ORIGINAL PAPER

STRUCTURAL HARDENING MECHANISMS OF LEAD-CADMIUM-MAGNESIUM ALLOYS FOR THE NEW GENERATION OF BATTERY GRIDS

L. ZERROUK[1], S. SAISSI[1], A. IBNLFASSI[1], E. SAAD[1]

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Abstract. *This study is focused on the structural hardening of ternary Pb-Cd-Mg alloys. The reequilibration of Pb-Cd-Mg alloys was studied by different experimental methods: hardness measurements, optical microscopy and X-ray diffraction. Alloys concerned are : Pb2%Cd1%Mg , Pb2%Cd2%Mg et Pb2%Cd3%Mg. Two structural states were considered: as-cast alloy and rehomogenized alloy. The explored temperatures were 20°C and 80 °C. The structure evolution of Pb -Cd -Mg alloys to the equilibrium state occurs in two stages: the first is characterized by a discontinuous transformation hardening; the second occurs after aging, it is characterized by softening coarse discontinuous precipitation. The addition of magnesium slightly increases the hardness and slow kinetics of the hardening transformation.*

Keywords: *Lead, Cadmium, Magnesium, Structural Hardening, precipitation, Rehomogenisation.*

1. INTRODUCTION

A lead-acid battery is a set of lead-acid batteries connected in series and included in the same box. This power storage system is widely used in industry as well as in motor vehicle equipment. It is an energy storage means particularly attractive since it is recyclable, with low cost and great maturity.

The lead battery industry requires materials allowing for lead accumulators a good mechanical resistance and better corrosion behavior. The use of lead in batteries alone is excluded because of its softness, malleability and lack of hardness and strength. But some of the solutes dissolved in the solvent liquid lead allow supersaturation of the first solid phase and thereby hardened alloys are obtained for the manufacture of battery plates.

Several studies were conducted to investigate the mechanical properties of lead alloys for the manufacture of battery grids. A systematic study of Pb-Cd alloys was carried out by Hilali and al [l]. Because of their good mechanical properties, the Pb-Mg alloys were recommended as a substitute for lead-tin alloy coating for phone [2]. Indeed, the curing of Pb-Mg alloy showed a hardness evolution since the latter has evolved from 14.1 Brinell to 19.1 Brinell after quenching after 1 day maintaining at room temperature for a composition of 3.5 % Mg. Hence the idea of adding Mg in Pb-Cd alloy according to defined proportions.

To our knowledge no structural hardening study for the ternary alloy Pb-Cd-Mg has been done so far .Our goal is to study systematically the structural hardening mechanisms of this alloy .The alloy Concerned are Pb2%Cd1%Mg, Pb2%Cd2%Mg and Pb2%Cd3%Mg.

[1] University Hassan 1 FST Settat, Laboratory of Physico-chemistry of Materials and Processes, Morocco.
E-mail: saadelmadani73@gmail.com.

Two structural states are considered: crude casting alloy and rehomogenized alloy. The explored temperatures are 20 °C and 80 °C. The latter temperature is selected because it corresponds to the temperature of ripening of battery plates as well as the extreme operating temperature. The techniques used are hardness, microhardness, optical microscopy and X-ray diffraction.

2. EXPERIMENTAL SETUP

2.1. PREPARATION OF ALLOYS

The alloys are prepared from pure metals: lead (99.99%), cadmium (99.99%) and Magnesium (99.99%). The phase diagrams of binary systems Pb-Cd and Pb-Mg are successively represented in the figures (Fig.1 and Fig.2), while the ternary diagram Pb-Cd-Mg is represented in the Fig.3.

For the Pb-Cd alloy [3] (Fig. 1), it represents a bearing eutectic at 248°C. The composition of the eutectic liquid is about 17.5% by weight of cadmium. The limit of solubility in α phase at the eutectic temperature is 3.3% by weight of cadmium and at room temperature is 0.15%. We therefore; chose a composition below the limit of solubility in primary solid phase which is 2% by weight of cadmium.

For the Pb-Mg alloy [2] (Fig.2), the binary phase diagram Mg-Pb is characterized by a eutectic at 248°C. The composition of the eutectic liquid is 2.25% by weight of magnesium. The limit of solubility in α phase at the eutectic temperature is 0.75% by weight of magnesium.

For Pb-Cd-Mg alloy [2] (Fig. 3), (Janecke studied carefully the structure of this ternary. Only lead corner of the ternary system is shown in Fig. 3. It is characterized by a ternary eutectic at the composition 18.9% cadmium, 1.8% magnesium and 79.3% lead to the temperature 194 ° C.

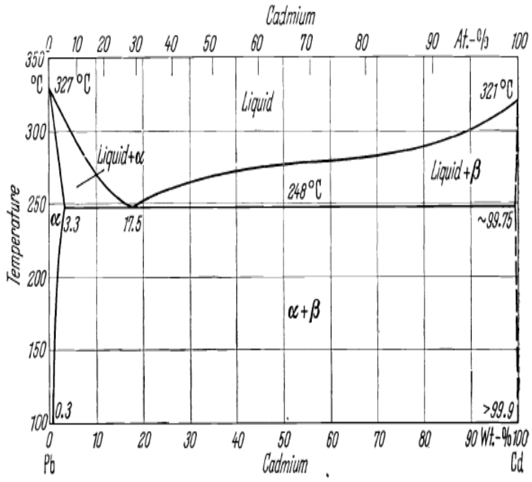

Figure 1. Pb-Cd phase diagram.

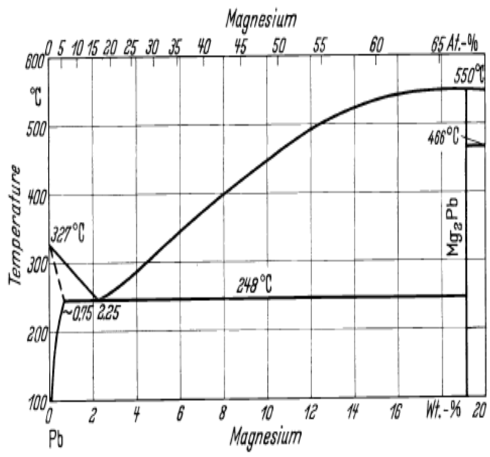

Figure 2. Pb-Mg phase diagram.

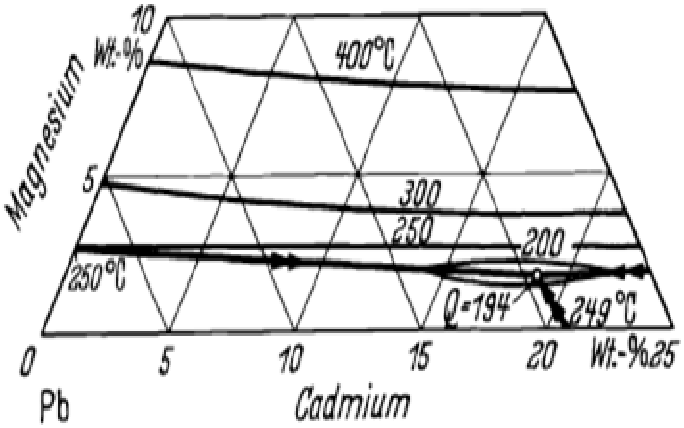

Figure 3. Pb-Cd-Mg phase diagram.

To study the structure of as-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 are 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 sealed under high vacuum. The entire bulb over samples is maintained at a temperature of 280°C for 2 hours (estimated optimal for rehomogenization) and then water quenched.

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 trucks 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= 0,3 R(MPa) can be used to evaluate the tensile strength (R) of these alloys.

Technical micrographic observation:

The physical properties of soaked solid solutions for lead alloys change from room temperature. The curing mechanisms correspond to transformations of continuous type and / or discontinuous. Indeed, this temperature corresponds to 0.5Tf, temperature at which the alloying elements can diffuse. The Observation of the structure of alloys corresponding to the continuous/discontinuous transformations is made by using the optical microscope, the samples must undergo mechanical polishing, chemical polishing using hydrogen peroxide 30% H_2O_2 and three share of glacial acetic acid for 20 seconds to 2 minutes, then chemical attack using 100g of ammonium molybdate; 250g citric acid and water in sufficient quantity to have a liter of the mixture [4].

3. RESULTS

3.1. STUDY OF THE ALLOY Pb2%Cd2% Mg:

Evolution of hardness

The hardening of the as-cast alloy Pb2%Cd2%Mg was carried out on aging at two temperatures 20°C and 80°C. Fig.4 shows the evolution of the hardness of this alloy as a function of time.

At 20°C, the supersaturated alloy has a hardness of about 14.5 HV exceeding twice that of pure lead whose hardness varies between 4 HV and 5 HV, which proves that the alloy undergoes a transformation during cooling.

The maximum of hardness (15.058 HV) is reached after 13 hours of aging. After this time, we see a stagnation of hardness which slightly decreased to achieve a value around 14.5 HV after 5 days and 12.48 HV beyond one month.

At 80°C, we find that there's an acceleration of the kinetic of hardening processing. Indeed, the maximum of hardness (14 HV) is reached after 10 minutes of aging, indicating that the discontinuous hardening processing is already completed at the time of solidification. After that, the hardness decreases to reach 13.28 HV after 2 days and 12.55HV after a month.

From the results obtained, magnesium stagnates hardness and increasing the temperature accelerates the hardening reaction.

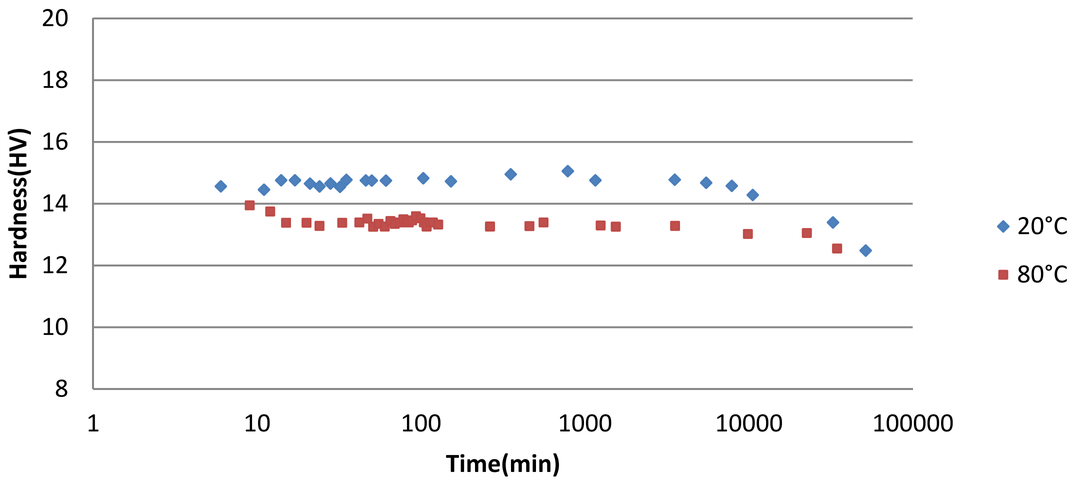

Figure 4. Evolution of hardness of crude casting alloy Pb2%Cd2%Mg at temperatures 20 °C and 80 °C versus time.

Evolution of quenching structure of the alloy Pb2% Cd2%Mg

The evolution of the quenching structure was observed under an optical microscope at 20 °C. After different maintains at that temperature; the Structural hardening of the crude casting alloy Pb2%Cd2%Mg is characterized by the appearance of a discontinuous transformations (Fig.5 and Fig.6).

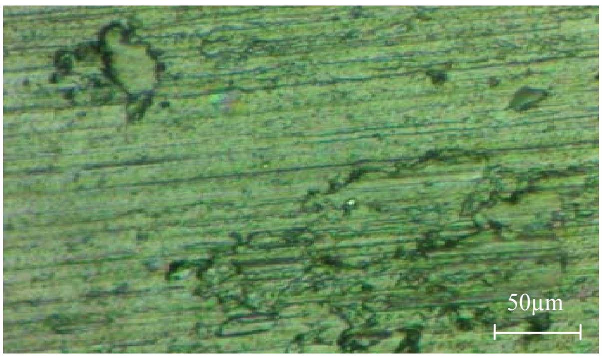

Figure 5. Visualization of discontinuous transformation of the crude casting alloy Pb2%Cd2% Mg quenched in water at 20°C after 2 days of quenching.

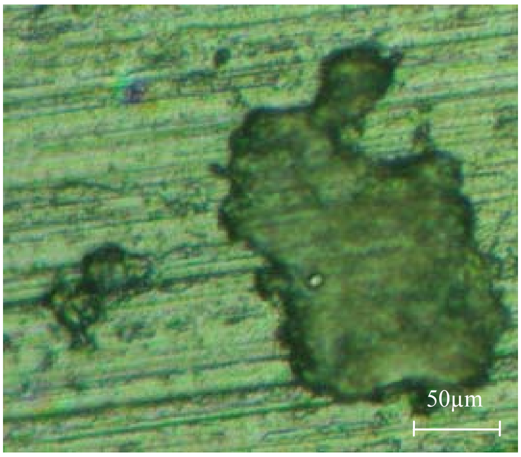

Figure 6. Visualization of discontinuous transformation of the crude casting alloy Pb2%Cd2% Mg quenched in water at 20°C after 2 days of quenching.

After three successive chemical attacks, we have been able to highlight; in a very clear manner; the displacement of transformation Front (Fig.7). This confirms that the transformations are discontinuous type.

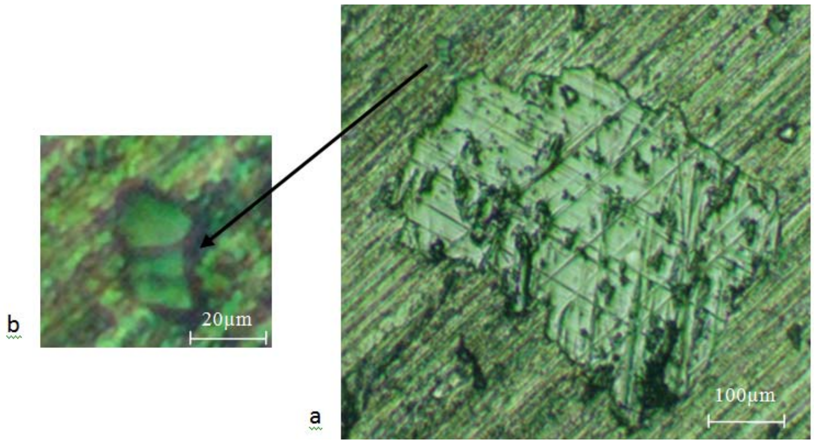

Figure 7. a) Visualization of discontinuous transformation of the crude casting alloy Pb2%Cd2% Mg quenched in water at 20°C after 3 days of quenching.
b) Visualization of displacement of transformation fronts after 3 successive chemical attacks of crude casting alloy Pb 2%Cd2% Mg quenched with water at 20 °C after 3 days of aging.

The development of the transformation is discontinuous during overaging. The precipitates of reactions that characterize aging coalesce into large precipitates. Indeed, observations with an optical microscope figures (Fig.8 and Fig.9) show the formation of large precipitates that characterize the over-aging.

Microhardness tests (Fig.10) performed on this alloy in areas transformed by the discontinuous processing and in areas non transformed by this transformations show that the latter are more hardened (about 15HV) and confirm that they are the seat of the continuous reaction.

Figure 8. Visualization of discontinuous transformation of the crude casting alloy Pb2%Cd2% Mg quenched in water at 20°C after 3 days of quenching.

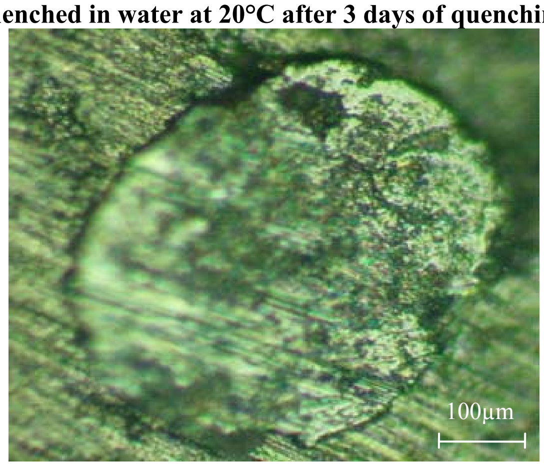

Figure 9. Visualization of discontinuous transformation of the crude casting alloy Pb2%Cd2% Mg quenched in water at 20°C after 3 days of quenching.

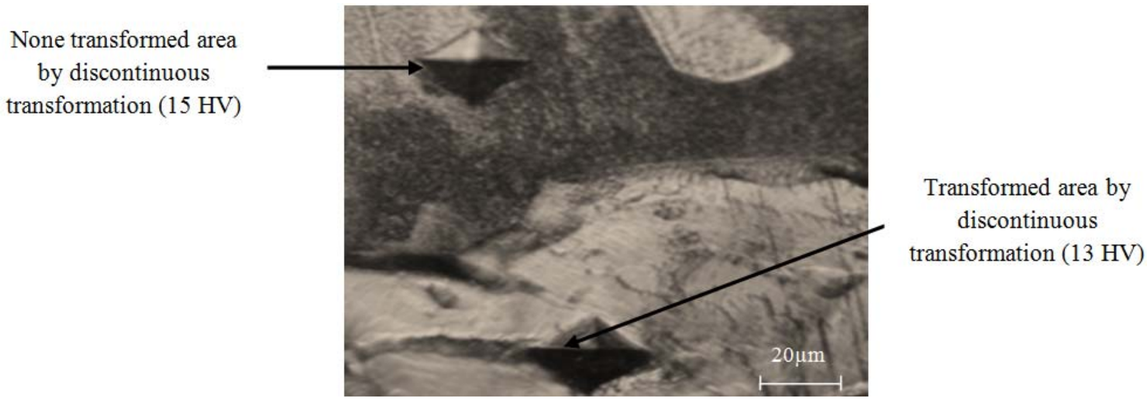

Figure 10. Visualization of footprints of micro hardness performed on the crude casting alloy Pb2%Cd2% Mg aged 2 days at 20 ° C.

Evolution of the structure at 80 °C

At 80 °C, structural hardening mechanisms are similar to those of 20 °C. Indeed, aging is characterized by the discontinuous processing and overaging by a coarse discontinuous precipitation. Moreover, the effect of the temperature results in acceleration of the kinetics of transformation that characterizes the structural hardening. Indeed, the appearance of the precipitate that characterizes overaging occurs after 10 minutes at 80 °C, whereas at 20 °C overaging does not appear just after 13 hours after tempering.

The optical microscope observation of the as-cast alloy Pb2%Cd2%Mg soaked with water and maintained at 80°C revealed the existence of the discontinuous processing that characterize overaging (Fig.11). Fig.12 shows the movement of discontinuous transformation fronts.

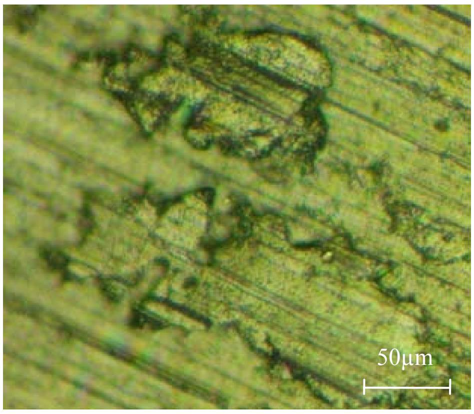

Figure 11. Visualization of discontinuous transformation of the crude casting alloy Pb2%Cd2% Mg quenched in water at 80°C after 6 hours of quenching.

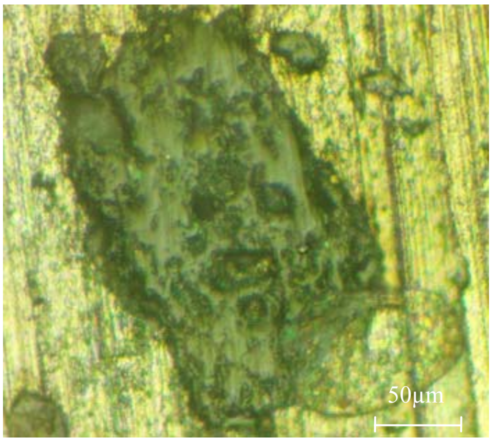

Figure 12. Visualization of discontinuous transformation of the crude casting alloy Pb2%Cd2% Mg quenched in water at 80°C after 7 hours of quenching.

For prolonged maintain at 80 °C, the discontinuous precipitation sweeps the majority of the matrix (Fig. 13) which coincides with the results of the hardness.

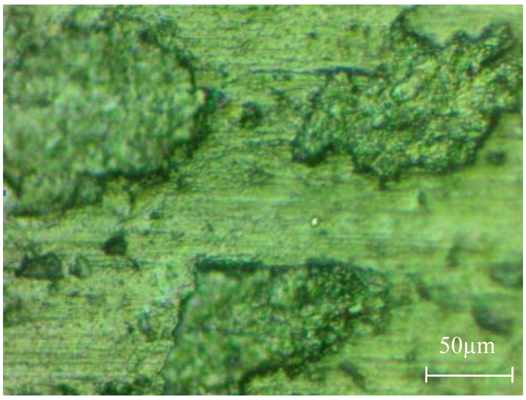

Figure 13. Visualization of discontinuous transformation of the crude casting alloy Pb2%Cd2% Mg quenched in water at 80°C after 2 days of quenching.

3.2. INFLUENCE OF CONCENTRATION OF MAGNESIUM (Mg)

To study the influence of the magnesium, three alloys PbCdMg with different compositions of magnesium were considered. The figure (fig.14) shows the changes of hardness with time on aging at 20°C for crude casting alloys Pb2%Cd1%Mg, Pb2%Cd2%Mg and Pb2%Cd3%Mg tempered in water.

By comparing hardness between the different compositions of magnesium, we acknowledge that a high concentration of magnesium delays the kinetic of the curing reaction and slightly increases the hardness.

Indeed, the value of the maximum hardness (14.652 HV) is reached after 4 hours for the alloy Pb2%Cd1%Mg, whereas the maximum hardness (15.058 HV) is reached after 13 hours for the alloy Pb2%Cd2%Mg, while the maximum value of hardness (15.2542 HV) is reached after 17 hours for the alloy Pb2%Cd3%Mg.

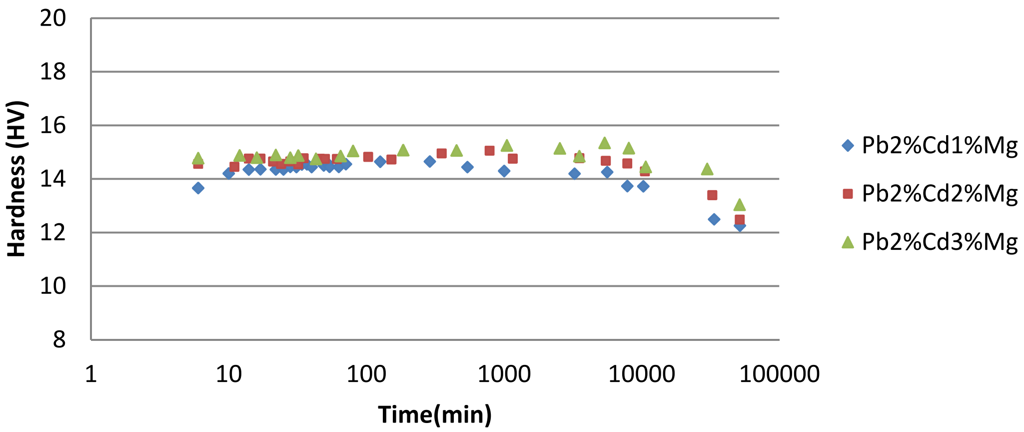

Figure 14. Evolution of hardness versus time at 20°C for as-cast alloys Pb2%Cd1%Mg, Pb2%Cd2%Mg and Pb2%Cd3%Mg.

The structures of the three alloys Pb2%Cd1%Mg, Pb2%Cd2%Mg and Pb2%Cd3%Mg were followed by optical microscopy; we found that the structural hardening mechanisms of these alloys are similar. Indeed aging is also characterized by a discontinuous transformation (Fig.15) and overaging is characterized by coarse precipitation (Fig.16 and Fig.17).

Furthermore, microscopic observations revealed the existence of transformation type S (Fig.18). This type of transformation was observed in PbCd and PbCa alloys [5].

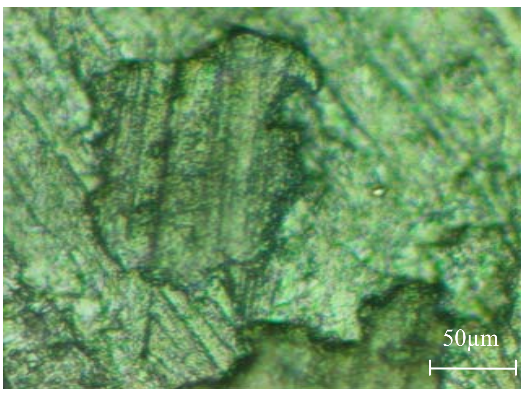

Figure15. Visualization of discontinuous transformation of the crude casting alloy Pb2%Cd3% Mg quenched in water at 20°C after 2 days of quenching.

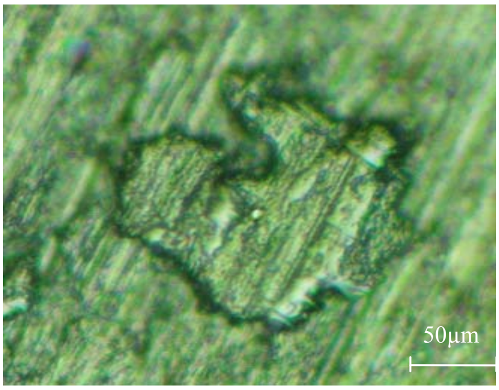

Figure 16. Visualization of discontinuous transformation of the crude casting alloy Pb2%Cd1% Mg quenched in water at 20°C after 4 days of quenching.

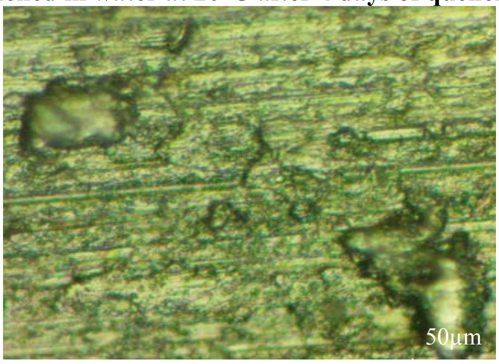

Figure 17. Visualization of discontinuous transformation of the crude casting alloy Pb2%Cd3% Mg quenched in water at 20°C after 6 days of quenching.

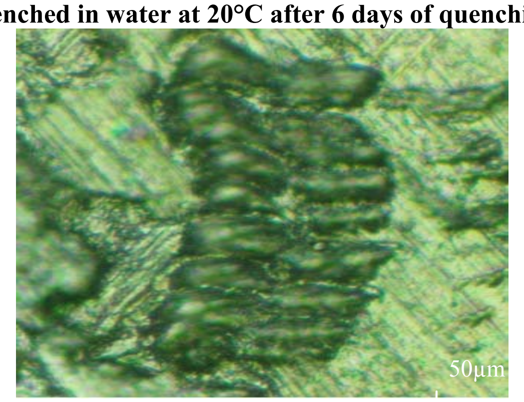

Figure 18. Visualization of discontinuous transformation type S of the crude casting alloy Pb2%Cd3%Mg quenched in water at 20°C after 6 days of quenching.

With a number of successive chemical attacks, we were able to highlight the movement of transformation fronts (Fig.19 and Fig.20).

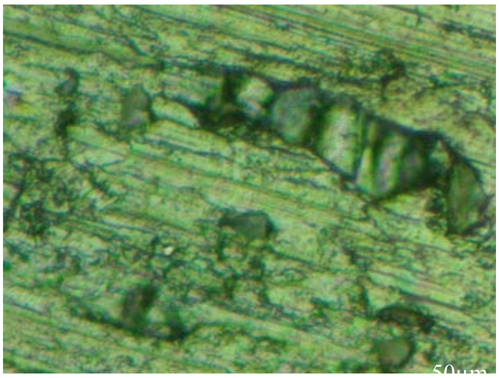

Figure 19. Visualization of movement of transformation fronts of the crude casting alloy Pb 2%Cd1% Mg quenched in water at 20°C after 4 days of quenching.

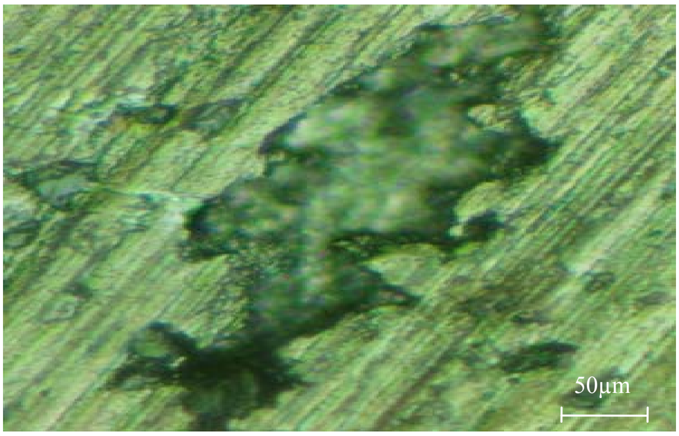

Figure 20. Visualization of movement of transformation fronts of the crude casting alloy Pb 2%Cd1% Mg quenched in water at 20°C after 4 days of quenching.

3.3. INFLUENCE OF REHOMOGENIZATION TREATMENT

Fig. 21 shows the variation of hardness as a function of time on aging at 20 ° C of the crude casting and rehomogenized alloy Pb2%Cd2%Mg. It is noted that the structural hardening mechanisms (Fig. 22) are similar in both cases, and the rehomogenization treatment has little effect on hardness. The effect of rehomogenization results in the disappearance of segregation cells which reduces precipitation sites. Furthermore, the transformation S (Fig. 23) was also observed in the rehomogenized alloy.

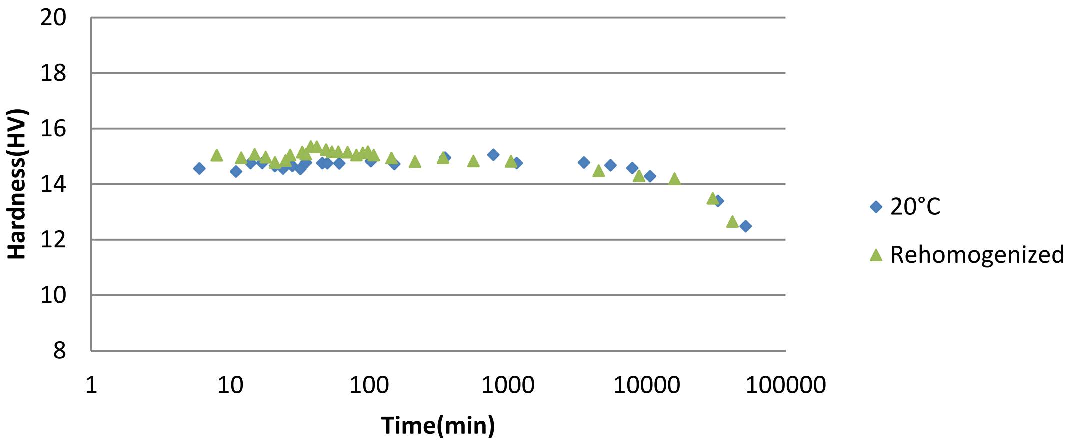

Figure 21. Evolution of hardness as function of time at 20°C, for the alloy Pb2%Cd2%Mg, as-cast and rehomogenized and then soaked in water.

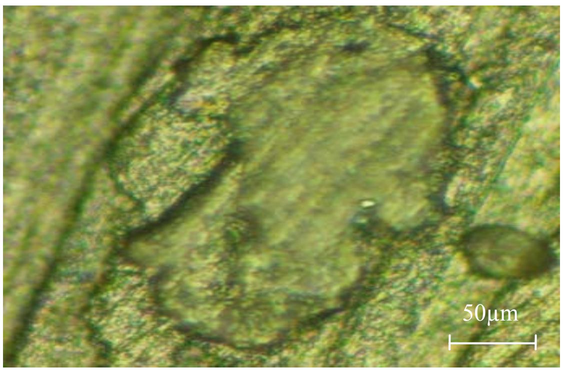

Figure 22. Visualization of the discontinuous processing of rehomogenized alloy Pb2% Cd2% Mg maintained at 20°C during aging after 1 day of quenching.

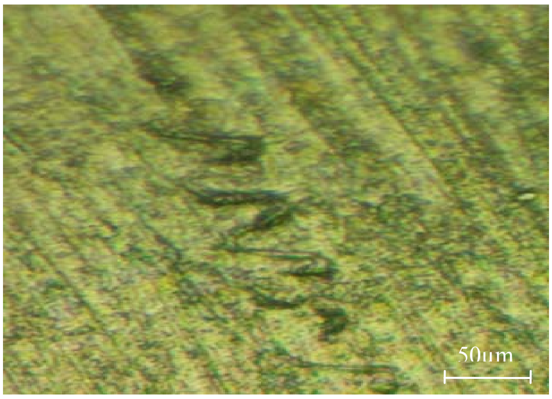

Figure 23. Visualization of discontinuous transformation type S of the rehomogenized alloy Pb2% Cd2% Mg quenched in water at 20°C after 1 day of quenching.

3.4. X RAY DIFFRACTION ANALYSES

Fig. 24 shows the result of XRD analysis of the alloy Pb2% Cd1% Mg.

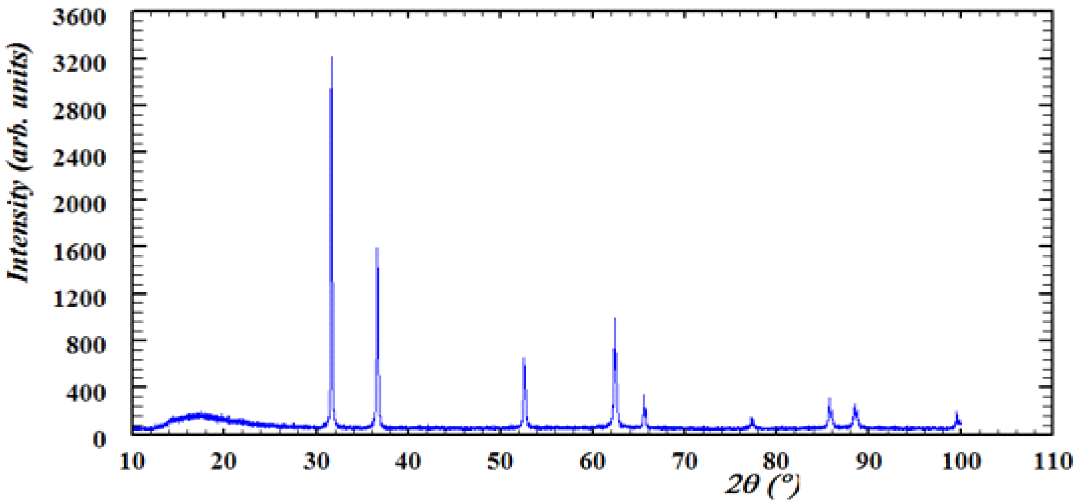

Figure 24. X-ray diffraction analysis of the surface of the crude casting alloy Pb2%Cd1%Mg.

According to X-ray diffraction analyzes (Table 1), we found that the alloy Pb2% Cd1% Mg is crystallized in a crystal structure Cubic face centered whose parameter a is of the order of 4.9167.

Table 1.Crystallographic parameters of the alloy Pb2%Cd1%Mg

2θ [6]	**2θ (Calculated)**	**d_{hkl}**	**hkl**	**Parameter a**
31.270	31.58789	2.80138	111	4.8521
36.262	36.50026	2.45088	200	4,9017
52.220	52.43229	1.73925	220	4,9193
62.139	62.52257	1.48433	311	4,9229
65.233	65.57621	1.42061	222	4,9211
76.985	77.12693	1.22942	400	4,9176
85.416	85.62401	1.13291	331	4.9382
88.189	88.41212	1.10370	420	4.9358
99.334	99.56453	1.00877	422	4.9419

Fig. 25 shows the result of XRD analysis of the alloy Pb2% Cd2% Mg.

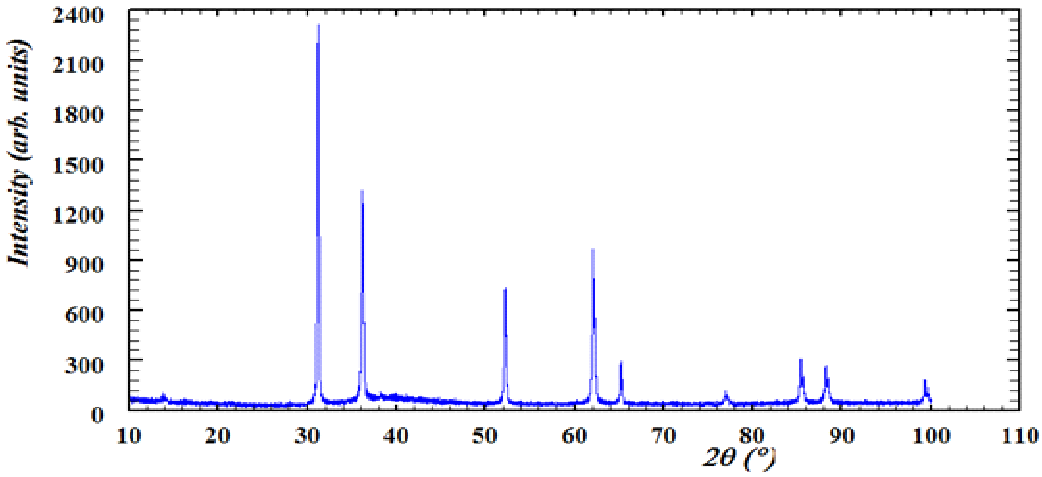

Figure 25. X-ray diffraction analysis of the surface of the crude casting alloy Pb2%Cd2%Mg.

According to X-ray diffraction analyzes (Table 2), we found that the alloy Pb2% Cd2% Mg is crystallized in a crystal structure Cubic face centered whose parameter a is of the order of 4, 9357.

Table 2.Crystallographic parameters of the alloy Pb2%Cd1%Mg

2θ [6]	2θ (Calculated)	d_{hkl}	hkl	Parameter a
31.270	31.05682	2.84387	111	4.9257
36.262	36.10196	2.47212	200	4,9442
52.220	52.03399	1.74987	220	4,9493
62.139	61.99150	1.48433	311	4.9229
65.233	65.17779	1.42061	222	4.9211
76.985	76.86139	1.22942	400	4.9176
85.416	85.35847	1.13383	331	4.9422
88.189	88.01381	1.10687	420	4.9500
99.334	99.16622	1.01008	422	4,9483

Fig. 26 shows the result of XRD analysis of the alloy Pb2% Cd3% Mg.

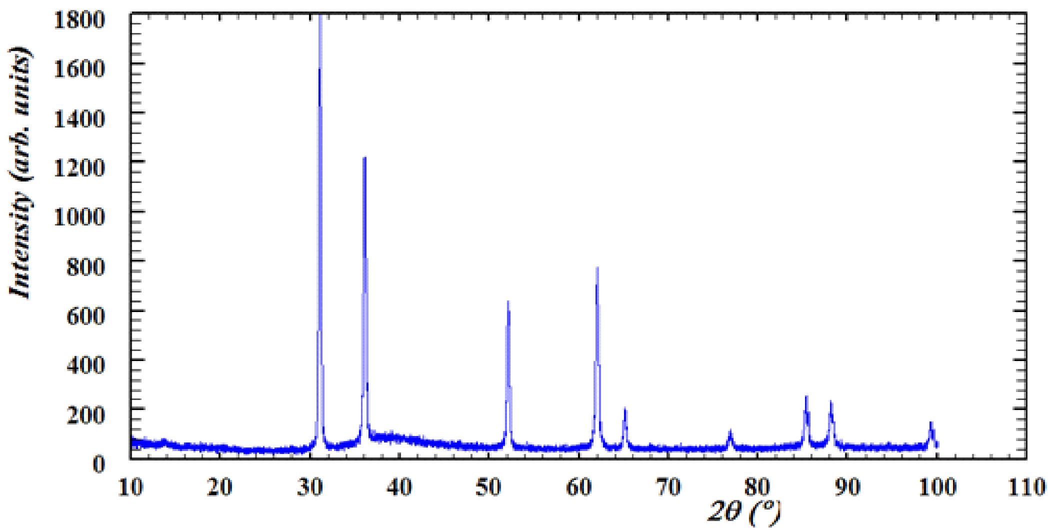

Figure 26. X-ray diffraction analysis of the surface of the crude casting alloy Pb2%Cd3%Mg.

According to X-ray diffraction analyzes (Table 3), we found that the alloy Pb2% Cd3% Mg is crystallized in a crystal structure Cubic face centered whose parameter a is of the order of 4, 9337.

Table 3.Crystallographic parameters of the alloy Pb2%Cd3%Mg

2θ [6]	2θ (Calculated)	d_{hkl}	hkl	Parameter a
31.270	30.92406	2.85449	111	4.94412
36.262	36.10196	2.48274	200	4.96548
52.220	52.03399	1.76049	220	4.97941
62.139	61.99150	1.48433	311	4.92296
65.233	65.04514	1.42061	222	4.92113
76.985	76.72862	1.22942	400	4.91768
85.416	85.22571	1.13383	331	4.94225
88.189	88.01381	1.09134	420	4.88062
99.334	99.19922	1.00637	422	4.93018

CONCLUSIONS

In this paper, we have described in a systematic way the hardening mechanisms of Pb-Cd-Mg alloys, whether from solidification temperature, or from rehomogenized temperature (280°C). We obtain an unstable supersaturated solid solution at 20°C. In this study, we concluded that:

– The evolution of quenching structure of Pb-Cd-Mg alloys to the equilibrium state occurs in two stages: the first is characterized by a hardening discontinuous transformation; the second occurs after overaging, it is characterized by softening coarse discontinuous precipitation.

– The kinetics of transformations characterizing the structural hardening mechanism of the Pb-Cd-Mg alloys is accelerated if the temperature is increased.

– Gradually as the magnesium concentration increases, the hardness increases slightly and the kinetics of changes characterizing the curing mechanisms of these alloys is slow.

– The dissolution of segregated phases during rehomogenization treatment increases the supersaturation after quenching by eliminating segregation cells from solidification structure. In the case of our PbCdMg alloys, rehomogenization treatment has made a slight increase in hardness because it increased by ~ 1HV.

– According to X-ray diffraction analysis carried out on the samples Pb2%Cd1%Mg, Pb2%Cd2%Mg et Pb2%Cd3%Mg; we see that it has able to highlight just the peaks corresponding to lead, this is due to the small size of additive elements.

Compared with the Pb-Cd alloys, we find that the addition of magnesium improved mechanical properties, particularly hardness which had a gain of about 2 HV for alloys maintained at 20 °C. Indeed the maximum hardness obtained at 20°C for Pb2%Cd is 13.8 HV, while those for alloys Pb2% Cd1% Mg, Pb2% Cd2% Mg and Pb2% Cd3% Mg are respectively 14,652 HV; 15,058 HV and 15,2542 HV.

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