STUDY OF STRUCTURAL HARDENING MECHANISMS OF PbSbAl ALLOYS FOR THE NEW GENERATION BATTERY GRIDS

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__Abstract.__ Structural hardening of PbSbAl alloys is characterized by two stages: the first is characterized by a hardening continuous reaction and a softening discontinuous transformation. The second is characterized by a softening discontinuous precipitation.

The influence of minor additions of aluminum results in increasing of hardness. Two structural states were considered: as-cast and rehomogenized alloys. The contents of Aluminium (Al) are 0.16%, 0.8% and 1.4% (in weight percent). Those of antimony (Sb) are 1.5% and 2%. The explored temperatures are essentially 20°C and 80°C. This last is chosen because it corresponds to the temperature of ripening of battery plates as well as the extreme temperature of its operation.

__Keywords__: battery, lead, alloy, aluminum, hardness, precipitation hardening.

1. INTRODUCTION

If it is desired to increase the hardness of lead for practical applications, then the readiest alloying element is, in general, antimony. The lead-antimony alloys have been known for long, simply as hard lead, and are used extensively as the most important group of alloys, i.e. for pipe and sheet, cable sheeting, collapsible tubes, storage battery grids, anodes, sulphuric acid fittings, and units for radiation protection [7]. However, Antimony has adverse effects on some of the characteristics of the battery. Thus, the overvoltage of antimony (Sb) into oxygen and hydrogen is less than that of pure lead. Antimony decreases the corrosion resistance of the positive grid, and the high content of antimony in the negative plate leads to formation of the stibine which is toxic.

One way to eliminate the negative effects of antimony without diminishing its beneficial role is to reduce its content in the alloy.

The reduction of the antimony content leads to degradation of mechanical properties. This may be compensated by the introduction of small amount of aluminum.

This work is part of a systematic study of the mechanical properties of lead alloys with a low percentage of Sb (1, 5.wt% and 2.wt %). The study is to examine the structural hardening mechanisms of PbSbAl alloys.

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2. EXPERIMENTAL SETUP

2.1. ALLOYS ELABORATION

We have prepared our alloys with defined proportions of each pure element; Lead (99.99%), Antimony (99.99%) and Aluminum (99.99%) which were melted at 700 ° C. The preparation is as follows; the molten lead and the minor components are mixed under vacuum and in a manner to avoid oxidation of the antimony and the casting surface. Once the molten alloy is solidified in the silica glass tube of 8 mm in diameter, the assembly (alloy + tube) is water quenched at room temperature.

All of the prepared samples are aged at room temperature to follow the evolution of the hardness and of the structure in a function of time.

Pb-Sb binary system shows a simple eutectic with two phases solid solution   (Pb) and   (Al) as shown in Fig. 1. The eutectic point is at a temperature of 252 °C and a composition of 11,1wt% [1].

The solubility of Sb in the lead is 3.5 wt% at the eutectic temperature and decreases to 0,3wt% at 50 °C [1].
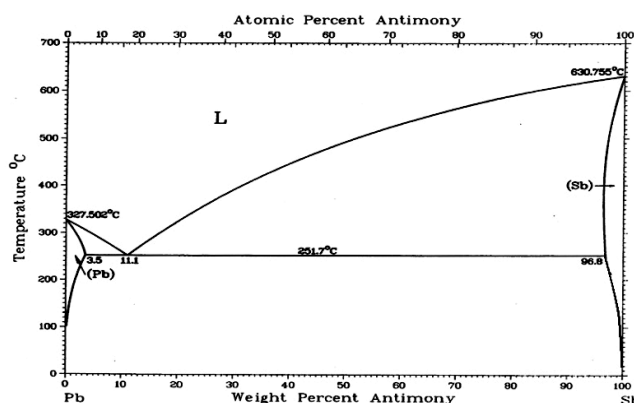

Figure 1. Binary phase diagram of Pb-Sb system [1].

Fig. 2 shows the system phase diagram Al-Pb [7]. This is a simple system with three phases: liquid L, the solid solution (Al) and the solid solution (Pb). A liquid immiscibility occurs below a critical threshold. The solubility of the solid lead in Aluminium and that of aluminium in lead (Pb) are extremely low. The critical composition is 55.2% of the aluminum to 1566 °C.
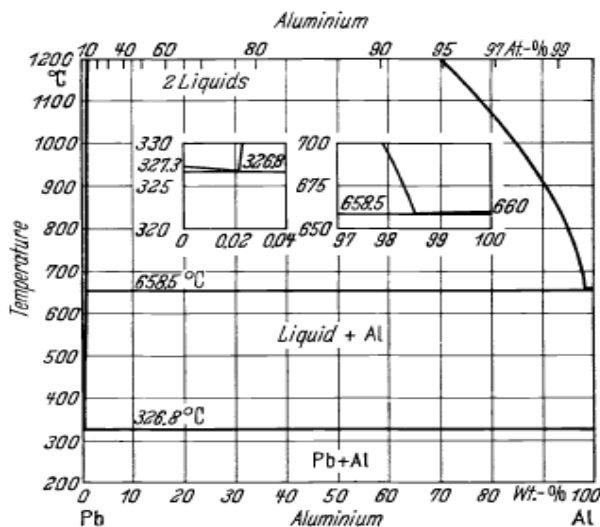

Figure 2. binary phase diagram of Al-Pb system [7].

The phase diagram Sb-Al (Figure 3) [8] shows a simple system with an intermediate single solid phase AlSb, it forms two eutectics, one with solid aluminum and the other with solid Antimony. Generally, the solubility of Antimony in Aluminum in the solid state is <0.1%.
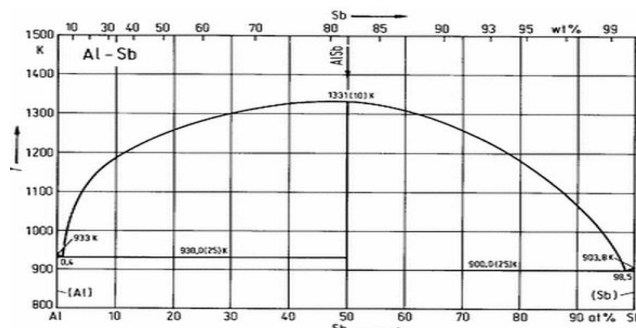

Figure 3. Binary phase diagram of Al-Sb system [8].

2.2. HARDNESS

Hardness tests are carried out by the Vickers method using a durometer Testwell under a load of 2 kgf. Each measurement corresponds to the average of a maximum of four imprints spread over a planar section corresponding to a diametrical plane or perpendicular to the axis of the cylindrical sample. The sections are obtained by sawing, mechanical abrasion and chemical polishing. Recall that the empirical relation HV = 0.3 R (MPa) can be used to evaluate the ultimate load (R) of these alloys.

2.3. OPTICAL MICROSCOPY - X-RAY DIFFRACTION

The physical properties of the quenched solid solutions of lead alloys evolve from room temperature. Hardening mechanisms correspond to continuous or discontinuous transformations. In fact, this temperature is 0.5 Tm (the melting temperature alloy). It is known that from 0.4 to 0.5 Tm, the alloy elements can diffuse. In the case where the kinetics of the discontinuous transformation is rapid at room temperature, the original technique developed by HILGER [2] is used in order to observe the structure before any transformation. It consists in an electrolytic polishing temperature of -50 °C (all transformation is blocked). In the case of our alloys, the sample to be polished, is immersed in a chemical solution composed of one part water oxygenated 30% H2O2 and three parts of glacial acetic acid. The immersion time varies between 20 seconds to 2 minutes depending on the state of the sample. The chemical polishing is followed by repeated chemical etching using a base mixture of citric acid and ammonium molybdate.

3. RESULTS AND DISCUSSION

3.1. HARDNESS EVOLUTION

Fig. 4 shows the evolution of the hardness of Pb 1, 5% Sb 0.8% Al as-cast alloy at 20 °C and 80 °C temperatures. It is noted that; the initial value of hardness (HV 11.26) is very high comparing it with that of basic element which is pure lead (5 HV). The hardness is high due to transformations that occur during the solidification of the alloy.

At 20 °C temperature, the maximum hardness is achieved in the order of 13 HV after 38 min. a slight decrease is noted. After 23 days, the hardness becomes stable (11.26 HV).

At 80 °C temperature, the Pb 1, 5% Sb 0.8% Al system is thermally activated which makes it difficult to follow the evolution of the hardness in the first minutes of quenching. From the first measure of the hardness we face softening transformations. After just 12 minutes of aging, the hardness rapidly decreases to stabilize after 5 hours. This is a slowing overaging.

Generally, at 20 °C temperature, the PbSb (1-3% Sb) alloys may not show signs of discontinuous overageing until after one year and a maximum hardness that does not exceed 11.5 HV [4-6]. However, the hardness of our system Pb1 5% Sb 0.8% Al is 13 HV just after half an hour and some minutes.
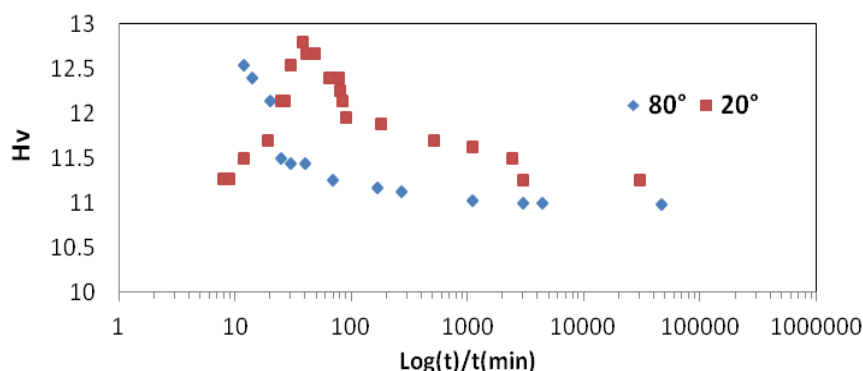

Figure 4. Evolution of the hardness of Pb 1, 5% Sb 0, 8% Al as-cast alloy in a function of time, aged at 20 °C and 80 ° C temperatures.

3.2. STRUCTURE EVOLUTION

The quenched structure evolution of Pb 1, 5% Sb 0, 8% Al as-cast alloy was followed by optical microscope. This structure is characterized by the appearance of finer grains, as shown in Fig. 5.
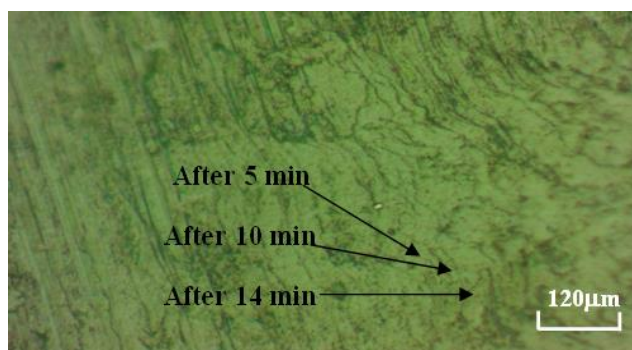

Figure 5. Structure evolution of Pb 1, 5% Sb 0, 8% Al as-cast alloy at 20 °C after quenching. Movement visualization of grain boundaries characterizing the beginning of discontinuous transformation after successive chemical attack 5, 10 and 14 minutes after quenching.

At the beginning of aging of the alloy, it is noted that the supersaturated matrix is not homogeneous; it is the beginning of the movement of the grain boundaries characterizing the discontinuous transformation of aging as shown in Figs. 6 and 7.

Figure 6. Quenching structure evolution of Pb 1, 5% Sb 0, 8% Al as-cast alloy at 20°C. Visualization of discontinuous transformation after 22 minutes.
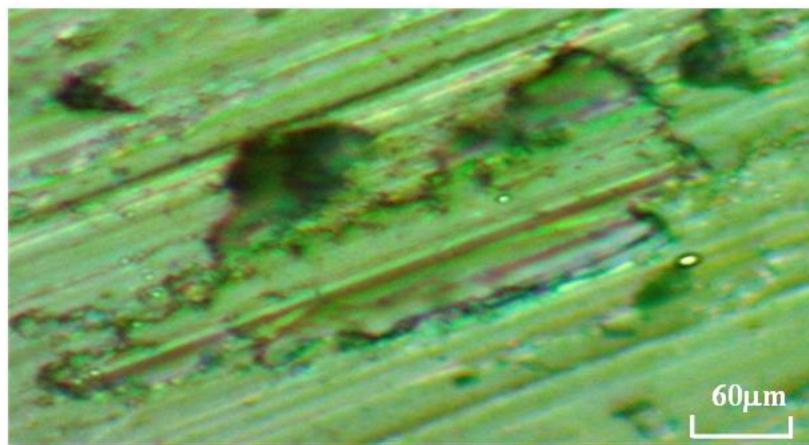

Figure 7. Quenching structure evolution of Pb 1, 5% Sb 0, 8% Al as-cast alloy at 20°C. Visualization of discontinuous transformation after 30 minutes.

The Micro-hardness testing performed on the transformed zones (10 HV) and non-transformed (12.33 HV) show that these are harder. Therefore, the aging of this alloy is characterized by a hardening continuous reaction and a discontinuous transformation. (Fig. 8).
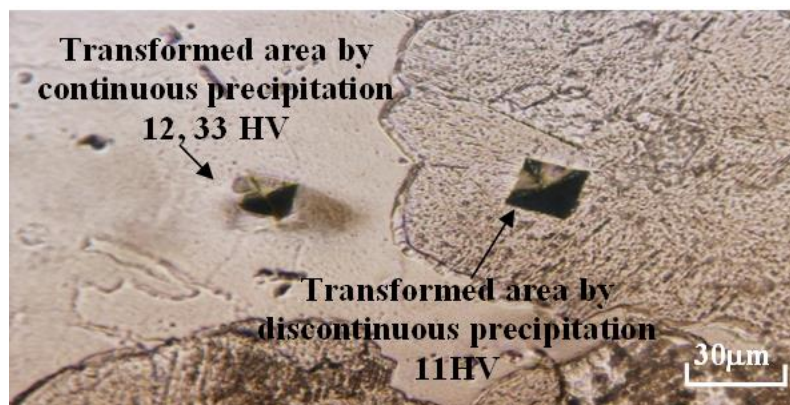

Figure 8. Visualization of microhardness prints performed on Pb 1,5% Sb 0.8% Al As-cast alloy after 20 minutes at 20°C.

For prolonged time maintain, a discontinuous precipitation is observed, which characterizes the overaging of Pb 1, 5% Sb 0, 8% Al As-cast as shown in Figs. 9 and 10.
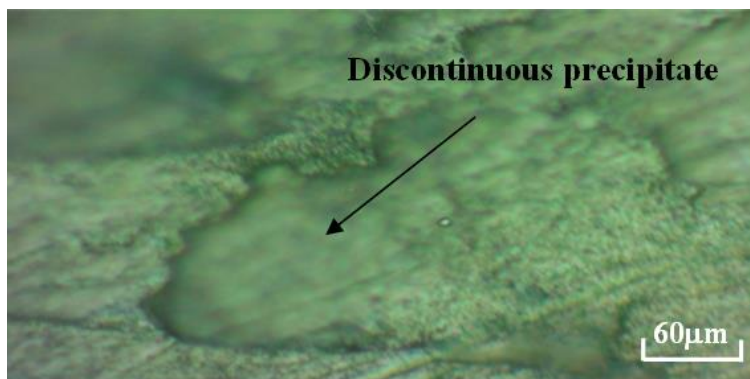

Figure 9. Discontinuous precipitation (overaging) of Pb 1, 5% Sb 0, 8% Al As-cast alloy at 20°C, after 22 aging days.
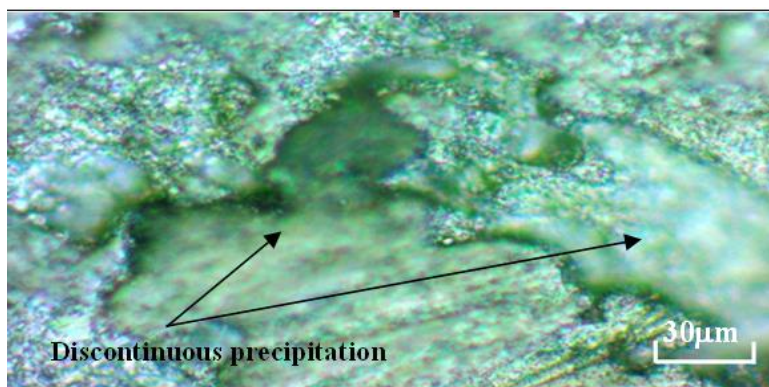

Figure 10. Discontinuous precipitation of Pb 1, 5% Sb 0, 8% Al, As-cast alloy at 20°C, after 51 aging days.

The X-ray diffraction shows that the precipitates are Pb and Sb (Fig. 11), moreover, the element Al is not involved in hardening mechanisms of PbSbAl alloys, the influence of the Aluminum results in the hardness increasing.
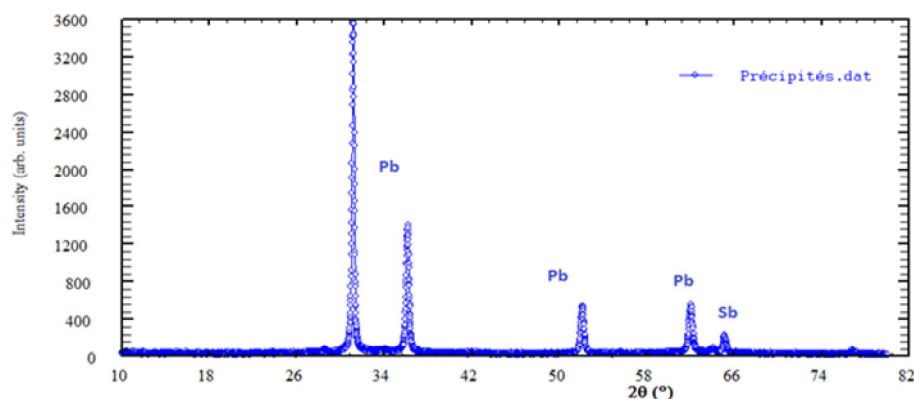

Figure 11. The X- ray diffraction spectrum of Pb 1, 5% Sb 0, 8% Al As-cast alloy at 20 °C.

3.3. THE INFLUENCE OF ALUMINUM CONTENT

In order to study the influence of Aluminum on lead-antimony alloys (PbSb), we varied the content of the additive. Fig. 12 represents the evolution of the hardness of Pb 1.5% Sb X% Al alloys a function of time at room temperature with (X = 0,8wt% 0,16wt%, 1.4% wt %).

The three curves of Fig. 12 have the same shape except that it is a phase difference between the aging and overaging of the three alloys as well as the maximum hardness achieved.

It is deduced that the Aluminum hardens the alloy at a defined percentage; among the three percentages studied 0,8wt% 0,16wt% 1,4wt% of aluminum, it is found that the alloy lightly loaded is more hardening than the other alloys, with a maximum hardness 14.03 HV.
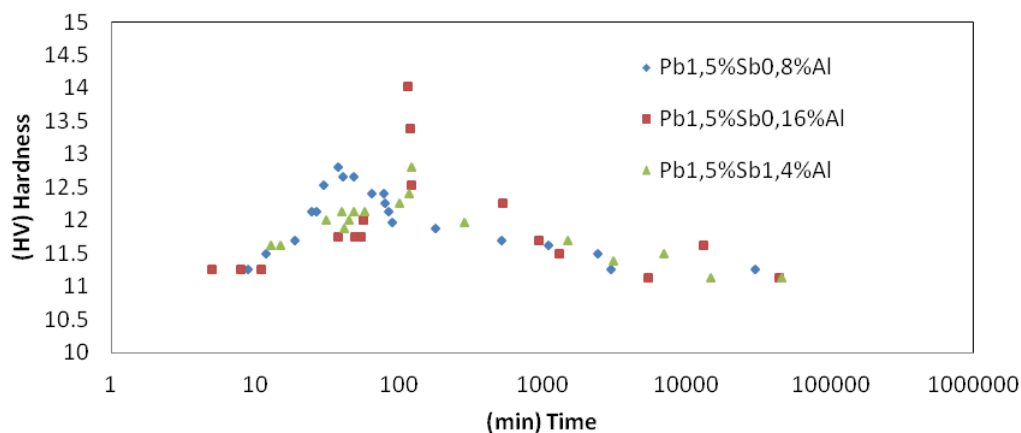

Figure 12. Hardness evolution in a function of time of Pb 1, 5% Sb 0, 8% Al, Pb 1, 5% Sb 0, 16% Al, Pb 1, 5% Sb 1, 4% Al As-cast alloys at room temperature.

The microscopic study of these three alloys shows that the transformations characterizing aging and overaging are similar (Figs. 13 and 14). Indeed, aging is characterized by a continuous reaction and discontinuous transformation while the overaging is characterized by a softening discontinuous precipitation.
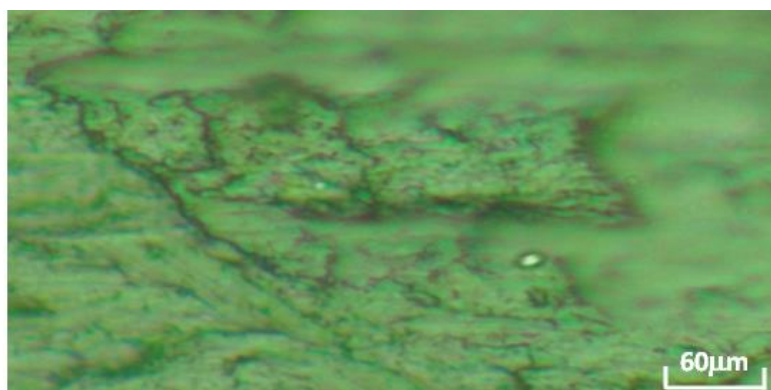

Figure 13. Structure evolution of Pb 1, 5% Sb 0, 16 % Al, As-cast alloy at 20°C. Visualization of grain boundaries displacement after successive chemical attacks after 20, 25 and 35 minutes after quenching.
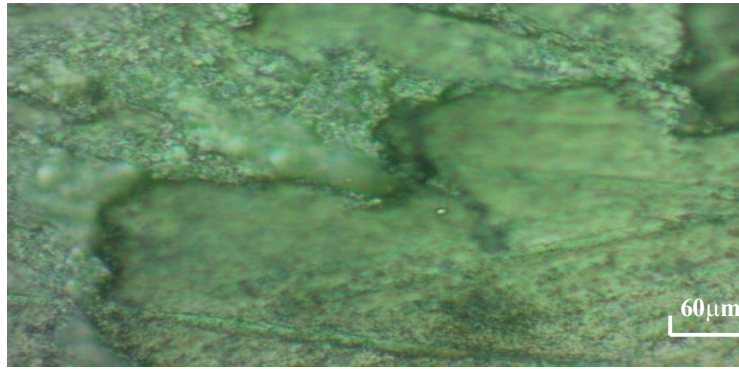
Figure 14. Discontinuous precipitation of Pb 1, 5 % Sb 0, 16 % Al As-cast alloy at 20°C, after 15 aging days.

3.4. THE INFLUENCE OF REHOMOGENIZATION

Fig. 15 shows the evolution of the hardness vs. time of Pb 1, 5 % Sb 0, 8 % Al As-cast alloy at room temperature for two structural states: alloy:-cast and rehomogenized.
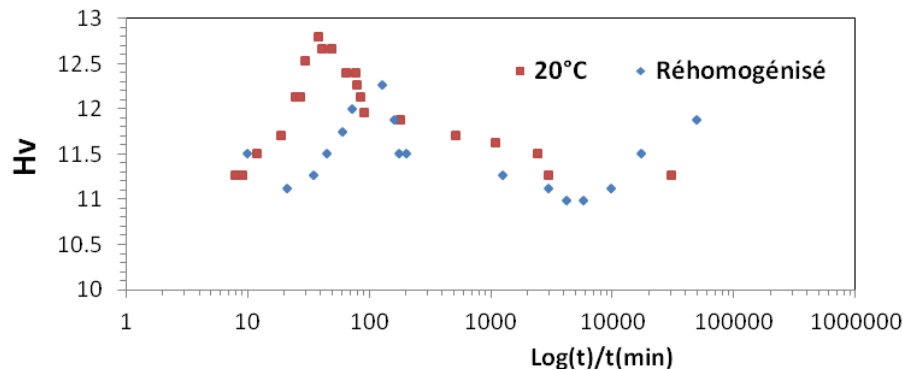

Figure 15. Hardness evolution in a function of time of Pb 1, 5 % Sb 0, 8 % Al As-cast and rehomogenized alloy at room temperature.

The Aluminum promotes the development and creation of grain germination sites contrary to rehomogenization which favors the reduction of these sites. The structural hardening mechanisms of the rehomogenized alloy are similar to those of the as-cast alloy. The influence of the rehomogenization results in a decrease in the hardness and a delay of the kinetics of the transformation characterizing the aging and overaging of the as-cast alloy. Indeed, the maximum hardness 12.25 HV for the rehomogenized alloy is reached after 3 days contrary to the as-cast alloy; the maximum hardness is reached after 38 minutes.
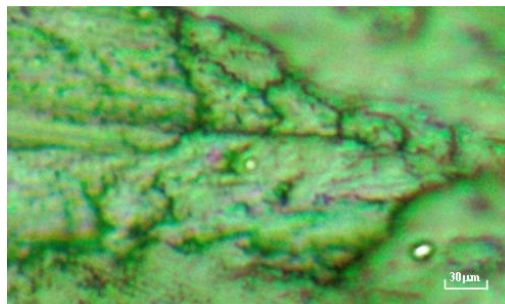

Figure 16. Structure evolution of Pb 1, 5% Sb 0, 8% Al rehomogenized alloy at room temperature, Visualization of displacement of boundaries grains after successive chemical attacks after 40, 45, 50 minutes after quenching.

The quenching structure of the rehomogenized alloy was followed by optical microscope; it is found that the structural hardening mechanisms of this alloy are similar to those of the as-cast alloy. Indeed, aging is characterized by a continuous reaction and discontinuous transformation (Figure 16). Overaging manifests by the appearance of a softening discontinuous precipitation.

For Pb 2 % Sb 0, 16 % Al rehomogenized alloy at room temperature (Figure 17). The rehomogenization delayed the aging of the alloy and decreased its maximum hardness. This is due to the elimination of development sites and grains germination of the alloy.
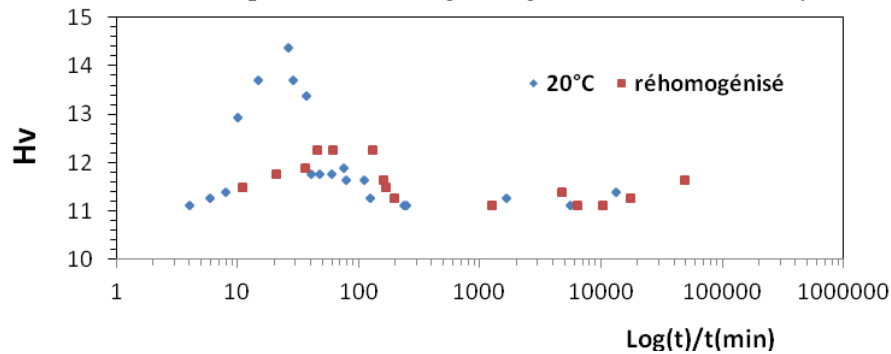
Fig. 17: Hardness evolution vs. time of as-cast and rehomgenized alloy Pb 2 % Sb 0, 16 % Al, at room temperature.

Kinetic study of the softening discontinuous precipitation of Pb 1, 5 % Sb 0,8% Al alloy

The degree of advancement of overaging reaction calculated by the Johnson and Mehl equation: [3]

After calculating the degree of advancement of aging softening discontinuous precipitation from the following relation:

with:
$$x = \frac{HV(t) - HV(0)}{HV(m) - HV(0)}$$

HV (0): The initial value of the hardness;
HV (m): The final value of the hardness;
HV (t): The hardness value at instant t.

We notice that the process of transformation is accelerated and the temperature better catalyzes the reactions in the crystalline structure, this is illustrated in Fig. 18.
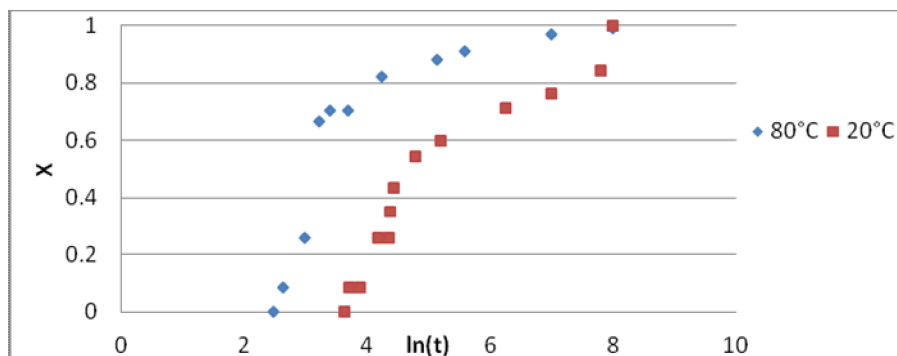
Fig. 18: Pb 1, 5% Sb 0, 8% Al alloy. Semi-logarithmic transformed for hardness tests curve at 20°C to 80°C temperatures relative to overaging softening transformation for as-cast alloy samples hardened quenched with water.

By calculating the exponents n and k coefficients for two straight lines in Fig. 19, we determined the apparent activation energy Q through Johnson and Mehl equation [3]:

$$LogLog\left(\frac{1}{1-x}\right) = nLogk + nLogt$$

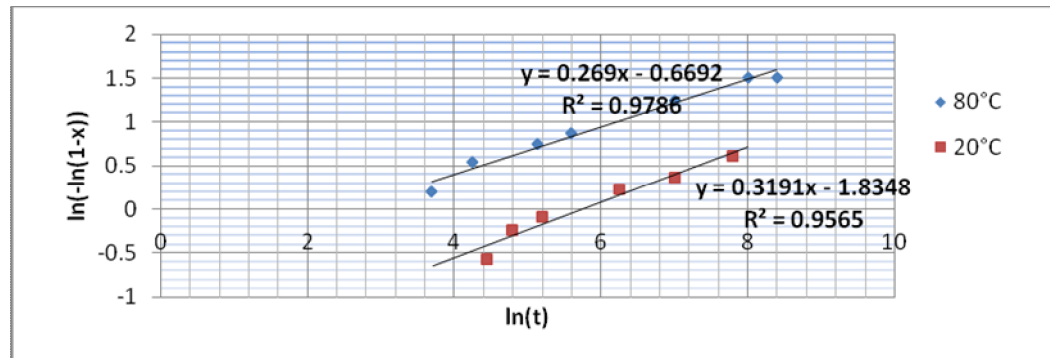**Fig. 19: log (-log (1-x)) representation as a function of Log (t) relative to the overaging softening transformation studied by isothermal hardness variations in the case of Pb 1, 5 %Sb 0, 8% Al as-cast alloy.**

Table 1 shows the values of n and k deducted from Fig. 19. According to this calculation method, we can say that the alloy transformations require 46.8 kJ / mol which represents the apparent activation energy.

Table 1: The coefficients of Johnson and Mehl equation at different temperatures for Pb1,5%Sb 0,8% Al as-cast quenched alloy.

Temperature (°C)	n	K
20	0,319	$3,185.10^{-3}$
80	0,269	0,083

Burke method [3]: To ensure this result, we use Burke method. The principle of this method is to calculate the activation energy Q for different values of the degree of advancement to prove that this energy does not depend on X variation. Figure 20 shows the Log t_x variation as a function of 1000 / T for different degree of advancement values (x = 0.6, 0.7, 0.8, 0, 9). The straight are almost parallel, which gives almost constant energies shown in Table 2 (é 45kJ / mol).

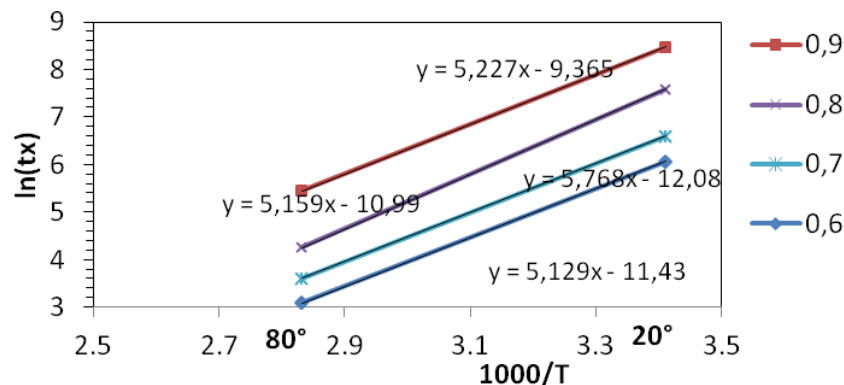**Fig. 20: Pb 1, 5% Sb 0, 8% Al alloy. The apparent activation energy determination associated to softening transformation. Log t_x variation as function of1000/T.**

Table 2: The apparent activation energy Q values for different degrees of advancement   characterizing overaging of Pb 1, 5% Sb 0, 8% Al quenched as-cast alloy.

X	Q (kJ/mol)
0,6	43,48
0,7	47,98
0,8	42,92
0,9	42,67

According to the previous results, the activation energy of the softening reaction is low (46.8 kJ / mol) comparing with the lead auto-diffusion (104 kJ / mol), therefore the reaction is isokinetic and the system is simple which is compatible with the obtained results in the case of PbSb alloys [9]. Indeed, the activation energy of these alloys is between 10 and 60 kJ / mol.

CONCLUSIONS

The phenomena of aging and over-aging of PbSbAl alloys are characterized by a continues hardening reaction and a softening discontinuous transformation with discontinuous precipitation Pb and Sb.

Minor Aluminium element has changed the structure of PbSb alloys and made it finer so hath he multiplied the transformations germination sites to harden the alloy better with a small percentage (0.16 wt %) and to accelerate transformations in play during aging and overaging.

The rehomogenization of PbSbAl alloys at room temperature delayed the reaction kinetics and decreased aging maximum hardness.

The activation energy of the softening reaction is low (46.8 kJ / mol) comparing it with lead auto-diffusion (104 kJ / mol), therefore the reaction is isokinetic and the system is simple.

Based on this study, we found that the mechanical properties of PbSbAl alloys are improved compared to those of PbSb alloys. The maximal hardness passes from 11.5 to 13 HV, which shows the beneficial effect of Aluminum (Al) on the structural hardening of PbSb alloys.

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