



How to decrease overaging in Pb–Ca–Sn alloys?

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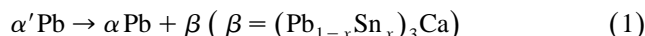
Abstract

It is known that lead–calcium–tin alloys are very well hardened by continuous precipitation since 20°C. But an overaging involving a decrease of the mechanical properties appears afterwards. It is proved in this study that with an adapted combination of the composition of the Pb–Ca–Sn alloys and a specific heat treatment it is possible to reach a hardness of 25 to 30 Vickers with a complete precipitation of $(\text{Pb}_{1-x}\text{Sn}_x)_3\text{Ca}$ and to suppress practically any overaging in as-cast or rolled specimens. © 1998 Elsevier Science S.A.

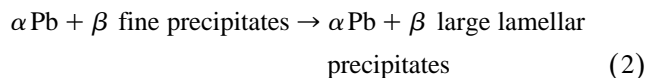
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1. Introduction

After quenching Pb–Ca–Sn oversaturated alloys with a high level of tin hardened by a continuous precipitation of $(\text{Pb}_{1-x}\text{Sn}_x)_3\text{Ca}$ in coherency with the matrix since room temperature [1]:



But an overaging corresponding to a new discontinuous transformation can also appear at room temperature with the reprecipitation of coarse β precipitates incoherent with the matrix.



The structural hardening depends on the total volume of the $(\text{Pb}_{1-x}\text{Sn}_x)_3\text{Ca}$ $L1_2$ phase given by the concentration of Ca and the ternary phase diagram [2], but also on the fineness and the coherency with the matrix of the $L1_2$ phase (lattice parameter a): ($a_{\text{Pb}} = 0.4950$ nm; $a_{\text{Pb}_3\text{Ca}} = 0.4916$; $a_{\text{Sn}_3\text{Ca}} = 0.4745$; $0.4916 < a_{(\text{Pb}_{1-x}\text{Sn}_x)_3\text{Ca}} < 0.4745$) With an increase of tin the solubility of calcium decreases [2].

Thermodynamically the most stable state corresponds to a minimum of the free enthalpy of the system. It is well known that the kinetics of the various solid states reactions

or phases transformations are diffusion controlled. It is possible that the first reaction is not complete at room temperature and that the matrix is still partially oversaturated after long time



So there is a competition between the two reactions: aging and overaging. The driving force for the discontinuous overaging transformation lies both in the residual oversaturation of the matrix and the energy of the boundaries of the β phase. The driving force consists of two contributions: a chemical volumic contribution and an interfacial contribution. Only in the special case where the composition of the two phases resulting from the first reaction are the same as those from the second, the chemical contribution is zero.

It is possible to reduce the driving force of the overaging transformation and to promote the complete aging reaction to prejudice of overaging by a decrease of the chemical contribution:

- decrease of the level of calcium according to the ternary Pb–Ca–Sn diagram,
- increase of the temperature of the aging transformation.

According to the *TTT* (Temperature, Time, Transformation) curves, Arrhenius law, and calorimetric measurements the start of the aging precipitation can be reduced and the kinetic increased by an elevation of the temperature (thermal treatment) up to 200°C [1,3].

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Discontinuous overaging transformation corresponds to grain boundary diffusion. The boundary structure is a complicated function of a large number of variables such as crystallographic parameters describing the misorientation of the adjoining crystals and the interface between them, the chemical composition (nature and distribution of the segregated atoms for example Ag [4]), the size of the grains. The discontinuous overaging transformation starts preferentially at a large-angle grain boundary. Plastic deformation changes the degree of distortion and the width of distortion of the interfacial region between two crystals and also the structure of the matrix (dislocations networks, subgrains) as it can be observed by TEM. So the grain boundary diffusion can be reduced but with a high reduction by rolling it appears a possibility of a third contribution of the driving force, the cold-work energy, which involves recrystallization.

To confirm the different hypothesis mentioned above a lot of Pb–Ca–Sn alloys were tested.

2. Experimental

Lead–calcium–tin alloys with or without Al and Ag selected for this study are the same as those used for earlier studies [4,5]. Further other alloys were prepared by mixing Pb–Ca–Sn alloys with pure primary or secondary lead (Bi 200 ppm, Cu 200 ppm, Ag 500 ppm, Al 150 ppm).

Alloys were recast at 650°C in a SiO₂ crucible with an 8 mm diameter. After solidification the samples were water quenched in the crucible.

For all compositions (about 20), the samples were divided into four pieces: two as-cast and two rolled. The ratio of rolling was lower than 80% to avoid recrystallization [6].

For all the compositions two samples (one as-cast and one rolled) are aged at 20°C, the two other samples are immediately aged between 60 and 200°C. Before and after the heat treatments, Vickers hardness tests (HV) were carried out on a Testwell durometer under a load of 2 kgf. Each reported value of hardness corresponds to the mean of five points distributed over the entire cross section or the rolled surface of the samples.

Samples were also polished and etched to reveal the grain structure and observed by optical microscopy.

3. Results

3.1. Structure and hardness of the alloys after different heat treatments

The best results obtained up today are summarized in Table 1 and can be observed with as-cast products as well

Table 1
Hardness of various Pb–Ca–Sn alloys after particular heat treatments

Alloy	As-cast			Rolled 80%		
	HV	θ°C	Time	HV	θ°C	Time
Pb–0.1% Ca–2% Sn	26	200	2 min 30	27	200	2 min 30
	20	90	2 h 30	17	90	2 H 30
	20	80	10 h	16	80	10 h
Pb–0.1% Ca–1.5% Sn	24	200	2 min 30	28	200	2 min 30
	20	90	1 h	19	90	1 h
	16	80	10 h	15	80	10 h
Pb–0.09% Ca–1.35% Sn	22	200	2 min 30	21	200	2 min 30
Pb–0.085% Ca–1.7% Sn	26	200	2 min 30	28	200	2 min 30
	29	100	1 h 30	21	100	1 h 30
Pb–0.08% Ca–1.2% Sn	25	90	2 h	27	90	2 h
Pb–0.07% Ca–2% Sn	27	90	2 h	28	90	2 h
	26	75	17 h	24	75	17 h
	23	60	14 h	26	60	14 h
Pb–0.07% Ca–2% Sn–500 ppm Ag	27	200	2 min 30	29	200	2 min 30
	29	110	3 h 30	26	110	3 h 30
Pb–0.06% Ca–1.8% Sn	27	90	2 h	26	90	2 h
	26	120	3 h	26	120	3 h
Pb–0.05% Ca–1.5% Sn	27	90	30 h	26	90	30 h
	26	120	3 h	26	120	3 h
Pb–0.05% Ca–2.5% Sn	25	90	3 h	27	90	3 h

as rolled products, with primary lead or secondary lead. When the level of calcium increases (for example 0.1%) a very short heat treatment (1–2 min) at high temperature (200°C) is necessary to obtain a high hardness, but we observe nevertheless a little overaging.

Conversely when the level of calcium decreases strongly (0.05%) the overaging is reduced even after a classical aging at room temperature. But a high level of tin has a similar effect to calcium. So after 4 yr aging at 20°C, Pb–0.044% Ca–2.5% Sn, Pb–0.044% Ca–5% Sn, Pb–0.022% Ca–3.5% Sn, Pb–0.022% Ca–5% Sn alloys present aged areas (HV = 23 to 25) and overaged areas (HV = 17 to 18), while Pb–0.044% Ca–1.3% Sn or Pb–0.022% Ca–2.5% Sn present only aged areas (HV = 20 to 21) and no overaged areas.

3.2. Stability of the aged structure

The stability of the aged structure is evaluated as follows. The minimum time necessary to obtain the end of the aging (maximum of hardness) is determined at two temperatures. After this the time necessary to observe the beginning of the overaging (beginning of the decrease of hardness and appearance of the overaging areas perceptible by microscopic observations) is also determined at two temperatures then plotted vs. $1/T$ (Arrhenius law) in a logarithmic scale. The stability at room temperature is extrapolated from the values at high temperatures (Fig. 1). The apparent activation energy is 60 ± 10 k J/mole for the two alloys tested: Pb–0.08% Ca–1.2% Sn and Pb–0.07% Ca–2% Sn. This is compatible with a grain boundary diffusion mechanism.

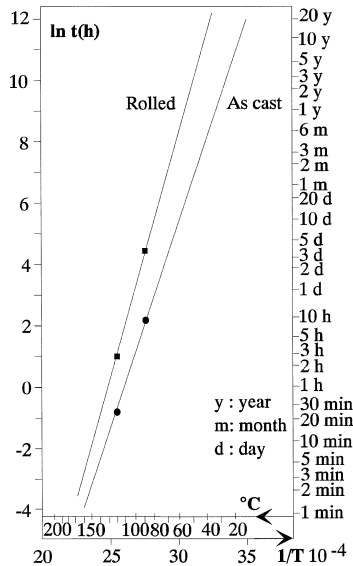


Fig. 1. Pb–0.08% Ca–1.2% Sn alloy: time of the beginning of overaging vs. temperature, as cast and rolled samples.

It appears that after plastic deformation (rolling up to 80% thickness reduction, without recrystallization) overaging starts later. This can be due to the pre-exponential term D_0 of the diffusion law $D = D_0 \exp(-Q/RT)$. D_0 is a function of the number of ways through which diffusion process is possible.

The stability of the as cast products and the rolled products at room temperature can be evaluated to 5 and 10 yr, respectively. Today we can confirm the stability after 18 months at 20°C (November 1995–June 1997) for the different alloys listed in Table 1 [7] (stability of hardness and no observation of overaging areas).

3.3. Influence of the time at 20°C before heat treatments

The rate of germination and growth of the $L1_2$ phase depends on the temperature. Pb–Ca–Sn alloys harden since room temperature. Figs. 2 and 3 show the hardness values before and after heat treatment vs. stay (time between solidification and heat treatment) at 20°C. Initial hardness increases (aging at 20°C) and final hardness (after heat treatment) decreases more and more with the importance of the intermediate stay at 20°C.

We confirm also that the time necessary at 20°C before heat treatment, to observe an important decrease of the hardness after heat treatment is much longer when the level of calcium is low (Figs. 2 and 3) with or without Ag. On the other hand with 0.08% Ca, silver blocks partially the overaging phenomenon. So the time available at 20°C before heat treatment is longer with the Pb–0.08% Ca–1.2% Sn–0.05% Ag as with the same alloy but without silver.

It was confirmed by microscopic observations that the overaging on the grain boundaries and perhaps on the dendritic subboundaries is responsible of the decrease of

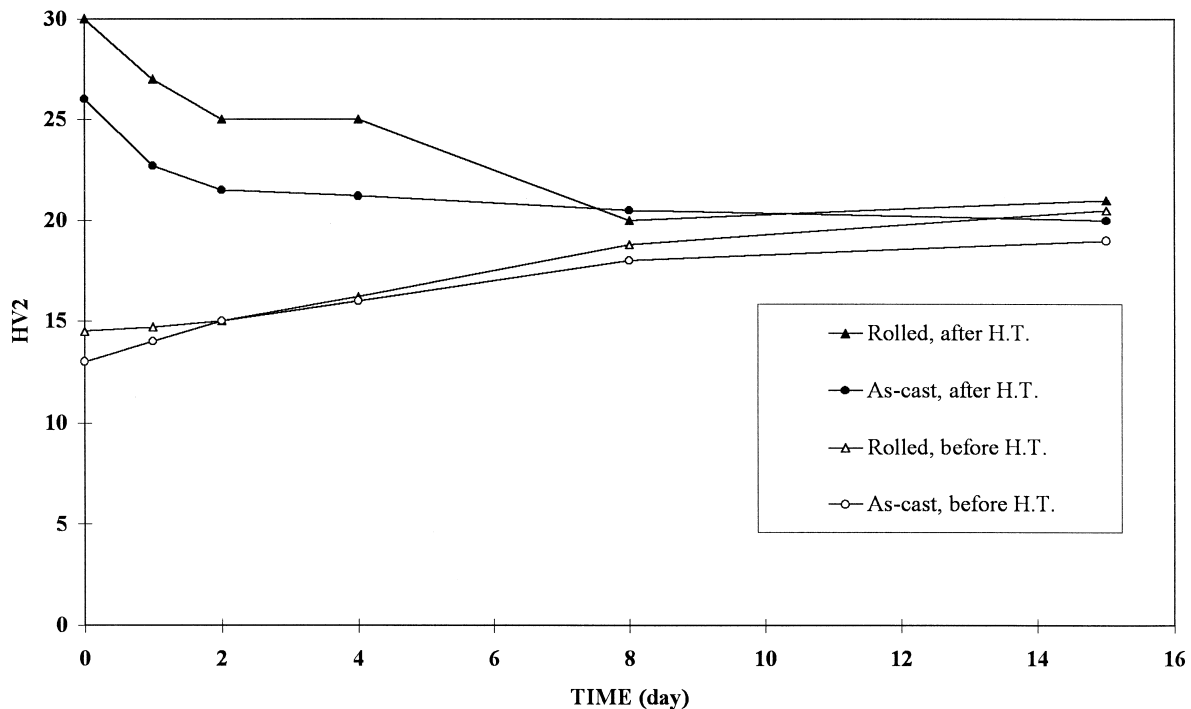


Fig. 2. Pb–0.08% Ca–1.2% Sn–0.05% Ag alloy: hardness values before and after a heat treatment (H.T.) of 1.5 h at 100°C vs. stay (time between solidification and heat treatment) at 20°C, as-cast and rolled samples.

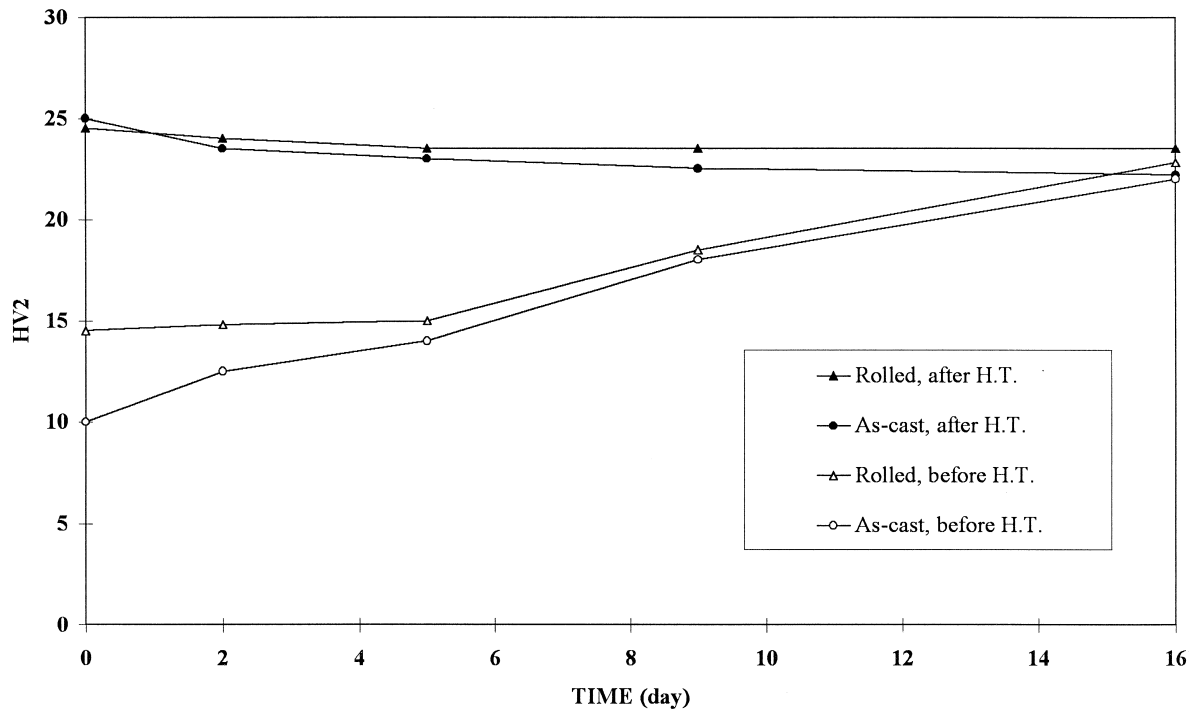


Fig. 3. Pb–0.05% Ca–1.5% Sn–0.03% Ag alloy: hardness values before and after a heat treatment (H.T.) of 1.5 h at 100°C vs. stay (time between solidification and heat treatment) at 20°C, as-cast and rolled samples.

the hardness in the as cast samples. For the rolled samples overaging and perhaps a beginning of recrystallization involve the decrease of hardness.

After 1 yr at 20°C the comparison of the heat treated and not heat treated samples shows that overaging is more important without heat treatment for the as-cast samples. For the rolled samples, restoration, recrystallization, aging and overaging are in competition. When the rolled ratio is less than 80% recrystallization doesn't appear or is very incomplete. It seems that a heat treatment (1.5 h at 100°C for example) immediately after casting and rolling accelerates and induces in a short time a complete precipitation of the $L1_2$ phase which hinders then restoration and recrystallization and stabilises the hardness at a high level.

For a same composition the evolution of the heat treated samples and the samples only aged at 20°C depends also on the grain size (possibilities of development of overaging process) which is in relation with the rate of cooling (temperature of the mould, dimensions of the as-cast samples). So the structure can be very heterogeneous from one grain to another or between the surface and the centre of a sample.

4. Comparison with other lead alloys

Borchers and Reuleaux [8] in Pb–Sb and Pb–Sb–As alloys have observed a similar phenomenon. At very low (200 days at –40°C) or high (1 h at 100°C) temperatures no overaging appears. Concurrently the prior treatment at

–40°C stabilize the structure at 20°C. But with the Pb–Sb (As) alloys the rate of germination of the precipitated phase (Sb) depends very much on the temperature. So the maximum of the hardness value obtained is about 32 HB (Brinell hardness) at –40°C, but only 17 HB at 100°C. With the Pb–Ca–Sn alloys it seems that there is no great difference of the rate of germination of the precipitated phase $(Pb_{1-x}Sn_x)_3Ca$ with the temperature. In all cases the maximum of hardness is very high.

5. Conclusions

In this study it was remembered how as a general rule in lead alloys and in particular in lead calcium tin alloys there is a competition between aging, overaging and recrystallization (in rolled samples). It was shown clearly that it is possible to reduce the driving force of the overaging transformation and to promote the complete aging reaction by a decrease of the calcium level according to the ternary Pb–Ca–Sn diagram and an increase of the temperature of the aging transformation according to the *TTT* (Temperature, Time, Transformation) curves.

The stability of the structure and the hardness (25 to 30 HV) can be estimated between 5 and 10 yr at room temperature. The ultimate tensile strength can be over 75 MPa with an elongation of 5 to 10% and a striction of 8 to 15%. A low level of calcium, high mechanical properties and the delay of the overaging phenomenon involve as a general rule an improvement of the corrosion resistance [4].

Industrially primary or secondary lead can be used. At this stage of the study it is important to know how this results can be used in battery performances. It must be taken into account the principle of the process of grid manufacture (gravity casting, continuous casting, rolling, expansion), the cooling rate which have an influence on the grain size, the temperature and the time of the curing as well as the time between the different stages.

Acknowledgements

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