Oxidation of Pb-17Li in Air between 25°C and 650°C
– Comparison with Lead –

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Abstract

The oxidation of solid lead is diffusion-controlled at all temperatures. On solid Pb-17Li, however, protective oxides are formed only below 158° C . The weight gain of samples is proportional to the time at higher temperatures. The effect of 'internal oxidation', the diffusion of oxygen into the solid metal, has to be considered. On the other hand, Li atoms diffuse in oxides and the metal as well. The formed oxides have semiconductor properties, the oxidation rate is higher at room temperature under light than in a closed cabinet.

Nevertheless solid Pb-17Li may be kept at room temperature in air for many years without excessive oxidation.

The oxidation of molten lead is diffusion controlled like that of the solid metal. The oxidation of molten Pb-17Li is much more complex. It follows a linear rate law only for the first time. Then a self-accelerating reaction starts with oxidation rates more than 100 times higher than before. Slags are formed, growing out of the crucible, until all of the lithium is oxidized.

This heavy reaction is not always observed. In some experiments the linear rate law reaction continues until all Li is removed. The start of the heavy reaction is influenced by traces of humidity : oxidation rates in dry air are lower than in room air, the heavy reaction starts not so frequently.

Lithium is oxidized preferentially from the molten alloy and its concentration in oxides is higher than in the metal. Its distribution in the oxide crusts or slags is not homogeneous. Spots were found in the same sample with as much as 14 wt.%, and such with less than 1 wt.% Li. Because of this 'leaching' of Li, smaller samples of molten Pb-17Li should be kept on air only for a short time. The effect seems to be not so important for larger samples or systems. No slag formation was observed when the molten metal was oxidized in thermal convection loops.

Only a few investigations were performed so far to study the behavior of impurities during oxidation. Probably oxidation cannot be used for the purification of the molten eutectic. On the other hand adding very small amounts of Al (and Be) could reduce oxidation rates to zero. However, more investigations are needed to decide if such an inhibitor can be useful for a fusion reactor blanket.

Die Oxidation von Pb-17Li in Luft zwischen 25⁰C und 650⁰C
-Vergleich mit Blei-

Zuammenfassung

Die Oxidation von festem Blei ist bei allen Temperaturen diffusionskontrolliert. Auf festem Pb-17Li hingegen werden nur unterhalb von 158⁰C schützende Oxide gebildet. Bei höherer Temperatur ist die Gewichtszunahme von Proben proportional zur Zeit. Sauerstoffatome diffundieren in das feste Metall, ein Prozeß, der als 'internal oxidation' bezeichnet wird. Andererseits diffundieren Li-Atome zur Oberfläche. Die auf Pb-17Li gebildeten Oxide haben Halbleitereigenschaften. Unter Belichtung wird eine erhöhte Oxidationsrate gefunden.

Trotzdem kann festes Pb-17Li jahrelang an Luft aufbewahrt werden, ohne daß eine zu starke Oxidation auftritt.

Wie die des festen Metalls, so ist auch die Oxidation von geschmolzenem Blei diffusionskontrolliert. Das Oxidationsverhalten des geschmolzenen Pb-17Li ist hingegen sehr komplex. Nur für die erste Zeit folgt die Gewichtszunahme dem linearen Zeitgesetz. Danach erhöht sich die Oxidationsrate plötzlich um einen Faktor von mehr als 100. Es werden Schlacken gebildet, die aus dem Tiegel herausquellen. Diese starke Reaktion ist beendet, wenn der Lithiumgehalt in der Probe unter 0.05 Gew.% abgesunken ist.

Die Schlackenbildung wird durch Spuren von Feuchtigkeit ausgelöst, sie wird jedoch nicht immer beobachtet. In trockener Luft ist die Oxidationsrate geringer als in normaler Raumluft, die Schlackenbildung tritt nur noch manchmal ein.

Unter allen Bedingungen wird Lithium bevorzugt oxidiert. Seine Konzentration in den Oxiden ist höher als im Ausgangsgemisch. Lithium ist in den Oxiden oder Schlacken nicht homogen verteilt. Es wurden Stellen mit bis zu 14 Gew.% Li, und solche mit weniger als 1 Gew.% Li gefunden. Die Verarmung der Schmelze an Lithium ist besonders bei kleineren Proben von Bedeutung. In größeren Thermokonvektionskreisläufen wurde auch keine Schlackenbildung beobachtet.

Nur in wenigen Versuchen wurde bisher das Verhalten von Verunreinigungen während der Oxidation untersucht. Wegen der bevorzugten Oxidation von Lithium können Verunreinigungen nicht durch Oxidation aus dem Pb-17Li abgetrennt werden. Andererseits könnte es möglich sein, durch Zulegieren geringer Mengen an Aluminium oder Beryllium die Oxidationraten von festem oder geschmolzenem Pb-17Li sehr stark zu reduzieren. Bevor jedoch ein solcher Inhibitor in einem Fusionsblanket eingesetzt werden kann, sind weitere Untersuchungen erforderlich.

Content

1. Introduction

The molten eutectic mixture Pb-17Li was proposed as one possible fusion reactor blanket material (1). The chemistry and physics of this material were studied extensively during the last decade (2-6). Its oxidation behavior is important for several reasons.

The release of energy, aerosols and radionuclides during a larger incident with contact between the molten eutectic and air or water has to be known. Corradini has summarized the current knowledge (7). However, for the normal operation of a blanket, and especially for experimental facilities, more questions are of importance:

   a. Is it possible to open a system at room temperature without formation of larger amounts of oxides; how long can samples be stored at room temperature under air?

   b. Oxides on molten Pb-17Li contain a larger concentration of lithium than the metallic phase, resulting in a depletion of lithium in the metal. Properties of the molten Pb-17Li will be changed, the breeding ratio reduced. How important is this effect ?

   c. Will it be possible to remove impurities from the molten eutectic by oxidation ?

We have investigated the oxidation of solid and molten Pb-17Li during the last seven years in many experiments. Some tests were also performed with pure lead in parallel.

2. Basic considerations

The eutectic mixture contains per definition 17 at.% Li. Because of the different atomic weights of Li and Pb these 17 at.% represent only 0.68% by weight. Therefore it is often assumed that the eutectic should be similar to lead. This is true in some cases (8). But many properties are very different from lead, e.g. the melting point is 100 degrees lower. This is more understandable if one considers that not 0.68 wt.% Li , but actually 21 wt.% PbLi (20 mol.%) are dissolved in lead.

The element lithium is chemically bound to lead in the eutectic, forming the intermetallic compound PbLi. Because of this, the chemical acivity of Li in the molten mixture is only in the range of 1.0E-5 to 1.0E-4. (e.g.Ref.9). Correspondingly, vapor pressure and evaporation rates are low (10). On the other hand, even with the low chemical activity, Li will remain very reactive in some cases. (Actually, writing Pb-17Li is as wrong as the old $Pb_{83}Li_{17}$. Pb-17Li, however, is used now worldwide, it will be used in this paper.)

The oxidation of solid and molten metals and alloys in air is described in a book by Kubaschewski (11). Simplified the following processes will occur:

The oxidation starts with the spontaneous formation of a very thin 'primary oxide layer' on the surface. The further oxidation depends on the properties of this oxide. In the case of a porous layer oxygen can reach the metal surface, the weight gain of a sample is proportional to the oxidation time :

$$dm = A1 + k1 * t .$$

/1/

*dm is the weight gain of a sample in (mg/cm^2), A1 is a constant including the effect of the primary oxide layer, k1 the rate constant in (mg/cm^2*h), and t the time in hours. *)*

In the case of a 'gas-tight' oxide the further oxidation is diffusion-controlled, the weight gain is proportional to the square root of time (Fick's law):

$$dm = A2 + k2 * t^{1/2}$$

/2/

Again A2 is a constant , and k2 the rate constant , given here in $(mg/ cm^2* h^{1/2})$.

Because of the large negative oxygen ions, usually the smaller metal cations will diffuse through the oxide, the reaction takes place at the oxide-air interface. For oxidation of lead, however, also a diffusion of oxygen was found (12).

Often it is not possible to make such clear distinction between these two kinds of processes. Oxides get formed with different compositions and modifications, transforming from one to the other. **Internal oxidation** is often found in alloys : oxygen diffuses into the solid metal and forms oxide deposits below the surface. Furthermore it should be mentioned that the formed oxides often have semiconductor properties, e.g. the sensitivity for light.

The temperature dependence of the rate constants k1 and k2 is given by the Arrhenius function

$$\ln k(1,2) = A + dH / R*T$$

/3/

Again A is a constant , including experimental factors and other physical effects, dH is called activation energy of the process, given in (kJ / mol*degree), R is the gas constant,and T the temperature in K.

*)In this report time will always be given in hours.

3. Materials

The purity of the used lead was 99.99+ wt.% Pb. It was obtained from the METALLEUROP company, Hanover and was remolten under purified argon.

Two kinds of Pb-17Li were used. The surfaces of Pb-17Li- bars, obtained from Metallgesellschaft, Frankfurt/Main had to be removed by machining. Then the metal was remolten in an argon atmosphere for several times, always removing oxide slags from the surface. The Li concentration after purification was only 0.64 wt.%, slightly lower than the eutectic composition. The second material was obtained from Metaux Speciaux, France. It was much cleaner (and more expensive), only one remelting step was done before use. The Li concentration was 0.66 to 0.69 wt.%. Because of the error range of the applied analytical method is is not possible to give information about the homogeneity of the eutectic.

For analysis, samples of 50 to 100 grams were dissolved by a special extraction technique in nearly stoichiometric amounts of nitric acid, the solutions were analyzed by ICP-AES (13). For some elements lead had to be removed as $PbNO_3$ or $PbSO_4$. Typical impurity concentrations for Fe, Cr, Ni, Mn, Sn, Se, Sb, and Cd were at or below 1 ppm, the alloy contained 2 ppm Zn, 3 ppm Ag, 8 ppm As , 10 to 20 ppm Bi, and 40 ppm Na (Pb-17Li from Metaux Speciaux).

There was no difference in the oxidation behavior of the two materials.

4. Oxidation of solid metals

Molten lead or Pb-17Li were poured on a clean cold plate of quartz in an argon glove box. There was no wetting, after cooling, solid disks with a metallic shiny surface could be taken away. The surface area was 20 to 30 cm^2. The samples were kept for oxidation in open air, free of chemicals , for experiments at higher temperatures in a cabinet dryer. The weight gain was determined from time to time. The formed oxides on solid Pb-17Li were analyzed after the experiments.

4.1 Solid lead

Oxidation rates of solid lead were low. Only during the first time a larger weight gain could be observed (Fig.1). However, the values are scattered over a wide range. The oxides are hygroscopic and absorb reversible small amounts of water.

The samples remained metallic lustrous for more than 2 months at room temperature. Then a colored tarnish appeared. After 2 years, the samples had a grey oxide layer. At higher temperature the oxidation was faster. At 90^0 C the colored tarnish appeared after 300 , the grey oxide after 1000 hours. A yellow oxide was observed at 225^0 C after 500 hours.

The oxidation is diffusion-controlled, the weight gain was proportional to the square root of the time. This can be seen in Fig.2 for room temperature, in spite of the scattered values

Fig.3 shows the weight gain during the first time for different temperatures. There was an incubation time of several days after the formation of the 'primary oxide layer', before the oxidation continued. Probably different oxides were formed (11). The temperature dependence of the rate constant k2 is given by

$$\ln k2 = -2.0 - 1413 / T \qquad /4/$$

The activation energy is only -11.7 kJ/mol. The data are included in Fig.4.

Discussion

There is a rapid formation of the very thin primary oxide layer at the surface of solid lead in air, followed by a much smaller oxidation rate. The effect has been known for more than 160 years (14). The oxidation rate is influenced by the humidity of the air and by chemical impurities (15,16).

From a paper by Vernon (15) a value of k2 = 5.8E-4 can be calculated for room temperature. The value found in this paper, derived from the scattered data of Fig.2, is 9.0E-4. This is a good agreement for different experiments with weight gains near the detection limit. (The value obtained with function /4/ is a factor of 2 higher).

Weber (17) studied the oxidation of solid lead between 254 and 321°C. The activation energy, taken from the diagrams, is -109 kJ/mol. Extrapolating its data gives a value of 2.0E-3 at 225° C. The value of this paper , obtained with function /4/, is only three times higher. However, extrapolating the function of Weber to room temperature results in an extremely low value of 3.0E-11 !

So far there is no explanation for the different functions of this paper and Weber's data at lower temperatures. In both cases the oxidation is diffusion-controlled over the entire investigated temperature range. Because both functions give the same value for 225° C it has to be assumed, that different types of oxides are formed below and above this temperature. This, however, has not been described in the literature.

4.2 Solid Pb-17Li

As expected, oxidation rates of Pb-17Li were larger than those of pure lead. Fig.5 shows the weight gain for the first weeks, Fig.6 for the time of 6 years. Fig.7 shows that the oxidation rate was not constant during the year : it was always higher in the summer time than in the winter. Such an effect was not observed for 90° C. Oxidation at higher temperatures was not followed over such a long time.

As for lead the oxidation was diffusion-controlled at room temperature and 90° C (Fig.8). It can be seen, from Fig.5, that at higher temperature the oxides were not any more protective: the weight gain was proportional to the time. At 158°C the oxidation was diffusion controlled during the first 100 hours. At 225° C no parabolic part could be identified any more.

The rate constants k2 for the diffusion-controlled part of the oxidation are included in Fig.4 . The values are about 10 times higher than those for pure lead; they show no temperature dependence.

Different oxides were observed. The surface remained metallic lustrous at room temperature for several hours. Then, grey oxides were formed. The oxides were brighter at higher temperature. Near the melting point a yellow oxide was seen after some time.

A breakaway point was found at 90° C after about 20.000 hours (Fig.6). At a weight gain of 5.3 mg/cm^2 white oxide rosettes and cracks were observed, the oxidation rate increased from time to time.

Chemical composition of oxides

The weight gain of samples at room temperature was 7.5 mg/cm^2 after 51.000 hours. The oxides were carfully scraped off until a metallic luster appeared. Only 8.7 mg/cm^2 reaction products could be removed, containing 96.2 wt.% Pb and 0.83 wt.% Li. After removing the oxides the surface kept the metallic luster for several weeks.

4.3 Discussion

Only at lower temperatures the oxidation is diffusion-controlled, the weight gain is proportional to the square root of the time. Oxidation rates are about 10 times higher compared to pure lead. At higher temperatures the formed oxides are no longer protective, the weight gain is proportional to the time. Probably different types of oxides are formed at different temperatures.

While after an oxidation time of 4 years a breakaway point was found at 90°C, such an effect was not seen at room temperature even after 6 years. Assuming that the oxidation would continue at the same rate, a sample of 1 mm thickness would be completely oxidized after several hundred years. This, however has to be considered hypothetical because even at room temperature a breakaway point may occur after a long time, followed by faster oxidation.

The performed measurements are not sufficient to give a satisfatory description of the formed reaction products. Only a small amount of CO_2 was formed when dissolving the scraped-off oxides in diluted nitric acid. The composition with 96 wt.% Pb and 0.8 wt.% Li points to PbO + Li_2O . Surprisingly small is the amount of obtained oxides. A weight gain of 7.5 mg/cm^2 as found after 6 years would mean, that about 100 mg/cm^2 oxides should be on the surface - only one tenth could be scraped off. It must be assumed that the major part of the oxygen diffused into the solid metal by the process of *internal oxidation* . After scraping away the thin 'outer oxides' the surface showed a metallic luster.

The concentration of lithium in the surface oxides is higher than in the original alloy. Obviously, Li diffuses not only in the oxides but also in the metal phase. The surface of the metal, therefore, should be depleted of Li, its behavior hence should be more like that of Pb. This was observed : the metallic luster remained for a much longer time than on the original Pb-17Li.

Fig.9 shows, that in the sample oxidized for 6 years at room temperature, the eutectic structure of Pb-17Li was destroyed down to a depth of 0.3 mm from the surface. This confirms the assumption of internal oxidation and Li diffusion to the surface.

The influence of the season on oxidation at room temperature is an interesting effect.The room temperature was constant within 10°C and had no influence . Different humidities could be responsible, but also the water concentration of the laboratory air was not very different during the year.

Most probably the following explanation can be given : *The oxides are semiconductors, whose properties are strongly influenced by (day-)light.* The samples at 90°C were kept in a dark closed cabinet and did not show the seasonal effect.

5. Oxidation of molten metals

The molten Pb or Pb-17Li was filled into crucibles in an argon atmosphere. During the first experiments crucibles of porcelain or Al_2O_3 were used. However, a larger fraction of the Li was lost by diffusion into the crucible material. Most of the experiments, therefore, were performed using crucibles made of alpha-Fe, stainless steel 4971, or Mo, depending on the temperature of the experiment. Samples of 50 to 100 grams Pb or Pb-17Li were used, the oxidizing surface was 4 to 6 cm^2.

Static experiments and such with stirring of the molten metal at up to 60 rpm were performed in a facility designed for other measurements (9,10). Fig.10 shows a photo of the apparatus.

The samples were heated under He-6.0, the He was replaced by air for the time of oxidation . Especially with Pb-17Li the heating rate around the melting point had to be small; otherwise sudden gas release expelled some metal from the crucible. Experiments were performed with room air and with dry air (molecular sieves and $MgClO_4$).

The weight gain of the samples was determined after cooling under helium to room temperature. The metal and the formed oxides were analyzed mainly for Li and Pb.

5.1 Molten lead

As for the solid metal the oxidation of molten lead in air was studied a long time ago . The low oxidation rates are strongly influenced by small concentrations of impurities in lead or in the atmosphere. (12,15,16,19).

In the experiments samples were heated up to 25 hours, mostly under static conditions.

As for the solid metal, also the oxidation of molten lead is diffusion-controlled. The reaction constant k2 follows the Arrhenius function

$$\ln k2 = 13.1 - 11370/T. \qquad \text{/5/}$$

The activation energy is -95 kJ/mol. The results are included in Fig.4. Fig.11 shows the data compared with values from the literature. It was reported that the oxidation of molten lead takes place in two steps, depending on the temperature and oxidation time (12,19). The oxidation in this work belongs to step 1, that means without a change in the oxide modification. The agreement of the results with values from the literature is reasonable. Only Gruhl found nearly no temperature influence on oxidation rates for temperatures below 500° C.

We found that stirring had no influence on oxidation rates in our experiments. Stirring was probably not strong enough to destroy the oxide layer mechanically.

5.2 Molten Pb-17Li

5.2.1 Static molten Pb-17Li, room air

The behavior of Pb-17Li is much more complex than that of pure lead. For the solid metal the oxidation followed at lower temperatures a parabolic, at higher temperatures a linear rate law. The oxidation of the molten eutectic followed always a linear rate function, at least for the first time. Fig.12 shows this for three temperatures. Fig.13 shows the temperature dependence of the rate constant k1. It is given by

$$\ln k1 = 13.7 - 8190/T \quad . \qquad \text{/6/}$$

The activation energy is -68 kJ/mol.

The lithium of the eutectic was preferentially oxidized and extracted from the molten mixture. The oxidation rate was comparable to lead if the Li concentration was reduced to levels below 0.05 wt.%. (Fig.12d). However, the oxidation often did not follow the linear rate function up to such low Li concentrations.

In most of the experiments the oxidation rate increased suddenly by a factor of more than 100 after some time of oxidation. Very porous slags were formed, growing out of the crucible to form a dome or to fall beside. Rate constants during the strong oxidation step were scattered over orders of magnitude. Often pores were filled with molten metal. This reaction stoped at Li concentrations below 0.05 wt.%.

The time before this strong reaction starts was not constant. Typically it started at 275°C after 40 hours. At 400 and 500°C the reaction started often after less than one hour, sometimes, however, not at all (Fig.12d). Immediate formation of the slags was observed when a sample, after an initial oxidation and cooling under helium, was brought to room air for a short time, e.g. for determining the weight gain, and heated again to continue the oxidation.

Fig.14 shows an example for the formation of slags. The strong reaction starts at cracks in the oxide layer.

5.2.2 Static molten Pb-17Li, dry air

In some experiments the used air was dried by molecular sieves and $MgClO_4$. The resulting dew point was below $-80°C$, the concentration of water vapor below 0.5 ppm.

The strong reaction with slag formation was observed only at about one third of the tests.

The linear oxidation rates before slag formation were much smaller in dry air compared to normal room air. The data are shown in Fig.13. The temperature dependence of the linear rate constant is given by

$$\ln k1 = 17.2 - 12642/T \quad . \qquad\qquad /7/$$

The activation energy is -105 kJ/mol.

5.2.3 Other observations

As in the case of lead, stirring had no influence on the oxidation behavior during the linear rate range. Slags, however, were often pulled out of the crucible by the stirring blade. Especially in this case, some oxides were also transported below the metal surface. As a result, average Li concentrations near the surface were found to be higher than in the bulk metal.

Li concentrations between 0.2 and 0.7 wt.% in the original alloy had no influence on oxidation results. With concentrations below 0.05 wt.% the oxidation was similar to that of lead, as mentioned before.

5.2.4 Chemical composition of oxides

As expected from the literature the oxides were not homogeneous. Layers containing more PbO or Li_2O, probably with some carbonates, were found.

Linear rate law : The oxides contained between 1.5 and 7 wt.% Li and 82 to 95 wt.% Pb. Li was extracted from the molten eutectic, its concentration in the remaining metal was correspondingly lower. Only 2 to 20 % of the Li were converted into carbonate (indirect analysis), the major fraction was found in the form of oxide. Probably no lead carbonate was formed. It was not possible to correlate Li or Pb concentrations in oxides to any experimental parameter.

Slags : Slags were even more inhomogeneous . In the same experiment some parts contained up to 14 wt.% Li and 60 wt.% Pb, others only 1 wt.% Li and 92 wt.% Pb. Often pores were filled with a metal phase.

5.2.5 Discussion

Some of the decribed observations were published in 1949 by Gruhl (12). Small amounts of Li in Pb increased the oxidation rates considerably. Enhancement factors of 100 were found with 1 wt.% Li for the oxidation rate at 400°C in air. Even with 0.01 wt.% Li this factor was still 3.5 . Gruhl described the formation of slags with lithium concentrations above 0.1 wt.% in the alloy. He mentioned the linear rate function, however only for temperatures below 500° C; at higher temperatures slag formation occured immediately. Slag formation was called 'main reaction' and explained as follows:

> Because of unknown effects Li gets enriched at certain spots.
> Oxidation of this Li gives locally a higher temperature, which
> in turn increases the reaction rate. This self-accelerating
> reaction is only possible for oxidations following the linear
> rate law (11).

It could be shown in this work, that linear rate law oxidation is possible also for higher temperatures. Sometimes no 'main reaction' was observed. Obviously humidity is responsible for this effect. Linear oxidation rates are more than 10 times lower in dry air. Formed oxides are hygroscopic, even less than 1 mg of water, absorbed during the determination of the weight gain, were sufficient to start the formation of the slag. Different humidities are probably also responsible for the widely scattered data.

In the eutectic 0.2 Li atoms are available for each atom of lead. From the composition of the reactions products it can be seen that Li and Pb are oxidized as well. During the time with linear rate law, 0.5 to 2 atoms of Li are oxidized for each oxidized Pb atom, with most of the values around 1. The composition of the oxides was independent on the initial Li concentration in the alloy between 0.2 and 0.8 wt.%. This would point to the oxidation of the intermetallic compound LiPb; but the strong inhomogeneous composition of the oxides needs further explanations.

The 'main reaction' with slag formation starts after non-reproducible times. Our obervations confirm Gruhl's assumption of a local enrichment of Li atoms. Spots with up to 14 wt.% Li were found, 4.9 atoms of Li for each oxidized atom of Pb.

More experiments under better controlled conditions must be performed to understand all occuring reactions.

One important question is : can the data be used for technical systems ? In such systems the total amount of Li is large, depletion of the molten alloy is not so important. Furthermore the interacting surface is usually not static.

In the decribed crucible tests slow movement of the surface had no influence on oxidation rates. Two other tests were performed with thermal convection loops . In these 4.6 kg Pb-17Li were circulating; the interface liquid metal - covergas was 31 cm^2, with strong movement (21). In one loop the surface was oxidized with room air for 30 minutes at 400° C. 800 mg oxides were formed with an average of 2 wt.% Li, corresponding to a weight gain of 4.2 mg/cm^2*h. From function /6/ a value of 4.6 would be expected for the linear rate range. In the second loop the metal was oxidized for 1 hour at 536°C. The oxygen consumption was measured by gas chromatography. 1.5 to 3 grams oxygen reacted, the weight gain therefore was 48 to 96 mg/cm^2*h. The value from function /6/ for the linear rate range would be 36.

In both cases the oxidation followed the linear rate law. Probably a local enrichment of Li atoms was not possible because of the movement of the surface. Nevertheless the question remains what happens if the surface is static, e.g. in a drain tank. We plan to make some experiments in this direction.

6. Behavior of impurities during oxidation

There is a wide field of literature concerning the behavior of impurities during the oxidation of lead. Only some general remarks will be given in this paper.

The elements Sn, As, Sb and Zn are removed from lead by oxidation. The remaining concentrations are between 10 and 300 ppm (19,22), much higher than required for a fusion reactor blanket. Furthermore not Pb, but Pb-17Li has to be considered. On the other hand, the mentioned elements are probably not important for the eutectic, contamination with them can be avoided during the production steps when using high-purity lead.

The influence of a large number of elements on the oxidation of lead was investigated in several experimental studies (12,19,22). Li as an impurity was described in the chapters before. While Li has a strong enhancing effect on oxidation, Al acts as an inhibitor. Nearly no oxidation can be seen with only 200 ppm Al in lead. Al is also an inhibitor in alloys. The classical train alloy contained 0.7 wt% Ca, 0.6% Na and 0.04% Li, and as an inhibitor against corrosion 0.02% Al (22).

(Possibly also Be in low concentrations may be an inhibitor of oxidation, as found for molten magnesium (18).)

It might be possible to add Al to Pb-17Li in a fusion reactor blanket. Reduced oxidation rates would allow to open even heated systems in air. On the other hand, the impact on the behavior of radionuclides needs to be investigated, as well as the Al behavior in purification systems.

In our experiments we found that Bi, Ag and especially Po (23) are enriched in oxide layers. These elements, however, cannot be removed from the eutectic by oxidation. The enrichment factors are not high enough, too much Li would be removed.

The migration of Ag into oxides is remarkable. This is an influence of the Li content, no Ag is found in oxides of pure lead.

7. Summary and conclusions

The oxidation of solid lead is diffusion-controlled at all temperatures. On solid Pb-17Li, however, protective oxides are formed only below 158⁰ C . The weight gain of samples is proportional to the time at higher temperatures. The effect of 'internal oxidation', the diffusion of oxygen into the solid metal, has to be considered. On the other hand, Li atoms diffuse in oxides and the metal as well. The formed oxides have semiconductor properties, the oxidation rate is higher at room temperature under light than in a closed cabinet.

Nevertheless solid Pb-17Li may be kept at room temperature in air for many years without excessive oxidation.

The oxidation of molten lead is diffusion controlled like that of the solid metal. The oxidation of molten Pb-17Li is much more complex. It follows a linear rate law only for the first time. Then a self-accelerating reaction starts with oxidation rates more than 100 times higher than before. Slags are formed, growing out of the crucible, until all of the lithium is oxidized.

This strong reaction is not always observed. In some experiments the linear rate law reaction continues until all Li is removed. The start of the strong reaction is influenced by traces of humidity : oxidation rates in dry air are lower than in room air, the strong reaction starts not so frequently.

Lithium is oxidized preferentially from the molten alloy and its concentration in oxides is higher than in the metal. Its distribution in the oxide crusts or slags is not homogeneous. Spots were found in the same sample with as much as 14 wt.%, and such with less than 1 wt.% Li. Because of this 'leaching' of Li, smaller samples of molten Pb-17Li should be kept on air only for a short time. The effect seems to be not so important for larger samples or systems. No slag formation was observed when the molten metal was oxidized in thermal convection loops.

Only a few investigations were performed so far to study the behavior of impurities during oxidation. Probably oxidation cannot be used for the purification of the molten eutectic. On the other hand adding very small amounts of Al (and Be) could reduce the oxidation rate to zero. However, more investigations are needed to decide if such an inhibitor can be useful for a fusion reactor blanket.

References

(1) M.A.Abdou et al., Blanket Comparison and Selection Study BCSS,
     Fusion Power Program, ANL/FPP 83/1 (1983)

(2) G.Kuhlboersch and F.Reiter,
     Physical Properties and Chemical Reaction Behavior of Li17Pb83
     Related to its Use as a Fusion Reactor Blanket Material
     Nuclear Engineering and Design/Fusion 1 (1984) 195-203

(3) U.Jauch,V.Karcher, and B.Schultz, Thermophysical Properties
     in the system Li-Pb, KfK-4144 (1986)

(4) H.U.Borgstedt, Chemische Eigenschaften des flüssigen Blanketstoffs
     Pb-17Li, KfK-4620 (1989)

(5) R.E.Buxbaum,A chemical theory analysis of the solution
     thermodynamics of oxygen, nitrogen and hydrogen in lead-rich Li-Pb
     mixtures, Journal of Less Common Metals 97 (1984) 27-38

(6) V.Coen, F.T.Dadd, H.Kolbe, L.Orecchia,
     Chemical reactivity of 17Li-83Pb with nitrogen, oxygen and its
     compatibility with AISI 316L under known partial pressure of
     these gases, Proc. 3rd Int. Conf. on Liquid Metal Eng. and
     Technology, London,9.-13.Apr.1984, Vol.1, p.347-354

(7) M.L.Corradini and D.W.Jeppson, Lithium alloy chemical reactivity
     with reactor materials: current state of knowledge,
     Fus.Engin.Design 14 (1991), 273-288

(8) H.U.Borgstedt and H.Feuerstein, The Solubility of Metals in
     Pb-17Li Liquid Alloy, 5th Intern.Conference on Fusion Reactor
     Clearwater, Nov.17-22, 1991,
     To be published in J.of Nucl.Materials 191-194 (1992)

(9) H.Feuerstein, J.Oschinski and S.Horn, Behavior of Po-210 in molten
     Pb-17Li, 5th Intern.Conference on Fusion Reactor Materials,
     Clearwater, Nov.17-22, 1991,
     To be published in J.of Nucl.Materials 191-194 (1992)

(10) H.Feuerstein, H.Gräbner, J.Oschinski, S.Horn and S.Bender,
      Evaporation of lead and lithium from molten Pb-17Li - Transport
      of aerosols, Fusion Engineering and Design 17 (1991) 203-207

(11) O.Kubaschewski und B.E.Hopkins, Oxidation of Metals and Alloys,
      London, Butterworth 1962

(12) W.Gruhl, Über die Oxidation ruhender Bleischmelzen,
     Z.f.Metallkunde 40 (1949) 225-240

(13) H.Graebner, H.Feuerstein and J.Oschinski, Compatibility of metals
     and alloys in liquid Pb-17Li at temperatures up to 650°C,
     Fusion Reactor Materials 155 - 157 (1988) 702 - 704

(14) P.A.von Bonsdorff,
     Über die Oxidation der Metalle in der atmosphärischen Luft
     Annalen der Physik und Chemie 41 (1837) 293-314

(15) W.H.J.Vernon, Second Experimental Report to the Atmospheric
     Corrosion Research Committee,
     Trans.of the Faraday Society 23 (1927) 113-265

(16) Gmelins Handbuch der anorganischen Chemie Vol.47, B1 (1972)
     Blei

(17) E.Weber and W.M.Baldwin, Scaling of Lead in Air,
     J.of Metals 4 (1952) 854-859   .

(18) F.Erdmann-Jesnitzer, H.Baramovsky and R.Görner,
     Beitrag zur Anreicherung verkrätzungsverhindernder Elemente
     an Oberflächen von Metallschmelzen,
     Z.f.Metallkunde 49 (1958) 133 - 140

(19) J.Gerlach and E.Müller,
     Beitrag zum Einfluß von geringen Sn, As und Bi-Gehalten auf die
     Oxidationsgeschwindigkeit von flüssigem Blei,
     Metall 18 (1964) 807 - 813

(20) E.Gebhardt, Über die Einwirkung von Luft auf flüssiges Zink,
     Z.f.Metallkunde 37 (1946) 87 - 96

(21) H.Feuerstein, H.Gräbner S.Horn and J.Oschinski, Behavior of
     deuterium and rare gases in convection loops with molten Pb-17Li ,
     Fusion Engineering and Design 14 (1991) 261-271

(22) W.Hofmann, Blei und Bleilegierungen, 2.Auflage
     Springer Verlag Berlin 1962
     Lead and Lead Alloys, Springer 1970 (Übersetzung der
     2.Auflage)

(23) H.Feuerstein, contribution in Nuclear Fusion Project Annual
     Report, KfK 4774 , EUR 13151 EN, Sept.1990 , page 85

Fig.1 : Oxidation of solid lead in air .
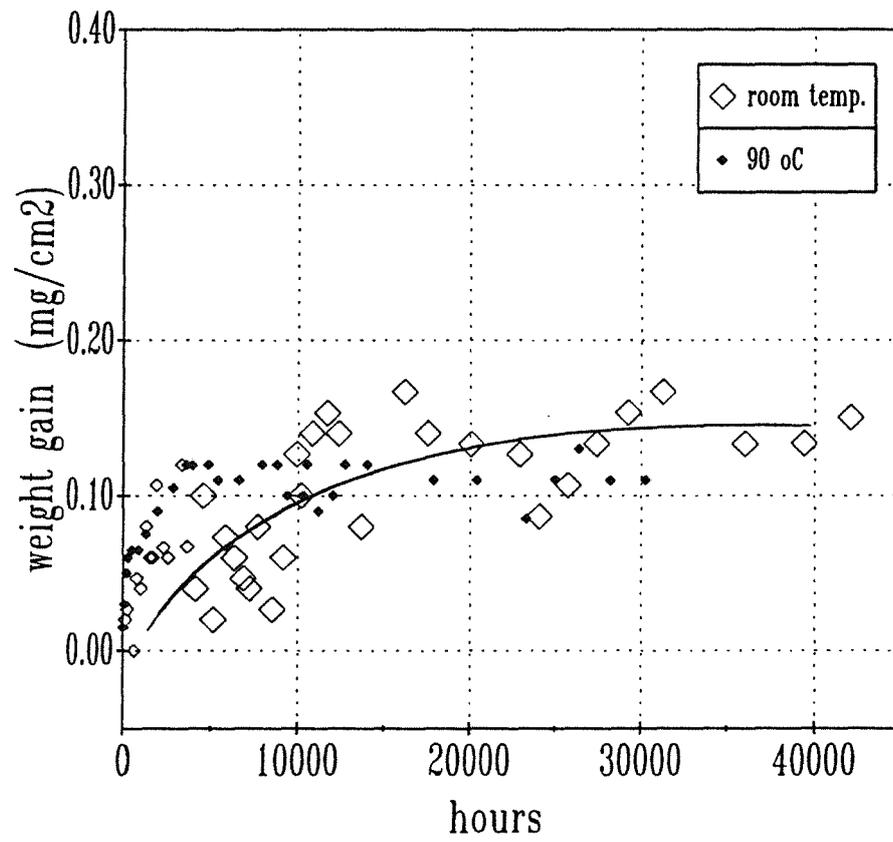
Fig.2 : Oxidation of solid lead in air at room
temperature; diffusion-controlled process .
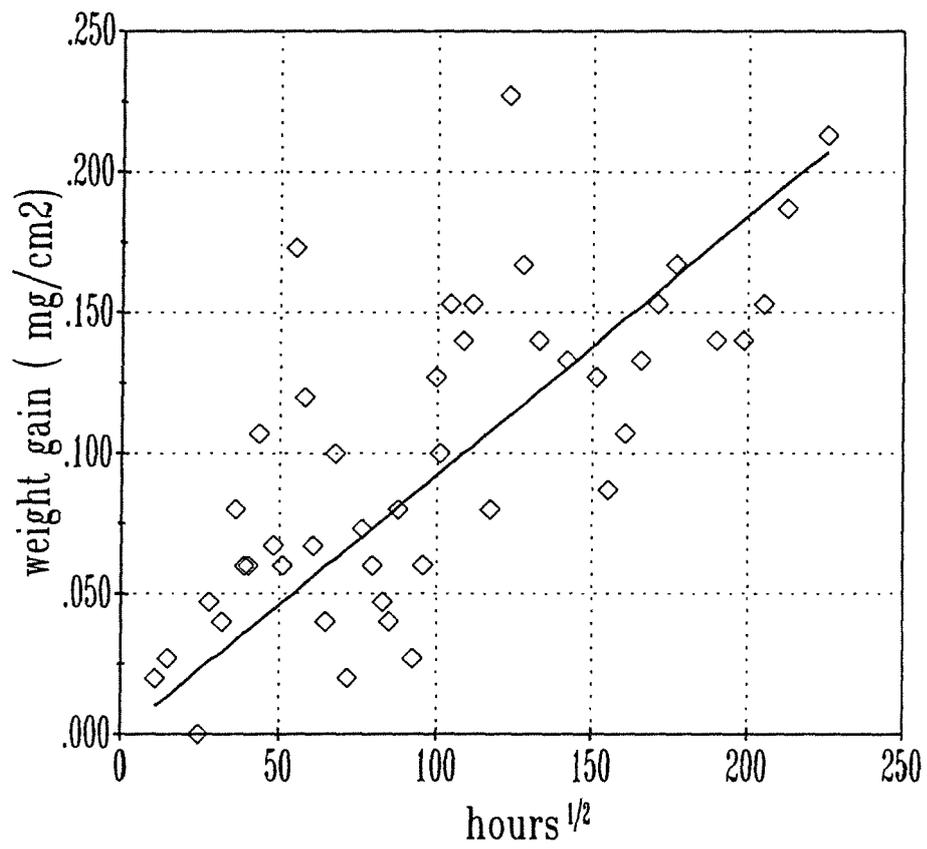
Fig.3 : Oxidation of solid lead in air; first 20 days.
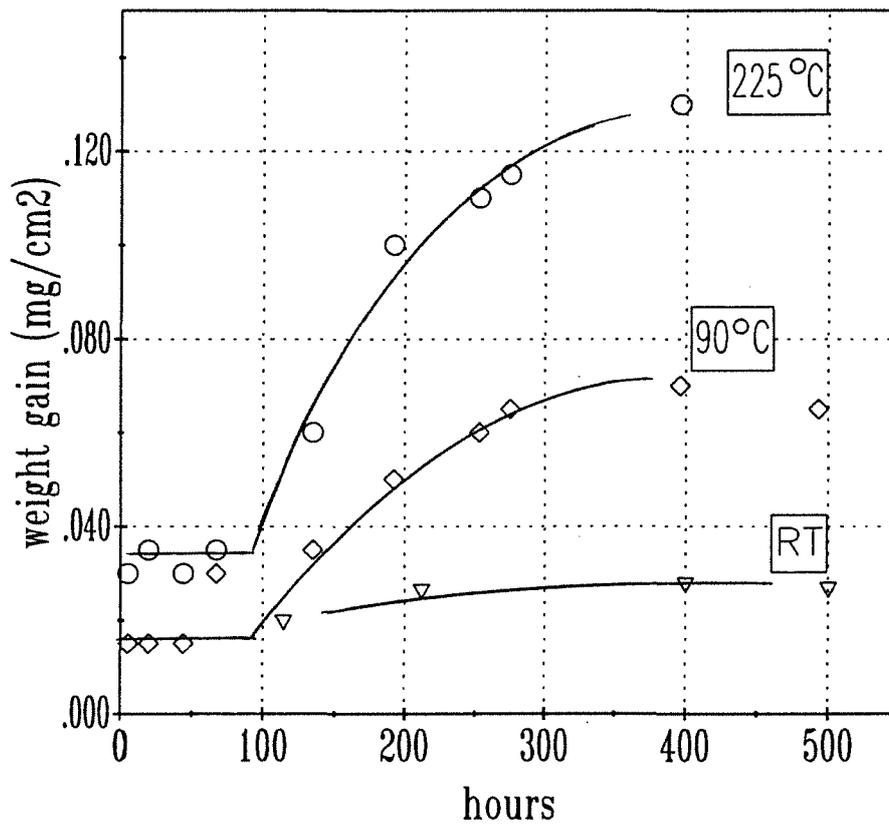
Fig.4 : **Oxidation of lead and solid Pb-17Li in air.**
Oxidation rates for the diffusion-controlled processes.
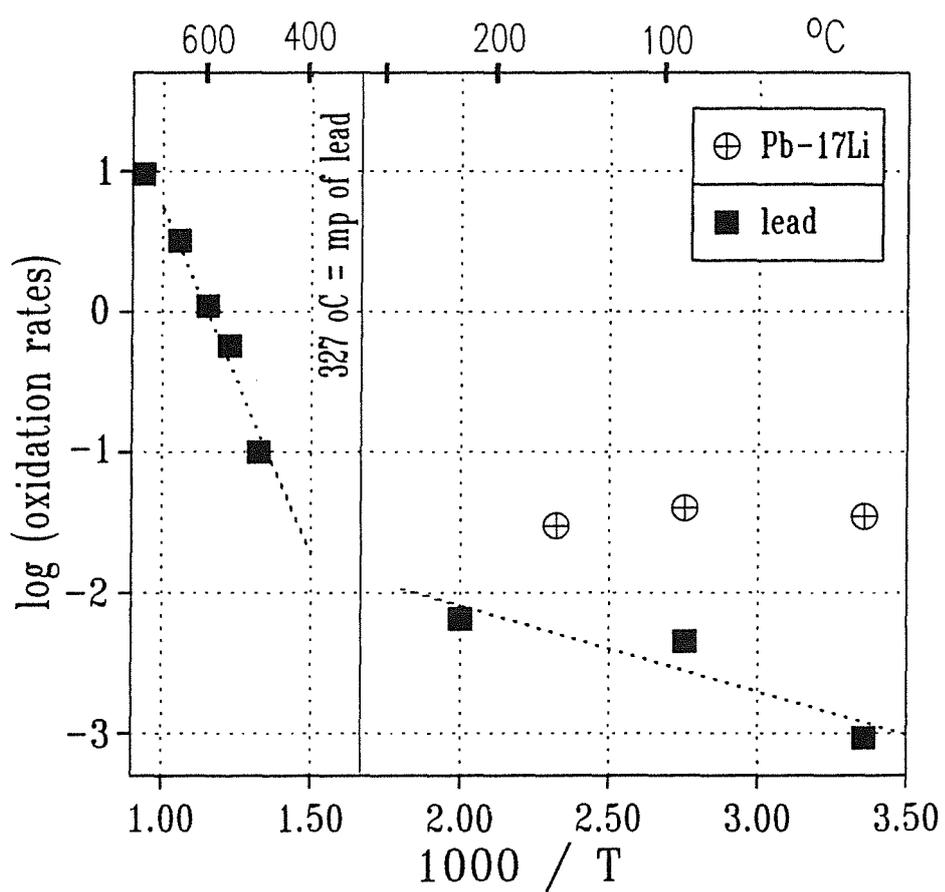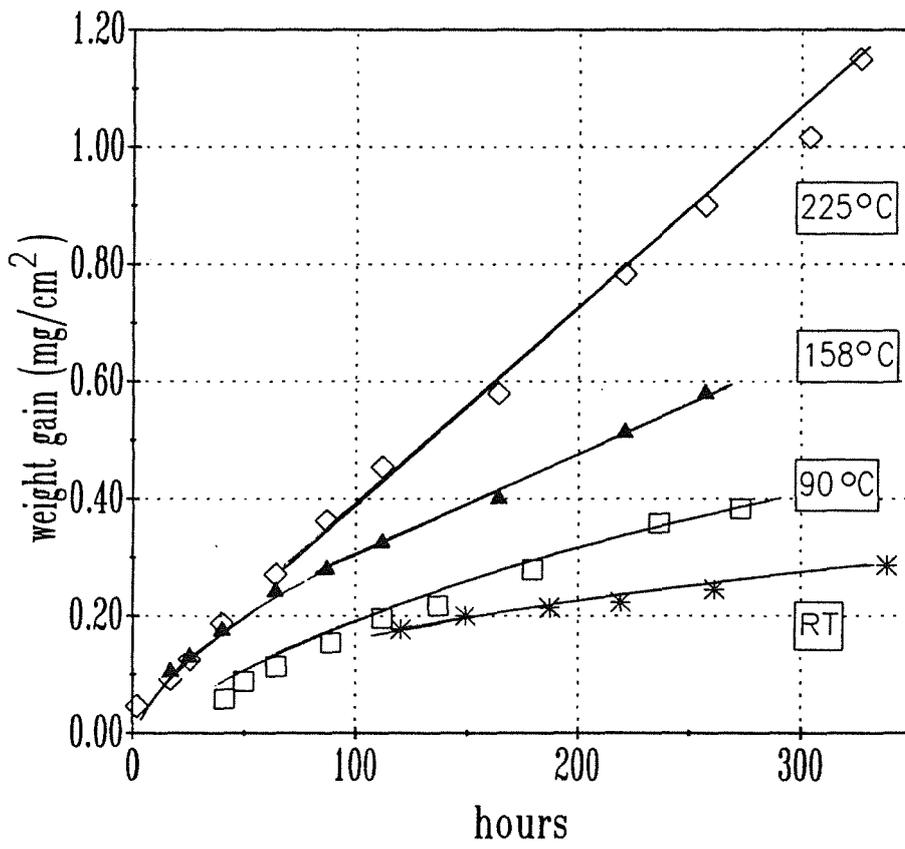**Values given in (mg/cm2*h1/2).**
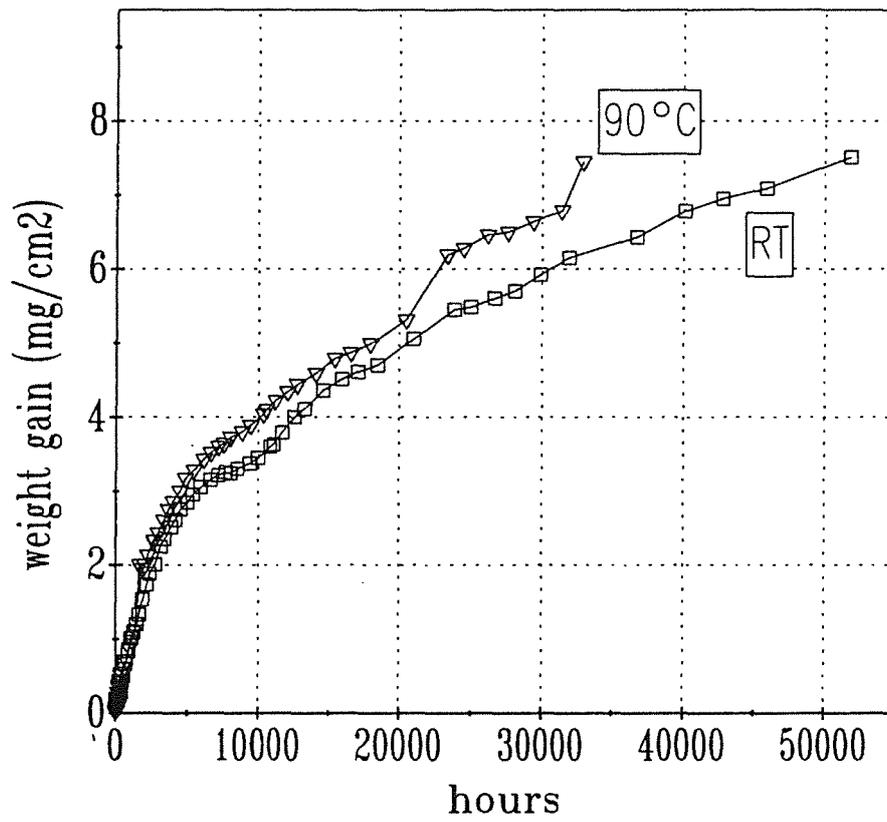
Fig.5 : Initial oxidation of solid Pb-17Li in air.

Fig.6 : Long-time oxidation of solid Pb-17Li in air.

Fig.7 : Seasonal effect of the oxidation of solid Pb-17Li in air at room temperature.
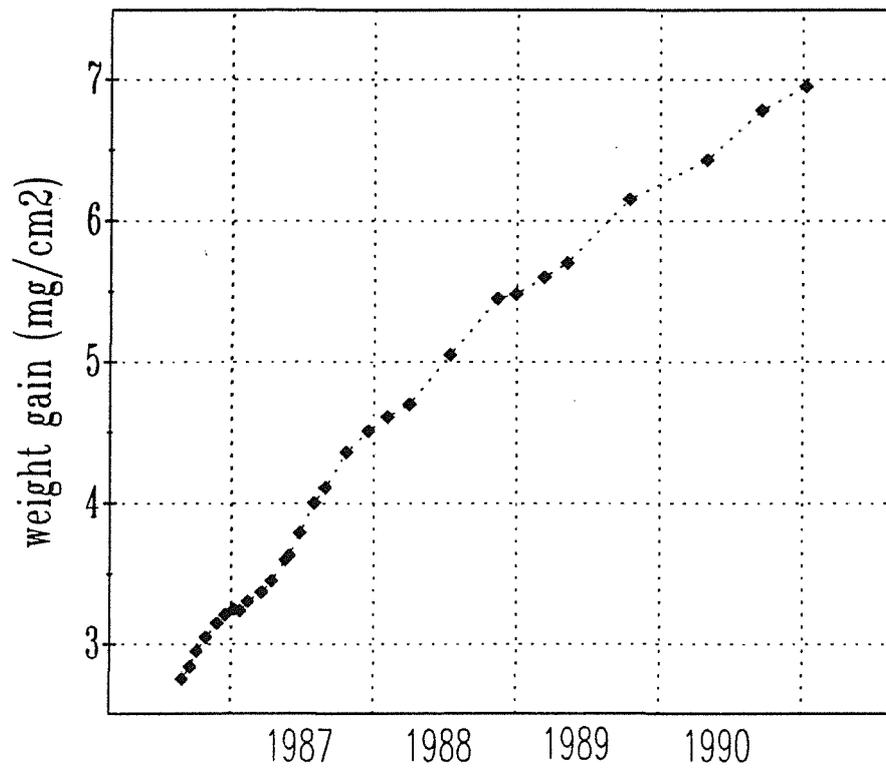
Fig.8 : Oxidation of solid Pb-17Li in air; diffusion-controlled process at room temperature and 90 oC.
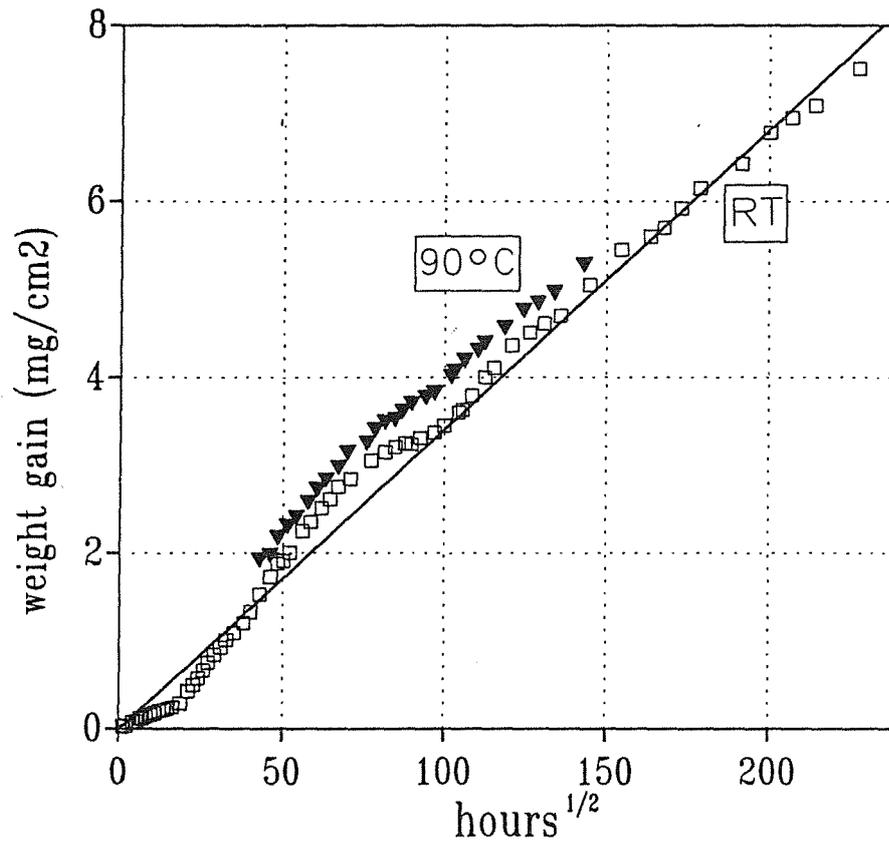
Fig.9 : Metallographic cross-section of a Pb-17Li sample, oxidized at room temperature for 6 years.
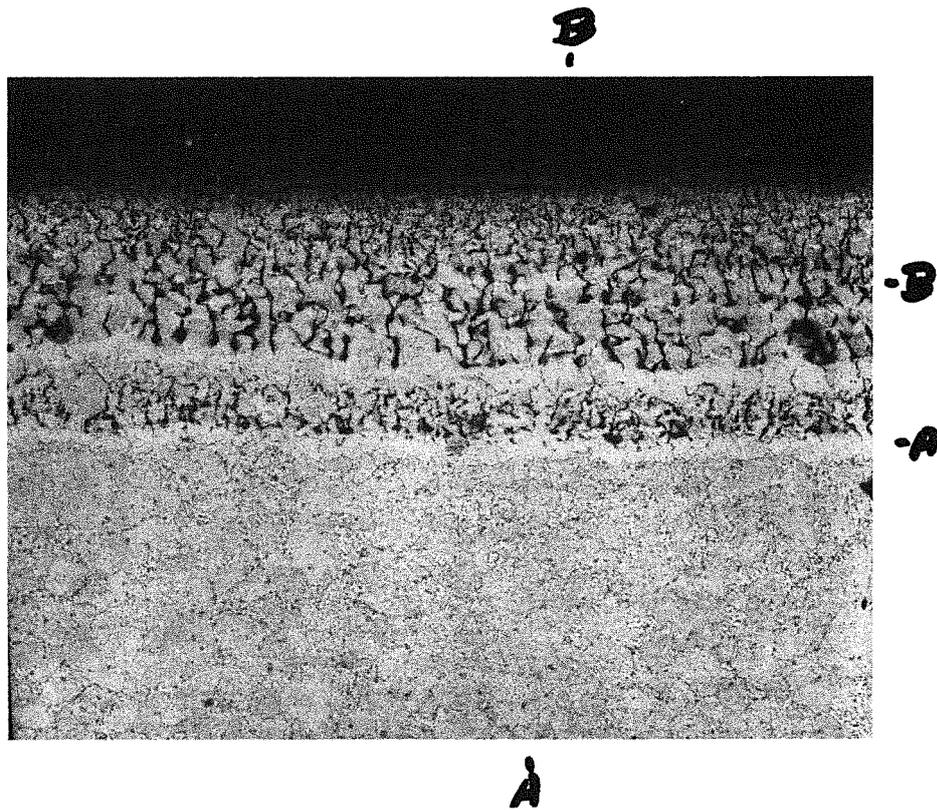
Fig.10 : Experimental facility for oxidation experiments.
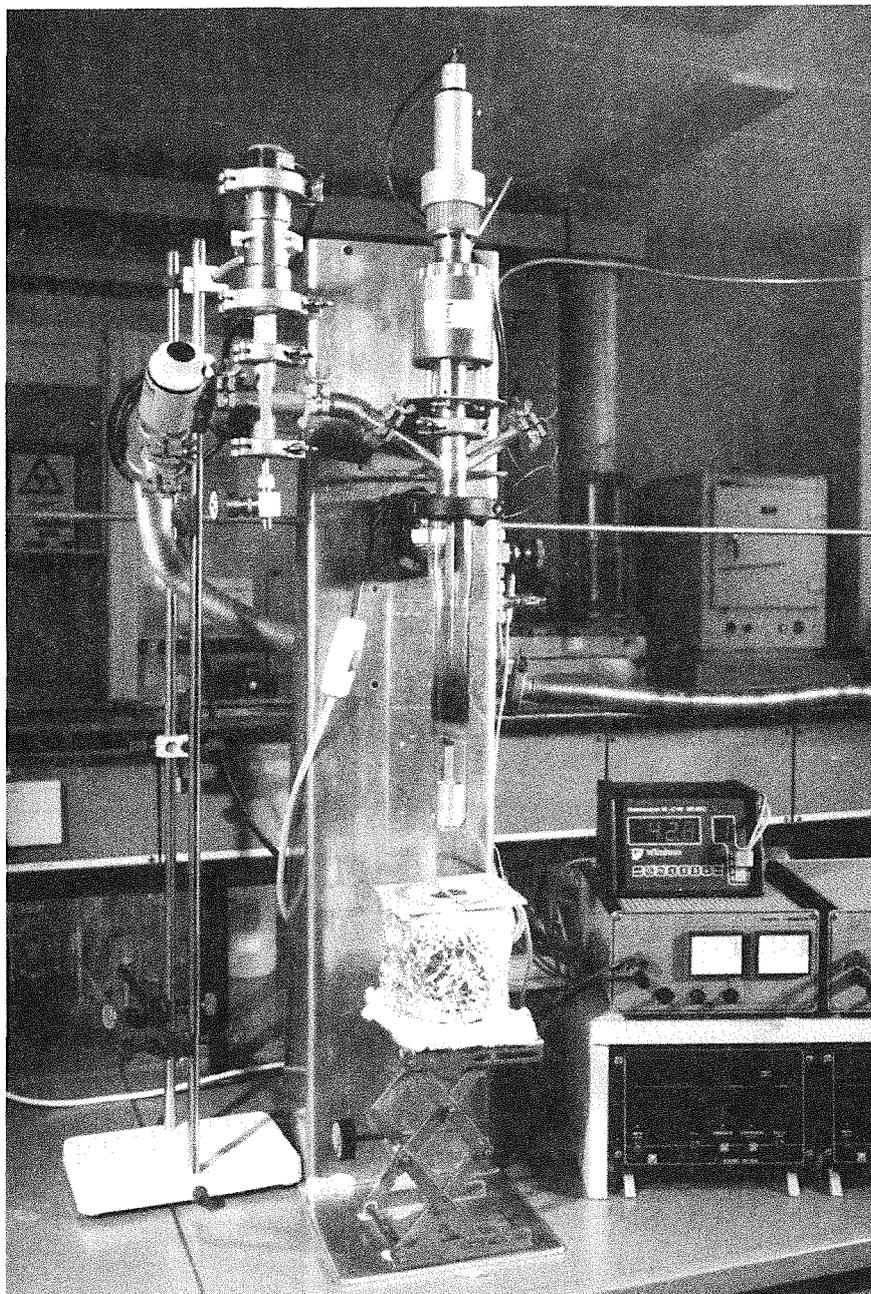
**Fig.11 : Oxidation rates of molten lead in air;
including data by Weber and Gruhl.**
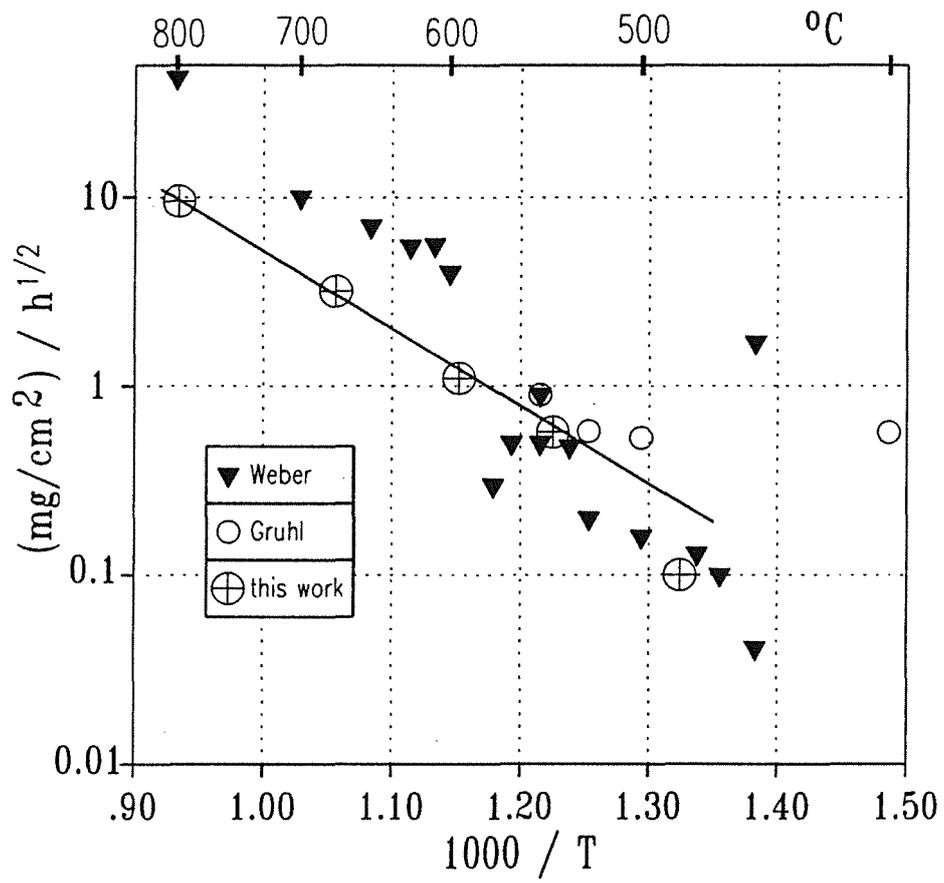
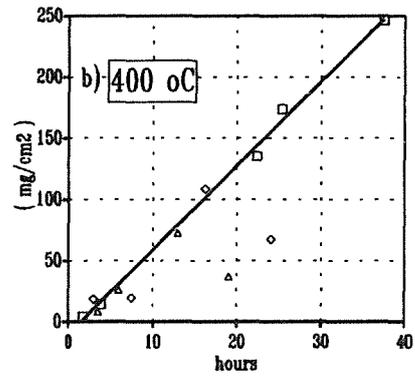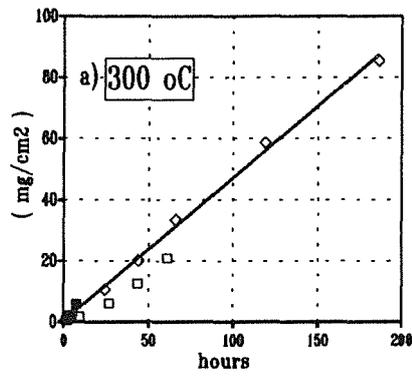**Fig.12 : Oxidation of molten Pb-17Li in air.**
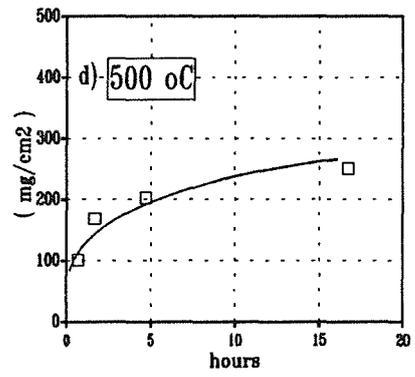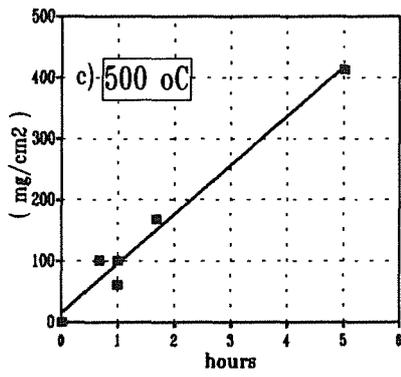
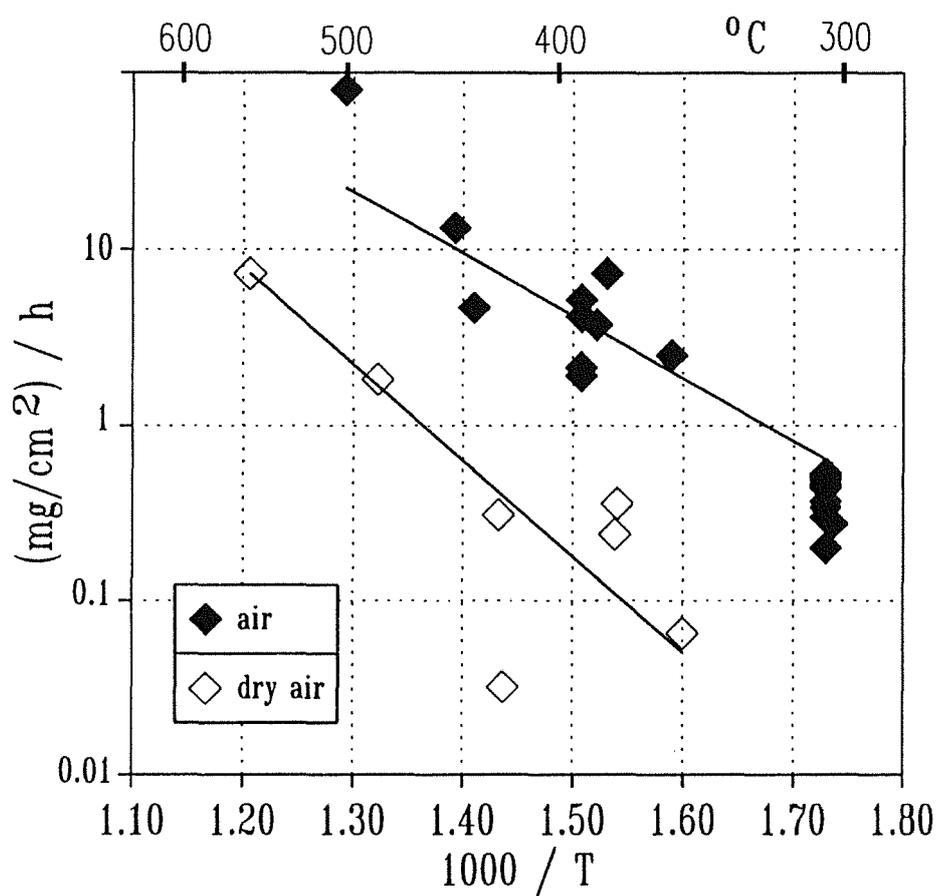Fig.13 : Oxidation rates of molten Pb-17Li in air.

**Fig.14 : Formation of slags during the oxidation of
molten Pb-17Li in air.**