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# Deformation and recrystallization texture, microstructure and kinetics of Pb-Ca-Sn alloy

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**Abstract:** A Pb-0.08Ca-2Sn alloy was subjected to rolling at room temperature to different final thicknesses. Annealing treatments at temperature ranging from 80 to 120 °C led to recrystallization of the samples as shown by resistivity and micro-hardness measurements. The deformation texture determined through X-ray diffraction is qualitatively the Brass type. The measured Lankford anisotropy parameter *R* and its evolution are close to the determined one using a self consistent approach. The *R* value evolution with angle to rolling direction shows the presence of planar anisotropy and poor drawability. The recrystallization in annealing at 80−120 °C is achieved within time period up to $3\times10^4$ s. The recrystallization texture is a retained deformation texture with an emerging Cube component.

**Key words:** Pb-Ca-Sn alloy; cold rolling; recrystallization; texture

## 1 Introduction

During the last decades, the increasing market for maintenance-free batteries has promoted the development of Pb-Ca-Sn alloys. These alloys show better mechanical and electrochemical properties and are replacing progressively Pb-Sb alloys for the manufacture of grids. The different processes of the grid production (gravity casting, continuous casting, rolling expansion and casting expansion) are capable of imparting large plastic strain and high dislocation densities to the material [1]. The overall amount of these lattice defects is is the key factor determining the evolution of the morphology and the kinetics of the phase transformations that can occur during the service life of the grids [2].

Apart old and pioneer works [3−6], very little consideration has been given to the deformation and recrystallization kinetics, texture and microstructure of Pb-based alloys as well as their anisotropy. Recently, WANG et al [7−8] have determined the microtexture of Pb-Ca-Sn-Al alloy via EBSD analysis as being composed of strong multiple components including {011}⟨211⟩(Brass), {123}⟨634⟩(S) and {112}⟨111⟩ (Copper). A more detailed and quantitative study of the recrystallization kinetics is still lack. For this purpose, resistivity and micro-hardness measurements were undertaken to highlight the recrystallization kinetics, X-ray diffraction analysis was applied to assessing the deformation and recrystallization kinetics and texture in commercial Pb-0.08Ca-2Sn (mass fraction, %) alloy.

## 2 Experimental

Specimens of Pb-0.08 Ca-2Sn alloy were cut from a block furnished by an industrial company. These specimens were remelted in quartz sealed tubes and then subjected to a solution annealing and quenched in liquid nitrogen. They were immediately cold deformed by rolling and the ratio of the thickness reduction were 50% and 75%, respectively (slightly lower than 80% in order to avoid a dynamic recrystallization [9]). After rolling, the samples were directly quenched in water.

The texture was determined in the mid-plane of the as-deformed state and recrystallized state by measuring incomplete pole figures (5°≤$\alpha$≤75°) in the back reflection mode using Co-$K_\alpha$ radiation from an X-Ray texture goniometer. The measured pole figures were corrected for defocussing and background, and recalculated via orientation distribution function (ODF) determination

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using Harmonic method implemented in popLa package.

The anisotropy parameter *R* was determined by tensile test measurements as the ratio of the transverse strain to longitudinal strain changed.

Samples were prepared for optical, scanning and transmission electronic microscopy following the protocols described in Ref. [1−2, 10].

Isothermal annealing treatments were performed in a four-probe resistivity equipment at temperature ranging from 80 to 120 °C. Micro-hardness measurements were carried out in a Shimadzu Vickers facility, an average value of 5 indentations was obtained under load of 100 N.

## 3 Results and discussion

### 3.1 Deformation microstructure and texture

Figure 1 shows the typical elements of defects in deformed Pb-0.08Ca-2Sn. The structure is typical deformed polycrystals: dislocation networks on sub-boundaries and micro-slip lines. The dislocation density roughly estimated from a set of TEM micrographs was around $(2-5)\times10^{10}$ $cm^{-2}$. This value is smaller compared to that of other FCC alloys; however, it is consistent with the value reported in Ref. [11].

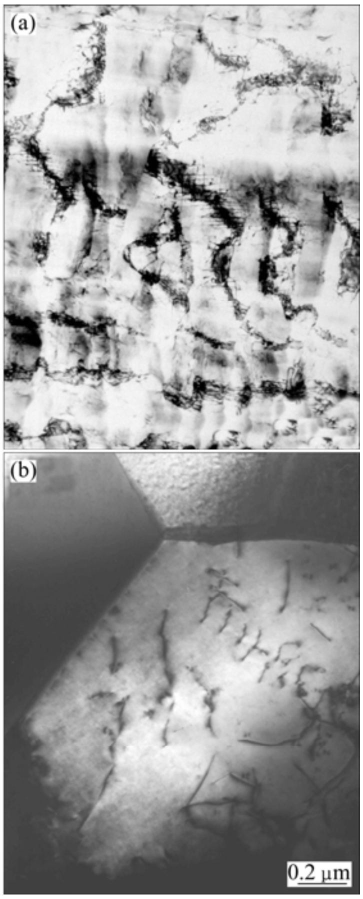


**Fig. 1** TEM micrographs showing typical elements of defects in deformed Pb-0.08Ca-2Sn alloy: (a) Dislocation networks on sub-boundaries; (b) Micro-slip lines

The experimental {111} pole figures of the cold rolled samples to thickness reduction of 50% and 75% are respectively shown in Figs. 2(a) and (b). Weak texture of multiple components including essentially Brass {011}⟨211⟩, S {123}⟨634⟩ and Goss {011}⟨100⟩ orientations is developed. The result is in agreement with the study by WANG et al [7−8] which evidenced that the texture of cold rolled Pb-Ca-Sn belongs to the commonly observed cold deformation texture of FCC alloys. It is known that the value of the stacking fault energy ($\gamma_{SFE}$) determines the type of texture of the material. It is estimated the value of $\gamma_{SFE}$ of Pb-Ca-Sn alloy in deformed state from the results of X-ray line profile analysis results. In Ref. [12] $\gamma_{SFE}$ is given as:

$$\gamma_{SFE} = \frac{\mu a_0^3 \rho}{24\sqrt{3}\pi\alpha} \tag{1}$$

where $\mu$, $a_0$, $\rho$ and $\alpha$ are respectively the shear modulus, the cell parameter, the dislocation density and the net stacking fault probability. The dislocation density value is estimated from an X-ray line profile analysis (XRDLPA) using a procedure called convolutional multiple whole profile fitting [13−14] while the net

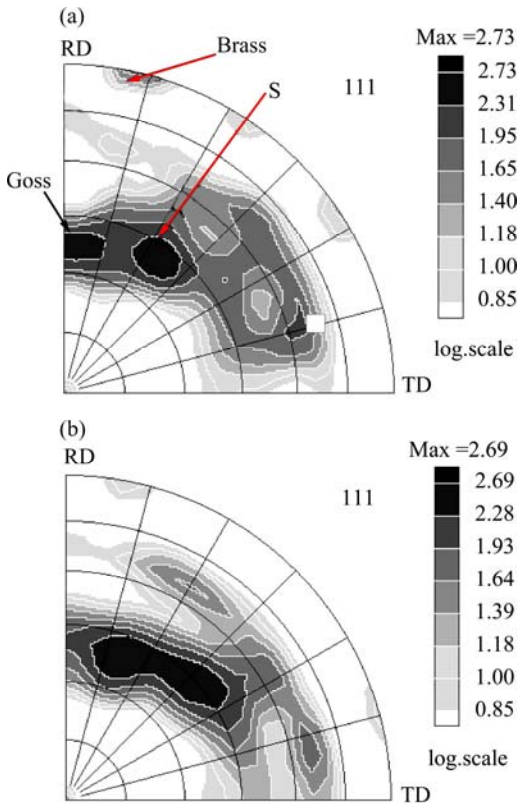


**Fig. 2** {111} pole figures of cold rolled Pb-0.08Ca-2Sn samples to thickness reduction of 50% (a) and 75% (b) (White filled square represents $\{\bar{2}\bar{1}1\}$ ⟨011⟩ shearing texture component)

stacking fault probability is determined from the relative shifts of neighbouring X-ray diffraction reflections using Eq. (1). The values of $\rho$ and $\alpha$ range around $5\times10^{10}$ $cm^{-2}$ and $5\times10^{-3}$, respectively. The deduced value of $\gamma_{SFE}$ is around 20 $mJ/m^2$, which indicates that Pb-Ca-Sn alloy has an intermediate value of $\gamma_{SFE}$. HOFMANN [15] reported the value of $\gamma_{SFE}$ of pure lead to be 25 $mJ/m^2$, that is of the order of magnitude of the $\gamma_{SFE}$ of silver and lower than that of aluminium. This explains the texture type in part, and in other part, the fact that deformation and recrystallization twins are abundant in lead alloys as observed in Refs. [7−8] after iterative thermomechanical processing of Pb-Ca-Sn-Al alloy.

### 3.2 Deformation anisotropy

Figure 3 shows the stress—strain plot for a Pb-0.08Ca-2Sn alloy, which was cold rolled to a thickness reduction of 70% under tensile deformation with a strain rate of $2\times10^{-4}$ $s^{-1}$. It evidences a short elastic domain and a very weak work hardening of lead alloys.

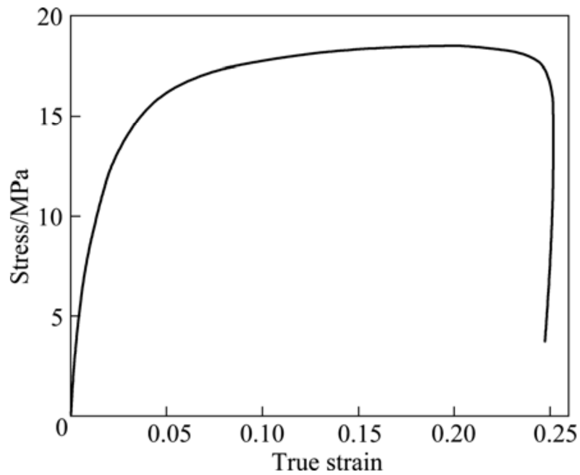


**Fig. 3** Stress—strain plot for Pb-0.08Ca-2Sn alloy cold rolled to a thickness reduction of 75% with strain rate of $2\times10^{-4}$ $s^{-1}$

Figure 4 presents the planar Lankford anisotropy or $R$ value that was measured and averaged from strain values at true strain of 0.075, 0.125 and 0.175, respectively. $R$ value varies with the direction in the sheet and is the lowest along the rolling direction (RD), and it increases towards transverse direction (TD), indicating the presence of planar anisotropy. The average $\overline{R}$ and its variation $\Delta R$ is given as [16]:

$$\overline{R}=\frac{R(0)+2R(45)+R(90)}{4} \tag{2}$$

$$\Delta R=\frac{R(0)-2R(45)+R(90)}{2} \tag{3}$$

where $\overline{R}$ and $\Delta R$ are found to be equal to 0.425 and 0.356, respectively. Such values are indicative of a weak drawability of Pb-Ca-Sn alloys. In comparison, experimental results obtained from Fe-based alloys are $\overline{R}$=1.7, $\Delta R$=0.68 [17] and the theoretical ones calculated in Ref. [18] are in the ranges of $\overline{R}$ from 0.45 to 25.43, $\Delta R$ from −0.88 to 49.38. As pointed out in Ref. [16], $R$ values characterizing face-centered cubic metals are rarely greater than 1 and often substantially less.

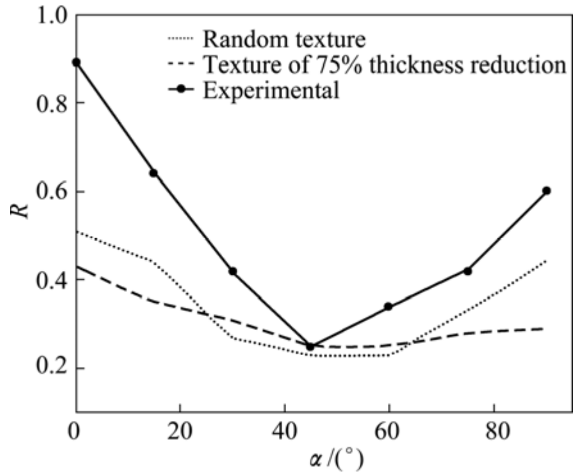


**Fig. 4** Evolution of planar Lankford anisotropy or $R$ value versus angle ($\alpha$) to rolling direction for Pb-0.08Ca-2Sn samples cold rolled to a thickness reduction of 70% (Dotted and dashed lines represent plots of $R$ value calculated using texture data with random and that of experimental pole figures)

The calculated $R$-values on the basis of Taylor model are plotted together and show very good agreement with experimental ones. The calculation was done on the basis of Hosford-Backofen model implemented in popLA package for two initial texture taken from experimental pole figures of Pb-Ca-Sn alloys deformed to thickness reduction of 50% and 75%. The global evolution of calculated $R$ versus the angle to rolling direction varies very slightly and is less than experimental ones. As pointed out in Ref. [18], the deviation between the experimental and calculated values can be explained by the dynamic evolution of texture during the tensile tests.

### 3.3 Recrystallization texture and kinetics

Figure 5 presents SEM micrographs showing features of recrystallization of cold rolled Pb-0.08Ca-2Sn. In Fig. 5(a), islands of small recrystallized grains can be depicted by grain with mean size of 2−10 μm imbedded in grains with large grain size probably in initial microstructure. Figure 5(b) shows a quasi fully recrystallized microstructure consisting of large non-equiaxed grains with grain size ranging from 100 to 200 μm.

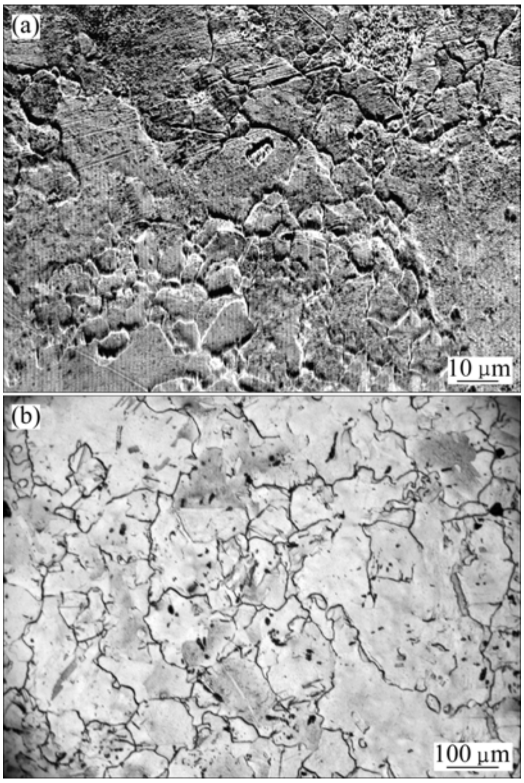


**Fig. 5** SEM micrographs showing features of recrystallization of cold rolled Pb-0.08Ca-2Sn alloys: (a) Annealed at 100 °C for 1 h; (b) Annealed at 100 °C for 6 h

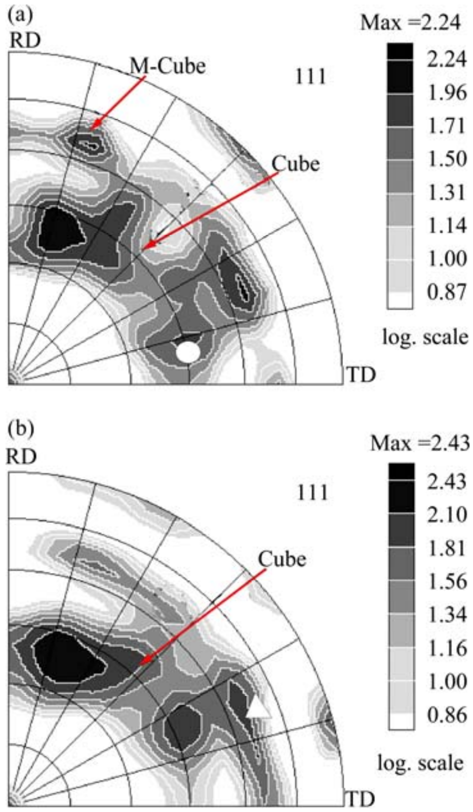


**Fig. 6** {111} pole figures of cold rolled Pb-0.08Ca-2Sn samples with thickness reduction of 50% (a) and 75% (b) (White filled circle and triangle represent the Sh1 $\{1\bar{1}\bar{4}\}\langle 1\bar{3}1\rangle$ and Sh2 $\{1\bar{1}\bar{1}\}\langle\bar{1}\bar{2}1\rangle$ shearing texture components, respectively)

Figure 6 presents the {111} pole figures of the cold rolled samples with thickness reduction of 50% and 75% and recrystallized at 120 °C for 2.5 h ($9\times10^4$ s). Manifestly, the maximum intensity levels in the pole figure are lower than those of the deformed alloy. The textures are not fairly flat and some components can be recognized from the pole figures.

The texture of the recrystallization and annealing texture at 120 °C is unambiguous and not very different from the deformation texture. It is depicted any relative tendency towards a randomization in recrystallization, but some components that have always been reported in recrystallization texture of deformed and recrystallized FCC alloys and metals [19] still exist. These components are Cube {001}⟨100⟩, M-Cube {122}⟨221⟩, Brass {011}⟨211⟩, S {123}⟨634⟩ and Goss {011}⟨100⟩. There also exist some other components such as Sh1 $\{1\bar{1}\bar{4}\}\langle 1\bar{3}1\rangle$ and Sh2 $\{1\bar{1}\bar{1}\}\langle\bar{1}21\rangle$ that are typical shear components. The results are slightly different from those in Ref. [7] in the fully recrystallized alloy. It is evidenced that the major Cube component contrasts with the present results.

The alloy cold rolled and annealed at 120 °C seems to have a retained deformation texture but with an emerging Cube component. The difference may be attributed to the recrystallization conditions. In Ref. [7], 250 °C was used as recrystallization temperature, at which no precipitation was expected to occur. A lower recrystallization temperature is applied in this work where in the domain of $(Pb,Sn)_3Ca$ intermetallic precipitation, the recrystallization process is considerably hindered.

Figure 7 presents the evolution of the relative resistivity versus annealing time under isothermal conditions. The relative resistivity decreases monotonically without apparition of any peak that may be inferred to multiple phase transformation in the material. The monotonous decrease of the resistivity has already been observed by previous studies for non-deformed and non-aged Pb-Ca-Sn alloys [20−21] and was explained by the precipitation of intermetallic $(Pb,Sn)_3Ca$. The kinetics of precipitation in the present study upon ageing at 80 °C seems to be in agreement with the results in Refs. [20−21]. The resistivity evolution may be correlated to the micro-hardness evolution versus ageing time. In Fig. 8, a classical evolution of deformed and recrystallized material microhardness is depicted. More or less, the time to reach total recrystallization (full softening of the material) is close to that determined by

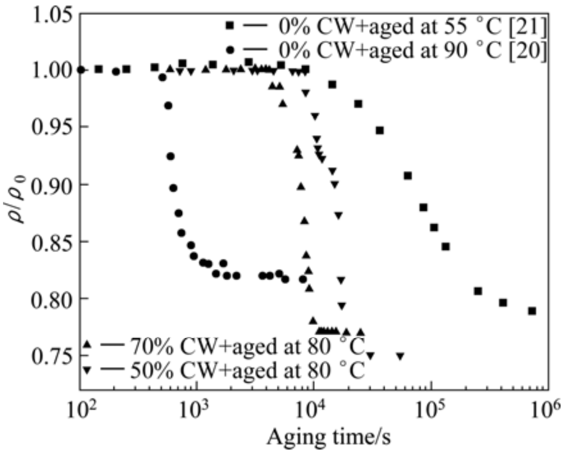


**Fig. 7** Evolution of relative resistivity versus isothermal annealing time of cold rolled Pb-0.08Ca-2Sn samples (Results in Refs. [20] and [21] are given for comparison)

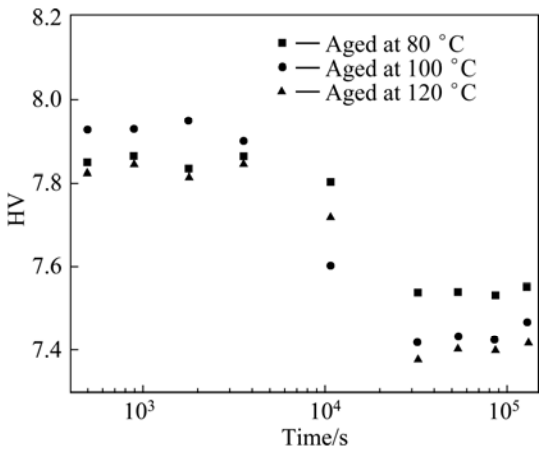


**Fig. 8** Evolution of Vickers hardness versus isothermal annealing time of Pb-0.08Ca-2Sn samples cold rolled to thickness reduction of 70%

resistivity measurements after full precipitation, which is around (2−4)×$10^4$ s. As pointed out in Refs. [1−2, 9−10, 22], it was established that Pb-Ca-Sn alloys with low molar ratio of tin to calcium may undergo several kinds of precipitation reactions. In aging, these alloys with high molar ratio of tin to calcium are evidenced by a suppression of all the preliminary transitional decompositions and the evolution of a continuous precipitation and subsequent over ageing. For example, a heat treatment (at 100 °C for 1.5 h) of a Pb-Ca-Sn alloy immediately after casting and rolling accelerates and induces a complete precipitation of the ordered $L1_2$ intermetallic phase in a short time which hinders the recovery and recrystallization [9−10, 22].

The order of occurrence of the precipitation and recrystallization reactions and the influence of temperature, super saturation and annealing time were discussed qualitatively in Ref. [23]. The Pb-Ca-Sn alloy seems to obey to the proposed schemes [23] for aging temperature ranging from 80 to 120 °C for which the precipitated particles influence both the rearrangement of dislocations to form recrystallization front and the migration of the latter. Aging at temperature ranging from 80 to 120 °C induces a combined continuous precipitation and recrystallization reactions that are dissimilar to the second part of the scheme proposed in Ref. [23], in which the recrystallization is influenced only by segregation and the precipitation occurs after the completion of the recrystallization.

## 4 Conclusions

1) The deformation texture of cold rolled Pb-0.08Ca-2Sn samples (to 50% and 75% thickness reduction) determined through X-ray diffraction is qualitatively the Brass type.

2) The Lankford anisotropy parameter *R* evolution with angle to rolling direction shows the presence of planar anisotropy and poor drawability.

3) Annealing treatments at temperature ranging from 80 to 120 °C lead to recrystallization within time periods up to 3×$10^4$ s. The recrystallization texture of Pb-0.08Ca-2Sn samples at 120 °C is retained deformation texture with an emerging Cube component.

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# Pb-Ca-Sn 合金的变形与再结晶组织、微观结构和动力学

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**摘　要：**在室温下将 Pb-0.08Ca-2Sn 合金轧制到不同厚度。电阻率和显微硬度的测试结果表明，样品在 80~120 °C 的温度区间退火时发生再结晶。XRD 检测确定变形组织为 Brass 型，所测得的 Lankford 各向异性参数 *R* 及其变化与用自洽方法所推导的结果接近。*R* 值随轧制方向角度的改变表明该合金具有平面各项异性和较差的延展性。合金在 80~120 °C 的温度范围内退火时，在 $3\times10^4$ s 内完成再结晶，显示出保留变形组织并有新 Cube 组元出现。

**关键词：**Pb-Ca-Sn 合金；冷轧；再结晶；织构

**(Edited by FANG Jing-hua)**