Micro-chemical clustering phenomena in liquid lead-bismuth alloy

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Abstract—Eutectic Pb-Bi alloy in the liquid state is considered as a good candidate for application in cooling device of an accelerator driven systems (ADS), such as MYRRHA. Our previous studies, based on the measurements of mechanical spectroscopy and high temperature X-ray diffraction, evidenced the instability of the alloy structure in liquid phase, with many changes at increasing temperature. In order to understand, if these changes involve the clustering phenomena of constituent elements, the alloy has been quenched at different temperatures, in order to freeze its liquid structure. It is expected that during the quenching, the liquid structure remains unchanged at least on the surface of the sample. Therefore, the surface of the quenched samples was investigated by means of X-ray Photoelectron Spectroscopy (XPS) and Scanning Photoemission Microscopy (SPEM), trying to determine the lateral distribution of the elements. Obtained results revealed the presence of a large number of clusters enriched in Pb or Bi which are enclosed in the eutectic matrix. The SPEM experiments revealed a rearrangement and redistribution of Pb and Bi clusters with varying size and chemical composition depending on the quenching temperature. Basing on the SPEM chemical maps, the statistical distribution of these clusters was calculated, taking into consideration both the cluster size and their chemical composition.

Keywords—Pb-Bi eutectic alloy, high temperature, XPS, SPEM

I. INTRODUCTION

Eutectic alloy of Pb and Bi (LBE) is used in liquid state as a coolant and neutron spallation source for accelerator driven systems, such as the MYRRHA [1]. The compatibility of structural materials with liquid LBE coolant at high temperature is one of the key issues for the commercialization of new type reactors, where the corrosion and embrittlement of liquid metal are the main problems. Possible changes of the liquid at high temperature may affect the interaction of LBE with structural materials. Therefore, the understanding of LBE behaviour at high temperatures is crucial for this application.

Previously, the mechanical properties of LBE have been investigated by internal friction (IF) and dynamic modulus measurements from room temperature till 720 °C [2-3]. After the drop at the melting point of 125 °C, the modulus was steadily decreasing till about 400 °C, where was observed a remarkable drop till about 500 °C. Above this temperature, the modulus continued to decrease with a slope very close to the initial one. In correspondence to the drops of dynamic modulus, the maxima of IF were detected at 125, ~ 350 and ~ 460 °C. Zu et al. [4] have observed a maximum of IF centred at ~550 °C by using a modified inverted torsion pendulum. The same behaviour was observed also in Pb-Bi alloys with different compositions [4] and in other alloys [5-7]. The common model is based on the heterogeneous structure of the alloys after melting, containing residual minor crystals till the critical temperature is reached, when the residual conglomerates are broken and the uniform structure appears. Even if there is a little discrepancy between the temperatures of IF maximum, the same phenomenon, observed by all authors, can be explained by structural re-arrangement of metal atoms in the liquid. These results are also consistent with some anomalies of the electrical conductivity [8-9].

Recently, have been published also the first results of high temperature X-ray diffraction (HT-XRD) measurements on this alloy [10]. The radial distribution functions (RDF) have been calculated from the diffraction patterns [11] and fitted by pair functions in order to determine the mean distance in Pb-Pb, Bi-Bi and Pb-Bi pairs in the liquid. The dependence of average distance between the nearest neighbours on the temperature revealed the structural transformation starting at about 350 and finishing at about 520 °C [10].

The first attempts to investigate directly the micro-chemical structure of LBE at high temperatures have been done by using water quenching of liquid alloy and scanning photoemission microscopy (SPEM) at the Elettra synchrotron of Trieste, Italy [10,12]. This study has been done on the samples quenched at three temperatures of the melt: 313, 401 and 518 °C. Statistical analysis of obtained results confirmed that the distribution of Pb and Bi after melting is not

homogeneous: the liquid alloy consists of many micro-clusters enriched with Pb or Bi atoms. The size of these clusters was decreasing with increased temperature till 510 °C.

In the present work, the experimental investigation of quenched LBE alloy by using X-ray photoemission spectroscopy (XPS) and Scanning Photoemission Microscopy (SPEM) techniques was extended to the temperature range of 126 – 700 °C. Moreover, the statistical analysis of obtained surface chemical images was enhanced in order to reveal the changes in micro-chemical composition, corresponding to the transformations of mechanical properties of liquid LBE.

II. MATERIALS AND METHODS

The investigations were carried out on the Pb-Bi alloy with eutectic composition of Pb = 43.9 and Bi = 56.1 wt% , which corresponds to the atomic ratio Pb : Bi = 0.8. The melting temperature of this alloy is 125 °C. In order to quench the liquid and to obtain planar surfaces, required for photoemission experiments, was used a suitable sample holder. The LBE alloy was preliminarily cast inside a pipe of AISI 316L stainless steel closed at one extremity. Particular attention was given to the complete filling of the pipe, seeking to avoid the presence of air bubbles that could lead to inhomogeneous sample cooling during the quenching. The alloy temperature was monitored by using a thermocouple embedded into the sample. After metal solidification, the other extremity of the pipe has been sealed and the pipe pressed to get two planar surfaces [12]. Then the sample holder was heated for 1 h in a vertical furnace at selected temperature and quenched in water. This process was repeated for six samples at different temperatures: 126, 200, 313, 401, 518 and 700 °C. The sample cooling rate measured by the thermocouple was of about 520 °C s^{-1}. Of course, this rate depends on the distance from the sample surface, where occurs the fastest change of the sample temperature. In the conditions of our experiments, the free random shift of the atoms during cooling in the surface layer with 20 nm thickness was below 100 nm. Therefore, the SPEM chemical images correspond to original sample surface at high temperature with this experimental error, which is very near to the SPEM lateral resolution.

The XPS experiments were performed by using a monochromatized spectrometer Escalab 250Xi (Thermo Fisher Scientific, UK) equipped with six-channeltron detection system for spectroscopy.

Before the measurements, the samples surface was cleaned by using an EX-06 Ar$^+$ ion gun at 2.0 keV energy. All spectroscopic data were processed by the Avantage v.5 software.

Laterally resolved XPS measurements were performed by the SPEM apparatus hosted at the ESCA microscopy beamline of the Elettra synchrotron in Trieste, Italy. Monochromatic X-ray beam from synchrotron source is focused on the sample to a diameter of about 150 nm by using Fresnel zone plate optics. The scanning is performed by mechanical movements of the sample (about 50 nm resolution) with respect to the source microprobe. Photoelectrons are collected by a SPECS-Phoibos 100 hemispherical analyzer and detected by 48-channel detector. Photoemission spectra of selected regions and chemical maps were acquired with 0.2 eV resolution in energy by using photon energy of 667 eV. Before the measurements, the surface of all samples was cleaned by Ar$^+$ ion sputtering, operating at 2.0 keV energy and a sample current of 5 ÷ 10 µA. Chemical maps were processed by using the software Igor v.6.3. More experimental details on the SPEM technique have been reported elsewhere [13, 14].

III. RESULTS AND DISCUSSION

XPS analysis revealed on the samples surface the presence of Pb, Bi, O and adventitious C, that was removed only after few cycles of Ar$^+$ sputtering. Pb and Bi were initially present as PbO and Bi_2O_3 oxides with Pb 4f$_{7/2}$ and Bi 4f$_{7/2}$ peaks at binding energy BE = 138.4 and 158.5 eV, respectively. Moreover, the shape of the Bi 4f spectrum revealed also the presence of metallic Bi at BE = 156.0 eV [12]. After the removal of the surface sublayer of ~ 6 nm, the amount of Bi_2O_3 was significantly reduced, whereas PbO still remained without any trace of metallic Pb, thus confirming that the oxide of Pb is much more stable under ion sputtering than the one of Bi [15]. The multipoint XPS analysis carried out on the cross-section of the samples, showed that the Pb/Bi atomic ratio varied from the nominal value of 0.8, measured at 0.5 mm from the top of the sample, to the values near the surface, depending on the quenching temperature.
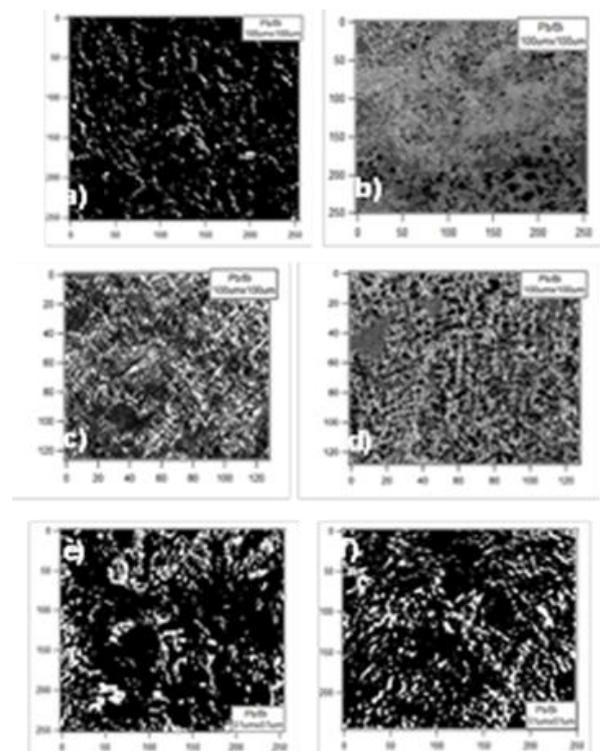
Fig. 1. SPEM images of the atomic ratio (AR) Pb : Bi for the samples quenched at: a) 126 °C, b) 200 °C, c) 313 °C, d) 401 °C, e) 518 °C, f) 700 °C.

Typical SPEM images acquired for the samples, quenched at 126, 200 and 700 °C, are shown in Fig. 1. From these images, it is possible to see the non-uniform distribution of the micro-clusters rich in Pb and its strong dependence on the quenching temperature. Remembering that the surface after quenching is very similar to the original surface of liquid alloy (see Experimental), it is possible to conclude that the size and distribution of micro-clusters in the liquid are changing significantly with temperature. This fact is better visible in the same images processed by Matlab software (Fig. 2), where different colours represent the surface areas rich in Pb or Bi. However, for the better understanding of these changes and for numerical comparison of the images some statistical criteria of the chemical maps are necessary.
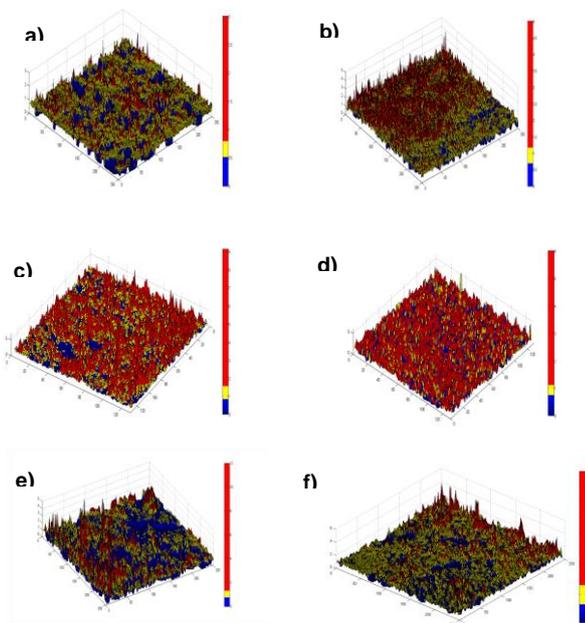
Fig. 2. 3D SPEM images processed by Matlab for the samples quenched at: a) 126 °C, b) 200 °C, c) 313 °C, d) 401 °C, e) 518 °C, f) 700 °C.

Let's start with the cumulative area of the chemical maps. This term means the percentage of total area (i.e., number of pixels in the image) with atomic ratio Pb : Bi (AR), which is higher than the nominal value of LBE (AR > 0.8). The equation for calculating the cumulative area (CA) in % is the following:

$$CA = \frac{100}{n} \sum_{i=1}^{n} p_i \qquad (1)$$

where n is total number of pixels in the image, p_i = 1, if AR > 0.8 and p_i = 0, if AR ≤ 0.8.

By plotting the values of CA versus quenching temperature, we obtained an interesting graph presented in Fig. 3. Two jumps of CA are observed in this graph: when the temperature is changing from 126 to 200 °C and from 401 to 518 °C. These jumps

correspond to the transitions observed in the experiments of mechanical properties: dynamic modulus and IF [2,3]. The second one corresponds also to the transformation observed in the dependence of average interatomic distance measured by HT-XRD [2,10].
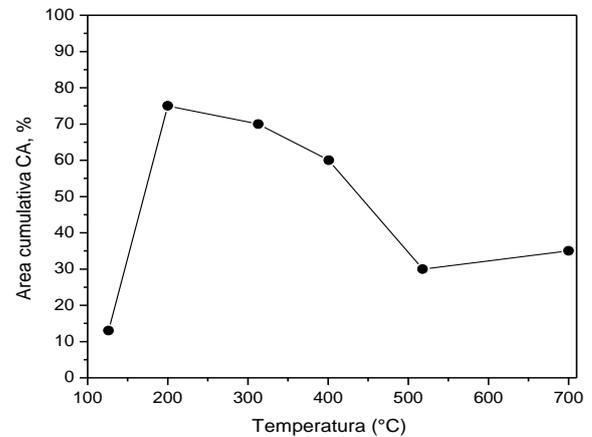
Fig. 3. Cumulative area (CA) of the zone enriched in Pb vs. quenching temperature.

If we have a look at the distribution of AR values through the area of chemical maps (Fig. 4), then
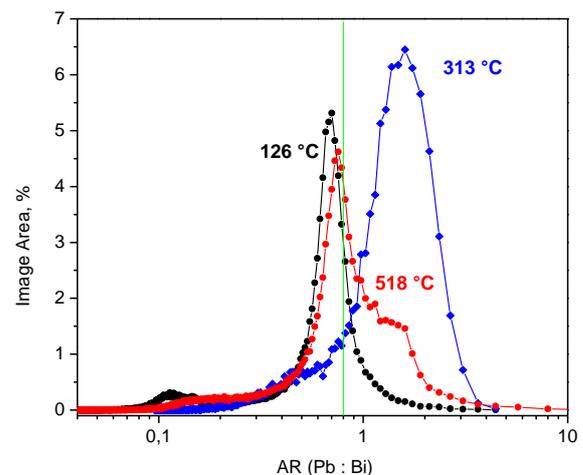
Fig. 4. Area distribution (%) of the chemical maps as function of AR (semi-logarithmic scale). The nominal value AR = 0.8 is marked with green line.

it will be possible to see how much the maximum of this distribution is shifted from the nominal AR value. At the beginning, i.e. very near to melting point, the maximum of distribution is very near to the nominal value of AR (indicated by green line). When the temperature is increased (see the curve at 313 °C), the maximum of distribution is shifted far away from the nominal value, because Pb-rich clusters are dominating on the surface, as it results also from the changes of CA shown in Fig. 3. After the liquid transformation between 400 – 500 °C, the maximum of distribution is returning back towards nominal value, even if its shape is still asymmetrical (see the curve at 518 °C). The dependence of AR value at the maximum of distribution on the temperature is plotted in the Fig. 5. In this figure, it is evident the sharp

transformation of the liquid alloy between about 400 and 500 °C.
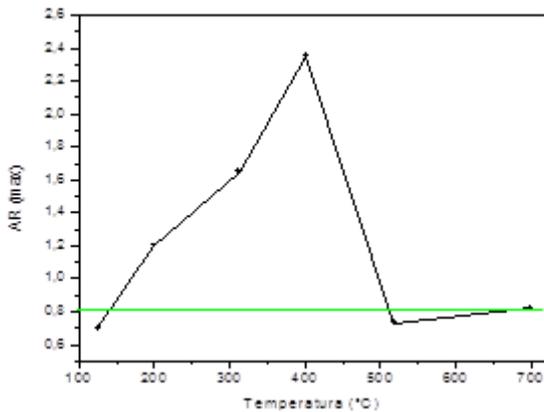
Fig. 5. Peak position of the maximum of the AR distribution as function of the quenching temperature. Green line indicates the AR nominal value.

One more statistical parameter, which could describe the structure of liquid alloy, is the average size of the clusters rich in Pb and in Bi. The determination of cluster size has been done from the wide line scans (width of 20 pixels, i.e. about 8 µm) on the chemical maps, manually measuring the distances between the starting and final point of every cluster rich in Pb (AR > 1) or in Bi (AR < 0.6). All the pixels with the values of 0.6 < AR < 1.0 were attributed to the alloy matrix with almost nominal value of AR = 0.8. From the obtained plots of the cluster size distribution on AR values, the average size was calculated after eliminating the few clusters with the values very far from the distribution cloud (see Fig. 6).
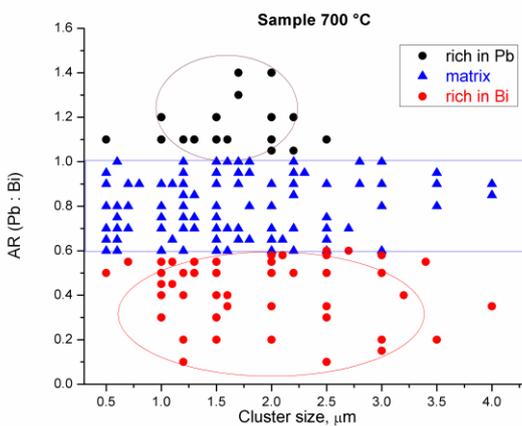
Fig. 6. Cluster size distribution calculated from the chemical map for the sample quenched at 700°C.

Obtained cluster sizes were plotted versus the quenching temperature in the Fig. 7. As we can see from this figure, the average size of both types of the clusters is decreasing with temperature till about 500 °C. There is only a jump in the size of Pb-rich clusters between the melting temperature till about 200 °C. From about 500 °C, the average size of the clusters is more or less constant.

Apparent increase of cluster size at 700 °C can be explained by the low number of clusters rich in Pb and Bi, remaining at this temperature. As we can see from the chemical maps (Figs. 1c and 2c) and the distribution of AR (Fig. 5), at this temperature the alloy matrix with AR near to its nominal value is dominating in the liquid LBE, therefore the sample surface is almost uniform.
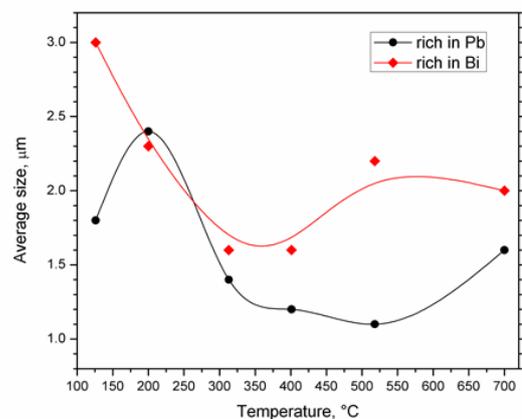
Fig. 7. Average size of the clusters enriched in Pb (black) and Bi (red) vs. quenching temperature.

IV. CONCLUSIONS

SPEM technique in combination with temperature quenching of liquid metal alloy enables to analyze the surface distribution of constituent metals and to reveal the micro-chemical structure of liquid alloy. In the case of liquid LBE alloy, it was demonstrated that the distribution of Pb and Bi is very unhomogeneous. After the melting, the alloy is contains many different clusters, enriched in Pb or Bi. As the quenching temperature is increased to about 500 °C, the average cluster size is decreasing.

All other statistical parameters of the surface chemical maps (AR at the maximum of surface distribution and cumulative area of the pixels enriched in Pb) in the LBE alloy, quenched at different temperatures, are indicating the transformation of alloy structure between 400 and 500 °C, i.e. in the temperature range which corresponds to the transformation of mechanical properties [2,3] and structural parameters revealed from the HT-XRD analysis [10]. All the changes of the liquid LBE properties (mechanical, structural and micro-chemical) can be explained by the transition from cuboctrahedral structure near to the melting temperature to icosahedral one at higher temperature, afterwards the

influence of thermal diffusion, which is breaking the Pb-Pb and Bi-Bi bonds in the micro-clusters and creating more uniform alloy with dominant Pb-Bi bonds an lower inter-atomic distances between the first neighbours.

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