ORIGINAL PAPER

SRUCTURAL HARDENING MECHANISM OF LEAD-CADMIUM-BISMUTH (TIN-SILVER) ALLOYS FOR BATTERY GRIDS

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Abstract. *The study back to the equilibrium state of Pb-Cd-Bi alloys was carried out by various experimental techniques such as hardness, microhardness, optical microscopy and X-ray diffraction. Two structural states were considered: raw casting alloy and rehomogenized alloy, their compositions are: Pb2% Cd1% Bi; Pb2% Cd2% Bi; Pb2% Cd3%Bi and Pb3.2% Cd2% Bi. The experimental temperatures are 20 °C and 80 °C. The latter one was chosen because it corresponds to the temperature of ripening of battery grids and the hot temperature for battery working. In general, the addition of bismuth accelerates the kinetics of transformation and hardness increases. While the addition of cadmium slightly increases the hardness and accelerates kinetics. The aging, which is the hardening step of the alloy, is still characterized by a discontinuous reaction and a hardening processing, while the overaging is characterized by a softening discontinuous precipitation.*

Keywords: *aging, alloys, battery grids, hardness, optical microscopy, continuous and discontinuous transformation*

1. INTRODUCTION

It is now widely recognized by the world that access to energy is a key element in developing societies. Lead-acid battery is a means having several applications in the automotive, a fact making it a major issue in energy storage in batteries, which reinforces more research and reinforces the fundamental study of its structural properties adapting to economic and ecological reasons. The choice of the lead acid battery requires the development of a grid characterized by corrosion resistance and improved mechanical properties.

The use of lead in batteries alone is excluded because of its softness, malleability and lack of hardness. 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.

Cadmium and bismuth are two additives that we have chosen to supplement the results found previously by Hilali et al. [1] in the case of adding cadmium to lead and Bouirden et al. [2] where bismuth was a minor additive. Cadmium is a malleable ductile metal having a good

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corrosion resistance in various atmospheres, while the element bismuth is deemed least toxic heavy metals.

Our goal is to study systematically the process of aging and over-aging of supersaturated solutions of PbCdBi hardened alloys. Indeed, two structural states are considered: the raw casting alloy and alloy rehomogenized. The influence of the addition of bismuth, cadmium and the kinetic study were studied. The techniques used are: hardness; microhardness, optical microscope 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 bismuth (99.99%). Phase diagrams of binary systems Pb-Cd; Pb-Bi; and Bi-Cd are shown successively in Figs. 1-3.

The binary system Pb-Cd alloy [3] (Fig. 1) represents a eutectic at 248 ° C. The eutectic liquid composition is about 17.5% by weight of cadmium. The solubility limit in the α-phase at the eutectic temperature is 3.3 wt% by weight of cadmium and at room temperature is 0.15% .We therefore chosen below the limit of solubility of the primary solid phase in compositions 2 and 3.2 % by weight of cadmium.

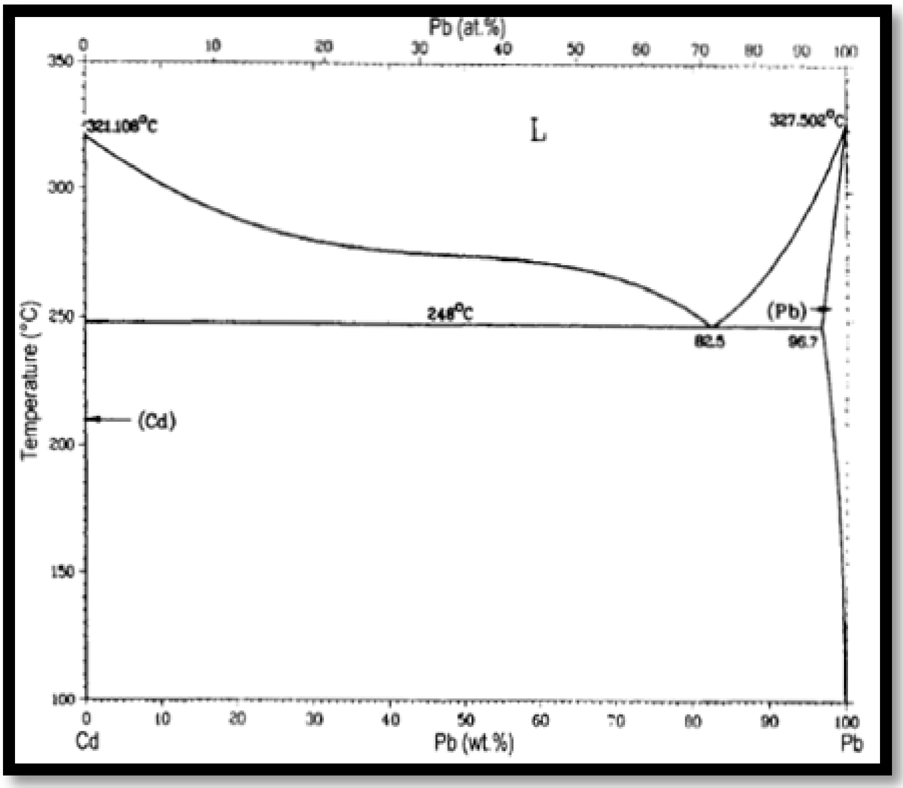

Fig. 1. Pb-Cd phase diagram [3].

The phase diagram of Pb-Bi alloys (Fig. 2) shows a large solid solubility of about 17.5 wt.% Bi in Pb at room temperature. The solubility at a temperature of 184°C is 23.5 wt. %. An eutectic reaction involving the intermediate β phase and the Bi terminal phase occurs at a composition of 56.5% Bi and a temperature of 125°C. So we chose the lower to the second terminal of the solid solution compositions.

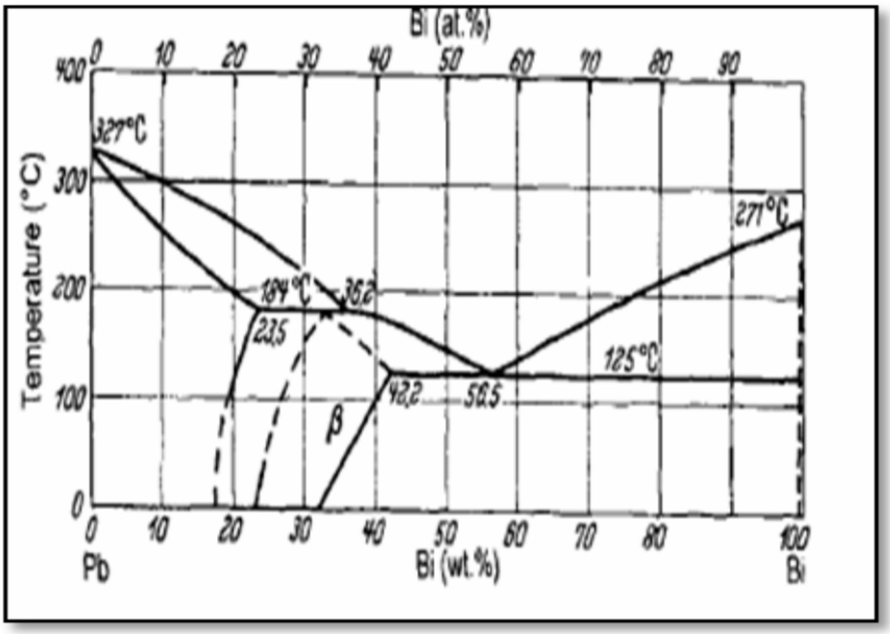

Fig. 2. Pb-Bi phase diagram [4].

For the binary system Bi-Cd alloys (Fig. 3), the Bi-Cd system is a simple eutectic with two solid phases (Bi) and (Cd). The eutectic composition is 55% Cd with a temperature of 146 °C.

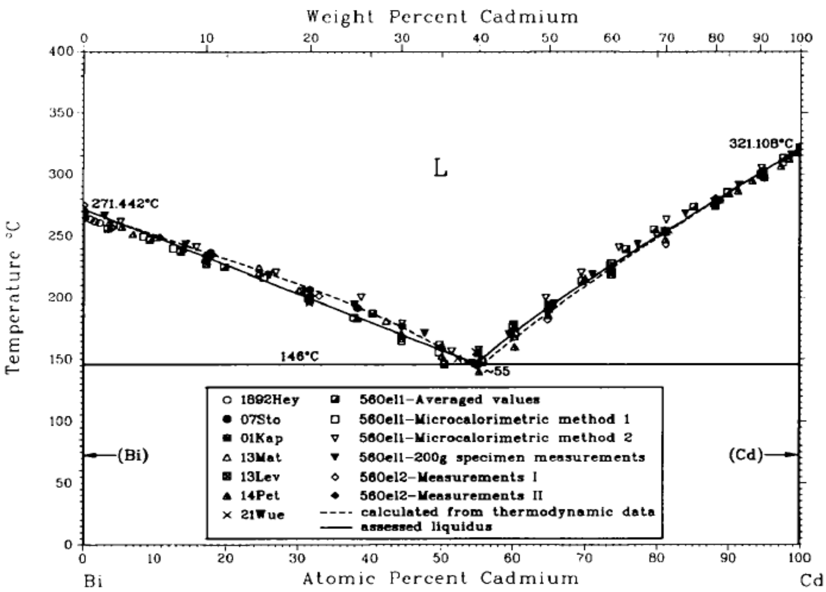

Fig. 3. Bi-Cd phase diagram [5].

We have developed alloys whose compositions are given in Table 1.

Table 1. Composition of the alloys studied.

Content weight %Cd	Content weight %Bi
2	1
2	2

2	3
3.2	2

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 in 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 264°C for 2 hours (estimated optimal for rehomogenization) and then water quenched.

2.2. HARDNESS

The hardness tests are carried out by the vickers method, using a duromètre 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 (MPa) can be used to evaluate the tensile strength (R) of these alloys.

2.3. TECHNICAL MICROGRAPHIC OBSERVATION

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 0.5Tf, temperature at which the alloying elements can diffuse. Observing 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; 250 g citric acid and water in sufficient quantity to have a liter of the mixture [6].

3. RESULTS AND DISCUSSION

3.1. STUDY OF THE ALLOY Pb2%Cd1% Bi

<u>3.1.1. Hardness measurement</u>

Fig. 4 shows the evolution of hardness depending on time of the alloy Pb2%Cd1% Bi gross of casting, temperature 20 °C and 80 °C. The alloy soaked oversaturated has a hardness of HV 11.38 which is almost double that of pure lead, the hardness varies between 4 and 5 HV, which proves that the alloy is partially transformed during cooling. At 20 °C; maximum hardness is 12.54 HV and is reached after 80 min, and then the hardness decreases slightly to 11.13 HV beyond one month. At 80 °C, the maximum hardening is reached after 84 min (13.1 HV), after 18 hours we see a stagnation of hardness decreases slightly after a month, peaking 11.3 HV. Furthermore, the influence of the temperature results in a slight increase in hardness.

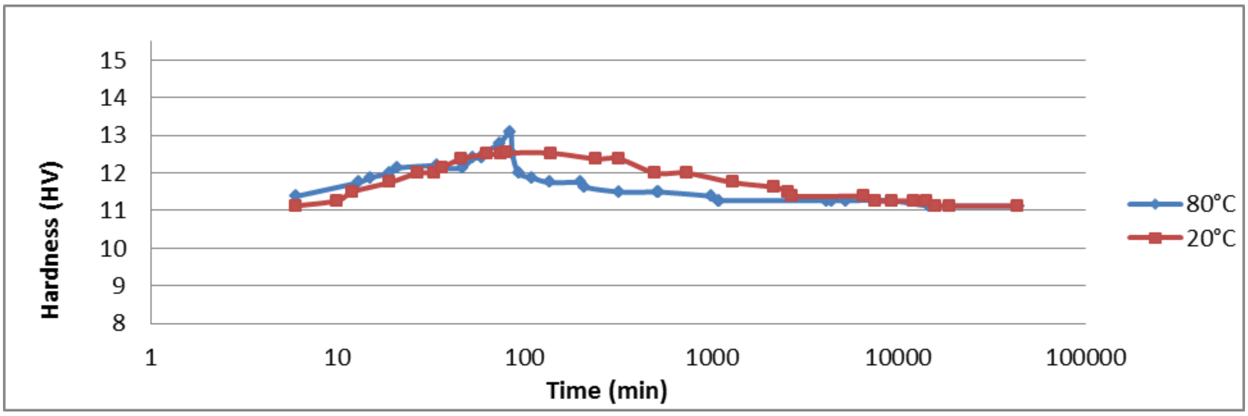

Fig. 4. Evolution of the hardness of the alloy Pb2%Cd1%Bi, as-cast as function on time-temperature 20°C and 80°C.

3.1.2. Evolution of the structure

The curing mechanisms can be determined by metallographic observations, when the increase in hardness is accompanied by displacement of the processing or fronts of the grain boundaries, is the batch type processing. Otherwise, it is a continuous reaction. Figure 5 shows the discontinuous transformation of the alloy Pb2% Cd1% Bi.

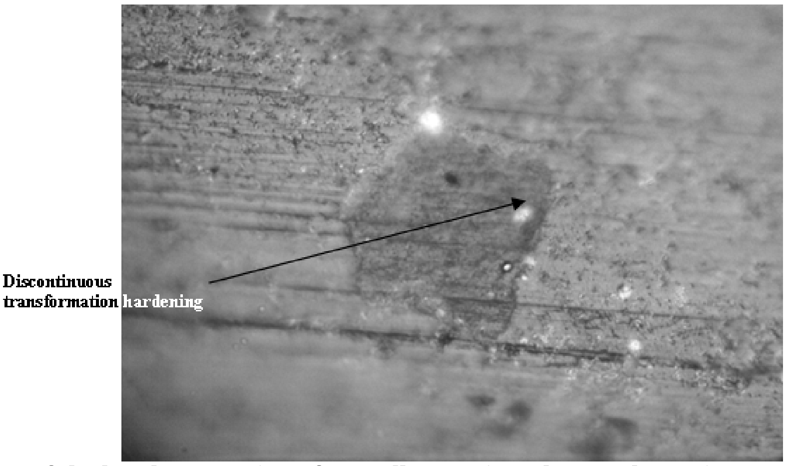

Fig. 5. Visualization of the batch processing of raw alloy casting Pb2% Cd1% Bi quenched with water at 20 °C during 10 min after aging hardening.

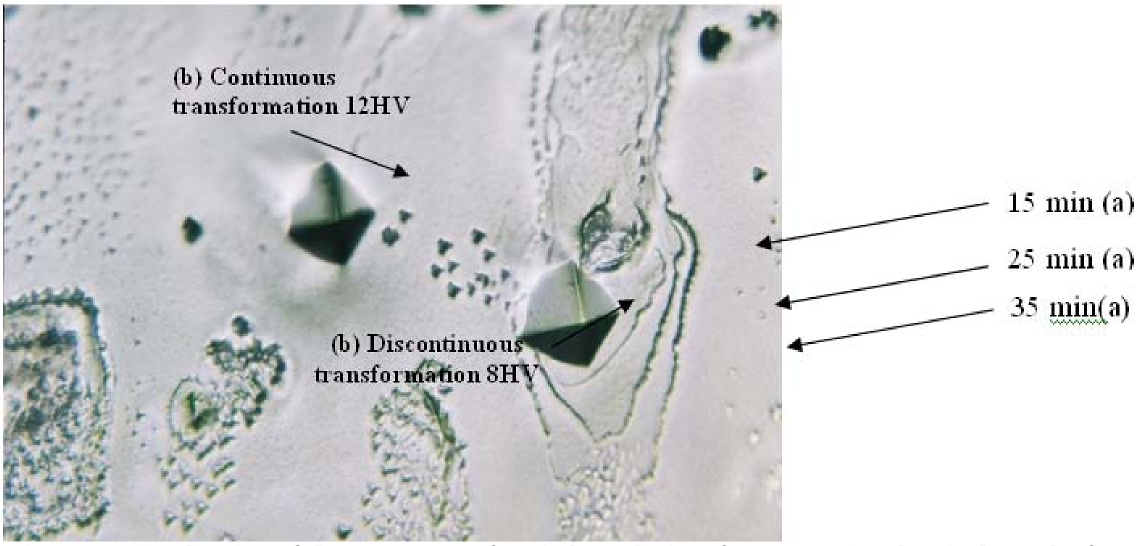

Fig. 6. a) Visualization of the movement of grain boundaries after successive chemical attack after quenching at 20 °C of the alloy Pb2%Cd1% Bi crude casting for 15 min, 25 min and 35 min. b) Viewing footprints micro hardness performed on the alloy Pb2%Cd1%Bi Gross casting aged 15 minutes at 20 °C.

For successive attacks, microscopic observations (Fig. 6a) show the progress of the batch reaction fronts transformation. Indeed, during the aging we observe the transformations movements fronts. They always grow in the grain boundaries. Microscopic observation shows the progress of these fronts after three successive attacks. After 15 min of aging, micro hardness testing (Fig. 6b) show that in the room temperature micro hardness of the batch processing is around 8 HV which is less than that processed by the continuous reaction with a hardness of about 12 HV. We therefore find that the aging of the alloy Pb2% Cd1% Bi is through a discontinuous transformation and continuous reaction hardening.

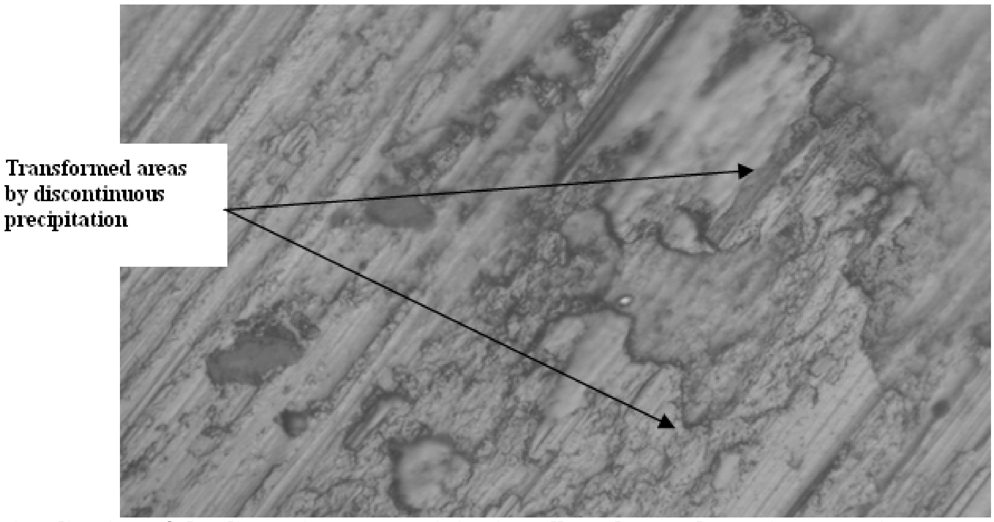

Fig. 7. Visualization of the discontinuous precipitation alloy Pb2%Cd1% Bi raw casting at 20°C after 1 hour and 40 minutes of quenching.

Precipitates characterizing overaging coalesce together to form large precipitates as shown in Fig. 7. Figs. 8 and 9 show the development of the discontinuous precipitation during the averaging; the supersaturated matrix was scanned by precipitates, which provides further evidence of the reduced hardness.

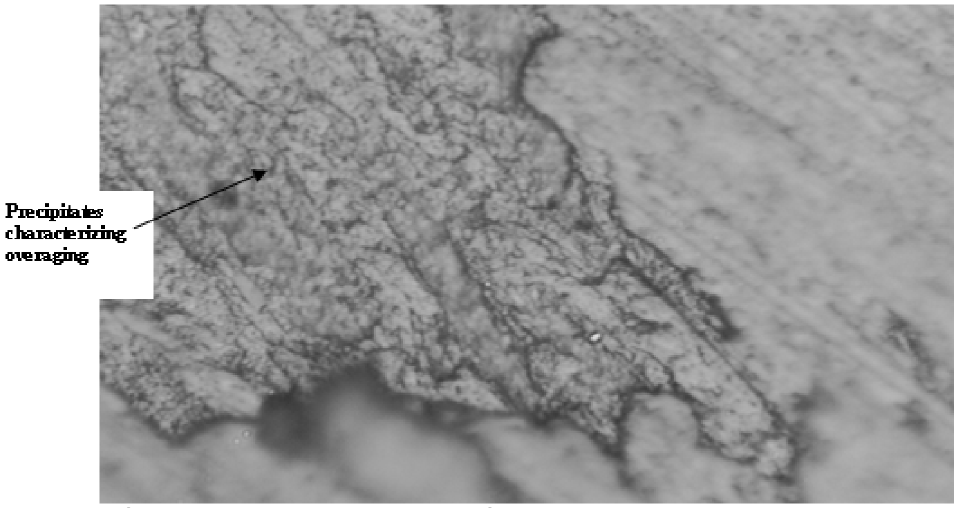

Fig. 8. Visualization of the discontinuous processing of the alloy Pb2%Cd 1% Bi raw casting at 20°C after 15 days.

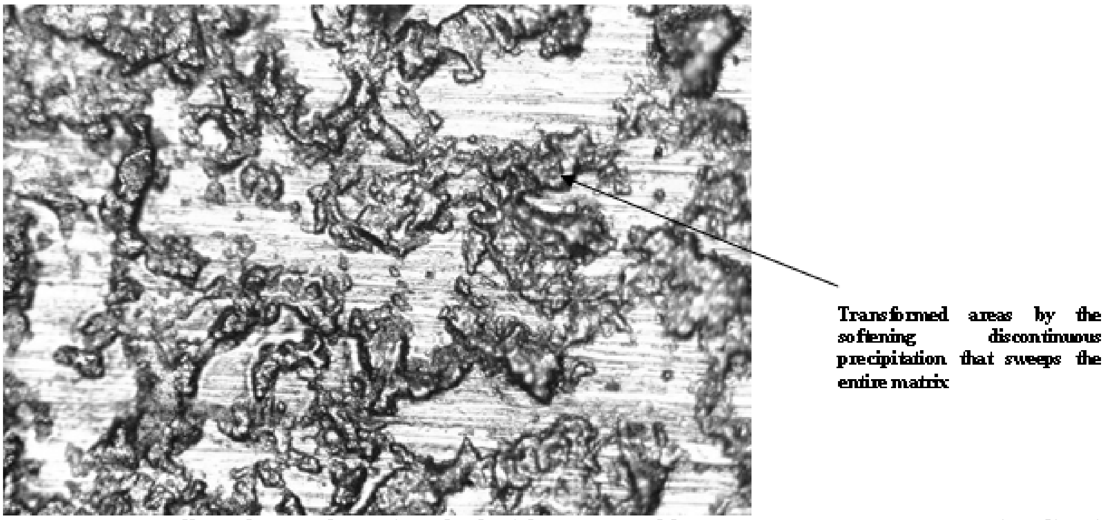

Fig. 9. gross cast alloy Pb2%Cd1%Bi soaked with water and kept at room temperature. Visualization of the discontinuous precipitation after 1 month 3 hours and 45 min.

3.1.3. INFLUENCE OF CADMIUM (Cd)

To study the influence of cadmium, we worked on two different compositions: Pb2% Cd2% Bi and Pb3.2% Cd2% Bi. The evolution of the hardness is shown in Fig. 10 below.

Cadmium as shown in Fig. 10 amplifies the maximum hardening which further allows the distinction of continuing precipitation. Indeed; increasing the concentration of cadmium leads to the attenuation of the movement of grain boundaries and thus decrease the speed of movement of these joints which influence the transformation. Concerning overaging; and in the case of low levels of cadmium; processes are accelerated.

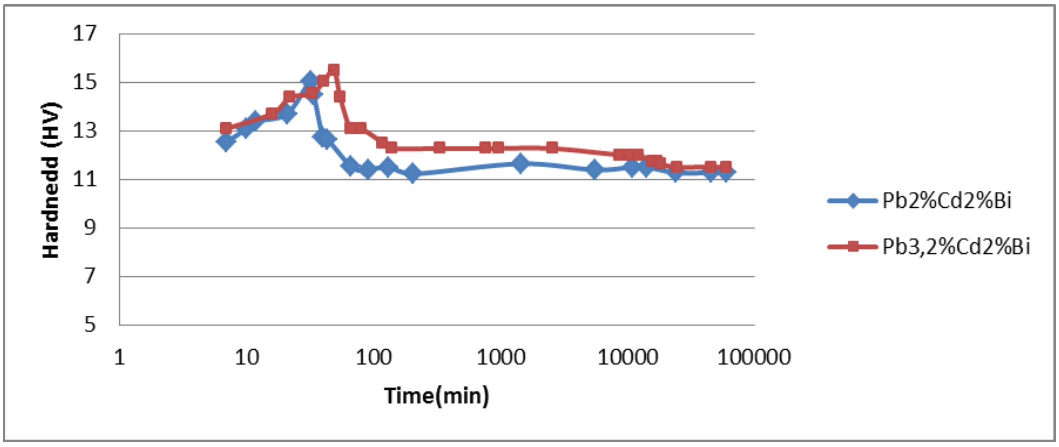

Fig. 10. Evolution of the hardness as a function of aging time at room temperature of gross casting alloys Pb2%Cd2%Bi and Pb3, 2%Cd2%Bi, soaked later with water.

Fig. 11 shows the discontinuous transformations of gross cast alloy Pb2%Cd2%Bi during aging (a) and overaging (b).

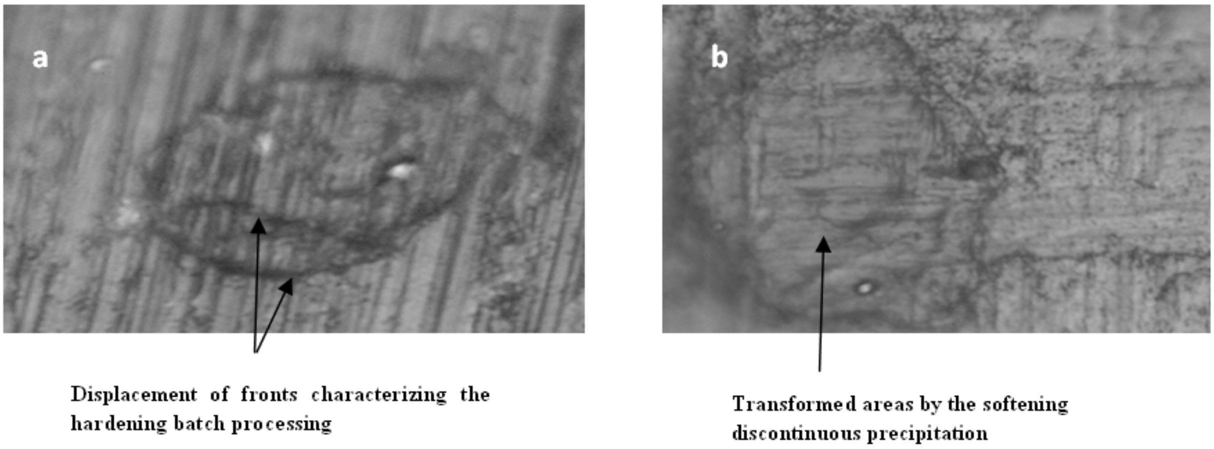

Fig. 11. a) Evolution of the structure of tempering at 20°C for alloy Pb2%Cd2%Bi, as-cast. Visualization of the discontinuous transformation after several successive chemical attacks for 10 min.
b) Alloy Pb2%Cd2%Bi, as-cast, aging one day at room temperature. Occurrence of discontinuous precipitation characterizing the overaging.

3.1.4. INFLUENCE OF Bi

To study the influence of bismuth, we worked on three different compositions: Pb2% Cd1% Bi; Pb2 %Cd2% Bi and Pb2%Cd3% Bi. The evolution of the hardness is shown in Fig. 12 below.

By comparing between the different hardness of bismuth compositions, we notice that a high concentration of bismuth accelerates the kinetics of the curing reaction and increase the hardness. Indeed, in the case of the alloy of bismuth highly charged, the maximum hardness (16HV) is reached after only 22 min in contrast to the alloy lightly charged in Bi; the maximum hardness (12.5) is reached after 80 min.

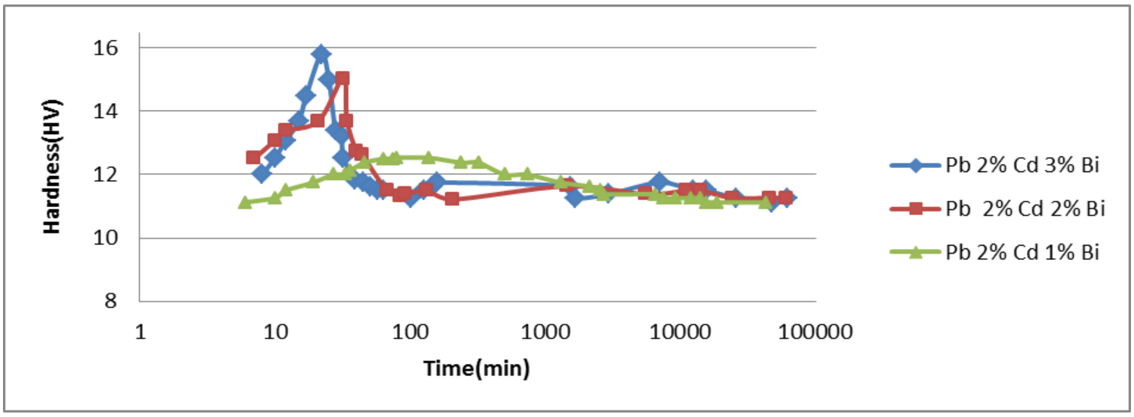

Fig. 12. Evolution of the hardness as a function of aging time at room temperature of gross casting alloys Pb2%Cd1%Bi, Pb2%Cd2%Bi and Pb2%Cd3%Bi, soaked later with water.

During overaging, there's no significant effect on the hardness and also the structure as shown in Figs. 13 and 14.

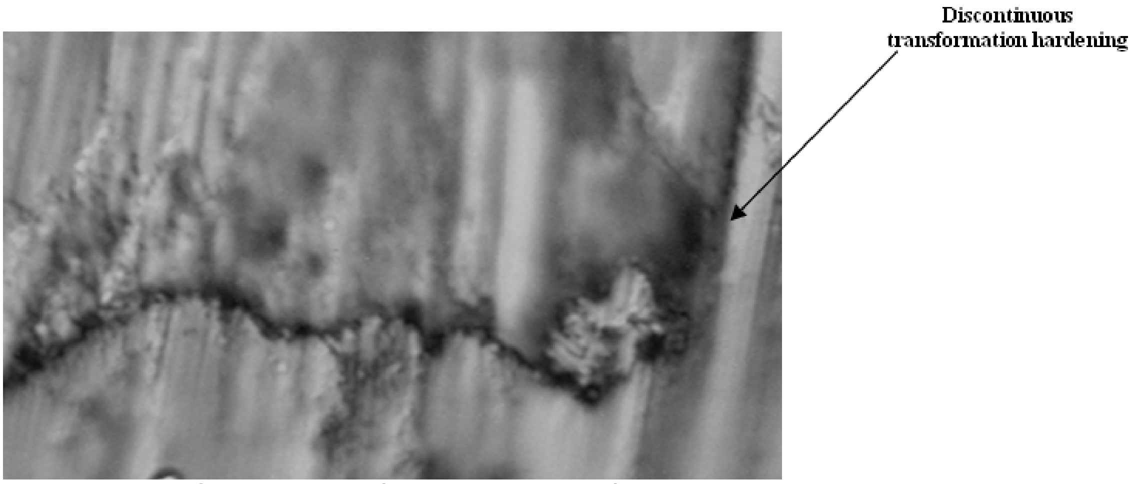

Fig. 13.Evolution of the structure of tempering at 20°C for alloy Pb2%Cd3% Bi, as-cast. Visualization of the discontinuous transformation after several successive chemical attacks for 8 min at room temperature.

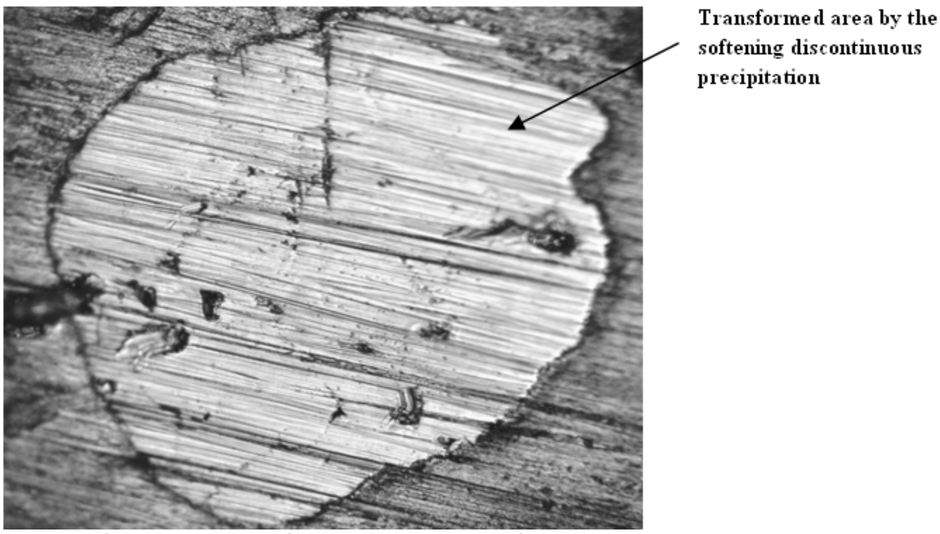

Fig. 14. Evolution of the structure of tempering at 20°C for alloy Pb2%Cd3% Bi, as-cast. Visualization of the softening discontinuous transformation after several successive chemical attacks for 20 days at room temperature.

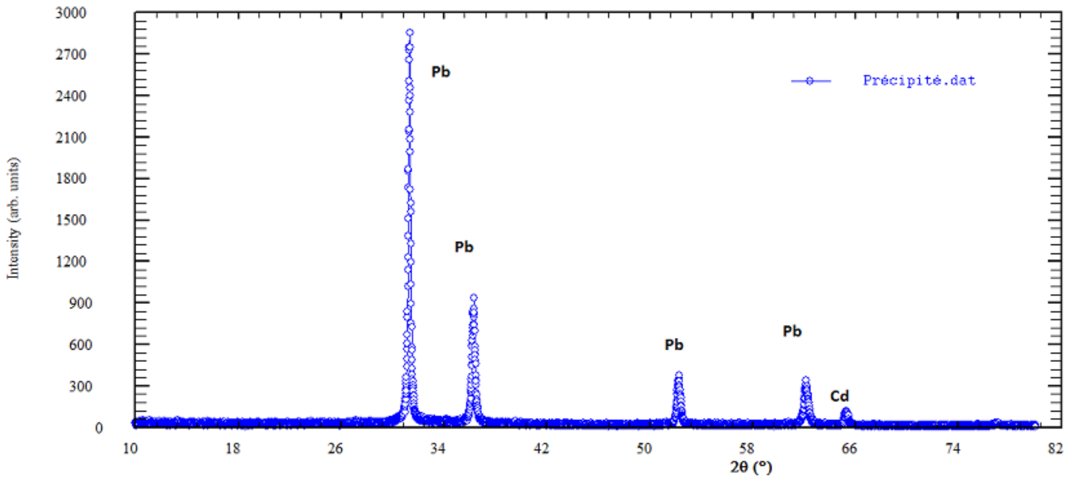

Fig. 15. X-ray diffraction of the alloy Pb2% Cd1% Bi raw casting, water quenched at 20°C after 3 months of aging.

The X-ray diffraction analyses (Fig. 15) shows that the precipitates are formed of lead and cadmium, Contrary to the matrix which is composed of lead and bismuth. The effect of that is explained by the influence on the kinetics of the transformations that characterize the hardening of the alloy Pb2% Cd1% Bi.

Table 2: values of maximum hardness at 20 °C for Pb-Cd [1], Pb-Cd-Bi and Pb-Ca-Cd [7], raw casting and then quenched in water.

Raw casting alloys		**Maximum hardness HV**
Pb-Cd[1]	Pb1%Cd	11
	Pb2%Cd	14
	Pb3,2%Cd	15
Pb-Cd-Bi	Pb2%Cd1%Bi	12.53
	Pb2%Cd2%Bi	15.05
	Pb2%Cd3%Bi	16
	Pb3,2%Cd2%Bi	15.5
Pb-Ca-Cd[7]	Pb2%Cd0,058%Ca	13
	Pb2%Cd0,093%Ca	16
	Pb2%Cd0,1%Ca	15

Compared to studies on PbCd [1], PbCaCd [7] alloys, which are reported in the literature, we find that PbCdBi alloys highly charged in bismuth (2% and 3% Bi) and highly charged in Cd (2% and 3.2% Cd) show a remarkable improvement in the hardness compared to other alloys (see table 2).

3.1.5. INFLUENCE OF REHOMOGENIZATION

Rehomogenization process reduces, by diffusion, the heterogeneity of composition due to segregation phenomena which appear in the solidification structure. In order to study, the influence of these cells of segregation on the aging and over-aging behavior of our raw casting alloys, we proceed by comparison with a parallel study on samples rehomogenized to 264°C.

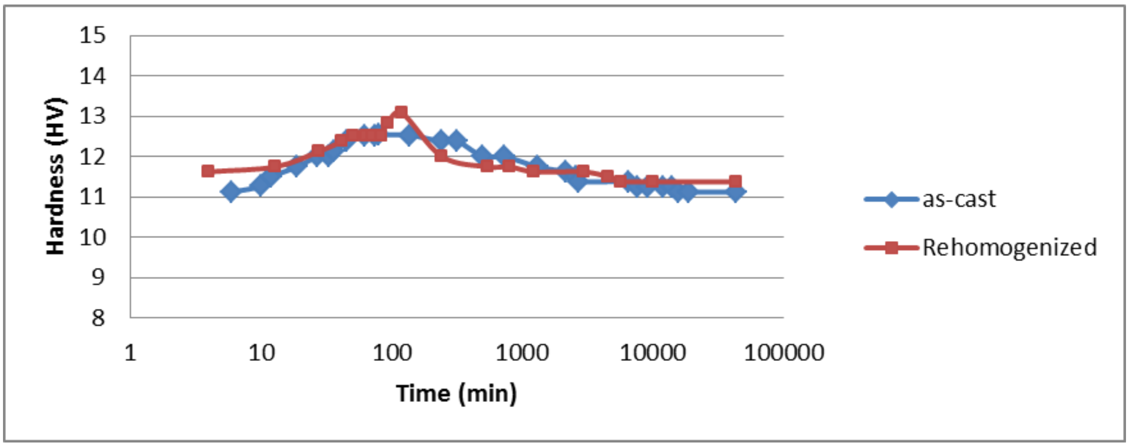

Fig. 16. Evolution of hardness as function of time at 20°C, for alloy Pb2%Cd1%Bi, as-cast and rehomogenized and then soaked in water.

Fig. 16 shows the variation of hardness as a function of time at room temperature for Pb2% Cd1% Bi alloys crude casting and rehomogenized and then soaked in water. Aging mechanisms for rehomogenized alloy are similar to those of the raw casting alloy, while the kinetics of the latter seems more accelerated. For overaging, no significant effect is observed; the hardness is the same in both alloys. Indeed, the final hardness observed after one month of keeping at 20°C of these alloys is in the order of 11,13HV for casting and 11.38HV for rehomogenized (See Fig. 16).

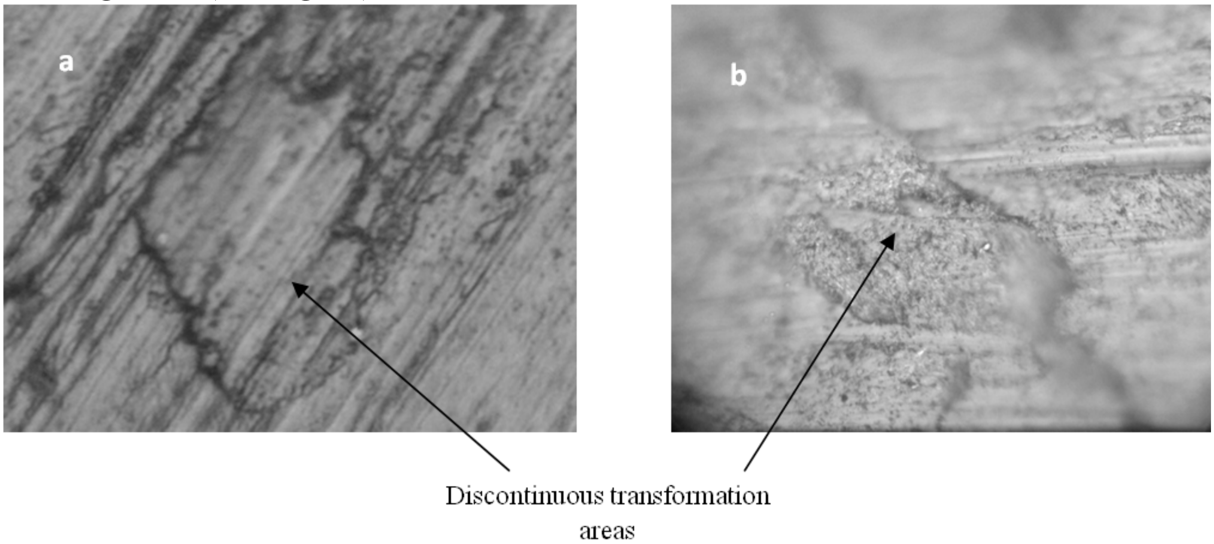

Fig. 17. a) Alloy Pb2% Cd1% Bi rehomogenized and then water quenched, aged 10 min at room temperature. Occurrence of discontinuous precipitation.
b) Alloy Pb2%Cd1% Bi rehomogenized and then water quenched, aged 2 hours at room temperature. Occurrence of discontinuous precipitation.

Furthermore, the influence of rehomogenization results in an increase in hardness, in fact, the maximum hardness goes from 12.5 HV (crude casting alloy) to 13.08 HV (rehomogenized alloy). Microscopic observations (see Fig. 17) show that the mechanisms of hardening of rehomogenized alloys are similar to that of the raw alloy casting. In fact aging is characterized by a discontinuous processing and a continuous hardening reaction and overaging is characterized by a softening discontinuous precipitation.

4. KINETIC STUDY OF THE SOFTENING DISCONTINUOUS PRECIPITATION WICH CHARACTERIZES THE OVERAGING OF Pb2%Cd1%Bi ALLOY

The kinetics of the softening discontinuous precipitation of the Pb2% Cd1% Bi alloy which characterizes the overaging was studied by jointly the hardness measurements. Heat treatments were performed at temperatures 20 °C and 80 °C for times ranging from 6 min to 1 month and applying the law of Johnson Mehl-Avrami [8]. We were interested in the kinetic study to the overaging. In fact, the kinetics of the transformations that characterizes aging is accelerated; and therefore we can not determine the initial hardness immediately after quenching.

4.1. DEGREE OF ADVANCEMENT OF THE REACTION

Fig. 18 shows the changes in the advancement degree x of the transformation according to ln (t) for different temperature 20°C and 80°C. Sigmoid curves, elongated along the time axis are obtained. Variations in the degree of advancement at temperatures 20°C and 80°C are deduced from hardness measurements of Fig. 4 relating to overaging.

The degree of advancement x is calculated from the following relation:

$$x = \frac{HV(t) - HV(0)}{HV(\infty) - HV(0)}$$

with:

- HV(t): hardness at the time (t)
- HV(0): The initial hardness of the discontinuous precipitation = the maximum hardness
- HV(∞): The final hardness

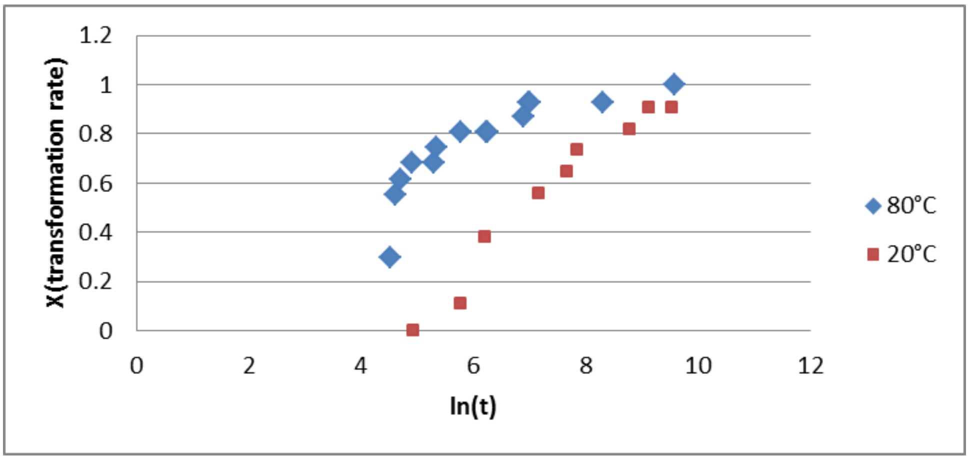

Fig. 18. Pb2%Cd1%Bi, semi logarithmic transformed of curves hardness testing in 20°C and 80°C temperatures for the softening discontinuous precipitation of raw casting alloy water quenched.

4.2. APPLICATION OF EQUATION MEHL AND JOHNSON

Fig. 19 represents the variations of $LogLog\left(\frac{1}{1-x}\right)$ as function of $Log\left(t-\tau\right)$.

The start time τ of this transformation are respectively 80 min and 84 min for 20°C and 80°C temperatures. This figure shows that the various points are placed on straight lines. The progress of this reaction is consistent to the johson and Mehl-Avrami [8].

Table 3 gives the values of the exponent n calculated from the slope of the lines in Fig. 19 and the rate constants k for the different temperatures. The value of n is close to 0.54 for both temperatures 20°C and 80°C.

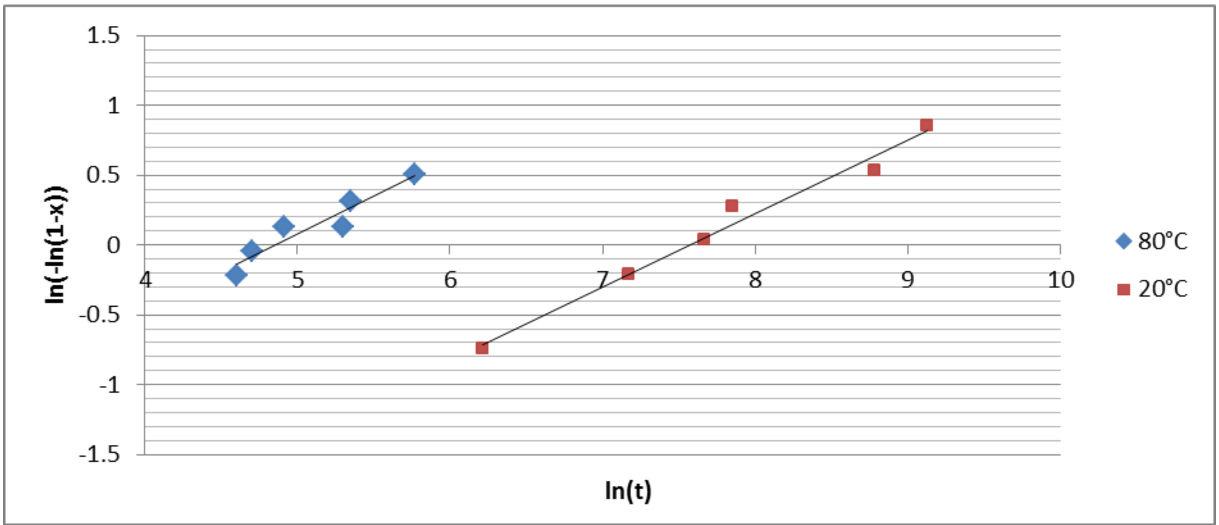

Fig. 19. Representation Ln (-ln (1-x)) according to ln (t) relative to the softening transformation by overaging studied isothermal changes in hardness of the alloy where% Pb2 Cd1% Bi raw casting.

Table 3. Coefficients of the equation of Johnson and Mehl-Avrami at different temperatures during overaging in the case of the alloy Pb2%Cd1% Bi crude casting water quenched.

Temperature (°C)	n	k [s^{-1}]
20	0.52	$5.12.10^{-4}$
80	0.54	$7.768.10^{-3}$

According to Table 3, we see that the values of n are almost the same for both temperatures, so, we can deduce that the reaction mechanism of the softening precipitation is simple.

4.3. DETERMINATION OF THE APPARENT ACTIVATION ENERGY

The apparent activation energy can be calculated from the variation of the coefficient k as a function of temperature. Indeed, in the case where it has an immediate saturation of the sites, the germination rate becomes null and the speed of the front obeys to the equation:

$$k = k_0 \exp\left(-\frac{Q}{RT}\right)$$

this is none other than the Arrhenius equation, with:

- k_0: rate constant
- Q: activation energy related to the progress of the reaction front.
- T: the absolute temperature in degrees Kelvin.
- R: universal constant of ideal gas R =8.32 J·mol^{-1}·K^{-1}

It should be noted however that this expression implicitly assumes that the total number of nuclei formed is independent of temperature. This expression allows reaching the activation energy value on the proposed kinetic regime. Through logarithmic representation linearized:

$$Log\left(\frac{k_1}{k_2}\right) = -\frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Assuming that k varies according to the Arrhenius law $k = k_0 \exp\left(-\frac{Q}{RT}\right)$ from the two values of the coefficient k of Johnson Mehl-Avrami Equation relating to temperatures 20°C and 80°C which characterizes the kinetics of transformation during overaging in the case of the alloy Pb2% Cd1% Bi crude casting quenched with water, the equation:

$$Log\left(\frac{k_1}{k_2}\right) = -\frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Gives a Q apparent activation energy associated with this reaction is about 39.03 KJ / mol.

To verify that the activation energy does not depend on the advancement degree, we will use the Bruke method [8] that can calculate the activation energy without explaining the function that represents the experimental curves. This method involves measuring the tx time to reach a specified rate x of precipitation. Log tx values are represented as a function of 1 / T in figure 20 for various values of x. The slope of these lines still substantially constant with x, and determines an apparent activation energy Q whose values are recorded in Table 4 These values are close to the value of the activation energy 39.03 kJ / mol given by Bruke method [8].

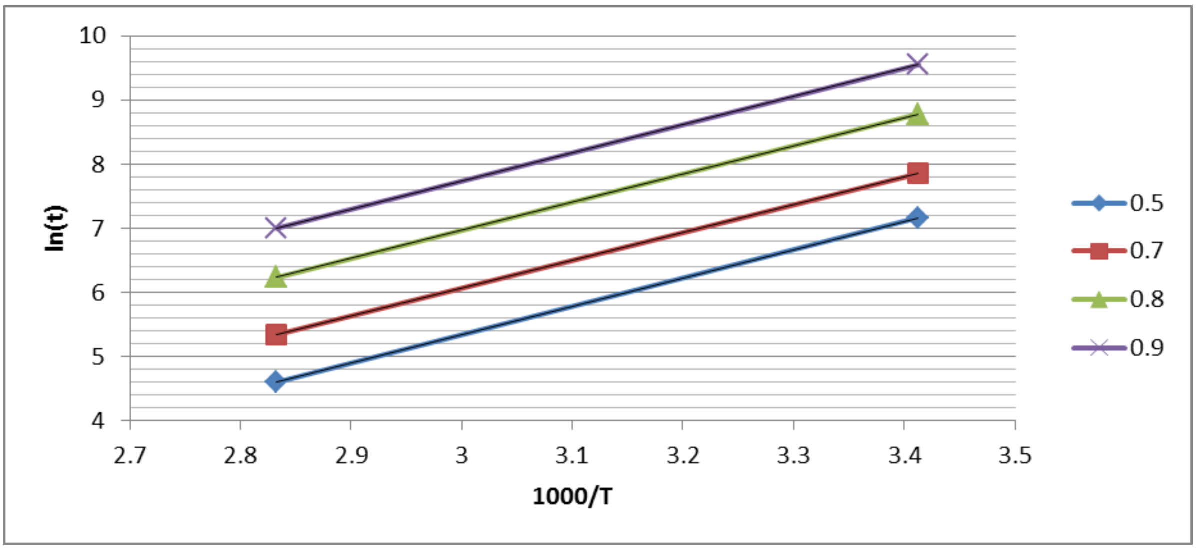

Fig. 20. Gross casting alloy Pb2%Cd1%Bi. Variation of Log t_x as function of 1/T.

Table 4: Values of the apparent activation energy Q for different rates of transformation in the case of crude casting alloy Pb2% Bi Cd1% water quenched.

Degree of advancement x	Apparent activation energy Q in [kJ/mol]
0.5	38.79
0.7	38.25
0.8	37.60
0.9	37.42

From Table 4, we find that the activation energy still constant, it does not depend on the degree of advancement, it is about 38.02 kJ / mol. The value obtained clearly explains the accelerator effect of bismuth on discontinuous precipitation that characterizes aging of Pb2%Cd1% Bi crude casting alloy.

5. CONCLUSIONS

The hardening of ternary alloys Pb-Cd-Bi is characterized by hardening and softening transformations. Indeed, aging is manifested by a curing discontinuous reaction which takes place in parallel with a discontinuous transformation initiating at grain boundaries. Furthermore overaging is corresponding to a discontinuous precipitation allowing the formation of precipitates Cd type, occupying; over time; the area of the matrix. The overaging is completed by softening and a decrease in the mechanical properties.

The increase in temperature has no significant influence on the hardness since it raised 0.5 HV at 80 ° C for the alloy Pb2% Cd1% Bi Gross casting.

Minor additions of cadmium lead slower kinetics hardening and a slight increase in hardness. We think that this retarding effect, promoting the continuous precipitation, is probably due to the presence of cadmium which makes the movement of grain boundaries more difficult.

The effect of ternary bismuth element results in acceleration of the kinetics of transformation and an increase in hardness. The effect of bismuth results in acceleration of germination of the continuous reaction and discontinuous precipitation.

The aging mechanisms of rehomogenized alloy are similar to those of raw casting alloy. Indeed, raw casting alloy seems accelerated in its kinetics. Comparing the hardness curves, with rehomogenized and gross casting for the same composition of Cd and Bi, we note that the presence of segregation cells has a significant effect on aging.

The calculation of the activation energy shows that it stays constant, it does not depend on the degree of advancement, and it is about 38 to 39 kJ / mol. The value obtained clearly explains the accelerator effect of bismuth on discontinuous precipitation that characterizes-aging of PbCdBi alloys.

Finally, comparing hardness levels achieved by PbCdBi alloys and given by PbCd and PbCdCa alloys emphasizes the beneficial effect of bismuth on the mechanical properties. As well, in view of economic requirements and improvements procured by minor additions of bismuth in mechanical properties, it appears that the alloys highly charged with Bismuth (2 and 3% by weight of Bi) and highly charged with cadmium (2 and 3.2% by weight of Cd) are the most conducive to industrial development.

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