

## STRUCTURAL HARDENING MECHANISM OF LEAD-CADIUM-CALCIUM-TIN-SILVER ALLOYS FOR BATTERY GRIDS

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**Abstract.** *The reequilibration of supersaturated Pb-Ca-Cd-Sn-Ag alloys was studied by several experimental methods: hardness measurements, optical and electron microscopy, electron microprobe. Two structural states were considered; as-cast alloy, rehomogenised alloy. The explored temperatures were 20 and 80°C. In addition, the processes of age hardening of the PbCaCdSnAg alloys are done in two stages. The first stage is characterized by a discontinuous transformation without precipitation and a continuous reaction. The second is done by a coarse discontinuous reaction. The influence of the silver results in an acceleration in the kinetics of the hardening transformations and a light increase in hardness. The effect of the rehomogenisation results in an acceleration in the kinetics of the processes of ageing and over-ageing thus involving a light increase in hardness. This acceleration in the kinetics is due primarily to continuous precipitation.*

**Keywords:** *aging, alloys, battery grid, electron microscopy, hardness, optical microscopy*

### 1. INTRODUCTION

Research works on alloys of lead are experiencing a growing boom in both the fundamental study of their structural properties and for their many applications in the automotive industry. Indeed, for ecological and economic reasons, a lot of research has been conducted to increase the performance of lead-acid battery for use as a source of energy in the electric car. The choice of lead-acid battery therefore requires the development of grids characterized by corrosion resistance and improved mechanical properties.

The use of lead single is excluded because this metal is soft and malleable, and lacking in hardness and strength. But the dissolution of some solutes in the solvent liquid lead allows the supersaturation of the solid phase primary and thereby obtains hardened alloys for the manufacture of battery plates.

We studied [1] in a systematic way the aging process and averaging of PbCaCdSn alloys. They are characterized by two stages. The first is due to the discontinuous process of transformation hardening, which is initiated on the grain boundaries or joints in DC. This

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reaction is characterized by the movement of reaction fronts. When this transformation occurs intermittently, a mode of continuous reaction occurs and characterizes the second stage of aging alloys PbCaCdSn. The overaging is caused by discontinuous precipitation reaction crude.

In order to improve the benefits of mechanical and electrochemical properties of these alloys, we have undertaken the study of the influence of minor additions of silver on the mechanisms of precipitation hardening alloys PbCaCdSn as lead alloys for in the manufacture of battery grids require minor additions of silver to improve their electrochemical properties. Our goal is to study in a systematic manner the mechanisms of precipitation hardening alloys PbCaCdSnAg. Indeed, two structural states are considered: alloy-cast alloy and rehomogenized. Temperatures explored are 20°C and 80°C. This temperature was chosen because it corresponds to the temperature of ripening of battery grids and extreme temperature operation. The techniques used are: hardness, optical and electronic microscopes and electron microprobe.

## 2. EXPERIMENTAL SETUP

### 2.1. Preparation of alloys

The alloys are prepared from pure metals: lead (99.99%), cadmium (99.99%), tin (99.99%). While the contribution of calcium occurs from a master alloy composition Pb0.135% pure calcium where Ca is nuclear grade (lack of magnesium and aluminum). This master alloy is synthesized as follows: the molten lead and minor element Ca were added under glass to prevent the rise of calcium in the bath surface to prevent oxidation. The liquid alloy is cast from 450°C in a steel mold, not preheated, internal dimensions 130x25x5 mm<sup>3</sup>. Once solidification is complete, the plate is removed from the mold to 100°C and then dipped directly into liquid nitrogen.

The binary system Pb-Cd [2] (Fig. 1) has a simple eutectic diagram. For the ternary system Pb-Cd-Sn (Fig. 2), only, isothermal sections at temperatures of 130, 145 and 180°C were studied by Osmura et al. [3]. These sections show the presence of three solid phases as follows: Pb, Cd and Sn. In addition, the solubility limit of Cd by weight in the lead at the eutectic temperature is 3.2%, it is 0.15% at 20°C [4]. The solubility of tin in lead at 20°C is not well known to a very precise manner. Indeed, several solubility values at 20°C have been published in the literature: 1.9% [5], 2-3% [6], 1.3% [7] and 1-2 % by weight of Sn [8, 9, 10].

In addition, there are two versions of phase diagram Pb-Ca (Fig. 3) for low levels of calcium (< 0.15% by weight). One, with a peritectic [11] and the other a eutectic [12]. As the difference between the melting temperature of pure lead and that of the eutectic or peritectic is only 1°C, Notin et al. [13] compared an alloy Pb0.135%Ca with pure lead by differential thermal analysis in a very fine Calvet calorimeter with the rate of rise in temperature of 10 K/hour. They showed that the temperature of the bearing in the case of the alloy is higher than the melting temperature of pure lead by 1°C. This result is consistent with the pattern that has a bearing peritectic at 328°C. The composition of the peritectic liquid is about 0.8% by weight of calcium. The solubility of calcium in the lead is about 0.1% by weight of Ca peritectic temperature near 328°C, whereas at room temperature lead does not dissolve about 0.01% by weight of Ca. We have developed alloys whose content by weight of cadmium is 2% that of calcium 0.1% and tin is fixed at 1.09%. The silver grades are 0.07% and 0.15%.

To study the structural-cast alloys, the elements taken in the proper proportions, are introduced into a silica ampoule of 8 mm in diameter, sealed under high vacuum, the mixture is heated to 500°C. After melting and cooling total, all-alloy tube and silica is soaked with water. The samples were examined directly or may be stored in liquid nitrogen. For

rehomogenization, the ingot obtained is cut into several pieces that are then polished by abrasion. Samples are introduced into silica ampoules under high vacuum sealed. The entire bulb over samples is maintained at a temperature of 280°C for 2 hours (estimated optimal for rehomogenization) and then water quenched.

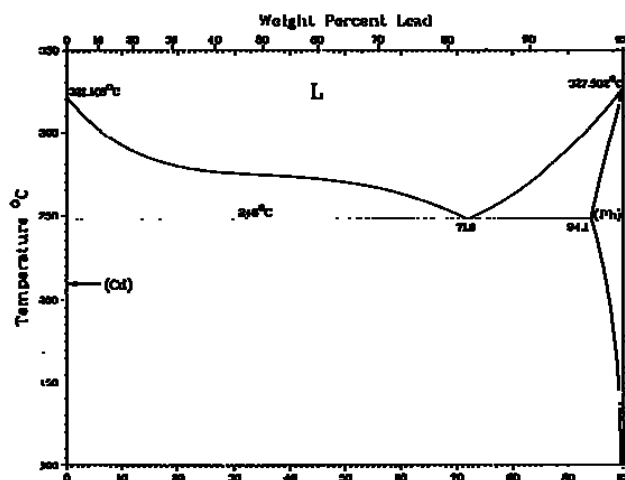


Fig. 1. Phase diagram Pb-Cd [2].

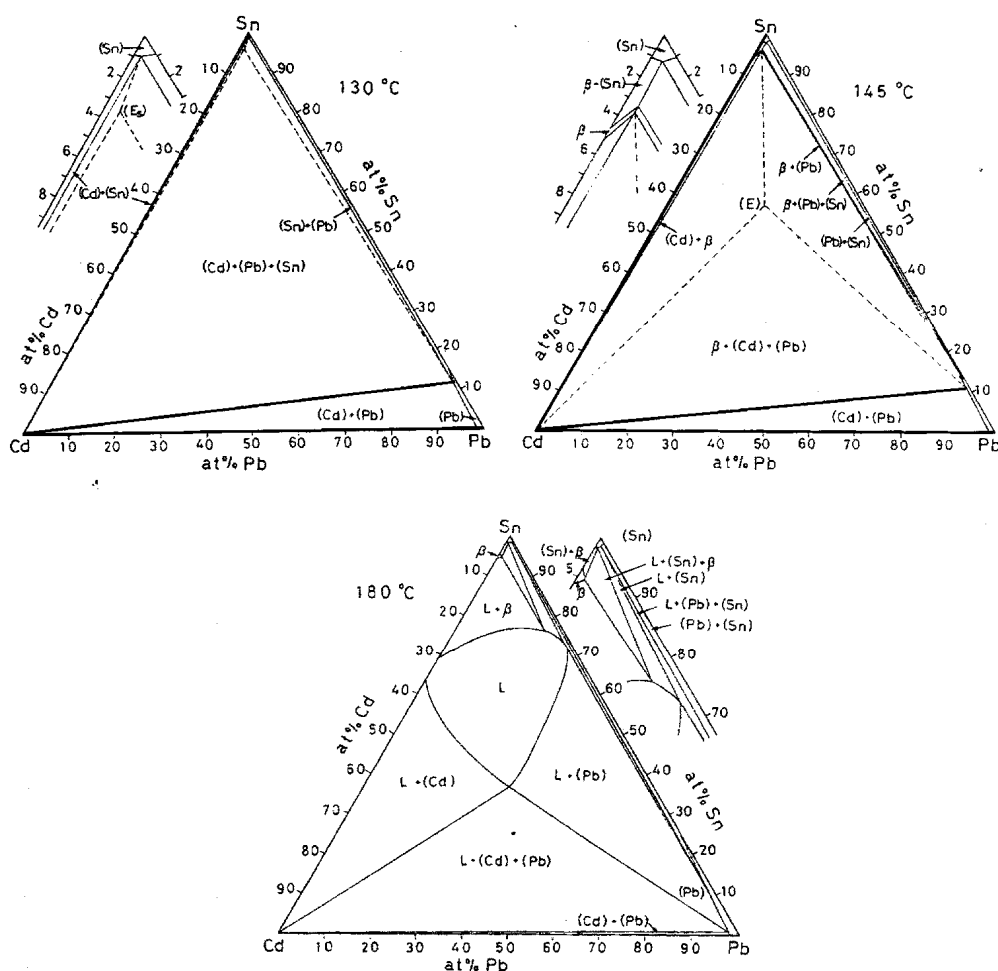


Fig. 2. Isothermal sections of the system Pb-Cd-Sn [3] at 130, 145 and 180°C.

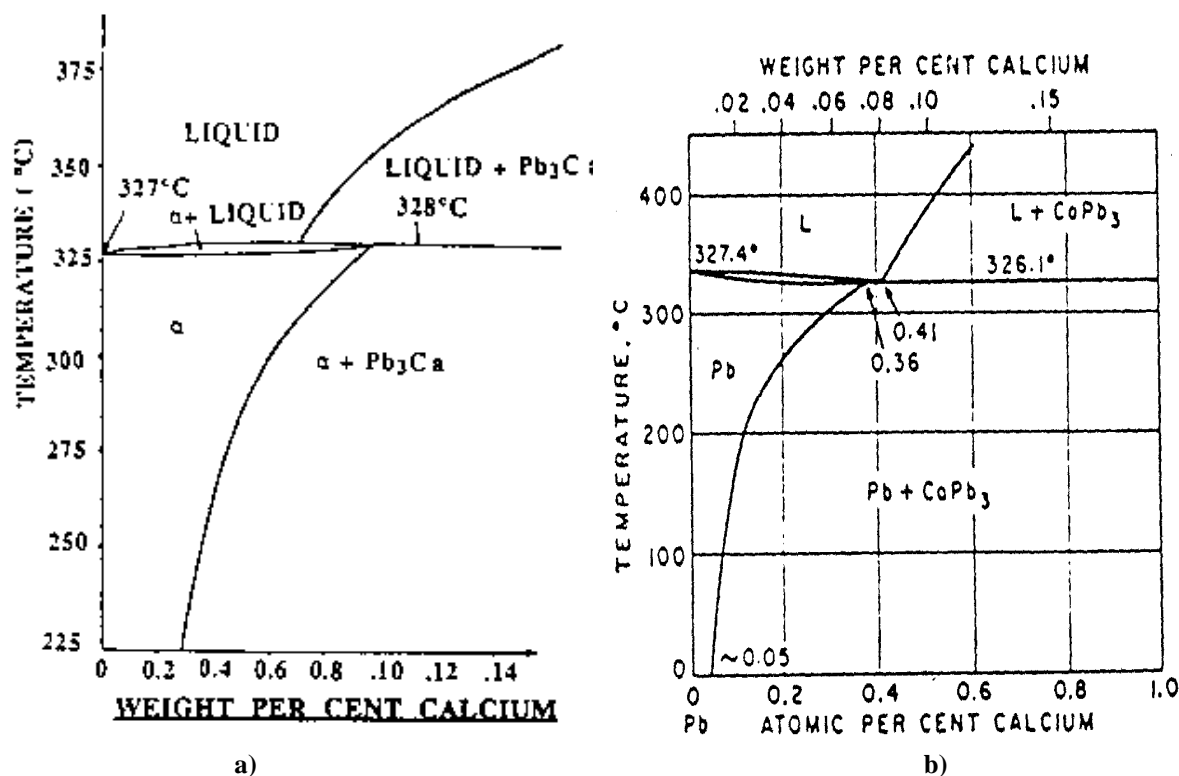


Fig. 3. Equilibrium diagram of Pb-Ca, in the rich of lead part.

a) Peritectic diagram [11]; b) Eutectic diagram [12].

## 2.2. Hardness

The hardness tests are carried out by the Vickers method, using a durometer Testweel under a load of 2 kgf. Each measurement is the average of up to five tracks spread over a flat section corresponds to a diametric 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  $HV = 0,3R$  (MPa) can be used to evaluate the tensile strength (R) of these alloys.

## 2.3. Optical microscope - Scanning Electron Microscope - Electron microprobe

The physical properties of solid solutions soaked lead alloys change from room temperature. The curing mechanisms correspond to transformations of continuous type and / or discontinuous. Indeed, this temperature corresponds to  $0.5T_f$ , temperature at which the alloying elements can diffuse. In the event that the kinetics of the discontinuous transformation is rapid at room temperature, the original technique developed by Hilger [14] is used in order to observe the structure before any processing. It consists of an electro-polishing at a temperature of  $-50^\circ\text{C}$  (blocked any transformation) in a mixture of 36 ml perchloric acid (70%) and 564ml ethyl alcohol followed by repeated chemical attacks at the temperature room with a mixture of citric acid (250g), ammonium molybdate (100g) and sufficient water to make one liter [15]. Indeed, the electrolyte is cooled to  $-50^\circ\text{C}$  by liquid nitrogen. The mixture was thermostatic in an insulated enclosure. The voltage is 20V. temperature is controlled directly using a thermometer or through the current density (0.1 to 0.2 A/cm<sup>2</sup>). To avoid localized the temperature rise at the sample surface low (<1 cm<sup>2</sup>). The sample is placed between two cathodes slightly domed stainless steel from a distance of 8 cm.

### 3. RESULTS

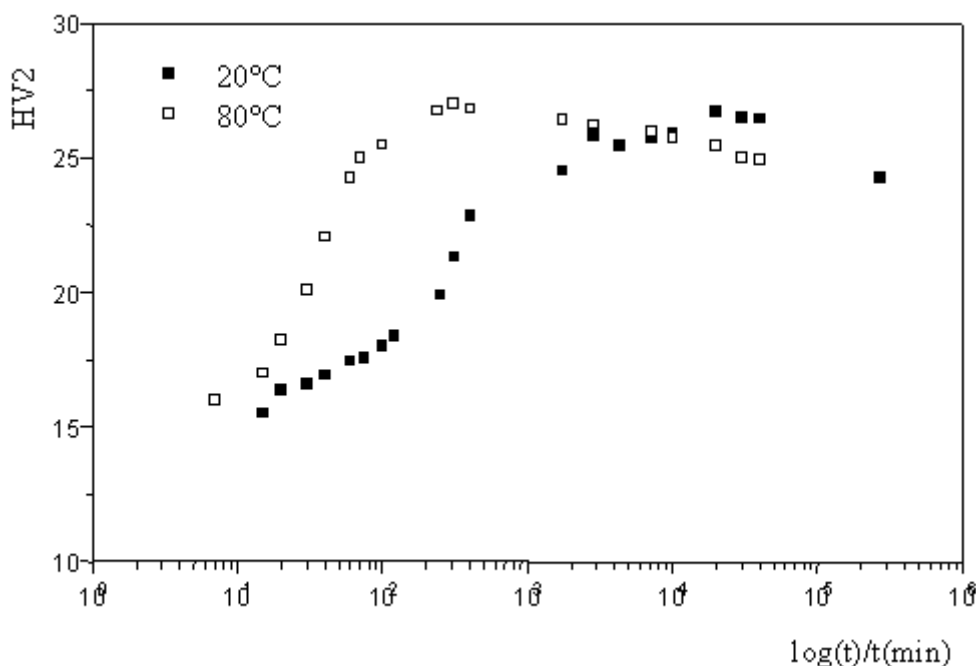
#### 3.1. STUDY THE ALLOY OF $Pb2\%Cd0.1\%Ca1.09\%Sn0.07\%Ag$

##### 3.1.1. Evolution of the hardness

Fig. 4 represents the evolution of hardness depending on time of the alloy  $Pb2\%Cd0.1\%Ca1.09\%Sn0.07\%Ag$  gross of casting, temperature  $20^{\circ}C$  and  $80^{\circ}C$ . The initial hardness is about 12.5 HV. This is a value greater than that of lead (4 up to 5 HV). This shows that this alloy has undergone a transformation during cooling.

At room temperature, the hardness increases to a value of 18 HV after one hour of aging. Then we see a rise again in hardness, which peaked at 26 HV after 15 days of maintenance. The hardness decreases to stabilize at 21 HV after two years of aging.

At  $80^{\circ}C$ , the curing process is accelerated. Indeed, the maximum (26 HV) hardness  $20^{\circ}C$  that is obtained here only after 4 hours of aging. This shows that the curing process at  $80^{\circ}C$  (ripening temperature grids batteries and extreme operating temperatures) appear identical to that of aging at  $20^{\circ}C$  except that the kinetic changes that characterize the aging and the overaging is accelerated.

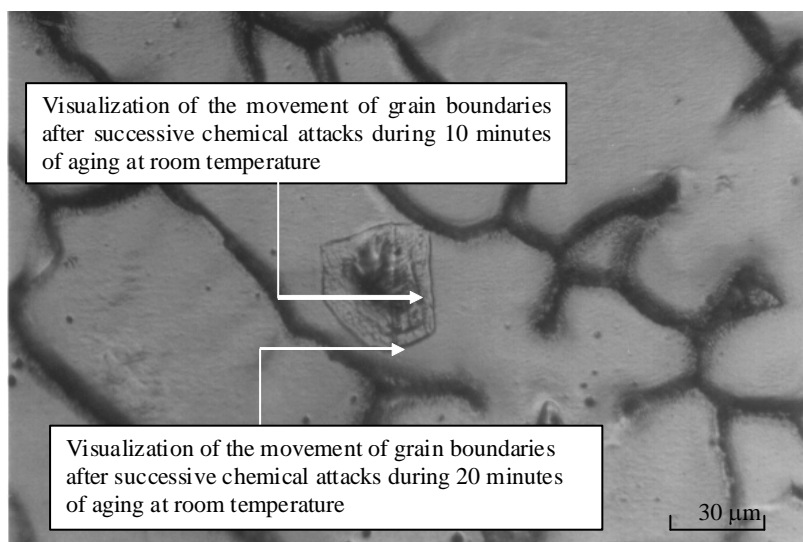


**Fig. 4. Evolution of the hardness of the alloy  $Pb2\%Cd0.1\%Ca1.09\%Sn0.07\%Ag$ , as-cast as function on time-temperature 20 and  $80^{\circ}C$ .**

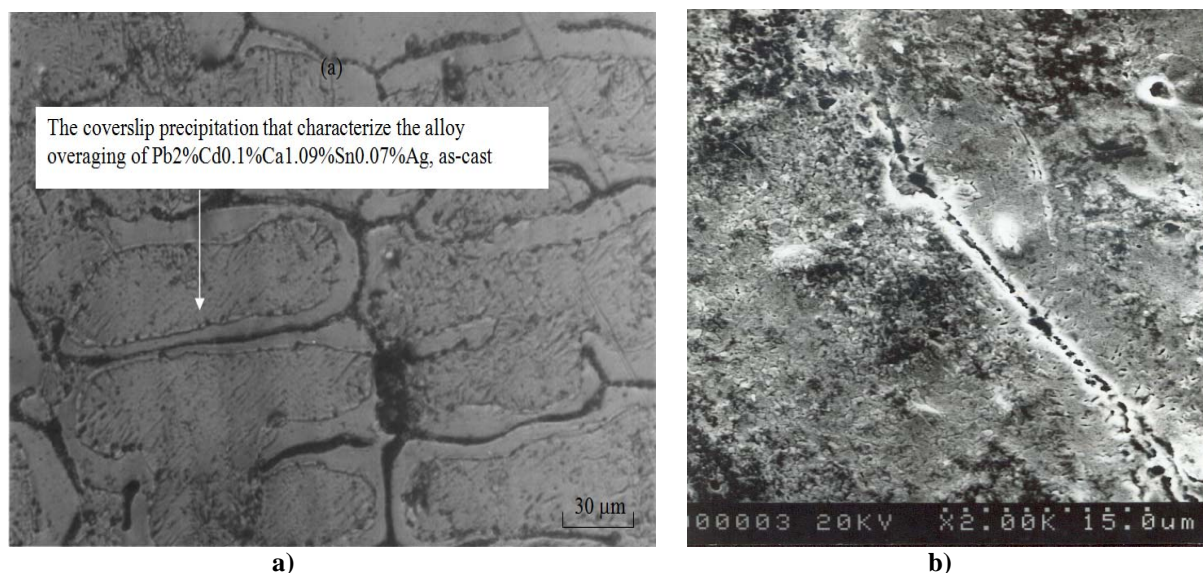
##### 3.1.2. Evolution of the structure

The changing structure of quenching was followed by the optical microscope. We have been able to highlight a few movements of front's discontinuous transformation characterizing the first stage of aging. This discontinuous transformation is nearly complete and is only in a few joints of the matrix mother (Fig. 5). The various microscopic observations at  $20^{\circ}C$  show that the movements of these grain boundaries are rare. After an hour of aging, continuous reaction occurs during this period of aging, we find no movement of fronts that characterize the discontinuous transformation.

For prolonged time, the microscopic observations of the gross alloy casting show that on aging (Fig. 6) is characterized by a discontinuous transformation course as in the case of the alloy free of silver [1]. The fine precipitates and consistent, resulting from the reaction continues, dissolve to the level of the grain boundaries and are transformed into big precipitated discontinuous non-coherent behind the joints in movement, resulting in a softening. Indeed, the overaging concerns almost all grains (Fig. 6 a), which explains the low values of hardness obtained in this stage of aging.



**Fig. 5.** Evolution of the structure of tempering at 20°C for alloy Pb2%Cd0.1%Ca1.09% Sn0.07%Ag, as-cast. Visualization of the movement of grain boundaries characterizing the discontinuous transformation after several successive chemical attacks for 10 and 20 minutes at room temperature.



**Fig. 6.** Alloy Pb2%Cd0.1%Ca1.09%Sn0.07%Ag, as-cast, aged one year at room temperature. Occurrence of discontinuous precipitation characterizing the coarse-aging.

In addition, the presence of 0.07% of Ag weight in the alloy Pb2%Cd0.1%Ca1.09%Sn, is marked by the presence of a eutectic mixture of areas that do not seem to contribute to the aging process and over-aging of these alloys.

The microprobe analysis showed the presence of lead, cadmium, tin and calcium in the precipitated but the different analysis do not allow us to determine exactly the actual concentrations of each element. These analyze show that the silver solution is not involved in the mechanisms of hardening of this alloy. In the joint of grain and the segregation cells, it detected a very small amount of silver by weight Ag. The presence of silver is due to the liquid eutectic Pb-Ag.

### 3.2. INFLUENCE OF SILVER CONCENTRATION

Figure (7) shows the evolution of hardness with time at room temperature of alloys Pb2%Cd0.1%Ca1.09%SnX%Ag (X = 0, 0.07, 0.15 in weight). Overall, the process of structural hardening of these alloys is similar to those of the alloy-free silver. Indeed, the first stage of aging is characterized by a discontinuous partial transformation and the second stage is a continuous reaction. The overaging is characterized by a discontinuous reaction course.

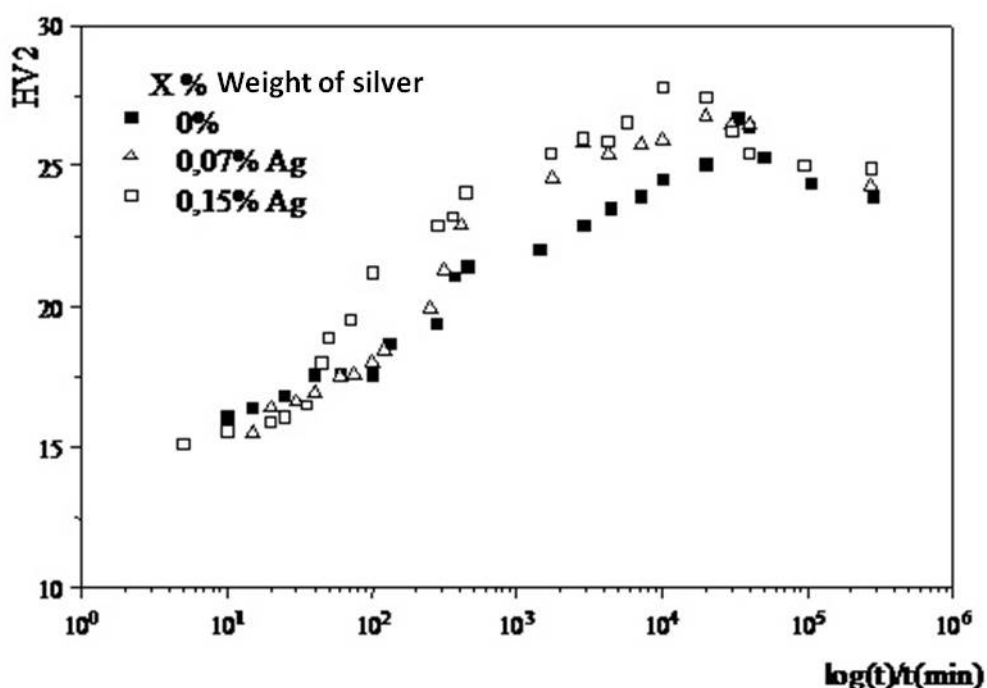
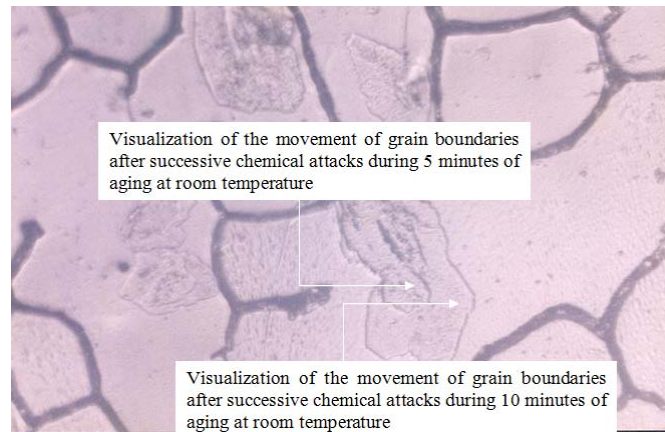
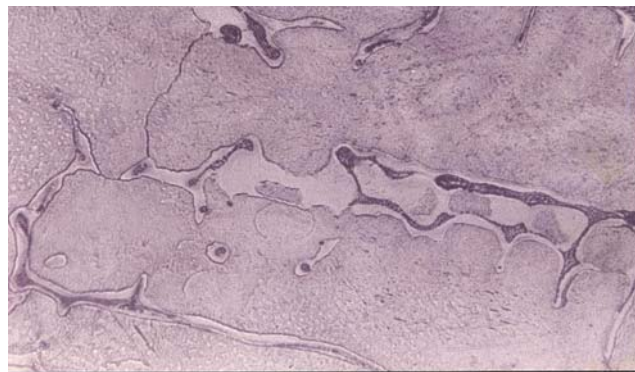


Fig. 7. Evolution of hardness as function of time at 20°C for alloys: Pb2%Cd0.1%Ca1.09%Sn, Pb2%Cd0.1%Ca1.09%Sn0.07%Ag and Pb2%Cd0.1%Ca1.09%Sn0.15%Ag, as-cast.

Gradually, as the silver content increases, the kinetics of hardening transformations is accelerated thus allowing a slight improvement in hardness. The maximum hardness is improved by 2.5 HV. In optical microscopy, this acceleration is reflected by the appearance of some movement of the grain boundaries which characterize the discontinuous transformation that characterizes the first stage of aging. Figure 8 shows the movement of fronts that characterize the discontinuous transformation after chemical attack for 5 and 10 minutes after quenching. For overaging, the rate of the batch reaction crude is important after 6 months of keeping only to the room (see Fig. 9) in contrast to the free silver alloy where the rate of conversion of the batch reaction crude is low despite a continuation of two years.

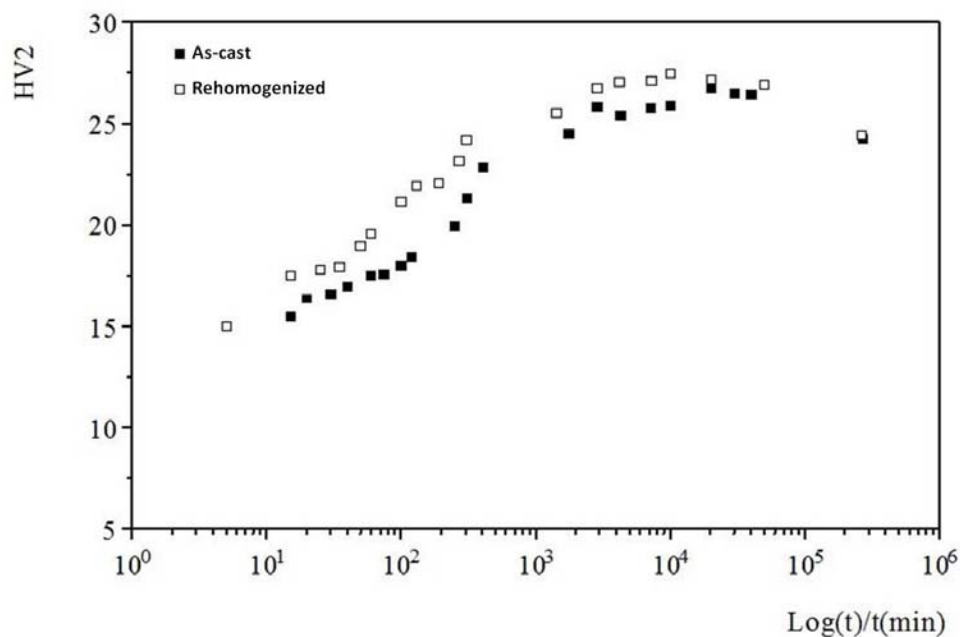


**Fig. 8.** Evolution of the structure of tempering at 20°C for alloy Pb2%Cd0.1%Ca1.09%Sn0.15%Ag, as-cast. Visualization of the movement of fronts that characterize the discontinuous transformation after several successive chemical attacks for 5 and 10 minutes at room temperature.



**Fig. 9.** Alliage Pb2%Cd0.1%Ca1.9%Sn0.57%Ag, as-cast. Aged 6 months at room temperature. Occurrence of discontinuous precipitation characterizing the overaging.

### 3.3. Influence of rehomogenization

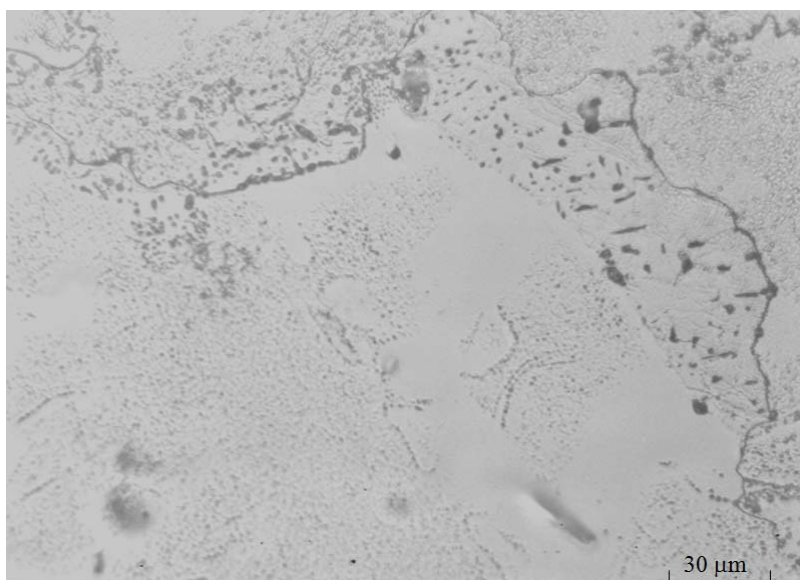


**Fig. 10.** Evolution of hardness as function of time at 20°C, for alloy Pb2%Cd0.1%Ca1.9%Sn0.7%Ag, as-cast and rehomogenized and then soaked in water.



Figure (10) shows the evolution of hardness with as a function of time at room temperature of the alloy Pb2% Cd0.1%Ca1.09%Sn0.07%Ag. We find that the aging process and overaging of the alloy rehomogenized are identical with those of the gross alloy casting, but with acceleration in the kinetics of the hardening process. This is mainly due to the precipitation continues. The maximum hardness of the alloy rehomogenized is higher than that of the as-cast alloy. This is due to the dissolution of segregated phases in the treatment of rehomogenization thereby increasing oversaturation after quenching. Microscopic observations of the alloy rehomogenized show that for the first time aging, the movements of reaction fronts that characterize the early stages of aging are rare.

For prolonged time, the over-aging occurs; it is characterized by a discontinuous precipitation course (Fig. 11). This is the discontinuous grow in the dissolution of fine particles from the continuous reaction at the grain boundaries which reprecipitate batch lamellar (magnification or discontinuous lamellar discontinuous precipitation). We also note that the influence of rehomogenization is reflected through the removal of cell segregation that characterizes the as-cast alloys (Fig. 6).



**Fig. 11. Alloy Pb2%Cd0.1%Ca1.09%Sn0.07%Ag, rehomogenized and then water quenched, aged one year at room temperature. Occurrence of discontinuous precipitation characterizing the overaging.**

#### 4. CONCLUSIONS

For alloys PbCaCdSnAg, the hardening process-cast alloys are similar to those PbCaCdSn alloys [1]. Indeed, the aging of these alloys is characterized by a discontinuous transformation without haste and a continuous reaction. The overaging is done by batch reaction crude. The influence of silver results in an acceleration in the kinetics of transformation hardening and a slight increase in hardness.

For the influence of temperature, we found that the hardening process at 80°C appear identical to that of aging at 20°C except that the kinetic transformations that characterize aging and over-aging is accelerated.

In addition, as and when the silver content increases, the hardening kinetics of transformations is becoming more and more accelerated simulating a slight improvement in hardness, the maximum value is increased by 2.5 HV.

The effect of mechanical stirring results in an acceleration in the kinetics of the aging process and over-aging resulting in a slight increase in hardness. This acceleration in the kinetics is mainly due to the precipitation continues. The improvement in hardness is due to

the dissolution of segregated phases in the treatment of rehomogenization thereby increasing oversaturation after quenching. We also note that the influence of rehomogenization is reflected through the removal of cell segregation that characterizes the as-cast alloys.

Based on these results, we concluded that:

- The influence of silvers results in an acceleration in the kinetics of hardening transformation and a slight increase in hardness.
- The mechanical properties of alloys PbCaCdSnAg are slightly better than those of PbCaCd alloys [16] and PbCaCdSn [1].

However, the expected performance of the batteries are good mechanical strength and good corrosion resistance. So what now, this work remains to be completed by an electrochemical study to investigate the electrochemical properties of these alloys.

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