. In order to be used in the manufacturing process, the alloys from which Cd and As were extracted have to be elaborated again.

Taking into account the fact that for a pressure of 10^{-2} torr, even at high temperatures, Cd cannot be completely eliminated, we suggest that research should be continued on a new equipment capable of creating a vacuum of at least 10^{-4} torr and during the elaboration process the alloy has to be vibrated. It has been demonstrated that during vibrations, high pressures build up within the alloy which lead to an increase in the speed of gas evaporation (the pressures being equivalent to a vacuum of 10^{-3} torr). The same equipment could be used for the elimination of As in order to increase the evaporation speed and reduce the temperature.

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