



## Short communication

## Influence of the cooling rate on the ageing of lead–calcium alloys

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## ABSTRACT

Cast lead–calcium alloys were known to be sensitive to experimental parameters, which cause large variations on the ageing and overageing behaviour. From the study of these parameters, the quenching rate was the only significant parameter. A critical cooling rate was defined based on hardness, electrical resistivity and metallographical observations. The inconsistencies in the literature noticed on the evolutions of lead–calcium alloys can now be explained by whether or not this critical cooling rate was respected.

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## 1. Introduction

Calcium has been used to significantly improve the mechanical properties of lead by precipitation hardening from an oversaturated  $\alpha$  solid solution. Numerous studies have been done on the subject since the replacement of lead–antimony alloys by lead–calcium alloys in the lead–acid batteries [1–4]. Research has dealt with the determination of the mechanisms and the kinetics of hardening and softening transformations. The behaviour of the alloy is now well-explained [5] with the identification of five transformations.

The hardening was performed in three stages with (Fig. 1):

- A: a first discontinuous transformation initiated on the grain boundaries and sweeping the grains. The hardness of the alloy increases from 6 HV (Hardness Vickers) to 10 HV,
- B: a second incomplete and approximately 10 times slower transformation named “puzzling” lets the hardness increase by 2 HV,
- C: a last hardening process with the microprecipitation of  $\text{Pb}_3\text{Ca}$  (structure  $\text{L1}_2$ ) with mean size of 2.5 nm. The maximum hardness is about 15 HV.

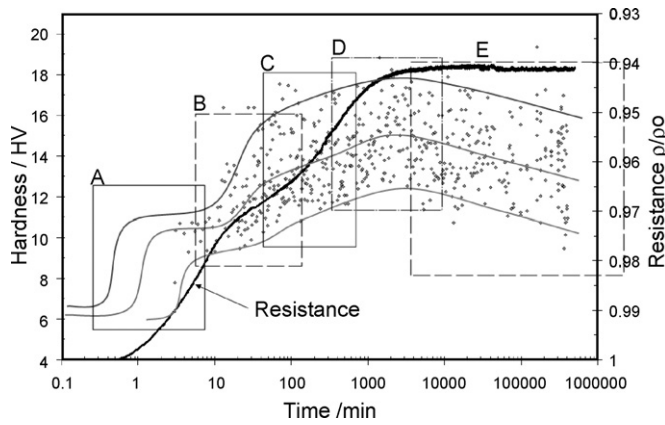
The hardening was then followed by two softening transformations (overageing) with (Fig. 1):

- D: a coarsening of macroprecipitates aligned in strings. Their growth is due to the progressive dissolution of the thin hardening precipitates (state C),
- E: a final softening with the coarsening of the macroprecipitates to form lamellar ( $\text{Pb}_3\text{Ca}$ ) structures.

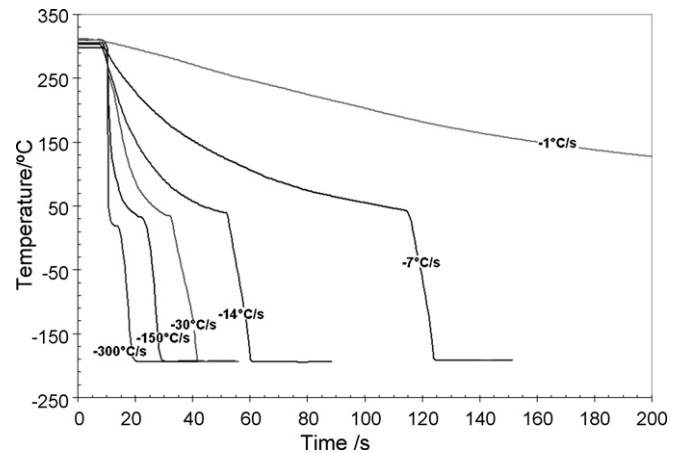
Among the studies on these alloys, many inconsistencies remained during decades on the identification of the transformations. Differences in the observations and interpretations arise on the one hand from the numerous transformations undergone by these alloys and the inherent difficulties in working on lead alloys (soft material and transformations kinetics in a range of several minutes to several years at room temperature). On the other hand, differences in behaviour have been attributed to the sensitivity of the alloy to its chemical composition and its thermal history. We have studied the effect of the process and heat treatment parameters on the transformation of the alloy. Experiments were designed to study the effect of each parameter (casting temperature of the alloy, preheating temperature of the mould, temperature of the quenching bath, etc.) [5]. Results have shown that most of the process parameters had no significant effect on the transformations of the alloy except the quenching rate. This paper is devoted to the analyses of the effect of this main parameter.

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**Fig. 1.** Typical microhardness and resistance curves for a Pb-0.1 wt.% at 20 °C. In black the value of the resistance over the resistance at initial time (oversaturated alloy). The points correspond to hardness measurements  $HV_{0.01/5}$  on a single sample. As samples were heterogeneous in hardness due to the presence of discontinuous transformations, fitted grey solid lines are added to represent the mean and the maximum, minimum curve to visualise the hardness range. The frames represents the five transformations undergone by the alloy.



**Fig. 2.** Evolution of the temperature measured in the middle of the samples during the quenching operation.  $300\text{ °C s}^{-1}$  (water),  $150\text{ °C s}^{-1}$  (oil),  $30\text{ °C s}^{-1}$  (stirring air),  $14\text{ °C s}^{-1}$  (low stirring air),  $7\text{ °C s}^{-1}$  (air),  $1\text{ °C s}^{-1}$  (oven). After the quench, samples were immediately dropped and kept in liquid nitrogen to stop any further transformations.

## 2. Experimental procedure

### 2.1. Alloys preparation

The samples have calcium levels around the peritectic composition (0.08 wt.% Ca) [6]. Alloys were obtained by mixing industrial lead–calcium alloys (calcium content 0.108 wt.%) with “pure” lead (99.97%). Some of the chemical compositions measured by ICP-MS (inductive coupled plasma-mass spectrometry) and ICP-AES (inductive coupled plasma-atomic emission spectroscopy) are summarized in Table 1.

The alloy was melted in a crucible at 600 °C under a protective atmosphere. In order to maximise their electrical resistivity, the samples obtained by casting present a specific size with a very long dimension (2 mm × 3 mm × 100 mm). Samples were then rehomogenised (310 °C during 1.5 h) and quenched in different media to achieve cooling rates of  $300\text{ °C s}^{-1}$  (water),  $150\text{ °C s}^{-1}$  (oil),  $30\text{ °C s}^{-1}$  (stirring air),  $14\text{ °C s}^{-1}$  (low stirring air),  $7\text{ °C s}^{-1}$  (air),  $1\text{ °C s}^{-1}$  (oven) (Fig. 2). As cooling rates were non-linear, the values presented were measured at 290 °C. After the quench, samples were immediately dropped in liquid nitrogen to stop any further transformations until the beginning of the observations in isothermal ageing conditions. Samples were obtained from a same casting batch to guarantee an identical chemical composition. Further sampling and preparation was performed in liquid nitrogen, or possibly for short times at temperatures under  $-50\text{ °C}$  for the metallographic preparation.

### 2.2. Resistivity measurements

Resistivity measurements have been widely used to identify the kinetics of lead alloy transformations [2,3,7–11] due to its sensitivity at the atomic scale and more precisely to the elements in solid solution. For supersaturated lead–calcium alloys, it was then pos-

sible to identify the transformations by monitoring the resistivity as a function of the time in isothermal conditions. The four-points method was used with spark welded copper probes in line on the sample extremities whereas the sample was kept in liquid nitrogen. The measurements were performed in situ at annealing temperatures in the range of  $-20$  to  $275\text{ °C}$  on an especially designed experiment device [5]. An example of a resistivity curve at  $80\text{ °C}$  is presented on Fig. 1.

### 2.3. Hardness measurements

The first two transformations occurring in lead–calcium alloys were of discontinuous type, so it was necessary to have local information of the evolution of the alloy. Usually, hardness is used to measure only the mean evolution of the sample [2,8,12]. We were the first to use in situ microhardness measurements to characterise both the mean of the hardness and the heterogeneity of the sample (Fig. 1). Heterogeneity of the sample has appeared to be a main parameter of the discontinuous transformation. Measurements were performed in situ with a specific redesigned microhardness tester. The samples were electrochemically polished at  $-50\text{ °C}$  [13] to prevent any microstructural transformations before the indentation. The samples were thermoregulated (from 20 to  $80\text{ °C}$ ) and a 10 N load applied during 5 s with a micro-Vickers hardness tester LECO AMH2000.

### 2.4. Metallographic observations

The metallographic observations were performed on aged samples, so the time and temperature preparation were not important parameters as their evolution is very slow. The softness of the alloy necessitated a final chemical polishing after a polishing under water with sandpaper of grade 800 to obtain a plane surface. The chemical polishing was performed by 3–5 min in a solution of one-third

**Table 1**

Chemical composition of the used alloys measured by ICP-MS (Inductive Coupled Plasma-Mass Spectrometry) and ICP-AES (Inductive Coupled Plasma-Atomic Emission Spectroscopy).

Chemical composition (wt ppm)	Ca	Al	Sn	Bi	Mg	Ag	Ni	Cu	Sb	As	Zn	Cd	Pb
Pb–Ca alloy (METALEUROPE)	1080	161	1	130	/	36	1	4	1	1	3	1	–
Pure lead (BUDIN et Fils)	/	/	3	250	/	10	/	10	3	2	10	3	–
Pb–0.06 wt.%Ca	593	31	17	50	2	22	4	3	<1	<1	<1	<1	–
Pb–0.1 wt.%Ca	1027	67	13	89	2	33	6	4	<1	<1	<1	<1	–

hydrogen peroxide (30%) and two-third of acetic acid [12]. Chemical polishing removed the strain hardened surface of the sample.

This chemical polishing was usually not sufficient to reveal the sample microstructure properly. An etching of 10–30 s was necessary with a solution of ammonium molybdate (100 g) and citric acid (250 g) in 1 l of water [14]. After each polishing and etching, samples were successively washed with alcohol and dried.

### 3. Results

#### 3.1. Effect of quenching rate on electrical resistivity measurements

Samples obtained with different quenching rates (Fig. 2) were followed up by electric resistivity measurements at a more elevated temperature (80 °C) in order to achieve the overageing in a few weeks. Measurements presented on Fig. 3 show a nearly identical evolution of the electrical resistivity for quenching rates below 7 °C s<sup>-1</sup>. The resistivity was sensitive to the amount of calcium in solid solution, so the range of variation of 4.4% certifies an identical supersaturation state after quenching. For the sample quenched at a rate of 1 °C s<sup>-1</sup>, the cooling is so slow that the first transformations were activated during its course. When the first measurement was started, some lead matrix depletion in calcium had already occurred. So the sample has no longer fully supersaturated in calcium. At first sight, the resistivity curve for this sample seemed only to move shifted to higher values. The resistivity evolution was similar to one of the other samples but the second transformation (“puzzling”) has an incubation time and a duration 50% longer than for the higher quenching rates.

#### 3.2. Effect of quenching rate on the hardness measurements

Fig. 4 represents the hardness after 2700 min (45 h) at 80 °C of samples quenched at different cooling rates. The hardness obtained is very nearly the same (a slight decrease can be noticed) when the quenching rate is below 7 °C s<sup>-1</sup>. For the quenching rates of 0.5 and 1 °C s<sup>-1</sup>, the hardness is lower by, respectively 2 HV<sub>0.1/5</sub> and 5 HV<sub>0.1/5</sub>, confirming the apparent hardening delay noticed in the resistivity measurements. The huge standard deviation (between 1 and 2 HV) of the hardness measurements is typical of lead–calcium alloys properties and is due to the heterogeneity of the samples caused by the discontinuous aspect of the two first transformations (Figs. 1 and 5).

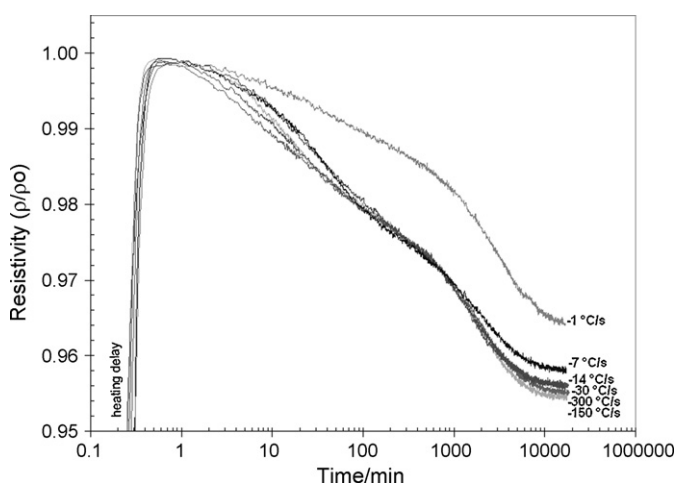


Fig. 3. Evolution of the electrical resistivity over the resistance at initial time (oversaturated alloy) in isothermal in situ ageing at 80 °C for a Pb–0.08 wt.%Ca rehomogenised 1.5 h at 310 °C and quenched at different cooling rates.

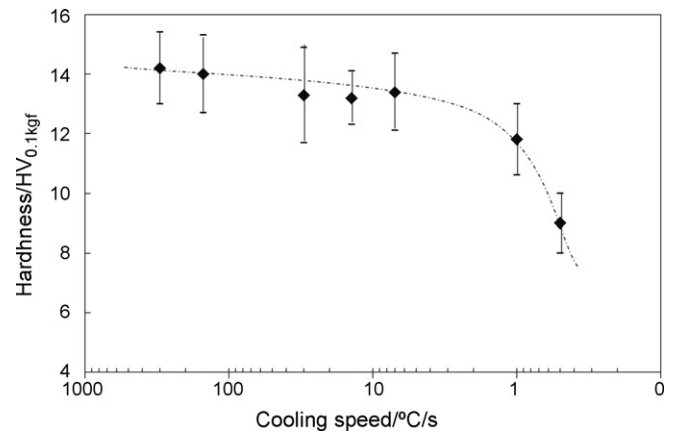


Fig. 4. Hardness and standard deviation (mean of 30 measurements) after 2700 min of ageing at 80 °C for Pb–0.08 wt.%Ca alloys rehomogenised 1.5 h at 310 °C and quenched at different quenching rates. The dashed line through the data points is curve fits.

The previous results point out an evolution of the hardness level for the quenching rate of several degrees per second. To clarify this observation, microhardness filiations were performed in situ at 80 °C. Fig. 5 presents the hardness evolution of samples quenched at a fast rate (40 °C s<sup>-1</sup>) and a slow rate (0.5 °C s<sup>-1</sup>). For the lower quenching rate, the first transformation (already achieved in the first minute of ageing at 80 °C, Fig. 5) arose the hardness only at 7 HV<sub>0.1/5</sub>, that is to say 3 HV<sub>0.1/5</sub> less than for higher quenching rate. The following transformations had only a minor effect on the hardness increase, which gained only 2 HV<sub>0.1/5</sub>. The range (maximum value minus minimum value at an ageing time) of measurement was only of 2 HV<sub>0.1/5</sub>, that is to say four times lower than for the more quickly quenched samples. The mechanical properties of the grain size of the sample seemed to be far more homogeneous. It is important to notice that the heterogeneity of hardness was due to the incomplete aspect of the “puzzling” and was not related to the solidification microstructure as has been proved with the study of recrystallised samples [5].

#### 3.3. Effect of quenching rate on the microstructure

The previous observations by electrical resistivity and hardness measurements have been confirmed by metallographic observa-

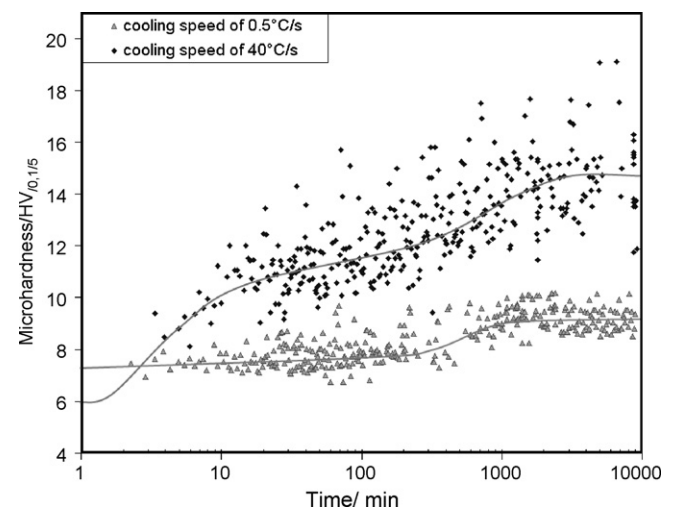
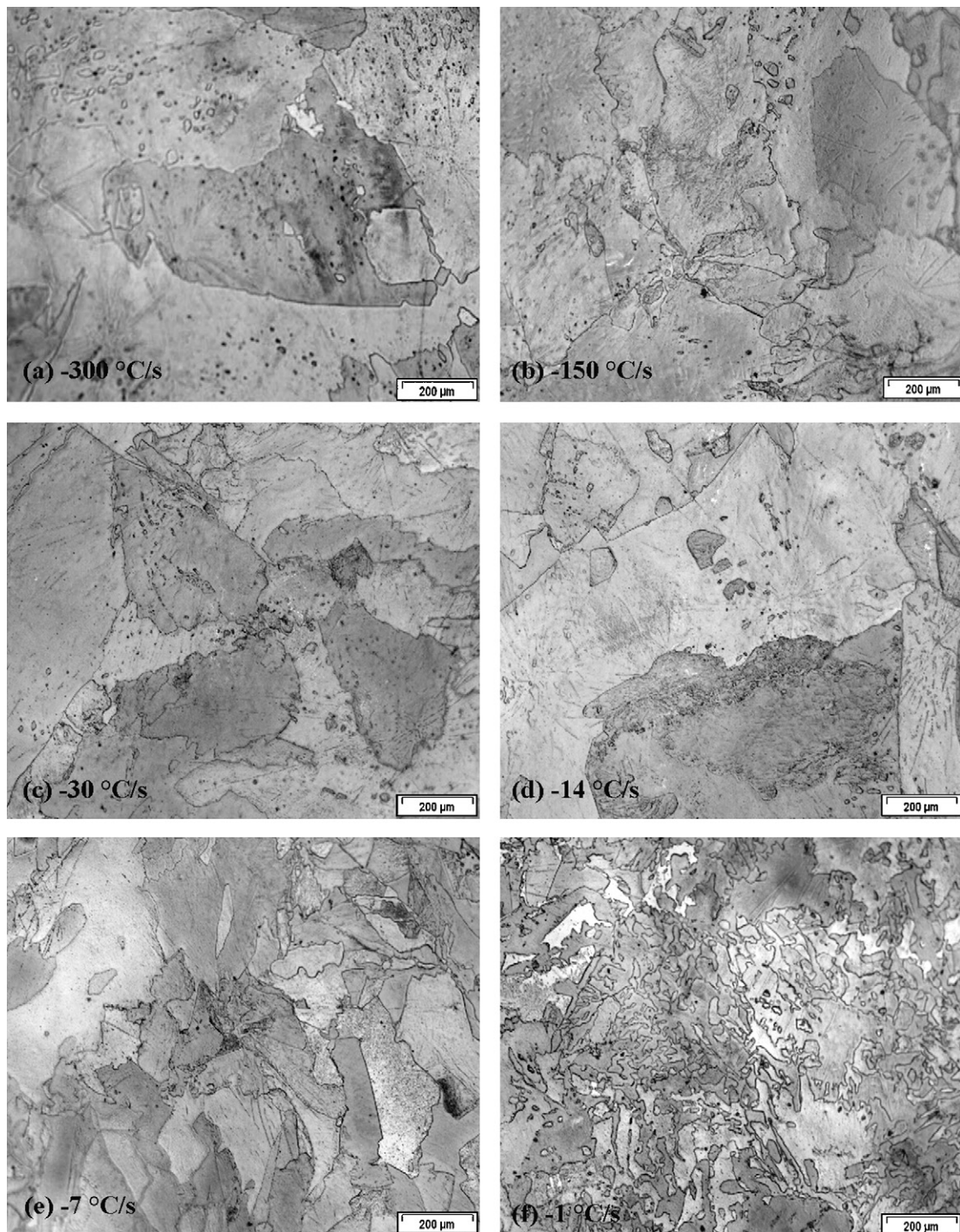


Fig. 5. Evolution of the microhardness measured in situ at 80 °C for Pb–0.08 wt.%Ca alloys, quenched from the liquid phase state at rates of 0.5 and 40 °C s<sup>-1</sup>. The curves represent the hardness mean.

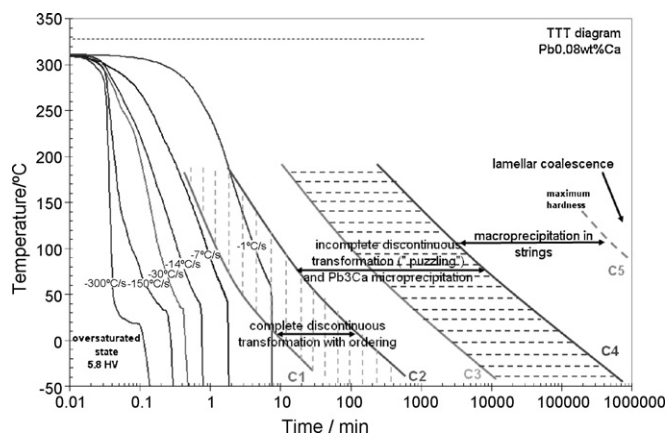


**Fig. 6.** Metallographic observations after 2700 min of ageing at 80 °C for Pb–0.08%PdCa alloys rehomogenised 1.5 h at 310 °C and cooled at different rates. Aged microstructure is significantly thinner with the disappearance of the solidification microstructure for cooling rate under 1 °C s<sup>-1</sup>.

tions. Samples cooled at rates between 300 and 7 °C s<sup>-1</sup> were partially affected by the “puzzling” and show similar microstructures (Fig. 6a–e). On these metallographic observations, it is clearly possible to recognise the initial casting microstructure and the newly formed boundaries (Fig. 6a–e). The sample obtained with the lower quenching rate (1 °C s<sup>-1</sup>) showed a thinner ageing microstructure. The microstructure was so affected by the “puzzling” that the casting microstructure was no longer observable (Fig. 6f). In these conditions, the name “puzzling” used in published research takes all its meaning. The slow cooling had favoured the

“puzzling” which was confirmed on the resistivity curves of Fig. 3 on which the variation amplitude corresponding to the “puzzling” and the microprecipitation was 30% more important, attesting that more calcium was consumed than for the high cooling rate.

This phenomenon can be explained by the fact that the first discontinuous and complete transformation was so quick that it had the time to be performed during the cooling at temperatures higher than room temperature. When the alloy pursued its cooling, the supersaturation in calcium increased as the first transformation was already initiated or even finished. At the end of a slow



**Fig. 7.** Continuous cooling temperature of the samples indicatively superposed on a TTT diagram for the alloy Pb–0.08 wt.%Ca. The TTT diagram curves are fits obtained by resistivity and hardness measurements performed in a subsequent in situ heat treatments carried out in the temperature range  $-20$  to  $180$  °C on samples cooled in liquid state at a minimum of  $40$  °C  $s^{-1}$  from  $310$  to  $-196$  °C.

**Table 2**

Evolution of the critical quenching rate with the calcium content.

Calcium content (wt ppm)	Critical quenching rate (°C $s^{-1}$ )
600	2
800	7
1000	10
1200	14

cooling, the second transformation (“puzzling”) showed an alloy which had undergone the first transformation with a lower calcium supersaturation. When the second transformation took place, the supersaturation was higher and it had more energy (calcium in solid solution) to develop and tended to be more complete (Fig. 6f).

#### 4. Discussion

The critical parameter for the quench corresponded to the beginning of the first discontinuous transformation. The cooling rate had to be high enough to avoid any first transformation during the quench.

The domain of transformation can be represented versus the temperature with TTT diagrams (Time–Temperature–Transformations). Even if the TTT diagram of Fig. 7 [5] is not a CCT (Continuous Cooling Transformation) diagram, the cooling curves of the samples have been represented on it to allow a qualitative interpretation. If the quenching rate were higher than a critical rate, the sample would evolve always in the same way, following the five transformations (Figs. 3 and 6a–e).

It is then possible to confirm qualitatively that, for a Pb–0.08 wt.%Ca alloy, the critical rate was about  $7$  °C  $s^{-1}$ . For a slower cooling, the first discontinuous transformation began during the quench. Kinetics of transformation of lead–calcium alloys is known to be dependent on the calcium amount [2], so the critical rate increases when the calcium decreases (Table 2). The design of the CCT diagrams will be needed to determine the real value of the critical cooling rate.

These results are coherent with those of Boulahrouf [12] which, even if he has identified only one single hardening transformation in lead–calcium alloys, have shown that transformation took place during the quench for a Pb–0.125 wt.%Ca when the cooling rate was under  $1$  °C  $s^{-1}$ . In these conditions, he has shown that the hardening effect was significantly lower.

#### 5. Conclusion

This study has enabled us to define the effect of the process parameters on the ageing of lead–calcium alloys. Quenching rate has been shown to be the only significant parameter on ageing with the determination of the critical cooling rate function of the calcium content. Aged microstructures available in published research can present different aspects. Sometimes the microstructure was fully puzzled and sometimes the initial casting microstructure remained clear (Fig. 6a–e and f). We know now that these microstructural and mechanical differences among the authors were due to the use of different cooling rates. If the quenching rate is over the critical value, the first transformation will be avoided during the quench. Whatever the values of cooling, if it is higher than the critical cooling rate, the evolution (hardness, microstructure, etc.) will be the same. With a cooling rate under the critical rate, the transformation of the alloy took place during cooling, refining the ageing microstructure and lowering the achieved hardness.

Complementary studies [5] have proved that, if the cooling rate is not sufficient during the solidification of the alloy, that is to say under the defined critical value (due to process impositions), it is possible to perform a treatment of rehomogenisation close to the peritectic point (for example 1 h at  $310$  °C) followed by a quench. The evolution of the alloy (kinetics of transformation, hardness, microstructure, etc.) will then be identical to that of samples quenched from the liquid.

#### References

- [1] E.E. Schumacher, G.M. Bouton, *Met. Alloys* 1 (1930) 405–409.
- [2] D.E. Kelly, The influence of ternary additions on the kinetics of discontinuous precipitation of lead–calcium alloys, Ph.D. Thesis, University of Waterloo, Ontario Canada, 1985.
- [3] H. Tsubakino, R. Nozato, Y. Satoh, *Zeitschrift für Metallkunde* 81 (1990) 490–495.
- [4] J.P. Hilger, L. Bouirden, *J. Alloys Compd.* 236 (1996) 224–228.
- [5] F. Rossi, Etude et compréhension des mécanismes de vieillissement des alliages de plomb–calcium, Ph.D. Thesis, Arts et Métiers ParisTech, Paris, France, 2006.
- [6] Y. Cartigny, J.M. Fiorani, A. Maître, M. Vilasi, *Thermochim. Acta* 414 (2004) 197–202.
- [7] H. Tsubakino, R. Nozato, A. Yamamoto, *Scripta Metall. Mater.* 26 (1992) 1681–1685.
- [8] H. Tsubakino, R. Nozato, A. Yamamoto, *Zeitschrift für Metallkunde* 84 (1993) 29–32.
- [9] H. Tsubakino, M. Tagami, S. Ioku, A. Yamamoto, *Metall. Mater. Trans. A: Phys. Metall. Mater. Sci.* 27 (1996) 1675–1682.
- [10] G. Bourguignon, Amélioration du comportement électrochimique des batteries plomb–acide à usage photovoltaïque, Ph.D. Thesis, University of Nancy I, France, 2003.
- [11] M. Dehmas, A. Maître, J.B. Richir, P. Archambault, *J. Power Sources* 159 (2006) 721–727.
- [12] A. Boulahrouf, Etude des alliages de plomb–calcium faiblement alliés en calcium destinés à la fabrication des grilles d’accumulateurs de la nouvelle génération, Ph.D. Thesis, University of Nancy I, France, 1989.
- [13] J.P. Hilger, A. Boulahrouf, *Mater. Charact.* 24 (1990) 159–167.
- [14] American Society for Metals, in: F. George, Vander Voort (Eds.), *Metals Handbook, Metallography and Microstructures*, vol. 9, 8th edition, ASM, 1973, pp. 415–423.