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Magnetic field effect on the deposition of nickel in molten Pb–17Li

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Abstract

Corrosion of structural materials by Pb–17Li liquid alloy may lead to deposit formation under the influence of the temperature gradient and the high magnetic field present in fusion reactors. Such a phenomenon can affect the operation of the liquid metal blanket. For this reason, the crystallization and deposition processes taking place in the liquid alloy under a magnetic field have to be studied. This work deals with the solubility and crystallization of nickel which occur in Pb–17Li under various magneto-thermal treatments. At 300°C, it is shown that the solubility of nickel in Pb–17Li is not affected by the magnetic field. The deposition process remains difficult to explain. However, from a qualitative point of view, differences are observed with regard to the size and distribution of deposited crystals, depending on the experimental conditions.

1. Introduction

The lithium-lead alloy, Pb–17Li (at.%), has been proposed as a tritium breeding source in the liquid metal blanket of fusion reactors. Corrosion studies have shown that the structural materials (austenitic stainless steel type 316 L and 1.4914 martensitic steel) exposed to high temperature Pb–17Li are subjected to dissolution. As a consequence, the dissolved elements can be deposited in colder parts of the blanket and ferromagnetic corrosion products can also be preferentially accumulated in regions of high magnetic field [1]. For fusion applications, deposition constitutes a problem because it may lead to flow restrictions which decrease the flow rate and therefore deteriorate heat and tritium transport. Furthermore, the activation of uncontrolled deposits by the neutron flux in the reactor can generate problems of maintenance.

In order to avoid such problems, methods for trapping the elements present in Pb–17Li are needed. A possible way to remove these elements is to use a cold trap and/or a magnetic trap in order to deposit impurities in dedicated zones. These purification methods are now under investigation [2–4]. However, the influence of various parameters such as temperature, magnetic field and hydrodynamics on the deposition process is far from being understood. In particular, the effect of a high magnetic field on the physico-chemical processes which occur in the flowing alloy is not well known. For example, it could be possible that the collision frequency of solute atoms which gives rise to crystal formation, or the coalescence of particles in suspension in the liquid be modified by the magnetic field. Thereby, the deposition of corrosion products would be affected. This aspect has been developed in another work [5].

The purpose of this work is to study the magnetic field effect on the formation of deposits in a relatively simple case. The element nickel, having a high solubility and a high rate of dissolution in Pb–17Li, has been considered [6]. In this preliminary experiment, the nickel crystals formed in static liquid alloy, in the presence of homogeneous and inhomogeneous fields applied for a fixed period, have been examined. Results are qualitatively discussed as a function of the various magneto-thermal treatments which have been used.

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2. Experimental procedure

2.1. Experimental device

Experiments have been carried out in the high field hybrid magnet of the Grenoble high magnetic field laboratory (GHMFL). Fig. 1 gives a view of the facility. A specific device placed in the gap of the coil, in a region of homogeneous or inhomogeneous magnetic field, has been designed. It consists of a large vessel which is continuously water-cooled in the external part during the experiment. The internal part of the vessel includes a holder to which the sample to be studied is attached, a furnace for heating and a water tank to quench the sample at the end of the test. The temperature is controlled by a thermocouple attached to the sample. In this design, the magnetic field is parallel to the vertical axis of the vessel.

2.2. Experiments

In the present case, the sample was a 316L stainless steel tube (internal diameter: 17 mm, length: 110 mm) filled under argon atmosphere with liquid Pb–17Li alloy containing a preset nickel concentration. The tube was not completely filled so that there was a free surface (≅2 cm from the top of the tube). After solidification of the alloy, the tube was sealed under vacuum.

Two series of experiments were carried out depending on the initial concentration of nickel in Pb–17Li. More precisely, nickel was added to Pb–17Li in order to obtain a low concentration (890 ± 30 wppm) and a high concentration (1930 ± 60 wppm), respectively. Pb–17Li analysis indicates that the alloy also contains some amount of tin (55 ± 5 wppm). The chemical analyses were made by atomic absorption spectroscopy (AAS) and by inductively coupled plasma optical emission spectroscopy (ICP-OES), respectively for Ni and Sn. Finally, three samples were prepared for each range of nickel concentration. Then, all the samples were exposed to the following sequence: heating to 550°C for 16 h to homogenize the liquid alloy, decreasing to 300°C in 90 ± 10 min and maintaining at 300 ± 2°C for 4 days, immersion in water for cooling to ambient temperature (solidification of Pb–17Li at 235°C in 4 s). During the thermal treatment, three different experimental conditions of magnetic field were used: (i) no magnetic field, in order to have a reference, (ii) homogeneous magnetic field, in an uniform magnetic field of 10 T, (iii) inhomogeneous magnetic field, in a magnetic field gradient ranging from 9 to 7 T.

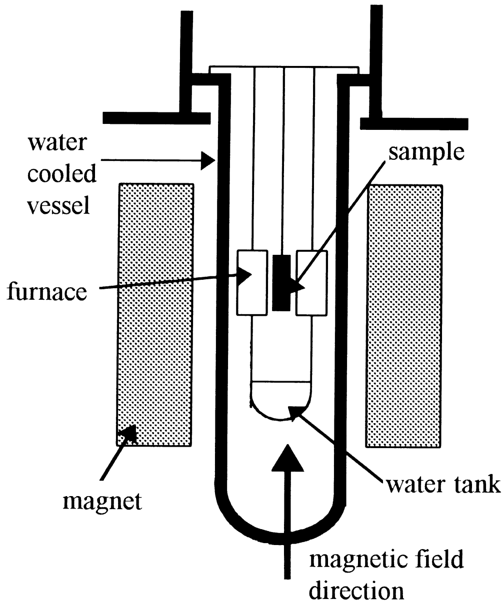

Fig. 1. Schematic view of the experimental facility.

2.3. Characterization

After cooling, the samples were sectioned longitudinally in order to obtain a quarter of the tube. The solidified Pb–17Li was removed from the tube by dissolution, using a chemical mixture (1/3 acetic acid, 1/3 hydrogen peroxide and 1/3 ethanol). The solution thus obtained was analysed by AAS to determine the Ni concentration remaining in Pb–17Li at the end of the test. The walls of the tubes, free of Pb–17Li alloy, were also examined by scanning electron microscopy (SEM) coupled with energy dispersive X-ray analysis (EDX) in order to characterize the crystals formed and deposited during the magneto-thermal treatment (distribution, size, shape...).

3. Results

3.1. Low nickel concentration

3.1.1. Experiment without magnetic field

At the end of the test performed without magnetic field, a small decrease of the initial Ni concentration is observed. The Ni content falls from 890 to 740 wppm, indicating that some deposition should occur during the thermal treatment. This is in agreement with Fig. 2(a) which shows Ni–Sn particles deposited on the wall of the tube. No significant difference is observed between the top and the bottom of the tube. According to [6], the nickel solubility (s) in Pb–17Li is given by: $\log s$ (wppm) $= 4.832 - 981.2/T$(K). Thus, no Ni deposition is expected at 300°C (solubility being equal to 1317 wppm). Furthermore, Ni deposition is unlikely to occur during the rapid cooling from 300°C to ambient temperature. Therefore, the Ni depletion can only be

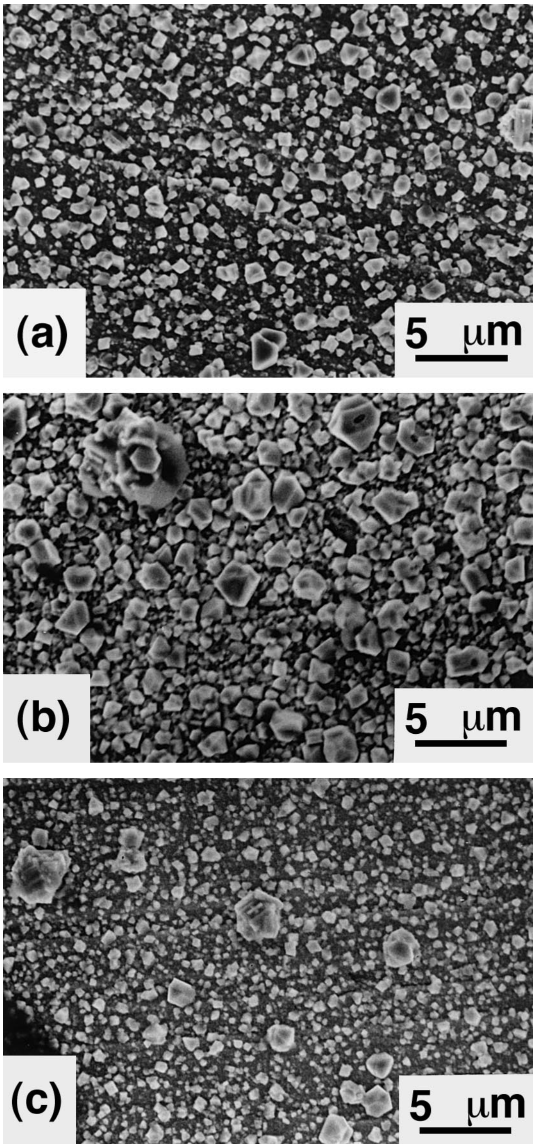

Fig. 2. SEM micrographs showing Ni–Sn crystals in the case of low Ni concentration: (a) without magnetic field, (b) with a homogeneous magnetic field $B = 10$ T, (c) with an inhomogeneous magnetic field.

explained by the formation of Ni–Sn crystals. Although some tin was found in Pb–17Li, it was not expected to react so easily with nickel [7].

3.1.2. Experiment in homogeneous field

The results indicate that the Ni concentration in Pb–17Li falls to 750 wppm. This value is similar to that obtained in the case of the experiment carried out without magnetic field. As already explained, this decrease results from the Ni–Sn particle formation. Although the magnetic field does not seem to affect the Ni concentration in Pb–17Li, differences are observed in the distribution of particles on the walls of the tube. Fig. 2(b) shows that the particles are larger. It can be deduced that the average size of crystals is increased by a factor of two with the field. No significant difference is observed between the top and the bottom of the tube.

3.1.3. Experiment in inhomogeneous field

The Ni concentration in Pb–17Li has also fallen to 740 wppm. This value is similar to that obtained in the previous experiments. Fig. 2(c) shows that the Ni–Sn crystals are smaller and somewhat more scattered than in the case of the homogeneous field (Fig. 2(b)). It is however difficult to see if there is a significant effect of the field by comparing Fig. 2(a) with Fig. 2(c).

3.2. High nickel concentration

3.2.1. Experiment without magnetic field

The results show that the Ni concentration falls from 1930 to 1360 wppm. This is correlated with the crystal deposition observed in Fig. 3(a). In the present case, the crystals were mainly composed of pure nickel (<3 μm). Only a few Ni–Sn crystals with a specific shape (small stick) were observed. The influence of Sn on the deposition process appears thus strongly reduced, this results from the large amount of nickel initially dissolved in the alloy. The nickel concentration found in Pb–17Li at the end of this experiment is consistent with the solubility of nickel at 300°C as reported in the literature (1317 wppm from Ref. [6]). Depending on the part of the tube, the size of Ni particles is changed. In particular, it decreases at the top of the tube. It is unlikely that the size change along the tube is caused by the effect of a thermal gradient since the temperature was isothermal during the experiment (±2°C).

3.2.2. Experiment in homogeneous field

The Ni concentration at the end of the experiment is found to be equal to 1330 wppm, which is close to the solubility limit expected at 300°C. With regard to the crystallization, Ni crystals (>3 μm) are uniformly deposited along the tube (Fig. 3(b)). A few very large crystals (10 to 20 μm) have been mainly found at the bottom of the tube. On the whole, the crystals are larger, than without a magnetic field.

3.2.3. Experiment in inhomogeneous field

The Ni concentration in Pb–17Li at the end of the experiment is similar to that obtained without a magnetic field and very close to the solubility limit of nickel in Pb–17Li at 300°C. Differences are only observed in the distribution of Ni crystals on the wall of the tube. In this case, crystals (>5 μm) are found along the tube with no significant difference between the top and the bottom (Fig. 3(c)). Their mean size looks larger than in the case

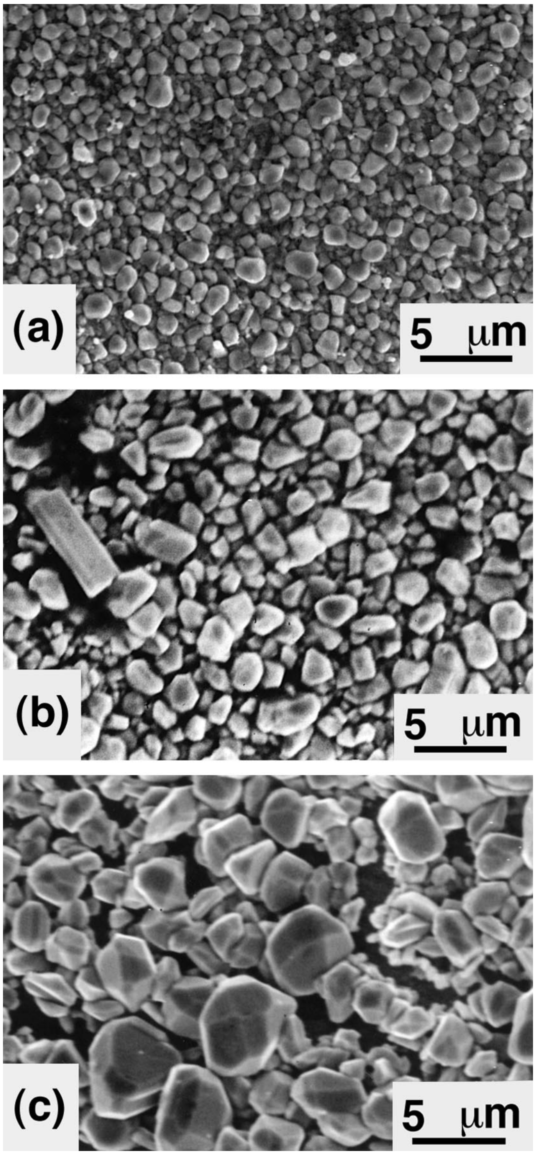

Fig. 3. SEM micrographs showing Ni crystals in the case of high Ni concentration: (a) without magnetic field, (b) with a homogeneous magnetic field $B = 10$ T, (c) with an inhomogeneous magnetic field.

of the experiment carried out without a field and with a homogeneous field.

4. Discussion

4.1. Solubility

Different magneto-thermal treatments have been carried out at 300°C with a Pb–17Li alloy containing a preset Ni concentration. For low Ni content (less than the solubility limit), a small Ni depletion (about 150 wppm) was observed at the end of the tests, whatever the experimental conditions. Part of this Ni depletion can be explained by the formation of Ni–Sn compounds. For high Ni content (more than the solubility limit), the concentration was also decreased and its value was equal to the solubility limit expected at 300°C. These results show that the nickel solubility is not affected by the magnetic field. Thus, the amount of nickel remaining in Pb–17Li at the end of the thermal treatment is not modified by the magnetic field, which means that the same quantity can be crystallized from the supersaturated solution.

4.2. Crystallization

In both series, the Ni depletion is related to crystallization. In the case of low Ni content, this process was not expected because the concentration of nickel was less than the solubility limit. However, formation of Ni-Sn crystals was detected due to the presence of tin in Pb–17Li. Although the Ni concentration was not modified by the magnetic field, some differences were observed in the distribution of crystals. Their size was larger in a homogeneous field. Such an increase may mean that fewer nuclei formed because the same amount was crystallized from the same supersaturated alloy and that the crystal growth was accelerated by the field. It is, however, difficult to see if there is a significant difference between the experiments carried out without a field and with an inhomogeneous field. No change was observed between the top and the bottom of the sample for the different experiments.

In the case of high Ni content, Ni crystals were observed as expected. In the experiment performed without a field, a uniform coating of Ni particles was formed but their size was found to be larger at the bottom. No explanation is found for this observation since insufficient thermal gradient is present. In the case of homogeneous field, crystals seem larger. In the case of an inhomogeneous field, Ni crystals were found uniformly along the tube and their mean size seems larger, than in the other cases. It is not clear why the particle distribution appears more regular with an inhomogeneous field and why very large crystals are only observed at the bottom of the tube tested in a homogeneous field.

Unfortunately, the various observations presently reported cannot be easily discussed and, they still remain unclear regarding the origin of the magnetic field effect. In particular, the two series of experiments (low and high Ni content) cannot be compared because the deposited crystals are not the same (Ni–Sn and Ni, respectively). The nucleation could also be affected in the temperature range 550–300°C, assuming that the cooling conditions were not exactly the same for each sample. Nevertheless, although only qualitative information can be deduced from this work, it seems to indicate that magnetic effects (not yet understood) can influence the crystallization process. However, experiments need to be duplicated to assess the reproducibility of the results.

5. Conclusions

Various magneto-thermal treatments have been applied to static Pb–17Li alloy containing preset (low and high) concentrations of nickel. In each case, a Ni depletion related to crystallization was observed. This depletion was independent of the experimental conditions. Therefore, the magnetic field does not seem to modify the solubility of nickel in Pb–17Li. For a low Ni content, the crystals resulted from Pb–17Li impurity, Sn, which demonstrates a strong interaction with nickel. The Ni–Sn crystals were found to be larger with a homogeneous field. For a high Ni content, mainly Ni crystals were formed. Their size seems larger in the presence of a magnetic field.

Only qualitative information can be deduced from this work which needs to be duplicated to assess the reproducibility and to better understand the results. Nevertheless, it shows that crystallization and deposition of metallic element in Pb–17Li could be affected by a magnetic field. Such effects are also expected to occur in a flowing liquid alloy because magneto-hydrodynamics could modify concentrations and local supersaturation (which is the driving force for crystallization).

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References

[1] T. Flament, P. Tortorelli, V. Coen, H.U. Borgstedt, J. Nucl. Mater. 191–194 (1992) 132.

[2] F. Barbier, F. Herbert, R. Terrasson, CEA Report No. RT SCECF 346 (1994).

[3] F. Barbier, B. Joseph, F. Herbert, R. Terrasson, CEA Report No. RT SCECF 347 (1994).

[4] F. Barbier, M.G. Barker, D.J. Siddons, J. Nucl. Mater. 233–237 (1996) 1436–1440.

[5] F. Barbier, A. Alemany, submitted to Fusion Engrg. Design.

[6] M.G. Barker, T. Sample, Fusion Engrg. Design 14 (1991) 219.

[7] F. Barbier, F. Herbert, R. Terrasson, A. Alemany, A. Pillot, CEA Report No. RT SCECF 395 (1996).