Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 20(2010) 1774−1779
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Semisolid lead-antimony alloys for cars batteries

A. POLA[1], M. GELFI[1], M. MODIGELL[2], R. ROBERTI[1]

1. Dipartimento di Ingegneria Meccanica e Industriale, Università degli Studi di Brescia, via Branze 38, 25123 Brescia, Italy;
2. Aachener Verfahrenstechnik, Chair of Mechanical Unit Operations, RWTH Aachen University, Turmstr. 46, 52056 Aachen, Germany

Received 13 May 2010; accepted 25 June 2010

Abstract: The application of semisolid process was investigated on Pb-Sb alloys that are normally used for metallic parts in car batteries, in order to increase their mechanical properties and corrosion resistance. The semisolid behaviour of a Pb-4%Sb alloy was analysed by means of rheological and calorimetry differential scanning experiments. The alloy was melted, treated by ultrasound to obtain the semisolid state and then poured into permanent moulds. Some of these samples were also heated in semisolid temperature range and injected in thixo-casting apparatus. Both poured and injected samples were characterized by metallographic analysis, mechanical test and electrochemical corrosion experiments. The results show an improvement of mechanical and corrosion resistance with respect to samples obtained by conventional casting technique.

Key words: Pb-based alloys; semisolid metal; corrosion resistance; viscosity

1 Introduction

Metallic parts used in car batteries, such as grid, connectors and terminals, are made in lead alloys. For these specific applications, lead alloys must guarantee some basic requirements as: 1) adequate hardness and strength, 2) low mechanical and heat distortion, 3) light intercrystalline corrosion and low corrosion rate, 4) good casting properties, 5) good weldability, and 6) low pollution and costs[1].

In order to fulfil all these properties, lead-acid batteries manufacturers have focused on modifications of production processes and on the alloys chemical analysis[2−7]. Typical chemical compositions for lead-acid batteries parts are: 1) low antimony alloys (0.8%−3% Sb), with small additions of As, Sn, etc; 2) high antimony alloys (3%−11% Sb), containing low amounts of As, Sn, etc; and 3) Pb-Ca-Sn alloys.

Hence, the main alloying system used in batteries is lead-antimony one. This alloy family is characterized by an eutectic transformation at 251.5 °C and 11% (mass fraction) of Sb; it is easy to cast into complex shapes as those for grids, connectors and terminals that are commonly obtained by foundry process. Being obtained by solidification into a permanent mould, Pb-Sb parts are commonly characterized by dendritic microstructure surrounded by nobler Sb-rich segregations, which can reduce the corrosion resistance. Moreover, porosities related to the foundry process can negatively affect the mechanical properties of castings.

Antimony is added to strengthen and harden lead as well because of its influence on conductive properties. It reduces corrosion resistance of the positive grid and, in high content in the negative plate, leads to the formation of stibin which is toxic[8].

The original antimony alloy concentrations are in the range of 8%−12%. Nowadays, the content is reduced to 3%−6%, in order to contrast the adverse effect of antimony without decreasing its advantageous role.

Lead-antimony alloys having low Sb content provide the desired strength. However, batteries parts containing 1.5%−3.5% (mass fraction) antimony show brittle behaviour and tendency for cracking, apparently because of the coarse dendritic microstructure. The reduction of Sb content causes a decrease in mechanical properties and in castability of the alloys. This can be partly compensated by the introduction of small amounts of other elements such as Se, As or Ag[8].

An alternative way to improve the performance of

Corresponding author: A. POLA; Tel: +39-0303715576; E-mail: annalisa.pola@ing.unibs.it
DOI: 10.1016/S1003-6326(09)60373-3

low-Sb lead alloys is most likely to be represented by the production of acid battery components by semisolid forming, in order to obtain a globular microstructure. In fact, recent studies on the influence of microstructural morphology and solute redistribution on corrosion resistance in HSO_4 solution for Pb-Sb alloys show that cellular structures and dendritic structures have different responses to the corrosion rate of such alloys[9].

In this work, the performances of semisolid Pb-4%Sb alloy were investigated in order to obtain car batteries parts characterized by improved mechanical properties and corrosion resistance compared with the traditionally solidified castings. In particular, improvements in the mechanical properties allow the reduction of the net section area and consequently of the weight, i.e. consumption, of lead which is carcinogenic.

The thixotropic properties were verified by measuring the alloy viscosity as a function of temperature; particularly, rheological experiments were carried out to study the shear rate and time-dependent flow behaviour in the semisolid state. Subsequently, some samples were produced by means of ultrasounds treatment to obtain a globular microstructure, both for rheocasting and thixocasting, i.e. with low and high solid/liquid ratio, respectively. These specimens were characterized from metallurgical, mechanical as well as corrosion resistance point of view.

2 Experimental

The experiments were carried out on a commercial Pb-4%Sb alloy, specific for the production of car batteries parts. The melting process of the alloys was experimentally studied via differential scanning calorimetry (DSC) analysis, performed with a TA instrument Q600 apparatus equipped with Universal Analysis 2000 software. The DSC analyses were carried out in a purified argon atmosphere with a scanning rate of 10 °C/min.

In parallel, rheological experiments were performed in a Searl rheometer, in order to evaluate the behaviour of the alloy under shear rate in the semi-solid range. The used rotational rheometer is characterized by a concentric cylinder measuring device. Rotational speed and momentum are measured at the rotating rod. Both rod and cup are made of graphite to avoid chemical interactions between the material under investigation and the measuring system. The rotating rod is evenly grooved to avoid the appearance of wall slip, which would lead to false viscosity evaluations. The measuring device is placed inside an oven. The heating mechanism is a combination of radiation and convection, where argon is used as the convective heat carrier, to prevent the oxidation of the sample surface. The temperature is monitored by a thermocouple placed at the bottom of the cup. The semi-solid alloy is generated in the rheometer by cooling down the liquid alloy with a cooling rate of 4 °C/min while simultaneously shearing at 100 s^{-1}. After the temperature corresponding to the desired solid fraction was reached, an isothermal shearing period of 1 h was applied. This part of the investigation is called material preparation. Then, the shear rate jump experiments (25, 50, 100, 150, 200, 250, 300 and back to 25 s^{-1} for 5 min each) were applied to the alloy in the semisolid range (25%, 30%, 35% and 40% of solid fraction) to investigate the shear-thinning and thixotropic flow properties.

For the casting experiments, the alloy was at first melted by laboratory furnace, by heating to a temperature 40−50 °C above the liquidus (known from previous DSC measurements) in a refractory crucible and subsequently poured into a permanent die for manufacturing small bars (7 mm×6 mm×100 mm, see sample B in Fig.1) suitable to undergo mechanical tests, as well as into a cylindrical mould (40 mm in diameter and 15 mm in height, sample D in Fig.1) for further investigations.

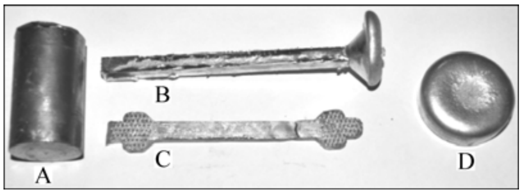

Fig.1 Cast Pb-Sb samples

Subsequently, liquid alloy was treated out of the furnace in order to obtain a globular microstructure typical of semisolid alloys. In particular, the method used consists of applying ultrasound (US) waves to the bath during its cooling within the liquid−solid temperature range. Nowadays, no off-the-shelf ultrasound equipments suitable for this specific application are industrially available; therefore, a US device was purposely manufactured, as already described in previous work[10].

The alloy was US treated while cooling down to around 10% of solid fraction and subsequently poured into the same dies as the full liquid metal.

The two sets of samples were named N (Not US treated) and U (US treated), respectively.

In order to assess the effect of US treatment on casting microstructure, metallographic investigations were carried out on etched sections ($CH_3COOH+H_2O_2$) by means of optical microscope (Reichert-Jung MeF3) equipped with QWin image analyzer, and by means of scanning electron microscope LEO EVO 40, both in secondary electrons and backscattering mode, equipped with an EDS (Energy Dispersive Spectroscopy) probe.

To evaluate the mechanical properties of alloys, Vickers microhardness was measured by applying a 0.98 N load for 15 s. The HV values were obtained as mean of 10 measurements per sample. Tensile tests were performed at a crosshead speed of 0.5 mm/min on Instron 3369 machine, equipped with 50 kN load cell. For all the experiments at least 3 tests were carried out.

Electrochemical corrosion tests were also carried out on square section specimens (1 cm^2) machined from the cast disks as well as on sections (6 mm×7 mm) obtained from tensile samples, in a 0.5 mol/L HSO_4 aqueous solution at room temperature. The AMEL 7050 potentiostat used for the polarization experiments was set in the 3 electrodes standard configuration: platinum counter electrode, saturated calomel reference electrode and working electrode. The polarization curves were collected, after at least 30 min of immersion into the solution, by stepping the potential at a scan rate of 0.16 mV/s from −200 mV to +200 mV with respect to open-circuit potential. Using an automatic data acquisition system, the potentiodynamic polarization curves were plotted and both corrosion rate and potential were estimated by the Tafel extrapolation method.

Finally, the US alloy was also poured in small cylindrical mould (28 mm in diameter and 60 mm in height, sample A in Fig.1) for the production of feedstock material for thixocasting. These billets were heated up to the semi-solid state in situ by a vertical induction heating system and then the soft slurry was forced, by means of a hydraulic vertical press, through a permanent mould to obtain the injected tensile test specimens (sample C in Fig.1), named T. These thixocast parts were characterized according to the above mentioned procedure.

3 Results and discussion

3.1 Rheological behavior

The temporal evolution of the viscosity during material preparation for a solid fraction of 40% is shown as an example in Fig.2. In the full liquid state, the Pb-Sb alloy has a viscosity of about 0.01 Pa·s.

As soon as the alloy is cooled down into the semi-solid state, solid particles appear. During this period, the particles grow in a more or less dendritic way, hence a dramatic viscosity increase is measured. The applied shear field prevents further dendritic growth, thus the particle shape changes from dendritic to globular, inducing a noticeable viscosity decrease. The further decrease in the viscosity in the third part of the diagram is caused by the effect of Ostwald-ripening, achieving an equilibrium value.

The peak viscosity results equal 1.12, 1.75, 2.22 and

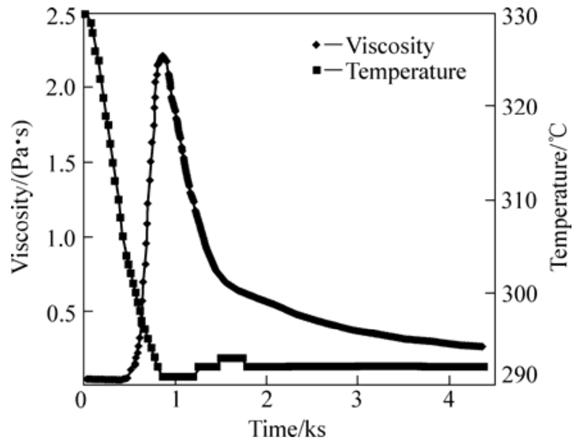

Fig.2 Temperature and viscosity of Pb-Sb alloy versus time during cooling (φ_s=40%) and shearing at shear rate of 100 s^{-1}

2.24 Pa·s for 25%, 30%, 35% and 40% of solid fraction, respectively.

Shear rate jump experiments were done, after material preparation at 100 s^{-1}, in order to evaluate steady state behaviour of the Pb-Sb alloy at different solid fractions. In Fig.3 the results for 35% of liquid fraction are shown, as an example. All the experiments, performed at different solid fractions, give the same behaviour.

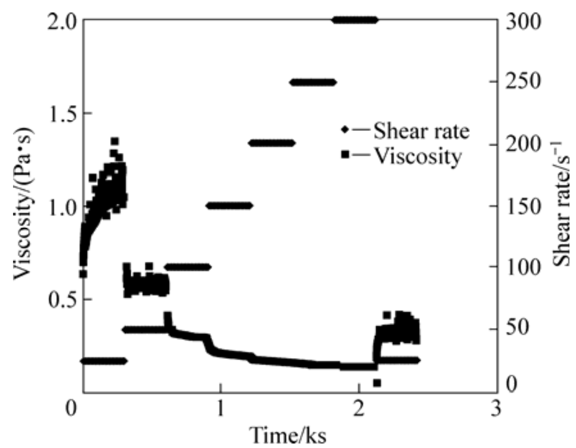

Fig.3 Shear jumps experiment results for 35% of solid fraction of alloy

The time-dependent and shear thinning behaviour of the alloy are clearly seen. As well known, thixotropic materials are essentially shear thinned but also thickened again when being allowed to rest[11].

In all the tests done, the time period needed to attain the steady state condition is a bit longer in the case of downward jumps than for upwards ones. It can be concluded that, the agglomeration proceeds slower than the disagglomeration, which is in good agreement with the result in Ref.[12]. Moreover, the viscosity in the very last jump (corresponding to the abrupt shear rate decrease to 25 s^{-1}) is lower than that in the first one (25 s^{-1}) due to Ostwald ripening.

3.2 DSC analysis

In Fig.4 the melting process of the investigated alloy is shown. According to DSC measurements, the alloy liquidus and solidus temperatures are respectively around 250 °C and 300 °C. Therefore, the solidification range is sufficiently wide, which is useful for semisolid processing. However, this single parameter does not necessarily ensure that the given alloy can be heated to any desired liquid fraction[13]. The DSC signals can be also integrated between the liquidus and solidus temperature in order to obtain the liquid fraction versus temperature curve, as shown in Fig.4.

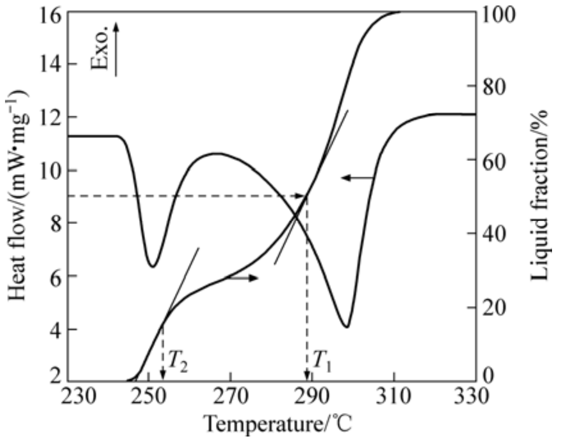

Fig.4 DSC heat flow and liquid fraction curves

The critical parameters on DSC curves, according to the Kazakov criteria[14], are: 1) The temperature (T_1) at which the slurry contains 50% liquid, which is equal to 288 °C; 2) The slope of the curve at φ_L=50% ($d\varphi_L/dT(T_1)$), which must be as flat as possible in order to minimize the reheating sensitivity (As shown in Fig.4, the investigated Pb-Sb alloy presents a slope of 0.021 $°C^{-1}$, which is lightly steep); 3) The temperature of the beginning of solid solution melting (T_2), which is around 253 °C. The difference between T_1 and T_2 determines the kinetics of dendrites spheroidization during reheating.

3.3 Metallographic analysis

In the case of the disk shaped samples, no particular differences are detected in the microstructure of the N and U samples, which are both characterized by the presence of a coarse dendritic microstructure (Fig.5). The U samples just offer a more homogeneous microstructure, almost free from porosity and lightly coarse phases. This similar appearance is probably due to the large thickness of the disks, which involves a slow cooling.

Concerning the bar specimens, the application of ultrasounds induces a strong variation in the microstructure. As shown in Fig.6, the N castings present the typical dendritic microstructure, surrounded by a small percentage of eutectics and also a second phase rich of Sb-As, as detected by SEM analysis shown in Fig.7 and Table 1.

On the contrary, the U samples are characterized by almost rounded Pb primary phase. It must be noticed that

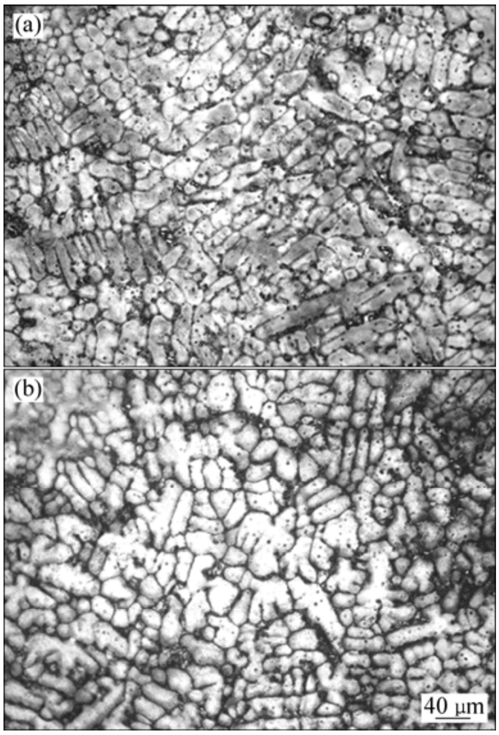

Fig.5 Microstructures of N disk (a) and U disk (b)

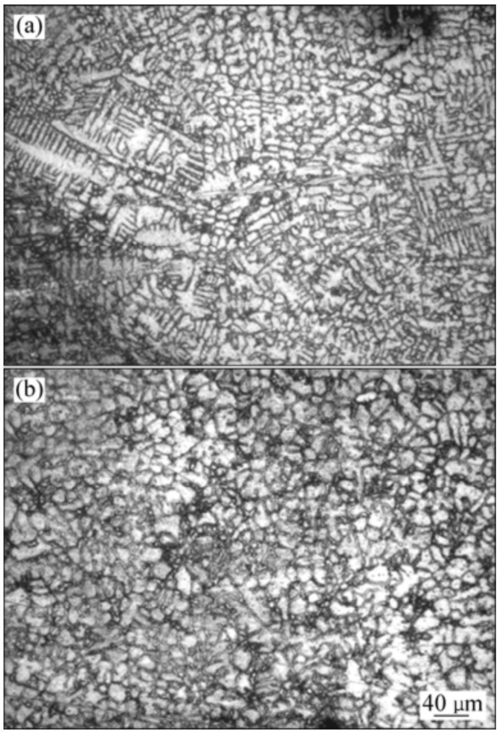

Fig.6 Microstructures of N bar (a) and U bar (b)

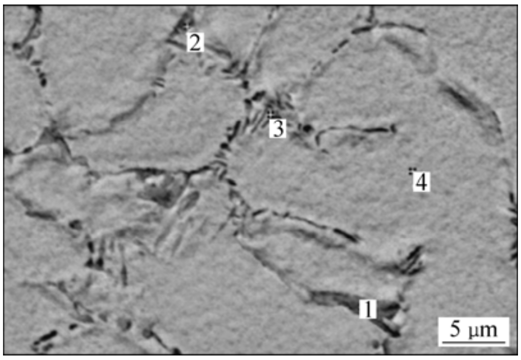

Fig.7 SEM image in back-scattering mode of N sample

Table 1 EDS results of selected zones according to Fig.7 (mass fraction, %)

Zone	As	Sb	Pb
1	27.08	37.04	35.87
2	−	16.45	83.55
3	−	16.71	83.29
4	−	2.97	97.03

the lack of dendrites, whose arms can interconnect and obstruct the eutectic liquid feeding, prevents from the formation of shrinkage micro-porosity.

The thixocast samples have a more homogeneous globular microstructure, finer than that of U samples, as shown in Fig.8.

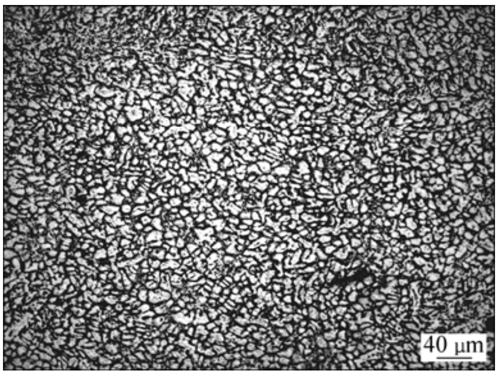

Fig.8 Microstructure of thixocast samples

3.4 Mechanical properties

The microhardness values of the N and U disks are similar, according to the comparable microstructure. Concerning the bars, the N samples offer a mean value of HV 14 and a standard deviation (σ) of 1.5, while the U specimens offer HV 16 and σ=0.9. The thixocast parts show a great improvement, reaching a mean value of HV 21.5 and also a lower standard deviation (σ=0.8).

In Fig.9 the results of mechanical tests, performed on the small bars (both N and U samples) as well as on thixocast specimens, are summarized. It can be observed that mean casting properties (σ_b, σ_Y) are quite similar for

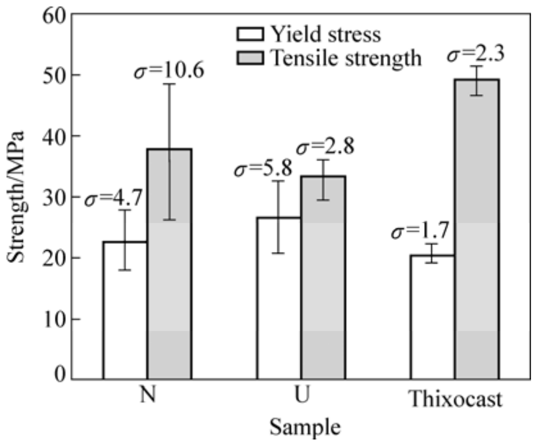

Fig.9 Mechanical tests results

the N and U bars.

The semisolid thixocast part shows an average tensile strength of 50 MPa, i.e. higher than that of N or U samples (around 35 MPa), probably because of the more homogeneous and globular microstructure as well as lack of porosity. It must be reminded that N and U castings were obtained by pouring respectively the liquid and 90%φ_L alloy into a steel die, while thixocast samples were produced by injecting the semisolid billet into a die, therefore, a lower porosity and a higher cooling rate induced by the applied pressure are expected.

3.5 Corrosion resistance

Fig.10 shows experimental potentiodynamic polarization curves for samples obtained from small bars. The mean corrosion current densities (J_{corr}) calculated by means of the Tafel extrapolation are reported in Table 2. The corrosion resistance appears to be increased for the US treated alloys (U and thixocast samples), which have corrosion currents less than half that of the sample N.

As reported in Ref.[15], the corrosion of Pb-Sb alloys in H_2SO_4 acid is mainly due to the micro-galvanic

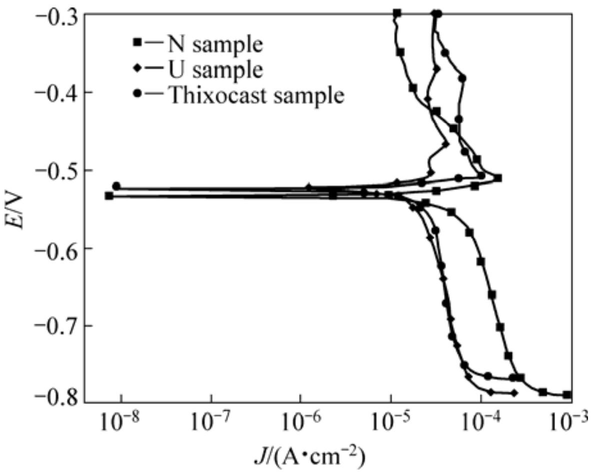

Fig.10 Polarization curves for N, U and thixocast samples

Table 2 Results of Tafel extrapolation

Sample	Corrosion current, J_0/(A·cm^{-2})	Corrosion potential, E_0/V
N	$(16.2±4.6)×10^{-5}$	−0.53
U	$(7.1±2.7)×10^{-5}$	−0.54
Thixocast	$(6.5±1.6)×10^{-5}$	−0.53

effect which develops at the interface between Pb-rich (less noble) and Sb-rich areas. For a fixed composition, the differences in corrosion velocities are principally related to the difference in microstructure and grain size which influences the distribution of solute, the extension and the shape of corrodible interfaces[16].

Ultrasound treatment has an homogenizing effect on sample composition because ultrasound promotes the evolution from dendritic to globular microstructure, which reduces the segregations and allows a more uniform solute redistribution. Moreover, the globular microstructure of US treated sample appears to be coarser than that of sample N, and consequently, the corrodible Pb/Sb interfaces are reduced.

In conclusion, the US treatment seems to be a convenient way to increase the corrosion resistance of Pb-4%Sb alloys as already demonstrated for alloy Al-5%Si[17].

4 Conclusions

1) According to DSC measurements the solidification range of Pb-4%Sb alloy appears sufficiently wide, which is useful for semisolid processing.

2) The rheological tests demonstrate the time-dependent and shear thinning behaviour of the alloy.

3) As detected by metallographic investigation, the application of ultrasound allows to obtain a homogenous globular microstructure in thin specimens. For wider ones, the structure remains dendritic, probably because of the inadequate power of ultrasound generator used, considering the high density of this material.

4) Concerning the mechanical properties, US treated thin samples do not show significant increase in hardness and strength with respect to the castings obtained from the full liquid alloy, even if the low dispersion of data indicates a better microstructural homogeneity. On the contrary, the thixocast samples show a great increase in mechanical properties, probably because of the more uniform and globular microstructure as well as lack of porosity.

5) Electrochemical corrosion tests indicate the superior corrosion properties of US treated and thixocast samples, confirming the ability of this process in reducing segregations and promoting a uniform solute distribution.

Acknowledgments

The authors wish to thank Lorenzo Montesano for the helpful support.

References

[1] GHASEMI Z, TIZPAR A. Studies on corrosion resistance and electrochemical behavior of Pb-Sb-As-S alloys as positive grids in lead-acid batteries [J]. Int J Electrochem Sci, 2007, 2(9): 700−720.

[2] PRENGAMAN R D. Challenges from corrosion-resistant grid alloys in lead acid battery manufacturing [J]. J Power Sources, 2001, 95(1/2): 224−233.

[3] PRENGAMAN R D. New low-antimony alloy for straps and cycling service in lead-acid batteries [J]. J Power Sources, 2006, 158(2): 1110−1116.

[4] ACHTERMANN M D, GREENLEE M E. Application of wrought lead calcium batteries in Europe [J]. J Power Sources, 1991, 33(1/2/3/4): 87−92.

[5] AL-GANAINY G S, MOSTAFA M T, ABD EL-SALAM F. Quenching media and temperature dependence of structural and stress-strain characteristics of deformed Pb-2at% Sb alloy during transformation [J]. Physica B, 2004, 348(1/2/3/4): 242−248.

[6] REZAEI B, DAMIRI S. Effect of solidification temperature of lead alloy grids on the electrochemical behavior of lead-acid battery [J]. J Solid State Electrochem, 2005, 9(8): 590−594.

[7] SHIOTA M, KAMEDA T, MATSUI K, HIRAI N, TANAKA T. Electrochemical properties of lead dioxides formed on various lead alloy substrates [J]. J Power Sources, 2005, 144(2): 358−364.

[8] GHASEMI Z, TIZPAR A. Influence of silver on the anodic corrosion and gas evolution of Pb-Sb-As-Se alloys as positive grids in lead acid batteries [J]. Applied Surface Science, 2006, 252(22): 7801−7808.

[9] ROSA D M, SPINELLI J E, FERREIRA I L, GARCIA A. Cellular/dendritic transition and microstructure evolution during transient directional solidification of Pb-Sb alloys [J]. Metallurgical and Materials Transactions A, 2008, 39(9): 2161−2174.

[10] POLA A, ARRIGHINI A, ROBERTI R, Ultrasounds: A new technology for alloys degassing, grain refinement and obtainment of a thixotropic structure [C]//11th ICAA Int Conf. Wiley-VCH, Aachen, 2008: 321−327.

[11] ATKINSON H V. Modelling the semisolid processing of metallic alloys [J]. Progress in Materials Science, 2005, 50(3): 341−412.

[12] KUMAR P, MARTIN C L, BROWN S. Shear rate thickening flow behavior of semisolid slurries [J]. Metall Trans A, 1993, 24(5): 1107−1116.

[13] ATKINSON H V, KAPRANOS P, KIRKWOOD D H. Alloy development for thixoforming [C]//6th Int S2P Conference. Turin, 2000: 443−450.

[14] KAZAKOV A A. Alloy composition for semisolid forming [J]. Advanced Material and Processing, 2000, 157(3): 31−34.

[15] ROSA D M, SPINELLI J E, OSORIO W R, GARCIA A. Effects of cell size and macrosegregation on the corrosion behavior of a dilute Pb-Sb alloy [J]. Journal of Power Sources, 2006, 162(1): 696−705.

[16] OSORIO W R, ROSA D M, GARCIA A. The roles of cellular and dendritic microstructural morphologies on the corrosion resistance of Pb-Sb alloys for lead acid battery grids [J]. Journal of Power Sources, 2008, 175(1): 595−603.

[17] ARRIGHINI M, POLA G A, ROBERTI R. Effect of ultrasound treatment of AlSi5 liquid alloy on corrosion resistance [J]. Materials and Corrosion, 2010, 61(3): 218−221.

(Edited by YANG Bing)