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Abstract

The compatibility of 31 metals, alloys and coatings with static eutectic mixture Pb-17Li was investigated in more than 300 tests. Most of the results have not been published before.

Wetting has no influence on **dissolution rates.** This is discussed in detail. Metals can be divided into three groups. Most stable are the refractories Nb, Ta, Mo, Re and W. Ferritic steels, Be, Fe, and V belong to the next group. However, Be is destroyed along grain boundaries. Not stable at all are Al, Ti, Zr, Y, U and their alloys.

Temperature functions for **solubilities in Pb-17Li** were obtained for 8 elements, single -one temperature- values for 3 others. The results are in good agreement with a theoretical work of Guminski. Remarkable high are solubilities of Al, Zr, Y and U while those of the refractories are low. Also, the **solubility of Pb in solid Ti** was determined, adding new data points to the phase diagram.

Because of the effect of mass transfer between dissimilar metals, **diffusion coefficients** in Pb-17Li could be calculated from dissolution rates and solubilities. Most reliable are the temperature functions for Be, Al, Fe and V. Those for Ti, Zr and U are influenced by the formation of compounds. All values are in an expected range, but not all effects can be explained.

Different kinds of **reaction zones** were found on surfaces. New is a very thin 'chemical reaction zone', identified for several metals during sample cleaning. It is probably formed as a first step before grain boundary attack of the eutectic.

The following new **intermetallic compounds** were identified: Ti_2Pb and Ti_3Pb_2, UPb_4, YPb_4 and Zr_4Pb. The compound Ti_3Pb_2 was investigated in detail. Lead and titanium can be replaced by other metals. With Y and U, there was even a reaction with lead in the gas phase above the eutectic. Other metals were embrittled in this area.

Generally, **alloys** are not more stable than their base metals. Leaching of elements from alloys and other effects were investigated. Especially with alloys, many open questions remain and more work has to be done to understand the chemistry of alloys in the eutectic.

Last but not least **Mo coatings** on getter metals were found not to be protective for the use in a blanket.

Verträglichkeit von 31 Metallen, Legierungen und Beschichtungen mit Statischer Eutektischer Mischung Pb-17Li

Zusammenfassung

In mehr als 300 Versuchen wurde die Verträglichkeit von 31 Metallen, Legierungen und Beschichtungen mit statischem Pb-17Li untersucht. Die meisten Ergebnisse wurden noch nicht publiziert.

Die **Benetzung** von Proben hatte keinen Einfluß auf das Lösungsverhalten der Metalle. Metalle können hinsichtlich ihrer Stabilität in Pb-17Li in drei Gruppen eingeteilt werden : Am stabilsten sind die Elemente Nb, Ta, Mo, Re und W. In der zweiten Gruppe folgen Be, Fe, V und ferritischer Stahl. Be wird jedoch entlang der Korngrenzen zerstört. Nicht stabil in Pb-17Li sind Al, Ti, Zr, Y, U und ihre Legierungen.

Temperaturfunktionen der **Löslichkeiten** in der eutektischen Mischung wurden für 8 Metalle erhalten, dazu Einzelwerte für 3 weitere. Die Ergebnisse stimmen gut mit einer theoretischen Arbeit von Guminski überein. Bemerkenswert hoch sind die Löslichkeiten von Al, Zr, Y und U, sehr niedrig die von Nb, TA, Mo und W. Die **Löslichkeit von Blei in Titan** wurde bestimmt, wobei neue Daten für das Phasendiagramm erhalten wurden.

Aus Löslichkeiten und Lösungsraten wurden **Diffusions-Koeffizienten** in Pb-17Li berechnet. Die Temperaturfunktionen für Be, Al, Fe und V sind diesen Metallen zuzuordnen, während die für Ti, Zr und U durch die Bildung chemischer Verbindungen beeinflußt sind. Nicht alle beobachteten Effekte können erklärt werden.

Auf den Metallen wurden unterschiedliche **Reaktionsschichten** gefunden. Wahrscheinlich als Vorläufer der Korngrenzenreaktion mit Blei wurde eine sehr dünne 'chemische Reaktionszone' identifiziert.

Die folgenden **intermetallischen Verbindungen** mit Blei wurden gefunden : Ti_2Pb and Ti_3Pb_2, UPb_4, YPb_4 and Zr_4Pb. Die Verbindung Ti_3Pb_2 wurde näher untersucht. Sowohl Ti als auch Pb können durch andere Metalle ersetzt werden. Selbst in der Gasphase über dem Eutektikum reagieren Y und U mit Blei.

Die untersuchten **Legierungen** sind nicht stabiler als ihre Basismetalle. Mehrere Legierungsbestandteile werden bevorzugt herausgelöst. Besonders zu erwähnen sind hier Nickel und Aluminium. Besonders mit Legierungen bleiben viele Fragen nach dem chemischen Verhalten in der eutektischen Mischung offen.

Mo-Beschichtungen auf Tritium Gettermetallen waren in Pb-17Li nicht stabil.

Preface

During the years 1982 to 1992 the compatibility of metals and alloys was tested in static Pb-17Li. More than 300 tests were performed. It was not really a systematic study. Tested materials were always of other interest. Gettering of tritium was the first goal and getter materials were studied. Later, with the construction of loop TRITEX, structural materials as steels, vanadium and molybdenum were of more interest. Beryllium was investigated because of its possible use in liquid metal blankets.

Only a few results have been published before. The main part of evaluations was postponed. Most of the experiments and analytical work was done by H.Gräbner and J.Oschinski, both retired several years ago. Therefore, it was difficult to reevaluate the data. Some informations may be lost. But still it was worth to compile the results.

Content

Part-I : General considerations and results

1. *Introduction*

The eutectic mixture Pb-17Li[1] is proposed as one possible blanket material for fusion reactors (1). Physical and chemical properties of this mixture are described in references (2) to (4). The eutectic contains 15.7 at.% lithium , its melting point is 234 °C (5,6,7).

In a fusion reactor the mixture will be in contact with different materials. The knowledge until 1990 about compatibilities is compiled by T.Sample (6). A number of corrosion experiments with steels have been done during the last years.

Because of the low chemical activity of Li in the eutectic it is assumed that most properties of the mixture will be similar to those of lead (3). This is only partly true. Solubilities in the eutectic of Mn, Ni, Th and Sm are up to a factor four higher (8,9). On the other hand many effects are comparable for different liquid metals. This was shown e.g. by Guminski (10) or Tortorelli (11). In this paper, results are often compared with those of pure lead. For some metals also results from liquid lithium experiments are included.

It was not possible to evaluate the literature for each investigated metal completely, but attempts were made to find most references. The start was always phase diagram considerations on the basis of Massalski's compilation (12). Furthermore some phase diagrams were picked from 'Bulletin Alloy Phase Diagrams'(13) and from the ASM monograph serie (14). The second starting point was the mentioned thesis of T.Sample (6).

2. *Experiments*

Details of the experiments are given in Part-III of this report.

The used materials were cleaned and/or vacuum annealed. The used eutectic mixture contained between 15.5 and 17.8 at.% Li (0.61 to 0.72 wt.%). Because of segregation effects (7) prior to the filling of crucibles, the concentration was not constant[2].

In an Argon filled glovebox, 60 to 80 grams of the eutectic were filled into Mo crucibles.[3] 15 cm^2 Mo were wetted by the eutectic.

Sheets of sample materials were inserted. The sample surface in contact with the eutectic was 3 to 8 cm^2. Any contact between the sample metal and the crucible wall was avoided. The assembly was then transferred - still inside the box -

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[1] The older value for the eutectic composition was 17 at.% Li. Most of the experiments were done with this concentration. However, the true Li concentration of the eutectic is 15.7 at.% (5,7). Nevertheless, the writing Pb-17Li will be used in this report.

[2] No influence of the Li concentration on results was seen. The Li concentration will not be mentioned any more.

[3] In a few experiments crucibles of Fe, W or alumina were used.

into a capsule for heating. Up to 6 crucibles with often different sample materials were in one capsule. During heating at constant temperature a flow of pure argon passed through the capsule.

After the exposure, crucibles were taken out from the capsule in the glove box. They were reheated und the samples extracted. The Pb-17Li was poured into alumina dishes. The eutectic was dissolved in stoichiometric amounts of nitric acid, using a special extraction technique. The solution was analyzed for dissolved metals by ICP-AES. Remaining Pb-17Li at the crucible wall was also dissolved and analyzed. Finally remaining eutectic from the sample surface was dissolved and analyzed. This was mostly done by an electrolytic technique. But depending on the material also other different chemical methods were used. There was a weight control of samples as well as metallographical examination. For some metals fractions of the sample were dissolved and analyzed for Li and Pb.

3. Basic considerations

A good description of all effects in connection with **static compatibility** tests of materials in liquid metals is given by Brasunas (15). The limited value of results from static tests for dynamic and non-isothermal systems is discussed. However, isothermal static tests contribute considerably to the knowledge of material behaviour. Loops are usually constructed from a material different from the sample. The surface ratio sample to loop is very small. The liquid metal becomes saturated by not wanted metals, and mass transfer of structural materials to the sample surface is possible (16). Furthermore different elements in solution influence solubilities.

The driving force for the dissolution is the different chemical activity in a sample metal and Pb-17Li. This activity is **one** at the metal surface, respectively equal to activities of metals in alloys. At equilibrium (saturation) the chemical activity is the same in the liquid metal. In most cases, dissolution rates are controlled by the mobility of atoms in the liquid, that means by diffusion in the eutectic, but other rate controlling steps are also possible (11). The dissolution process can be divided into the following steps :

3.1 Wetting

Wetting of the sample surface by the liquid metal is the first step. The physical definition of wetting does not help much for the understanding of liquid metal corrosion. Also it is not possible to see the shape of droplets of molten eutectic without special equipment. The practical definition as used in this report is :

> A wetted surface after removing from the molten eutectic at 350 to 400 °C retains a film of 30 to 100 microns of liquid metal equivalent to 30 to 100 mg/cm^2. Non-wetted surfaces are clean with droplets.

Often a gap between a non-wetted solid surface and the liquid is assumed, preventing the contact and dissolution. Sometimes it is observed that corrosion starts after a long incubation time. e.g. Borgstedt (17) found this effect for MANET-steel in Pb-17Li. It was assumed that a thin oxide layer on the steel prevented wetting.

Inspite of its low chemical activity Li is still a reducing agent for many oxides. Dissolution is accelerated after the removal of these oxides. Other authors did not find such an incubation period with steels (11,18).

The influence of wetting on corrosion processes is not completely understood. The model with a gap between the solid and the liquid is too simple. Robertson (19,20) found that the volume-diffusion coefficients for Fe and Cr in lead were the same for wetted and non-wetted surfaces. He observed 'grooving' at grain boundaries also when metals were heated in vacuum or an inert gas. Grooving in a liquid metal surrounding is caused by volume diffusion in the liquid; grooving in vacuum or an inert gas by diffusion in the solid metal and/or evaporation-deposition processes. But the rate for grooving was the same in his experiments.

To have a better wetting process samples are sometimes heated in the liquid metal for a short time to a higher temperature. This was done in our experiments occasionally. Such a process has to be selected very carefully. A reaction may start different from that at experimental conditions.

3.2 Dissolution

The next step after wetting depends on several parameters. In most cases a thin layer of liquid on the surface will be quickly saturated with the dissolving metal. Dissolved atoms have to diffuse through this layer into the bulk Pb-17Li. The concentration in the molten metal increases until finally the bulk material is saturated and dissolution stops. On the other hand dissolution can be controlled by the dissolution of the metal, that means by transport of an atom from the solid into the liquid. In this case saturation needs much longer, the dissolution rate remains approximately constant for a longer time. However, a constant dissolution rate is also seen in case of mass transfer. In our experiments it was isothermal mass transfer between dissimilar metals, in case of loops often non-isothermal mass transfer. In both cases dissolved atoms are removed from the liquid.

The equilibration time until saturation depends on the conditions of experiments. Solubility measurements are often done with equipments similar to those used in the experiments of this report (6). The liquid metal is stirred to reduce the equilibration time. Stevenson (21) investigated the dissolution of Cu and Ni in lead at 527 °C. The dissolution time constant increased by a factor of four when increasing the liquid metal velocity at the sample surface from 8 to 20 cm/s.[4] Extrapolating the function would give equilibrium in a static system after 2 hours. On the other hand, Ali Khan (22) found for the dissolution of iron in stirred lead equilibrium after 50 hours at 1000 °C. This is a long time compared with Stevensons results. The exposure time in our experiments was always long. **We assume, therefore, saturation in most experiments.**

Solubilities of metals are similar in different molten metals (10). Even in lithium solubilities are often reported similar to those in lead or Pb-17Li. Theoretical calculations depend very strongly on the used model. For example, V solubilities in lead calculated by different models scatter over 8 orders of magnitude (10) ! Therefore, casual similarities should not be used for predicting solubilities. Such theoretical considerations were not included in the discussions.

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[4] A different mechanism was found with velocities larger than 50 cm/s. This will not be discussed in this paper.

Only Guminski's model looks promising (10). It considers the electronic configuration of atoms in a 'cellular' model und finds similarities between different solvents. For example, Nb has a 1000 times lower solubility than Al in molten Li, Sn, Pb and Bi. This was shown by drawing solubilities as a function of atomic numbers. Our results will be compared with this model.

3.3 Mass transfer, diffusion coefficients

With most of the investigated metals, dissolution did not stop despite solubility limits were reached. Because of **isothermal mass transfer between dissimilar metals** (15) the dissolved metal deposited at the crucible wall. Different processes can reduce the chemical activity of a metal at the Mo wall, e.g.diffusion into Mo or the formation of compounds. In some cases, however, the process can not be explained.

The concentration gradient across the crucible remains constant and the First Fick's Law is valid. The Pb-17Li is saturated at the sample surface, the chemical activity at the deposition surface is lower. The constant dissolution rate is given by

$$R = D/x\ (Cs-Co).$$

An estimation of Co, the concentration at the crucible surface, is not possible. But assuming Co<<Cs and the distance sample-crucible wall for x, diffusion coefficients can be calculated. However, one has to keep in mind that Co is not determined and values should be considered with care.

3.4 Surface reaction zones

Different kinds of surface reaction zones can be formed : Penetration of Pb and Li into the sample metal, formation of chemical compounds or leaching of elements from an alloy. The formation of a Ni-depleted ferritic layer on austenitic steels is an example for the latter effect.

Chemical reaction zone

A new kind of a 'chemical reaction zone' was found. Reaction zones are usually identified by metallographic examinations. But often metallographic examinations showed no effect. However, the chemical behaviour during cleaning processes of metals after exposure was different from that of the original metal: More of the sample metal was dissolved. We assume that there was a more reactive surface reaction zone. The thickness of this was proportional to the exposure time. We believe that this zone is the first step before the 'metallographical' reaction zone is formed and indicates e.g. penetration of lead along gain boundaries (s.steel 4922 and other metals).

3.5 Intermetallic compounds

The formation of intermetallic compounds may occure with lead or lithium in solution or at the surface. Depending on solubilities and transport properties, compounds may form surface reaction zones or deposit at the sample or crucible surface. All these effects were seen in the experiments for different metals.

3.6 Mutual solubilities

The corrosion continues even if the dissolution of a metal stops. Dissolution is a mutual process. At the same time with dissolution in the eutectic, lithium and lead will dissolve into the solid metal. This process is often accompanied by modified mechanical properties (50) or embrittlement, as seen for many metals. A typical example is beryllium in our experiments. **Liquid metal embrittlement** is important with all liquid metals. Kamdar (81) gives a detailed description of the effect. He describes that embrittlement was often found even if there was no measurable penetration of the liquid metal into the solid one. That means that trace amounts of the liquid metal in the solid, e.g. dissolved at grain boundaries, are sufficient.

3.7 Gas phase reactions

The mentioned observation with grooving (19,20) leads to the question for reactions in the gas phase. Indeed embrittlement of steels in a lead atmosphere is reported by Kamdar (81).

The isothermal atmosphere in the capsule above the crucibles is nearly saturated with Li and Pb vapor [5], corresponding to the chemical activity of these elements. The upper section of a sample was exposed to this covergas. Reactions between the sample metal in this area and lead was observed with several metals, often causing embrittlement.

3.8 Complex mechanisms

Actually the dissolution and corrosion process is complex and all described mechanisms will occure in parallel. Furthermore not a simple binary system has to be considered. Solid phases are the sample, the crucible wall, and formed intermetallic compounds or deposits. In the liquid phase at least two components, Pb and LiPb, are mixed. Reaction zones or leaching of alloy elements change chemical properties of surfaces.

3.9 Some remarks on molybdenum crucibles

Crucibles of molybdenum were used in most of the experiments because of good compatibility of this metal with the molten eutectic. But with Mo, an additional solid metal phase was introduced, dissimilar-metals mass transfer occured. Mutual interdiffusion with Mo up to the formation of compounds is reported for many metals (25). The chemical activity of these metals at the Mo surface is reduced. The question, if there is still a Mo crucible after deposition of e.g. Fe or V, can be answered with 'yes'. Never any stop of the mass transfer process was observed.

At the beginning of the experimental program crucibles failed when a sample metal was in contact with the Mo-wall below the liquid metal surface. This was observed in our experiments with Ti, Zr, Fe, steels and vanadium at temperatures above 450 °C. Obviously the mobility of metal atoms is high enough at this temperatures for mutual interdiffusion and chemical reactions. There was no systematic investigation of this effect; instead samples were fixed in the crucible to avoid this contact. But the effect has to be considered in connection with **Mo coatings.**

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[5] Not exactly saturation because of a very slow covergas flow.

4. Results and discussion

All results are described in detail in Part-II of this report, together with a discussion of the literature. In this chapter a kind of **extended summary** is given. Not for every metal all investigations were done. Also some informations may be lost because of the long delay between experiments and evaluation. The reader should be aware that no mention of an effect can mean no remarks were found in laboratory notes. Nevertheless, a large number of valuable results were obtained.

4.1 Wetting by Pb-17Li

There was no systematic investigation of wetting behaviour, but some observations were registered in laboratory notes.

A wetted surface after removing from the molten eutectic at 350 to 400 ^{0}C retains a film of 30 to 100 microns of liquid metal, equivalent to 30 to 100 mg/cm^2. Non-wetted surfaces are clean with droplets.

Wetting at 300 ^{0}C was seen only with yttrium after 66 hours exposure time and with uranium after more than 350 hours. Also at 400 ^{0}C, a longer time was often needed for wetting. The wetting behaviour of different materials including Mo of the crucible was different. In agreement with Robertson's observations (19,20) however, **even in case of non-wetted samples, solubility and dissolution rate data fit well into the Arrhenius functions from higher temperature experiments.**

This important observation is in agreement with our experiments for gettering of hydrogen (65) with vanadium : wetting had no influence on the rate of hydrogen uptake. The rate determining step was diffusion in a liquid metal boundary layer. This diffusion is probably dominant also in cases where wetting has no influence on corrosion or dissolution, as seen for several metals.

Therefore, 'incubation times' as seen by Borgstedt (17) should be discussed better on the basis of protecting surface layers than with wetting effects.

4.2 Dissolution and mass transfer

Dissolution rates were obtained from the sum of dissolved metal found in Pb-17Li and at the crucible wall. This corresponds to weight loss data which were determined occasionally[6]. In case of Ti and Zr, reaction zones were growing at the surface, 'loss of sound metal' was higher than calculated from the dissolved amount.

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[6] Weight loss data were always in agreement with data from chemistry.

Only in a few cases an **incubation time** was observed before dissolution started. A delay of 1200 hours was seen with uranium at 300 °C. But then dissolution was fast. But even in this case it was not a wetting effect. An incubation time was seen with Ti and Zr metal (60), probably caused by remaining surface oxides. Exact informations for these elements are lost. An other example for an incubation time was with molybdenum coatings on Ti and Zr. Diffusion of Ti respectively Zr and Pb through the Mo layer caused the delay. Then dissolution rates were the same as with uncoated samples.[7]

In most cases a faster dissolution during the first few hundred hours was followed by a **steady state** dissolution rate. Usually dissolution did not stop at saturation of the eutectic because of isothermal mass transfer to the crucible wall (below). **Fig.1** shows the dissolution of iron and steel 4922.

A faster dissolution rate at the beginning was found e.g. by Chopra (74) for ferritic steels in non-isothermal systems. Because the initial period was not investigated in this work, only steady state dissolution rates will be discussed. As mentioned in chapter 3.2, a constant dissolution rate is caused by mass transfer.

All steady state dissolution rates as found in this work are shown in **Fig.2**, functions are summarized in **Table 1.** For Mo, upper limits were found, for Y only a lower limit at one temperature. No values can be given for Nb, Ta and W.

Tab.1

Steady state dissolution rates
R in g/m^2*d, T in K; heat of reaction in kJ/mol.

	ln R = A + B/T		heat of reaction
	A	B	
Al	13.6	-9560	-80
Be	6.89	-9300	-77
Fe	3.38	-7206	-60
Ti	11.6	-9260	-77
U	23.6	-12970	-108
V	2.37	-5431	-45
Zr	11.7	-8858	-74
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4922	4.06	-5195	-43

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[7] The pumped loop TRITEX (38) is constructed from this steel, the composition is similar to steel HT-9 or MANET.

Fig.1

Dissolution of iron and steel 4922
in Pb-17Li

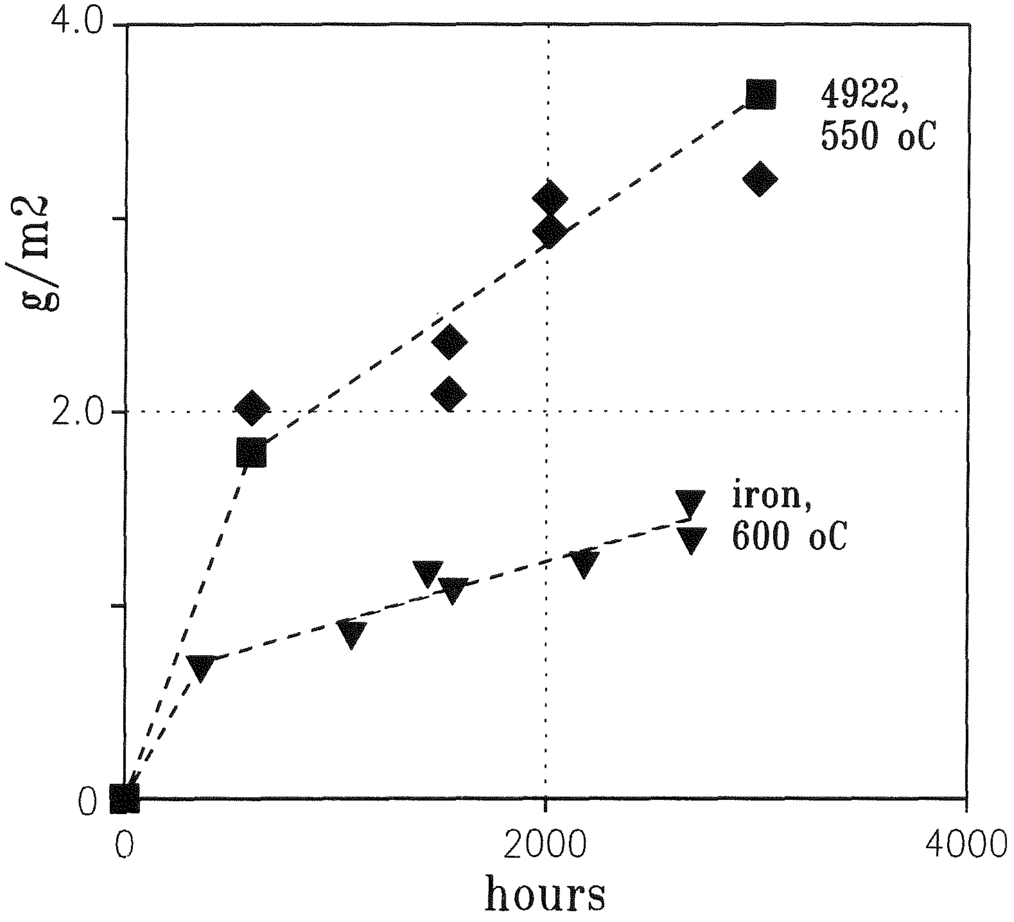
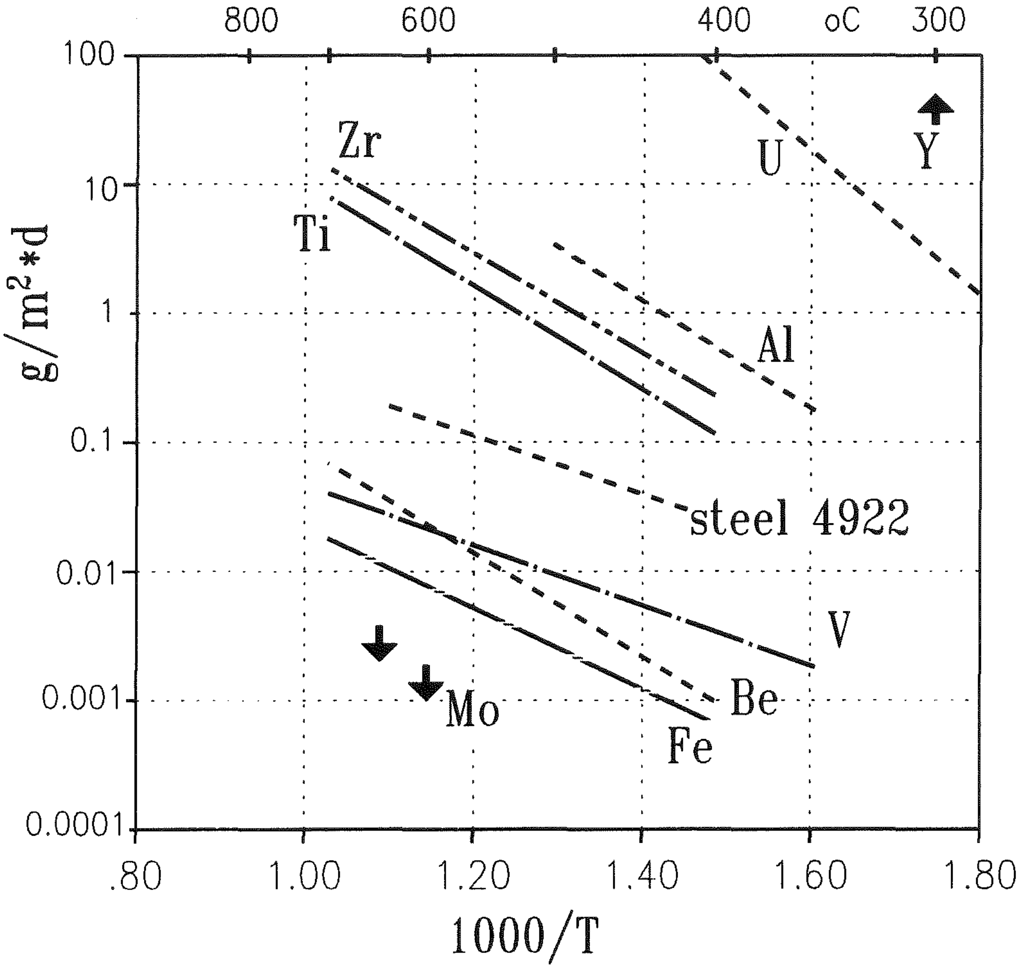


Fig.2

Steady state dissolution rates



All functions have nearly the same slope, pointing to the same mechanism for dissolution. Even in case of formation of compounds (Ti,U and Zr) this slope is found. From the work of Stevenson (21) it can be concluded that diffusion in the liquid phase is the rate controlling step.

For the maximum blanket temperature of 450 °C (1), dissolution rates are shown in **Fig.3** . Three groups of metals can be identified. Most stable are the refractory metals Nb, Ta, Mo, Re and W. The structural materials for a blanket belong to the second group. From this group, beryllium cannot be used in Pb-17Li because of severe attack along grain boundaries. Not usable in Pb-17Li are the elements of the third group because of their high dissolution rates.

Corrosion rates in non-static loop systems are higher than in static tests. This can be seen e.g. in Part-II, Fig.4922-2. Also the slope of the temperature function is steeper. Increasing the temperature from 400 to 450 °C causes a doubling of the steady state dissolution rate from our static experiments. The same temperature rise would give ten times higher corrosion rates for steels in loop systems(17). Nevertheless at least a comparison of metals whith each other can be done. **Figure 3** can be used for the prediction of corrosion rates in other systems.

Isothermal mass transfer

Mass transfer from a sample to the crucible wall was seen with many of the investigated metals. The effect is described in the literature (e.g.ref.15). The strongest deposition was seen with Al and compounds of U and Y. Be, Fe and V show also strong mass transfer, while probably the formation of compounds at the sample surface reduces mass transfer for Ti and Zr.

Mass transfer between dissimilar metals can play an important role for the interpretation of corrosion experiments. For example, Borgstedt found in loop PICOLO (16) a weight gain of vanadium alloys because of pick up of Fe from the eutectic. In our static isothermal experiments mass transfer caused a steady state dissolution rate and gave the possibility to calculate diffusion coefficients.

4.3 Solubilities of elements in Pb-17Li

The applied technique to investigate material behaviour in Pb-17Li is often used for solubility measurements (6). After longer exposure time, the eutectic is saturated with the dissolving metal. Temperature functions for solubilities were obtained for Al, Be, Fe, Mo, Ti, U, V and Zr; single -one temperature- values for Y, Nb and Ta; solubility limits for Re and W. **Fig.4** shows all results. Functions and single values are summarized in **Table 2.**

Fig.3

Steady state dissolution rates at 450 oC

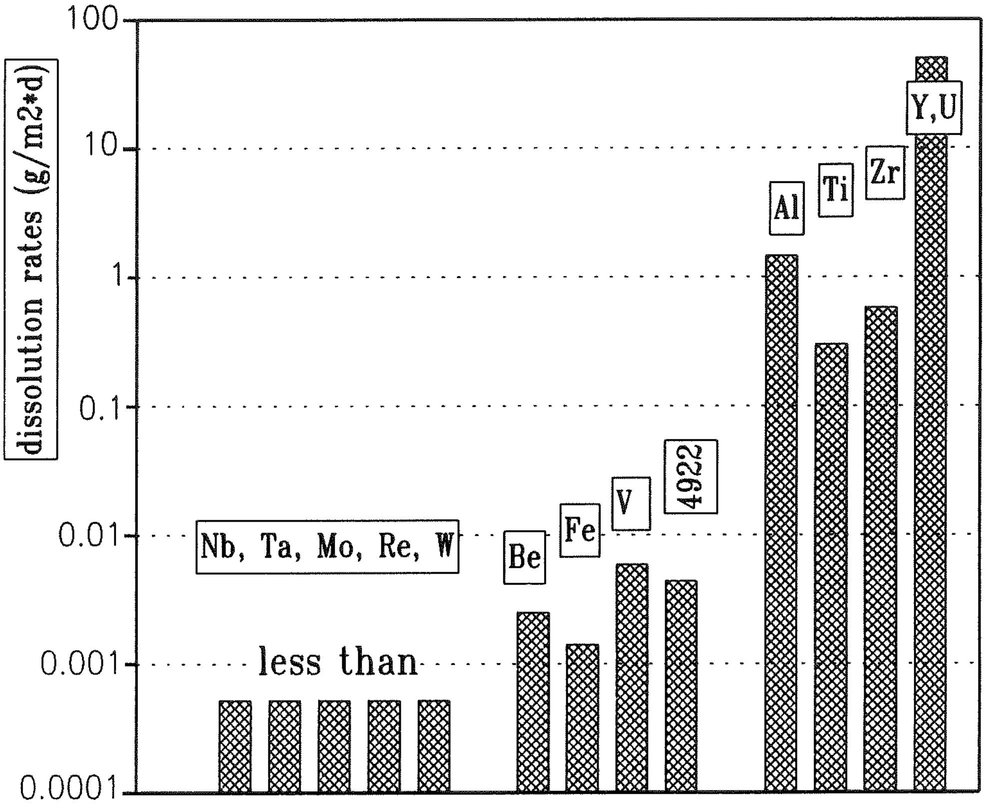
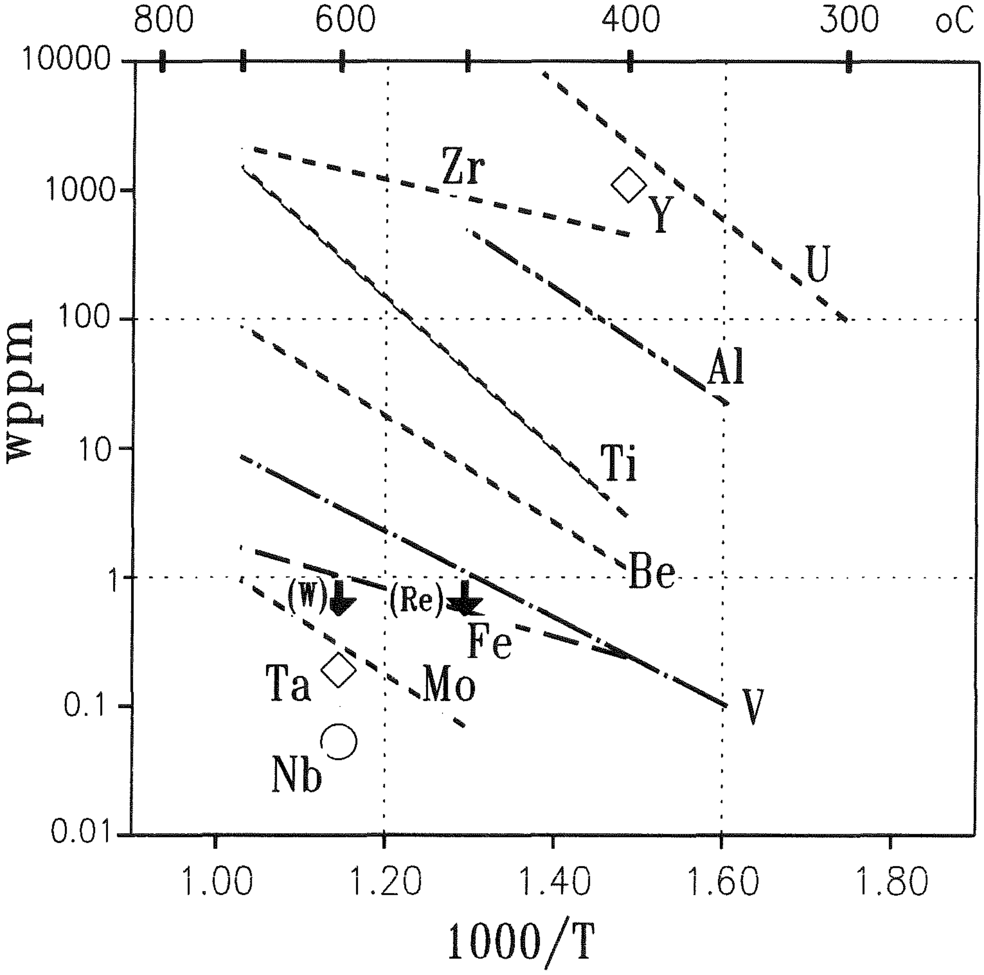


Fig.4

Solubility of elements in Pb-17Li



From these elements the solubility of Al in Pb-17Li was reported recently (44). The results are in good agreement. Only one value for the iron solubility at 450 °C is reported (8). It is much higher than values from our function. But this value was derived from stainless steel corrosion tests. Also we found higher 'Fe-solubilities' in experiments with steels 4300 and 4922. This will be discussed below.

The solubilities of Ti, U, Y and probably Zr are actually solubilities of compounds with lead (below).

Solubilities of a metal in different liquid metals are similar. In **Fig.5** our solubility values for 600 °C are given together with 'Guminski's function' (10) for lead. It is evident that the data follow the function.

An amazing fact is that also Ti, Zr, Y and U fit into the function. These four elements form intermetallic compounds with lead. Obviously solubilities are not much influenced for these elements. In the figure a value for **bismuth** is included (31). Again in spite of the formation of Li_3Bi (32), the value fits into the function. However, when considering the scale in Fig.5, the reader should not expect a high accuracy for predicted solubilities from Guminski's function.

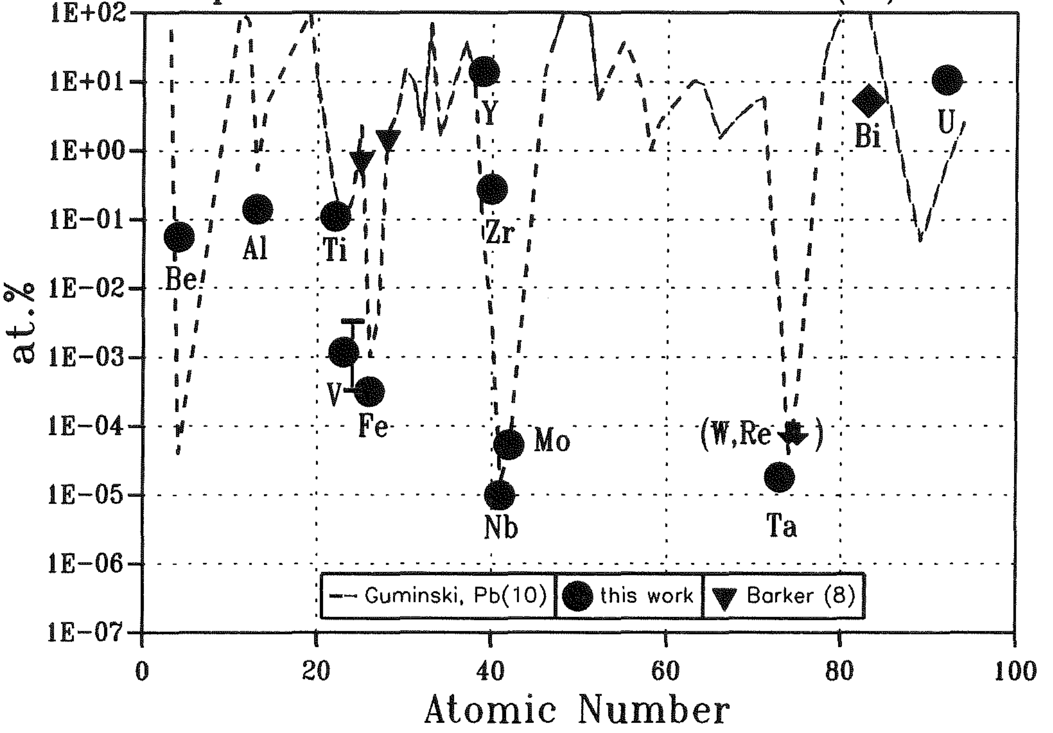
Tab.2

Solubilities of elements.
S in wppm; T in K; heat of dissolution in kJ/mol.

	ln S = A + B/T		heat of dissolution	single values	
	A	B		°C	wppm
Al	19.2	-10040	-84		
Be	14.2	-9446	-78		
Fe	4.94	-4292	-36		
Mo	10.0	-9784	-81		
Nb				600	0.053
Re				500	< 1
Ta				600	0.19
Ti	21.3	-13600	-113		
U	25.8	-12150	-102		
V	10.1	-7730	-64		
W				600	<1
Y				400	1100
Zr	11.2	-3423	-28.5		

Fig.5

Solubility of elements in Pb-17Li at 600 oC, compared with a function of Guminski (10) for lead



4.4 Diffusion coefficients in Pb-17Li

Comparing Fig.2 and Fig.4 it can be seen that metals with high solubilities have also high dissolution rates. From the First Fick's Law and assumptions as given in chapter 3.3, a linear relation is expected between steady state dissolution rates and solubilities:

$$R = D/x\ (Cs-Co).$$

Because of similar diffusion coefficients for different metals, this is found over the range of five orders of magnitude, **Fig.6** .

For 7 elements dissolution rates and solubilities were determined at the same temperatures. For these, diffusion coefficients were calculated, using x = 1.2 cm (0.012 m) for the average distance sample-crucible wall. The values are in an expected range (**Fig.7**). The functions are summarized in **Table 3.**

The elements U, Ti and Zr form intermetallic compounds at the surface. These compounds are in equilibrium with the solution. Fick's Law should be valid for compounds as for a pure metal and the data fit into the slope of Fig.6 . Diffusion coefficients, however, may be influenced by these compounds.

The functions for Al, Be, Fe and V are considered to be more reliable for these elements because no compounds are formed.

Included in the figure is a function of Robertson (19) for iron in lead. Inspite of completely different experiments (study of 'grain boundary grooving') it has the same slope as our Fe function, but the values are 10 times higher than ours. An iron value of Simon (27) is obviously to low, while a chromium value of the same author fits into the range of our functions. The low values of beryllium are probably influenced by the odd behaviour of this metal : relative low solubility and dissolution rate, strong grain boundary attack. Not explainable is the positive value of the diffusion energy for vanadium.

Table 3

Diffusion coefficients
D in m^2/s, T in K; heat of diffusion in kJ/mol.

	ln D = A + B/T		heat of diffus.
	A	B	
Al	-21.6	-920	- 7.7
Be	-25.4	171	1.5
Fe	-19.6	-2844	-24
V	-25.7	2300	19
Ti	-27.7	4348	36
U	-32.1	6302	52
Zr	-17.6	-5220	-43

Fig.6

Dissolution rate vs. solubility at 450 oC

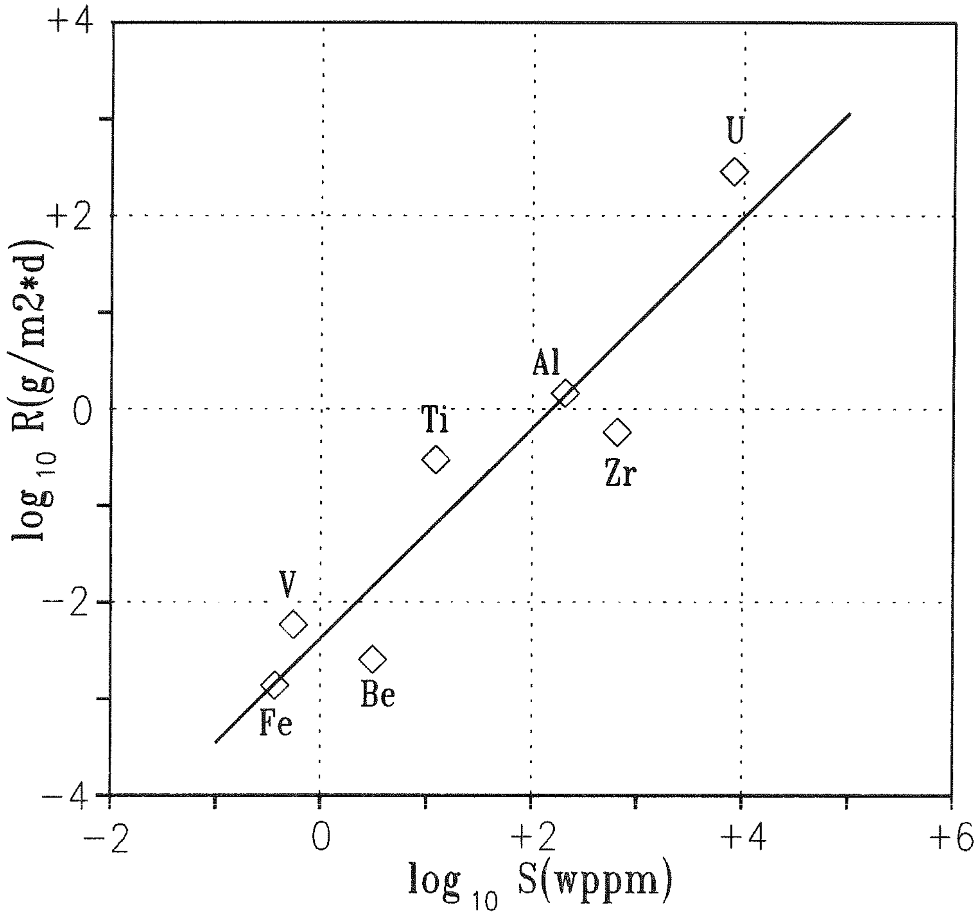
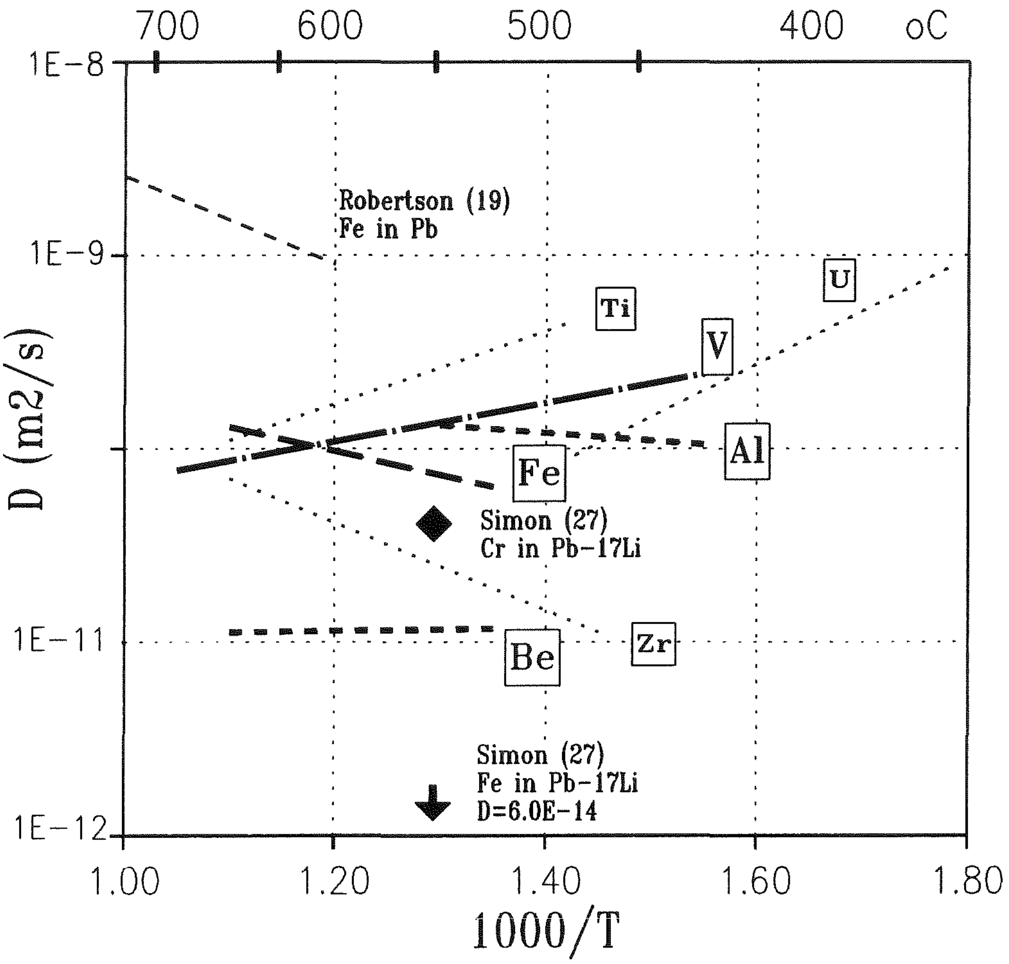


Fig.7

Diffusion coefficients of metals in Pb−17Li



4.5 Reaction zones and compounds

Some reaction zones and compounds were mentioned in the chapters before. Reaction zones at sample surfaces may be formed by different processes. The chemical activity of an element in a reaction zone or compound is smaller than for the pure metal. Therefore, the compatibility with the eutectic will be influenced. Different kinds of reaction zones were found in this work.

4.5.1 'Chemical reaction zone'

Chemical purification of samples showed for most investigated metals very thin reaction zones. The thickness was proportional to exposure times and larger at higher temperatures. Typically on vanadium the thickness was 0.04 mikrons after exposure to the eutectic for 3000 hours at 550 °C. These reaction zones can not be seen by metallographic examination. We assume that such chemical reaction zones point to the beginning of dissolution of lead into the metal. For example, the start of a grain boundary attack on iron was seen at 600 °C after 1560 hours, while the chemical reaction zone was seen also at lower temperatures and shorter exposure times.

4.5.2 Metallographical reaction zone

Metallographical reaction zones are most often reported in the literature. For pure metals and without formation of compounds they are caused by diffusion of solvent atoms into a sample metal. Mainly lead is penetrating along grain boundaries. Samples get brittle and can be destroyed, as seen with beryllium. **Grain boundary attack was seen also with Fe, Mo and other metals.**

4.5.3 Chemical compounds on surfaces

A different kind of surface layer is seen when compounds are formed.

Metals may pick up elements as O, N or C from the eutectic or atmosphere. This was seen with **vanadium**. But the reaction zone was thin and did not prevent the dissolution of this metal.

Much more important are reactions with lead from the eutectic. In all cases the formation of compounds caused destruction of the solid metal. The following compounds were found :

titanium : Ti_2Pb and Ti_3Pb_2
uranium : UPb_4
yttrium : YPb_4
zirconium : Zr_4Pb

From these compounds Ti_3Pb_2, YPb_4 and UPb_4 were not reported before. Ti_2Pb was proposed by Farrar (62) for the Ti-Pb system, but not experimentally verified.

Ti_3Pb_2 was investigated more in detail (23). Well shaped crystals were found in the experiments. The crystals are chemically much more stable than Ti metal. The composition of the crystals gives Ti_3Pb_2 or a more complex compound. In the literature no compounds are reported with more than 33 at.% Pb. From some selected crystals crystallographic parameters were determined : space group $P6_3/mmm$, with a=0.93 and c=0.58 nm spacing.

In this new compound Pb and/or Ti can be replaced by other metals. There was no systematic investigation of this effect. Other elements were found only when using Ti-alloys as discussed below. The crystals contained in our experiments the following elements:

Zr	up to	14	at.%
Al		40.6	at.%
V		0.27	at.%
Mo		0.27	at.%
Sn		0.63	at.%

A partly replacement of Ti by Zr over the whole concentration range was found e.g. for the intermetallic compound Ti/Zr_5Pb_3 (63,64). A very high concentration of Al, however, shows that a replacement of lead is also possible. More tests are needed to quantify these effects.

The dissolved titanium is obviously in equilibrium with the intermetallic compound Ti_2Pb. The same concentration in the eutectic was found with Ti metal and with all investigated alloys. Also zirconium is forming an intermetallic compound with lead at the surface. The equilibrium concentration, however, is proportional to X(Zr) in the alloy.

4.5.4 Chemical compounds in solution

The compound Ti_3Pb_2 is formed by crystallizing from the solution. Therefore, the replacement of Ti or Pb by other metals is possible. As in aqueous systems, deposition occurs if the concentration exceeds the solubility product. Depending on solubilities and the effect of mass transfer, deposition at the sample or on other surfaces is possible. Compounds with lead were found also at the crucible wall.

4.6 Behaviour of alloys

Results with alloys have been mentioned in the chapters before. The behaviour of alloys is often different from that of pure metals, even when considering reduced chemical activities of the components. **All investigated alloys showed no better behaviour than the pure base metals.**

Alloys of Ti and Zr were studied as possible getter metals for tritium. The concentration of Ti in Pb-17Li with these alloys showed that the compound Ti_2Pb, formed as a surface layer, determines the solubility of Ti : independent on X(Ti) in the alloy, the same value was found for the equilibrium concentration. The compound of the crystals, Ti_3Pb_2 has obviously no influence. On the other hand, equilibrium concentrations of zirconium in Pb-17Li are directly proportional to X(Zr) in the alloy, although the surface reaction product Zr_4Pb was formed. But the concentration for X(Zr)=1, derived from alloys, is lower than for pure Zr metal. That means that the chemical activity of Zr in alloys is lower than X(Zr).

Titanium and zirconium were leached from the Mo **alloy TZM.** The leaching rate is small. This alloy is as stable as Mo metal.

A few **alloys with aluminium** showed that this element is leached out from Ti-V-Al and Ti-Zr-Al. The Al-concentration in the eutectic was very low compared to the solubility, clearly indicating the formation of compounds. Nevertheless, crystals of pure Al were found at the crucible wall. The chemistry of aluminium should be investigated more in detail because of its importance for alumina coatings (30).

Austenitic steels showed the typical ferritic surface layer because of Ni-leaching. More important for a blanket is the behaviour of the **ferritic steels 4922 and 4301.** The dissolution rates are higher than for pure iron. Also the equilibrium concentrations of Fe in Pb-17Li are higher than the Fe-solubility ! At 450 °C we find for pure iron a solubility of 0.4 wppm, for the steels an equilibrium concentration of 0.8 wppm. Barker (8) found for the austenitic steel 316 an equilibrium value as high as 20 wppm. Probably not pure Fe is dissolved but a compound. On the other hand, nickel with only 0.3% in steel 4922 showed ideal behaviour. It was leached out even from ferritic steels. This leaching may have caused the chemical reaction zone and the start of an intercrystaline attack. For equilibrium concentrations of chromium data were scattered as usually (6,8). For manganese, the activity coefficient from equilibrium concentrations is in the range of 0.1. But there may be an other explanation for the 'too low' Mn values. Even if not found in static compatibility tests, the compound MnNi may be formed at the surface, with a much lower solubility. In a non-isothermal stainless steel convection loop MnNi was found at the coldest spot (33,34). This compound is proposed for the removal of Mn-54 from the eutectic in a blanket (35).

Summarizing the behaviour of alloys we have to conclude that alloys and the role of compounds in solution should be studied much more in detail in order to understand their behaviour in the eutectic. So far, not all effects can be explained.

4.7 Mo coatings

When sample metals contacted the molybdenum of the crucibles below the liquid metal surface, failures of crucibles were observed. It was mentioned in chapter 3 that inter-diffusion of solid metals or even chemical reactions are responsible for this effect (25). In the literature it was reported that Mo coating on steels was not stable (36,37). Nevertheless, Mo coatings on getter metals were investigated.

The coatings showed a very limited protection effect for Ti, Zr, Y and alloy Beta-3. In case of titanium, for example, Ti as well as Pb are diffusing through Mo at 500 °C. The described reaction layer of Ti_2Pb on Ti metal is seen below Mo. Also crystals of Ti_3Pb_2 are formed on the surface of Mo. The incubation time was discussed before in chapter 4.2.

4.8 Solubilities of Li and Pb in solid metals

The solubility of metals is a mutual process. Therefore Pb and Li will dissolve in the solid sample. Several attempts were made to determine Li and Pb in the sample metals.

Lithium: Li was never detected because of a too low sensitivity of the analytical method. The concentration in all materials was below 0.1 wt.%. However, Li is clearly penetrating into the metals. Steel 4922 samples from loop TRITEX were chemically cleaned, even a surface layer was removed. After some time in air, Li is diffusing from the metal to the surface, forming there alkaline reaction products. This is a well known effect from all sodium systems. Coen (28) found Li in austenitic steels always together with lead. He assumes a reaction of Li with oxygen or nitrogen in the steel. But intergranular penetration without such reactions is also possible as described e.g. by Wilkinson (29) for steel 21/4Cr-1Mo.

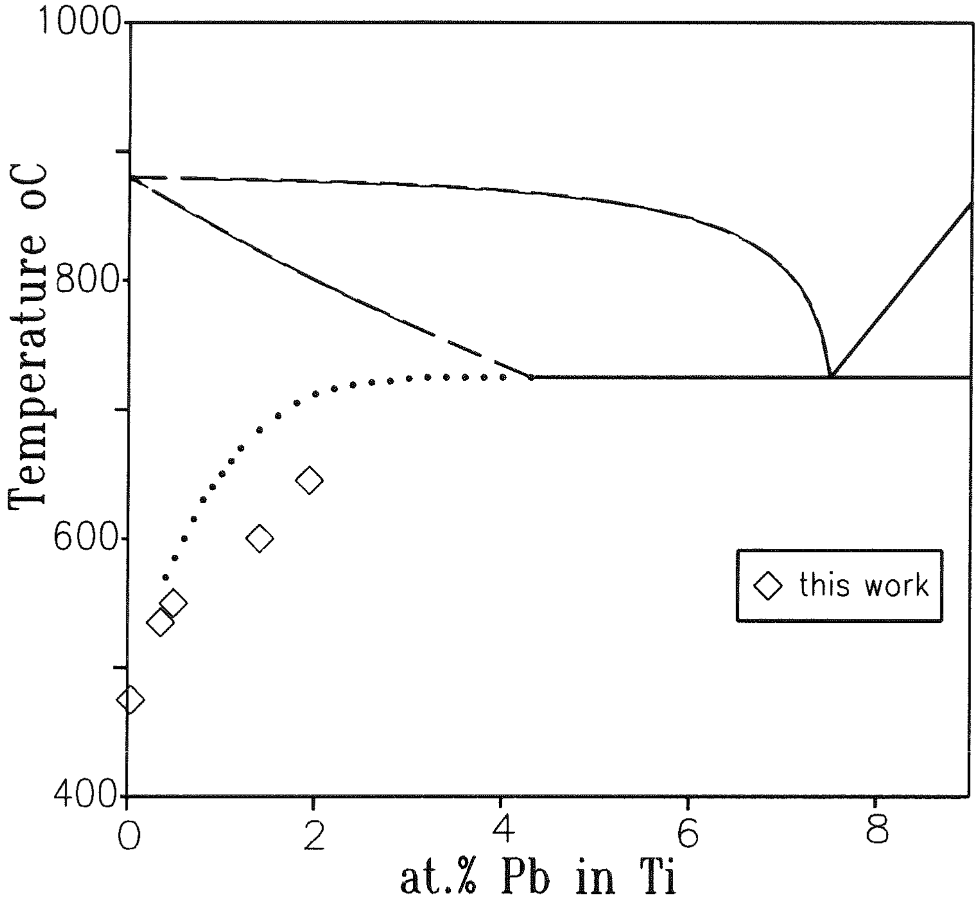
Lead: Also for Pb results are meager. Boundary concentrations e.g. for Al (<500 wppm), V (<200 wppm) or Be (<1000 wppm) are of limited value. Only for titanium the solubility for lead in solid Ti was found. It is given by

$$\ln S(\text{wt.\%}) = 19.9 - 15980/T \ .$$

The results add new data points to the phase diagram (23), (**Fig.8**).

Fig.8

Phase diagram Ti–Pb from ref.(61)



4.9 Gas phase reactions

Inspite of its importance for embrittlement no systematic investigation of the gas phase part of samples was done.

As mentioned in chapter 3 reactions between lead and U or Y were seen in that part of the sample which was exposed only to the gas phase above the eutectic. With these two metals even a kind of 'super wetting' was seen : 'creeping up' of the liquid into the covergas range of the sample. The mobility of lead in solid U and Y, therefore, is much higher than in other metals.

Embrittlement of the gas phase part of a sample was seen with some other metals. The effect was not investigated in detail. Only aluminium and beryllium should be mentioned in this chapter. Heavy embrittlement was seen in all parts of the sample.

5. *Summary*

The compatibility of 31 metals, alloys and coatings with static eutectic mixture Pb-17Li was investigated in more than 300 tests. Most of the results have not been published before.

No influence of the Li concentration on results was seen between 0.62 and 0.77 wt.%. **Wetting** has no influence on **dissolution rates**. This is discussed in detail. Metals can be divided into three groups : Most stable are the refractories Nb, Ta, Mo, Re and W. Ferritic steels, Be, Fe, and V belong to the next group. However, Be is destroyed along grain boundaries. Not stable at all are Al, Ti, Zr, Y, U and its alloys.

Temperature functions for **solubilities in Pb-17Li** were obtained for 8 elements, single -one temperature- values for 3 others. The results are in good agreement with a theoretical work of Guminski. Remarkably high are solubilities of Al, Zr, Y and U, while those of the refractories are low. Also, the **solubility of Pb in solid Ti** was determined, adding new data points to the phase diagram.

Because of the effect of mass transfer between dissimilar metals **diffusion coefficients** in Pb-17Li could be calculated from dissolution rates and solubilities. Most reliable are the temperature functions for Be, Al, Fe, and V. Those for Ti, Zr, Y and U are influenced by the formation of compounds. All values are in an expected range, but not all effects can be explained.

Different kinds of **reaction zones** were found on surfaces. New is a very thin 'chemical reaction zone', identified for several metals during sample cleaning. It is probably formed as a first step before grain boundary attack of the eutectic.

The following new **intermetallic compounds** were identified: Ti_2Pb and Ti_3Pb_2, UPb_4, YPb_4 and Zr_4Pb. The compound Pb_2Ti_3 was investigated in detail. Lead and titanium can be replaced by other metals. With Y and U, there was even a reaction in the gas phase above the eutectic.

Generally, **alloys** were not more stable than their base metals. Leaching of elements from alloys and other effects were investigated. Especially with alloys, many questions remain open and more work has to be done to understand the chemistry of alloys in the eutectic.

Last but not least **Mo coatings** on getter metals were found not to be protective for the use in a blanket.

Part-II : Results

Aluminium

Aluminium is not considered to be a structural material in contact with the molten eutectic. However to form layers of alumina on steels for electrical isolation or as barriers for tritium permeation, steels are aluminized in a first step before oxidation (30,39,40).

The phase diagram Al-Pb is not complicated; only the compound AlPb can be identified. A very low solubility of Pb in solid Al is assumed (41). The phase diagram Al-Li shows several intermetallic compounds (12). But because of the low chemical activity of Li in the eutectic probably no reaction products will be formed.

1. Experiments

The table shows the performed experiments. Most of the aluminium was obtained from Goodfellow with 99.99+ % quality. Some other materials were used too, all showed the same behaviour. In most cases, Al was etched with NaOH or HCl and vacuum degassed at 400 °C. Some tests were done without degassing, the behaviour in Pb-17Li was the same.

2. Results

Samples were always wetted at 400 and 450 °C. Poor wetting was seen below 400 °C, even after longer time. Probably samples had remaining oxides at the surface which prevented wetting. This is in agreement with observations during old screening tests (42), where no reaction was seen between Al and Pb at 350 °C. Indeed aluminium oxide should be stable in the eutectic in the whole investigated temperature range (30,39).

Dissolution

Dissolved amounts were obtained by two ways :

a) Weight change after electrolytic purification of the sample
b) By analysis of the Pb-17Li

In the latter case the weight of deposited Al-crystals was added (below). Both kinds of data are mixed in the figures, no difference could be seen. The dissolution is shown in **Fig.Al-1** . The dissolution rate at the beginning is a factor 10 higher than the steady state dissolution rate. In many experiments, especially at higher temperatures, the sample was completely dissolved. Steady state dissolution rates, **Fig.Al-2** , are given by

$$\ln R = 13.6 - 9560/T$$

(R in g/m^2*d). The heat of activation for the process is -80 kJ/mol.

Because of strong isothermal mass transfer most of the dissolved metal was deposited on the crucible wall in form of well formed crystals (**Fig.Al-3**). The driving force for the deposition of Al on Mo is not clear. A number of intermetallic compounds between Al and Mo are reported (25). However, chemical analysis as well as EDX- analysis of a cross section showed no Pb or Mo in the crystals (less than 0.1%). The crystals were pure Al. Non-isothermal mass transfer was found by Barker in thermal convection loops (43), pure Al-crystals were deposited in cooler parts of the system. It is clear from the results that no temperature gradient is needed for this mass transfer, it occurs also between dissimilar metals.

Solubilities

Most of the dissolved Al was transported by isothermal mass transfer to the crucible wall. The concentration of Al in the bulk Pb-17Li was constant over the time. (**Fig.Al-4**). **Fig.Al-5** gives this solubilities in Form of an Arrhenius plot. From two data points the **solubility of Al in Pb-17Li** is given by

$$\ln S(\mathrm{wppm}) = 19.2 - 10040/T .$$

The heat of dissolution is -84 kJ/mol.

Recently the solubility of Al in molten Pb-17Li was determined (44). The function is included in the figure. Solubility functions for lead (45,46) are nearly identical. The solubilities found in this work are well in this range, but the heat of dissolution is found higher.

From solubilities and the steady state dissolution rates **diffusion coefficients** were calculated : they are shown in **Fig.Al-6** The values are in an expected range. The Arrhenius function is given by

$$\ln D = -21.6 - 920/T,$$

the heat of activation is only -7.7 kJ/mol.

The **solubility of Pb in Al** in the sample material as well as in deposited crystals is below 500 wppm at all temperatures. The low solubility of Pb in solid Al is expected (41).

Reaction zone

Probably the high dissolution rate prevented the formation of a chemical reaction zone. Metallographic pictures of a sample (**Fig.Al-7**) show very large grains. This recrystallization can be influenced by lead, as observed with many other metals. It was not seen with samples heated without Pb-17Li in argon.

Other observations , gas phase reaction

As expected from large grains, remaining samples were very **brittle.** The same embrittlement was found for that part of the sample which was only in the gas phase above the eutectic. Lead vapor was probably responsible for this effect. Often a gray **foam-like material** was floating on the surface of the eutectic. Unfortunately this material was never analyzed. It was, however, included in the analysis of the bulk Pb-17Li. We assume that metallic aluminium was deposited at the cover gas interface.

3. Summary

The dissolution rate of Al in the eutectic as well as its solubility is high. Isothermal mass transfer between dissimilar metals has to be considered. Al crystallizes at the Mo surface or in cooler parts of a system. Large grains in the solid metal, probably caused by lead, cause strong embrittlement.

Table : List of experiments with **aluminium.**
Header line temperatures °C, other numbers hours
of exposure time.

300	400	450	500
	160	.	.
tests	300	305	.
up to	436	456	.
	.	.	504
2200 h	.	.	504
	.	765	.
	931	.	.
	1250	1200	.
	.	1293	.
	1776	.	.
	2592	2230	.

Fig. Al-1

Dissolution of Aluminium

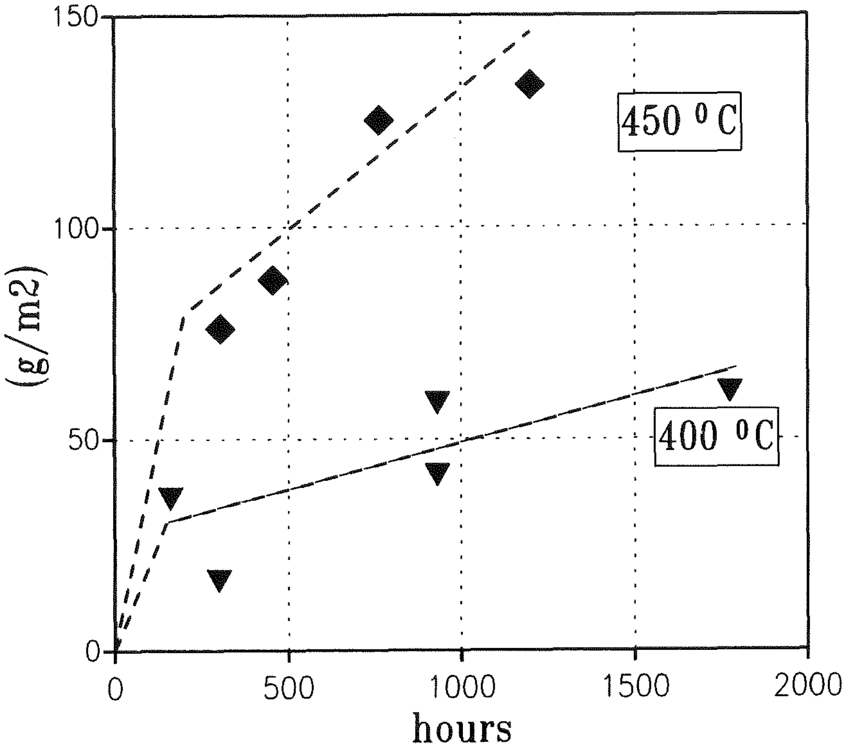


Fig. Al-2

Steady state dissolution rates

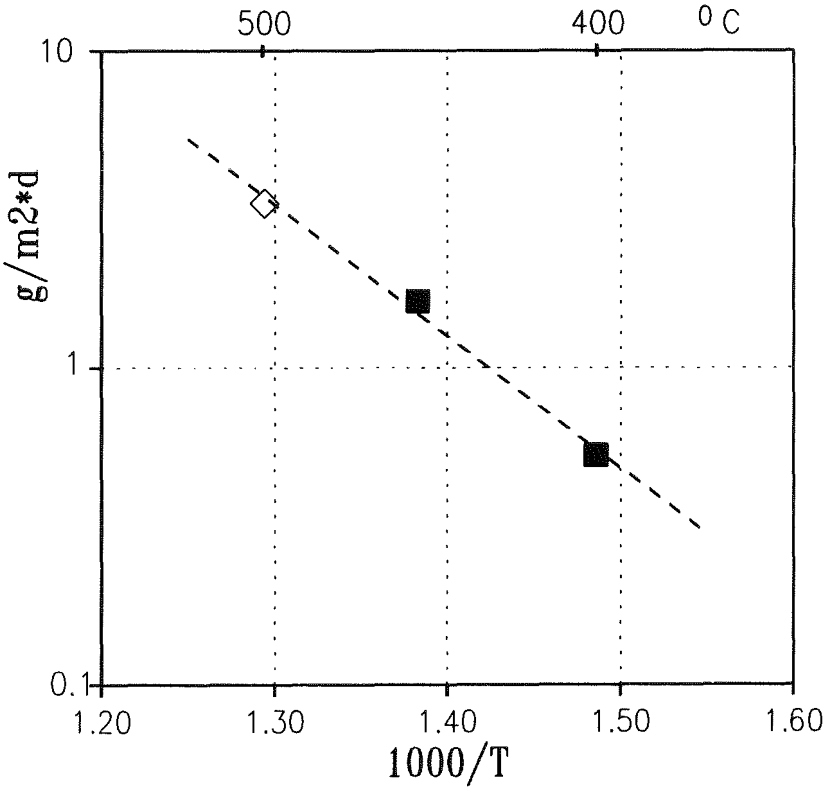


Fig.A1-3

Al crystals from the crucible wall

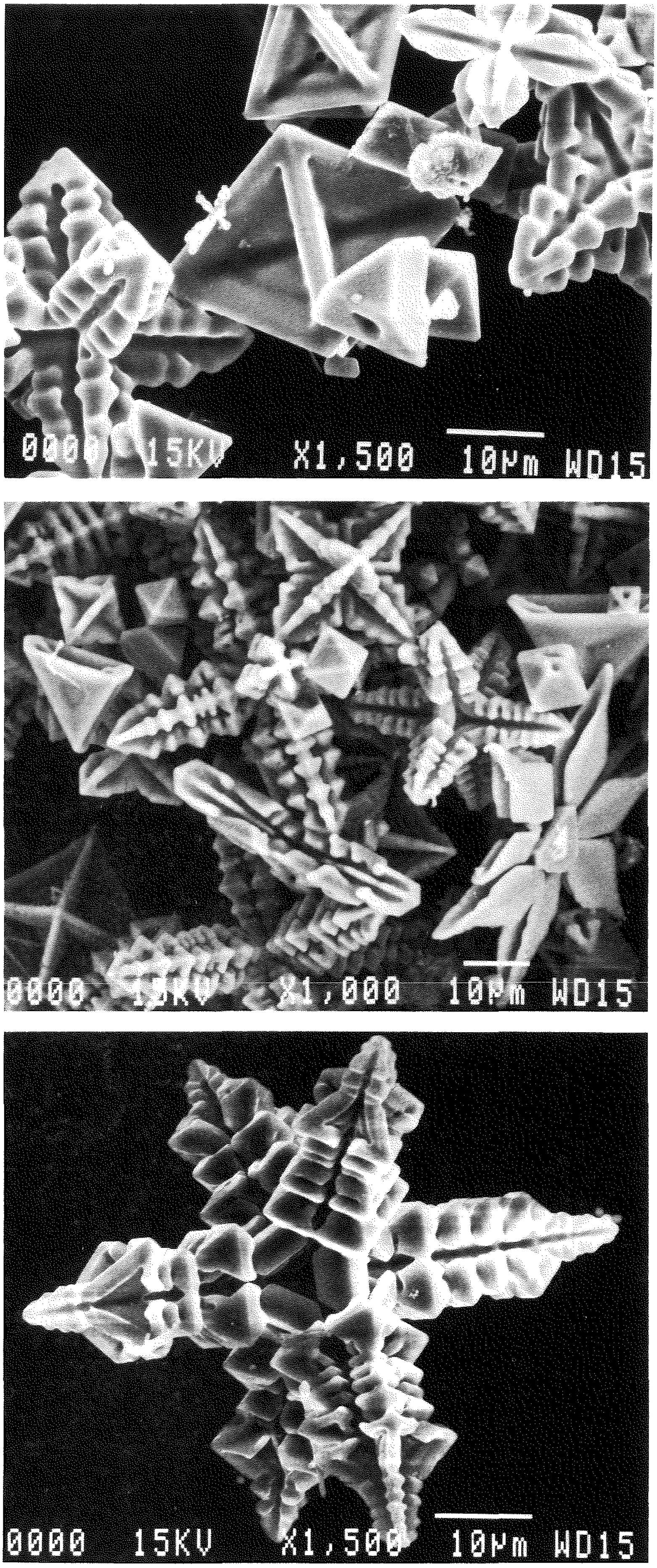


Fig. Al-4

Concentration of Al in bulk Pb-17Li

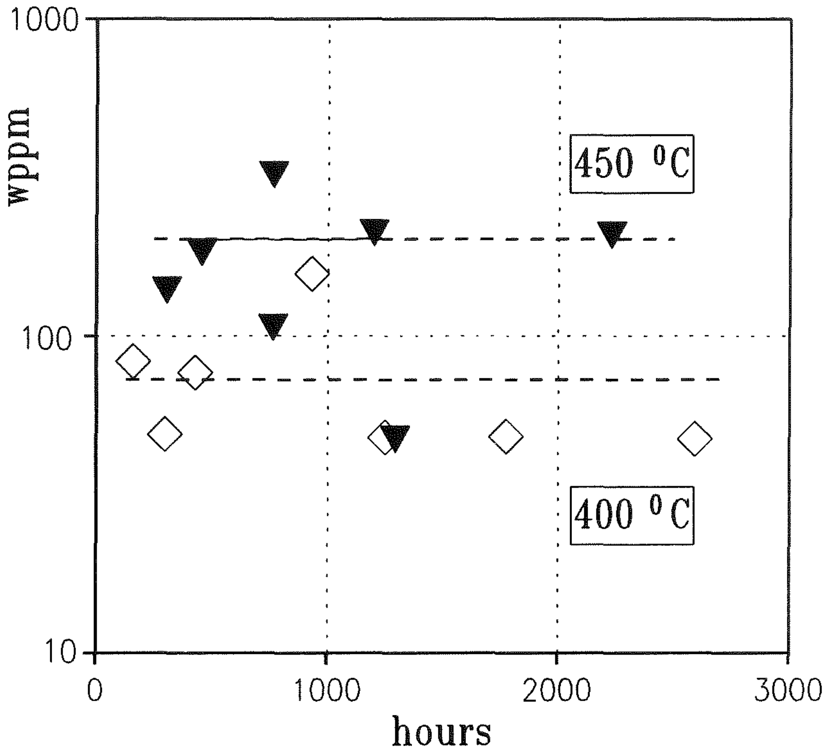


Fig. Al-5

Solubility of Al in Pb-17Li

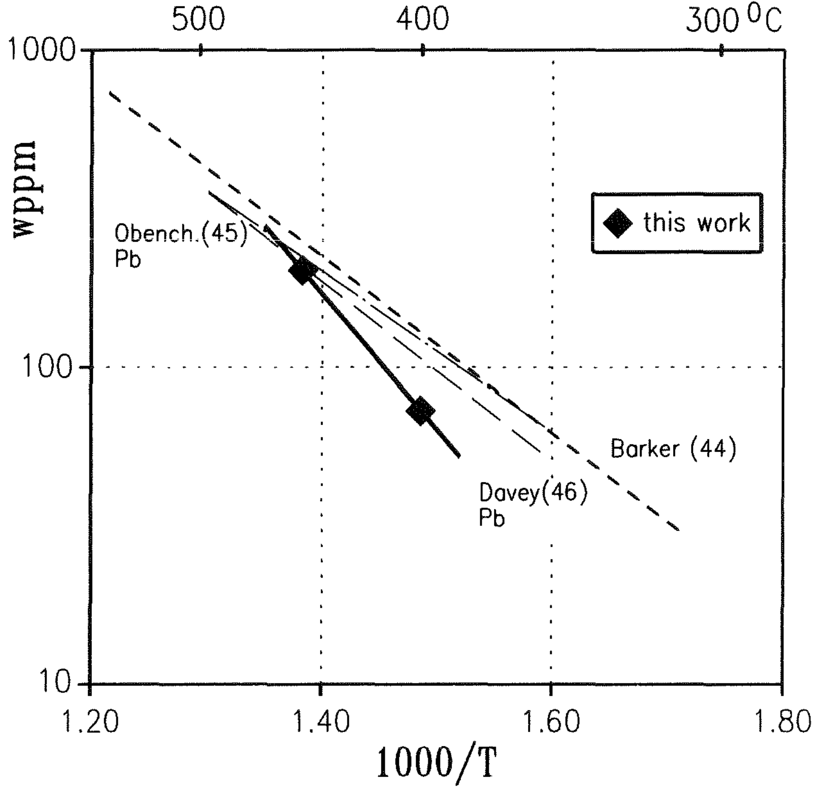


Fig. Al-6

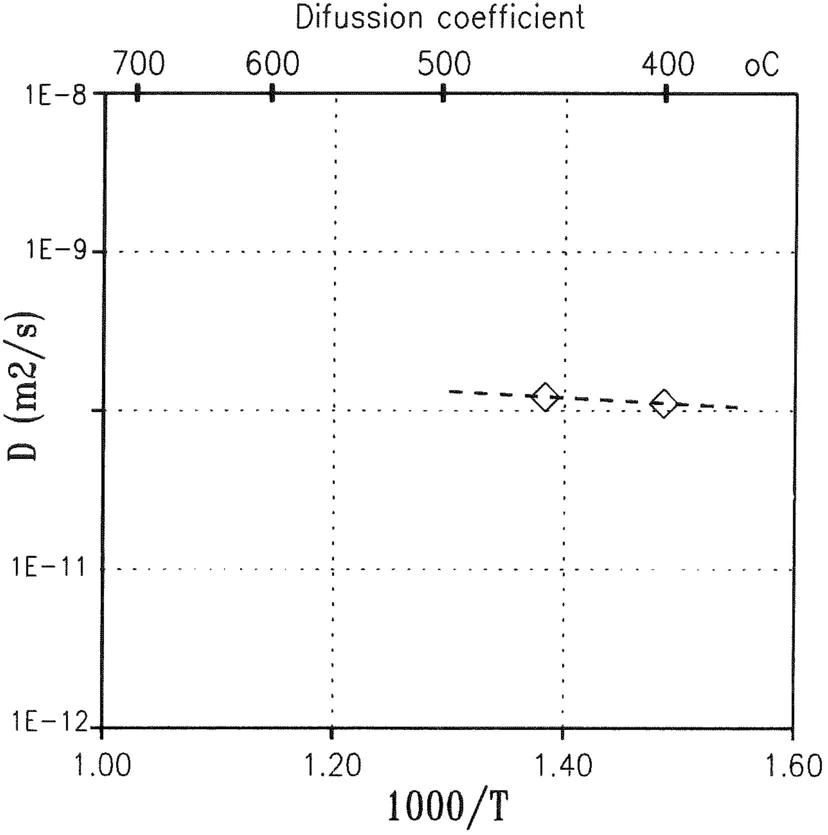
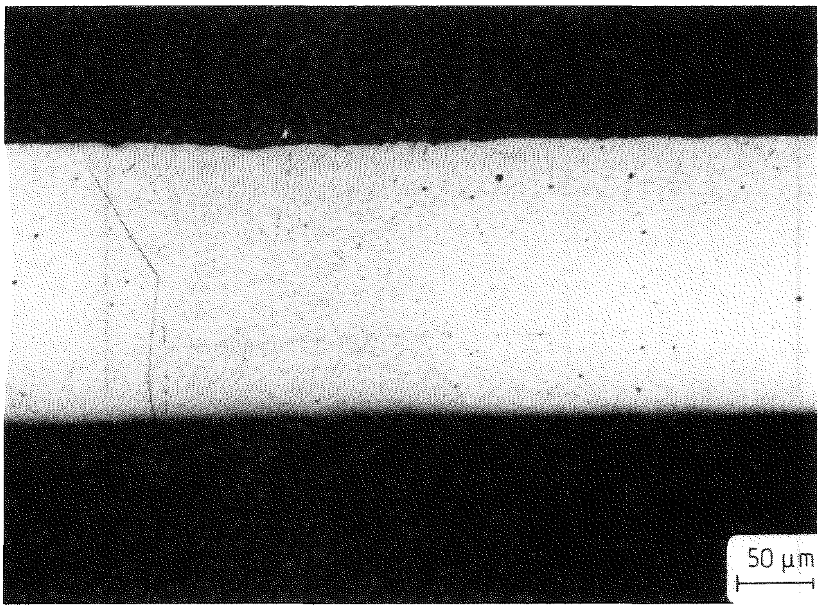

Difussion coefficient
700
600
500
400
oC
1E-8
1E-9
1E-11
1E-12
D (m2/s)
1.00
1.20
1.40
1.60
1000/T

Fig.Al-7

Al sample after 930 hours at 400 °C in Pb-17Li



Beryllium

Beryllium is proposed for nearly all blanket concepts as a neutron multiplier. No work has been published so far about the compatibility of Be with Pb-17Li, even if some work may be under way in different laboratories. No phase diagram was published for the Pb-Be system (79), more work was done for the system Li-Be (80). **In lead** Kelman (42) found no attack after 5 hours at 1000 °C. At the same temperature Brasunas (15) reports an 0.1 mm reaction zone after 40 hours. Therefore, Be should be very stable in the eutectic at lower temperatures.

1. Experiments

The table shows the performed experiments. Beryllium was obtained from Goodfellow with 99.8 % and from Ventron with 99.0 % quality. No difference in the behaviour of these materials was seen. Both materials were brittle. Cutting sample pieces had to be done under argon at 400-500 °C. Most of the samples were mechanically and chemically polished. All samples were vacuum degassed for 2-4 hours at a pressure below 10^{-5} mbar and at temperatures between 600 and 800 °C.

Beryllium metal which has been on air even for a short time, is always covered with an oxide layer. Some experiments were performed to investigate the influence of this oxide. The metal was preoxidized by heating in an atmosphere of 100 mbar oxygen for two hours at 750 °C , followed by 5 minutes at 1000 °C. The color of the oxidized Be was blue, corresponding to an oxide layer of 0.15 microns (47).

2. Results

No **wetting** was observed at 400 °C. Wetting was poor at 450 °C even after 3000 hours.

Dissolution

Fig.Be-1 shows that the dissolution was proportional to time. Data points for 400 and 450 °C were obtained only from Be, deposited on the crucible wall (mass transfer, below). The dissolution rate of preoxidized samples were smaller (**Fig.Be-2**). All straight lines have a positive offset : the dissolution during the first few hundred hours is faster.

Fig.Be-3 shows the Arrhenius-plot for steady state dissolution rates. The function is given by

$$\ln R = 6.89 - 9300/T$$

(R in $g/m^2 * d$). The heat of activation for this process is -77 kJ/Mol.

As for other elements **isothermal mass transfer** to the Mo-crucible was found. While Pb-17Li becomes saturated after longer time, the amount deposited on the crucible wall increases.

Solubility of Be in Pb-17Li

Fig.Be-4 shows the effect of saturation for 500 °C. Not so many data points were obtained for 600 °C. It is assumed, however that the eutectic was saturated after 1464 hours. Therefore two solubility values were obtained :

at 500 °C 7.4 ± 1.7 wppm
at 600 °C 30 ± 6 wppm.

This two data give the temperature dependence of the solubility:

$$\ln S\ (\text{wppm}) = 14.2 - 9446/T$$

The heat of dissolution is -78 kJ/Mol.
In **Fig.Be-5** solubility data from the literature for pure Li (46,48) and for eutectic Pb-Bi mixture (42) are included. Extrapolation of our function to 1000 °C would result in a value between solubilities in Li from Bychkov (48) and the found concentration in Pb-Bi given by Kelman (42). The values of Klemm for Li are 10 times higher. This can not be discussed in the scope of this report. On the other hand it is not clear if Kelman had equilibrium conditions.

From solubilities and steady state dissolution rates **diffusion coefficients** were calculated :

$$D\ (500\ ^{\circ}C) = 1.20 \cdot 10^{-11}\ (m^2/s)$$
$$D\ (600\ ^{\circ}C) = 1.17 \cdot 10^{-11}\ (m^2/s)$$

These values are in an expected range. The Arrhenius function from these two values is

$$\ln D = -25.4 + 171/T,$$

the heat of activation only 1.5 kJ/mol. **Fig.Be-6** shows the function.

Reaction zone

Metallographic examination showed that there was a strong reaction between the eutectic and the metal. Especially at 600 °C the metal was nearly destroyed after 1000 hours. But the attack is also visible at 500 °C after 3000 h **(Fig.Be-7 and Be-8)** . The extreme embrittlement of the samples is caused by this destruction. Brasunas (15) found an intergranular reaction zone of 0.1 mm after 40 h at 1000 °C in lead. Probably as for other metals Pb is dissolving in the solid Be. From chemical analysis, however, the concentration of Pb in Be was below 0.1 wt.%.

There is also a **chemical reaction zone** at the Be surface. A very mild electrolytic process for dissolving adhering Pb-17Li from the surface dissolved also some Be. From samples which have been for 1000 hours in the eutectic at 600 °C, this dissolved Be will correspond to 0.1 microns of the geometrical sample surface. After 3000 hours exposure time at 500 °C 0.15 microns, at 600 °C 0.25 microns were dissolved. For comparison : only 0.002 microns were dissolved from samples with less than 500 hours exposure time. The dissolved amount increases with longer exposure times. The increase of the actual sample surface with exposure time because of crack formation is not large enough to explain this reaction zone.

3. Summary

While dissolution rates and solubilities for Be in Pb-17Li are small, the metal is strongly attacked at higher temperatures. BeO will protect the surface only below 450 °C. However, despite of poor wetting, dissolution and reaction starts even at at 400 °C.

Table : List of experiments with **beryllium.**
Header line temperatures °C, other numbers hours of exposure time.

400	450	500	600	500ox.
.	.	.	254	360
.	.	.	.	360
.	768	864	.	.
984	1170	1032	1008	.
.	1536	.	1464	1515
.	.	.	.	1584
.	2160	2350	.	.
.	3000	3072	.	3072
.	.	3072	.	.
.	.	3280	.	.
.	.	3400	.	.
.	4536	5048	.	.
.	.	5376	.	.
.	.	5712	.	.

Fig.Be-1

Dissolution of Beryllium

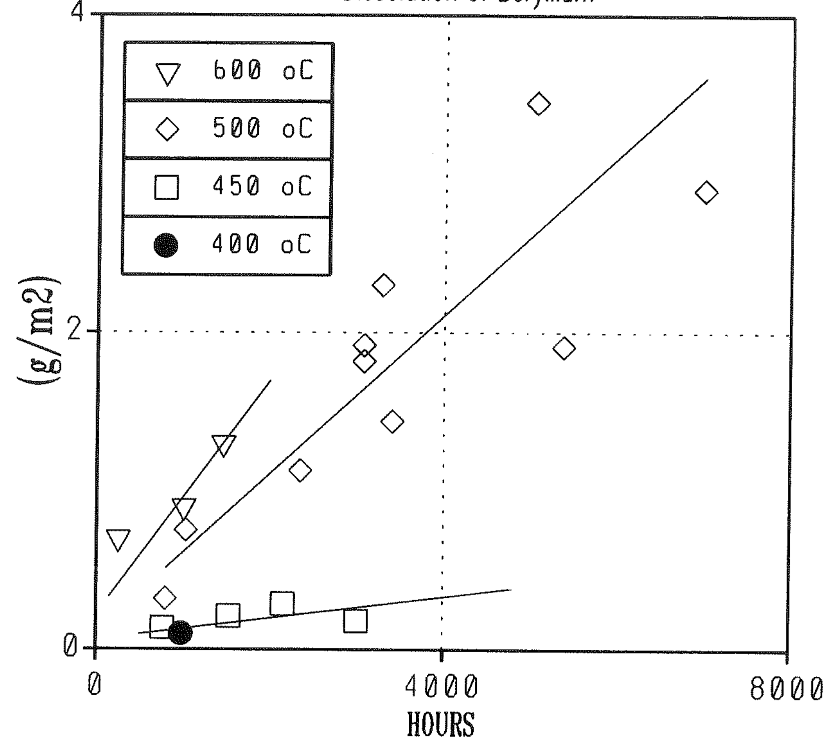


Fig.Be-2

Dissolution of Beryllium at 500 o C

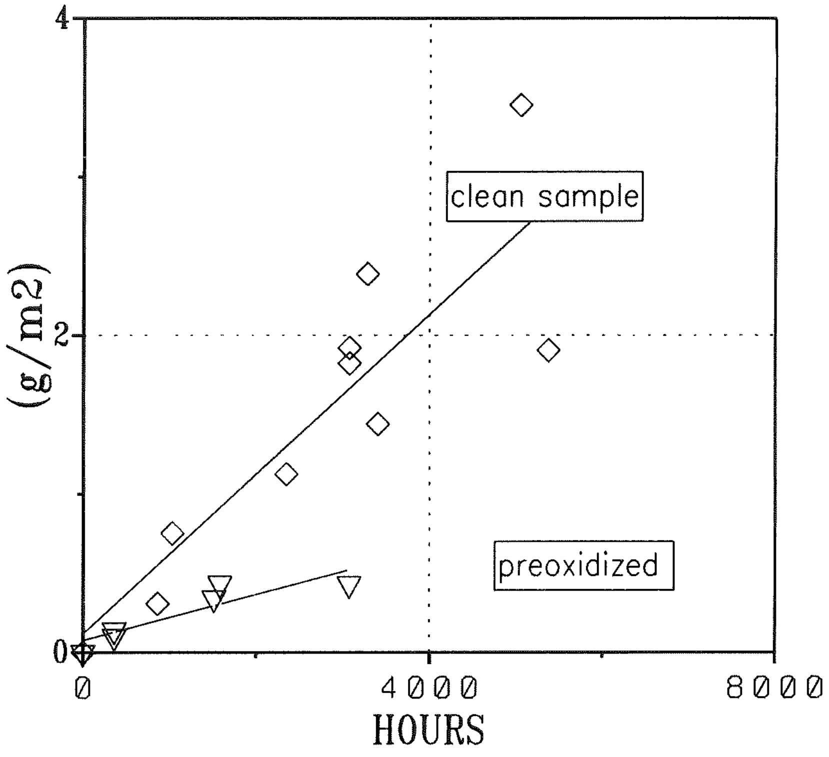


Fig.Be-3

Steady state dissolution rate of Beryllium

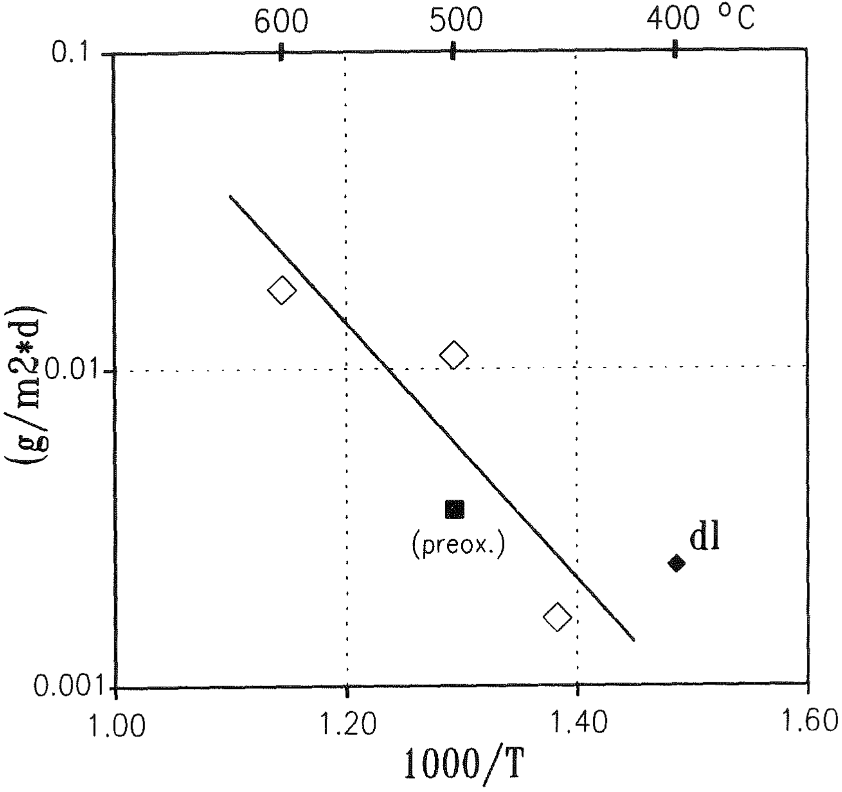


Fig. Be-4

Concentration of Be in Pb-17Li
(500 oC)

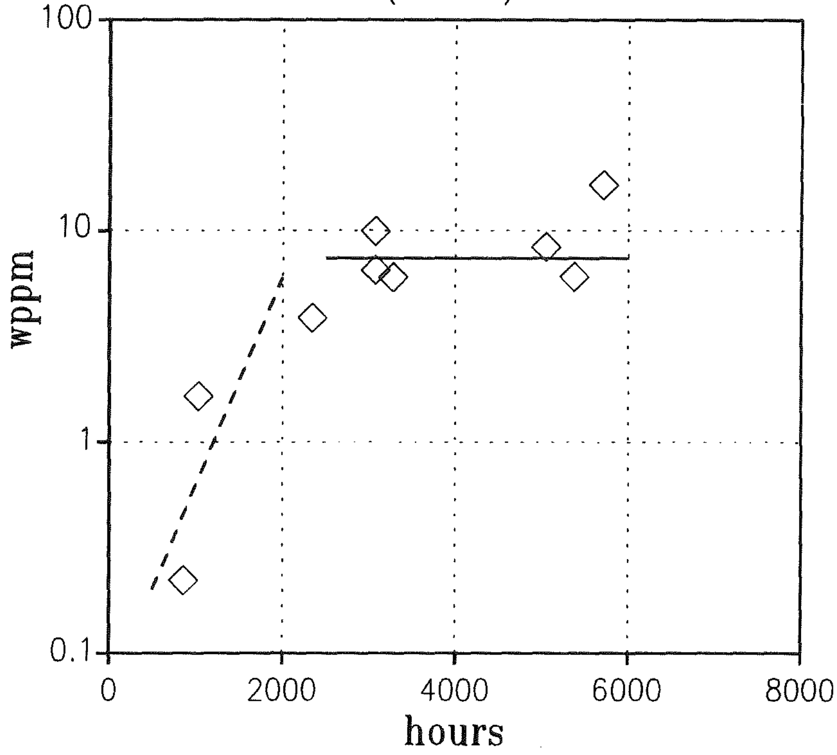


Fig. Be-5

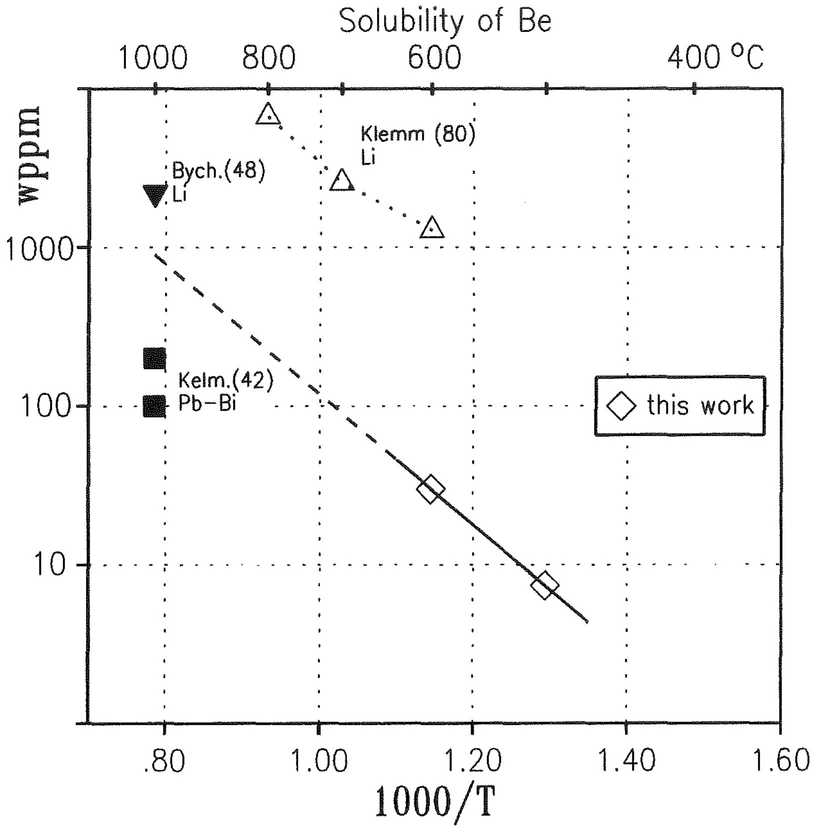


Fig. Be-6

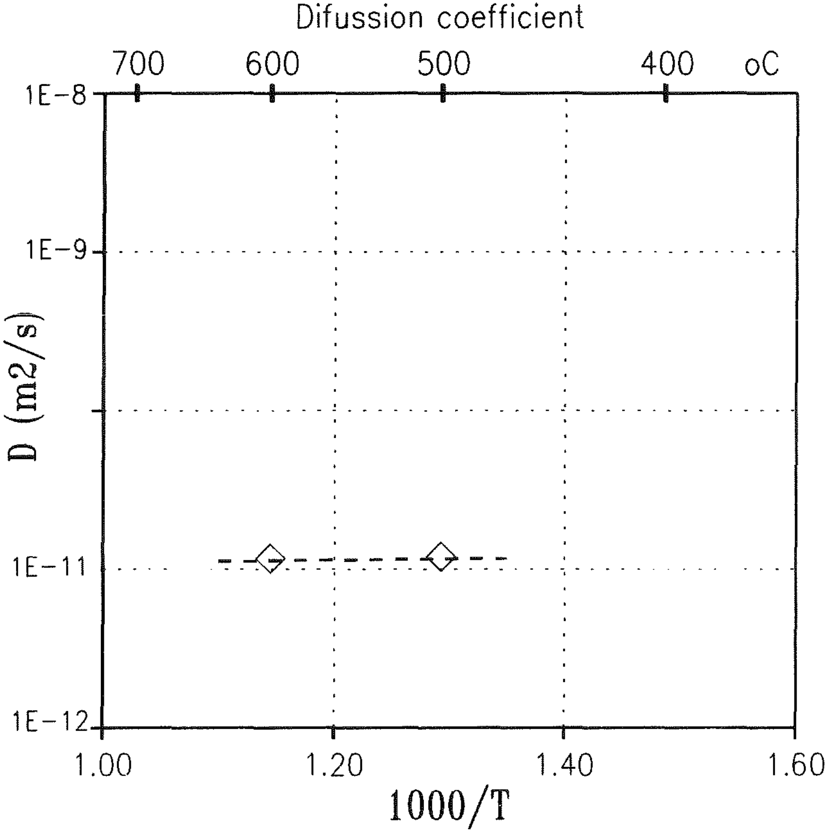
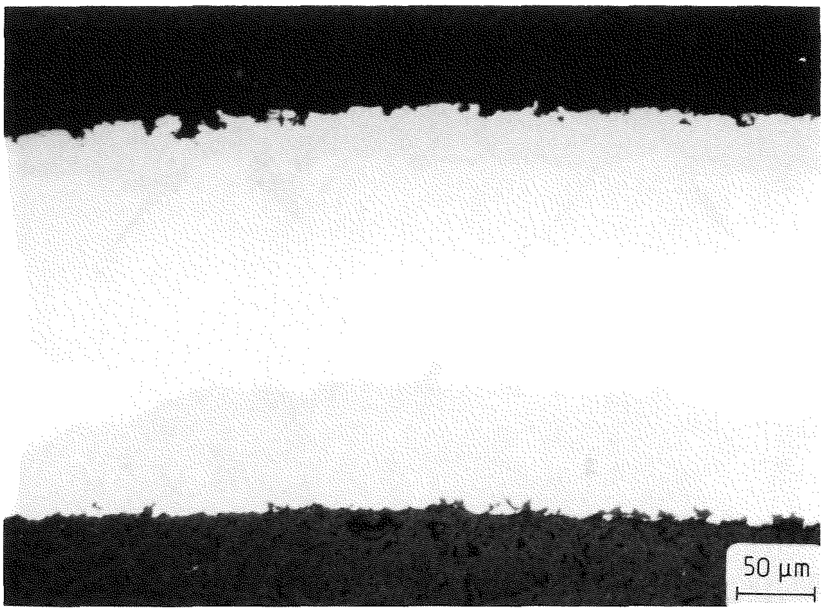


Fig.Be-7

Be metal after 3072 hours at 500 ^{0}C in Pb-17Li.
Intercrystalline corrosion.
(etching 25ml glycerol, 5ml HNO_3,
5ml HF)



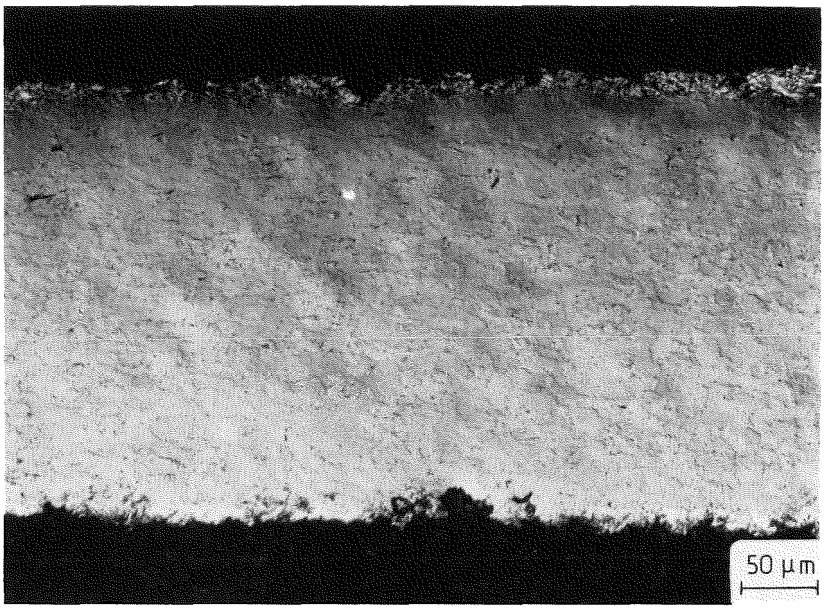
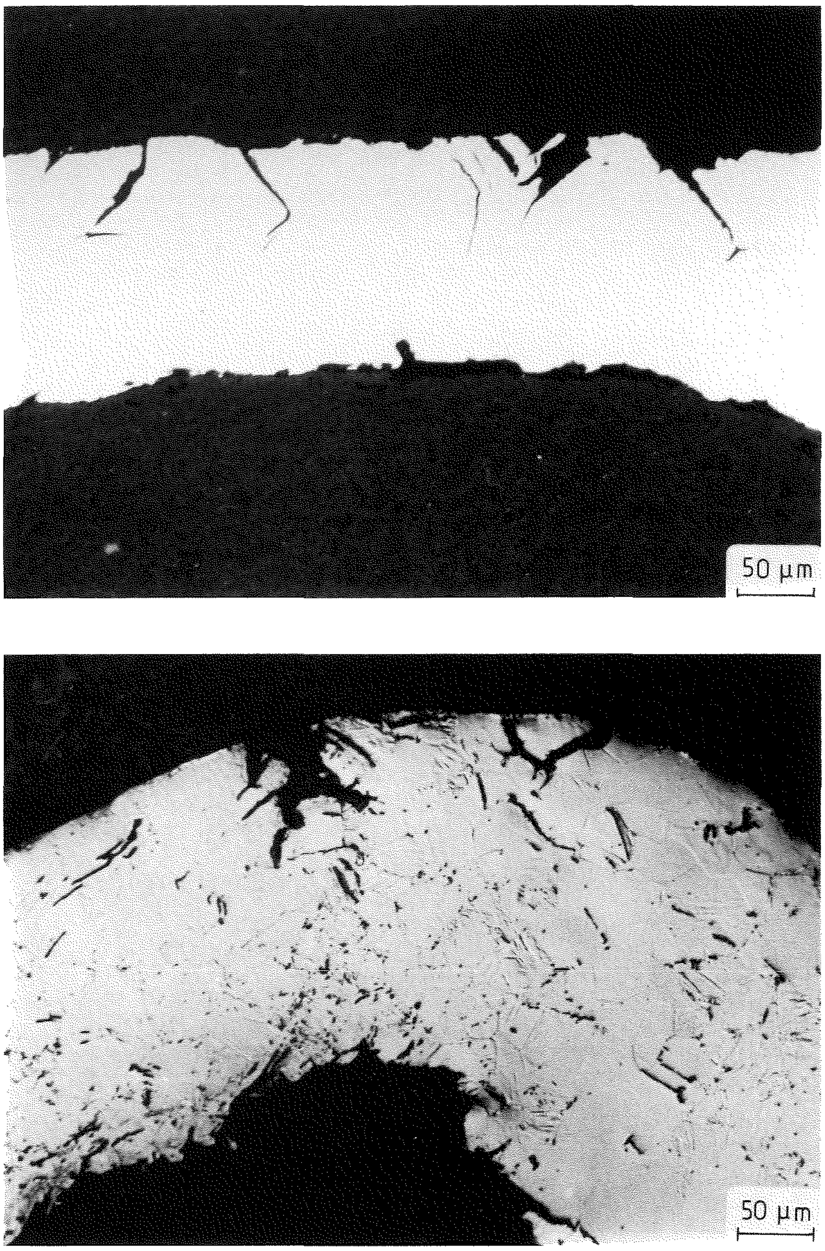


Fig.Be-8

Be metal after 1008 hours at 600 °C in Pb-17Li.
Intercrystalline corrosion.
(etching as in Fig.Be-7)



alpha-Iron

Only a few experiments are reported for pure iron in lead or Pb-17Li. But iron is the main component of steels and many corrosion experiments have been performed with steels. Barker (8) remarked that iron in ferritic steels should behave similar to pure iron. Not much is known about phase diagrams of Fe with Pb or Li. Mutual solubilities are low even at temperatures above the melting point of iron, no intermetallic compounds are reported (12,49).

1. Experiments

The table shows the performed experiments. Iron was obtained from Goodfellow, with 99.5 % quality. It contained 0.3 % Mn, 0.1 % Si, 0.08% C, 0.04 % P and 0.05 % S. The metal was cleaned and vacuum annealed for several hours at 600 °C.

2. Results

There were no remarks about wetting of iron in our laboratory notes. Because of high temperatures of the experiments we assume wetting in all experiments.

Dissolution

Fig.Fe-1 shows the results of all experiments. Because of mass transfer to the crucible wall, the dissolution does not stop after the initial period. Steady state dissolution rates, **Fig.Fe-2** , are given by

$$\ln R = 3.38 - 7206/T$$

(R in g/m^2*d). The heat of activation is -60 kJ/mol.
Of course, dissolution rates from flowing Pb-17Li as obtained e.g. by Borgstedt (50) or others for ferritic steels, are up to three orders of magnitude higher. But such dissolution rates should not be compared with each other. The dissolution mechanism is different, as can be seen from the high activation energy of -200 kJ/mol found by Borgstedt.

Solubility

Two solubility values were obtained in this work (**Fig.Fe-3**). From these the solubility is given by :

$$\ln S(\text{wppm}) = 4.94 - 4292/T$$

The heat of dissolution is -36 kJ/mol.

A solubility function from Coen (51) gives obviously too high values. Also a value of Barker (8) is much higher than solubilities found in this paper. Barker's value was derived from experiments with steel 316. We found also in experiments with steels higher 'solubility' values. They are inlcuded in Fig.Fe-3 and discussed below together with compatibility of steels.

Stevenson (52) found for the solubility in lead at 600 ^{0}C a value identical to ours, but his function is steeper. Ali Khan's functions (22,53) for lead are not clearly understandable. Data taken from fig.13 of ref.(53) are 10 times higher than from our function. The function from Weeks (54) is nearly identical to ours.

Two **diffusion coefficients** were calculated from values for steady state dissolution rates and solubilities :

$$D\ (500\ ^0C) = 7.48*10^{-11}\ (m^2/s)$$
$$D\ (600\ ^0C) = 1.14*10^{-10}\ (m^2/s)$$

The Arrhenius function is given by

$$\ln D(m^2/s) = -19.64 - 2844/T$$

the activation energy for the diffusion process is -24 kJ/mol. **Fig.Fe-4** shows the function.

The values are in an expected range. The extremely low value of Simon (27) for Fe in the eutectic with $6.0*10^{-14}$ m^2/s (500 ^{0}C) cannot be explained. The same author found for chromium a value of $4.0*11^{-11}$ m^2/s, in the same range as the iron value in our work. Robertson (19) measured diffusion coefficients of iron in lead. His values are 10 times higher than found in this work.

Mass transfer, reaction zone

There are a number of intermetallic compounds in the system Fe-Mo (49). No compounds could be identified by chemical analysis or metallographic examination of the crucible wall. Mass transfer was observed before in lead systems (15,36), also without identification of compounds. No reaction products could be seen at the iron side. But a thin chemical reaction zone as described for other elements points to a modified surface. An even dissolution at the surface at 500 ^{0}C can be seen in **Fig.Fe-5 . At 600 ^{0}C, Fig.Fe-6, a grain boundary attack starts.** Ali Khan (22,53) reports such a reaction between iron and lead, but for much higher temperatures.

3. Summary

Alpha-iron is relatively stable in Pb-17Li up to 600 ^{0}C. At this temperature grain boundaries are attacked. The solubility of alpha-iron in Pb-17Li was determined at 500 and 600 ^{0}C. The values are much lower than data from Barker or Coen, but in the range of values for lead . Also, from steady state dissolution rates, diffusion coefficients were calculated. These values are 1000 times higher than a value of Simon.

List of experiments with **iron.**
Header line temperatures °C, other numbers hours exposure time.

500	600
380	3600
960	.
1152	1080
	1440
.	1560
1776	1675
1800	.
2110	2180
.	2684
.	2690

Fig. Fe-1

Dissolution of iron in Pb-17Li

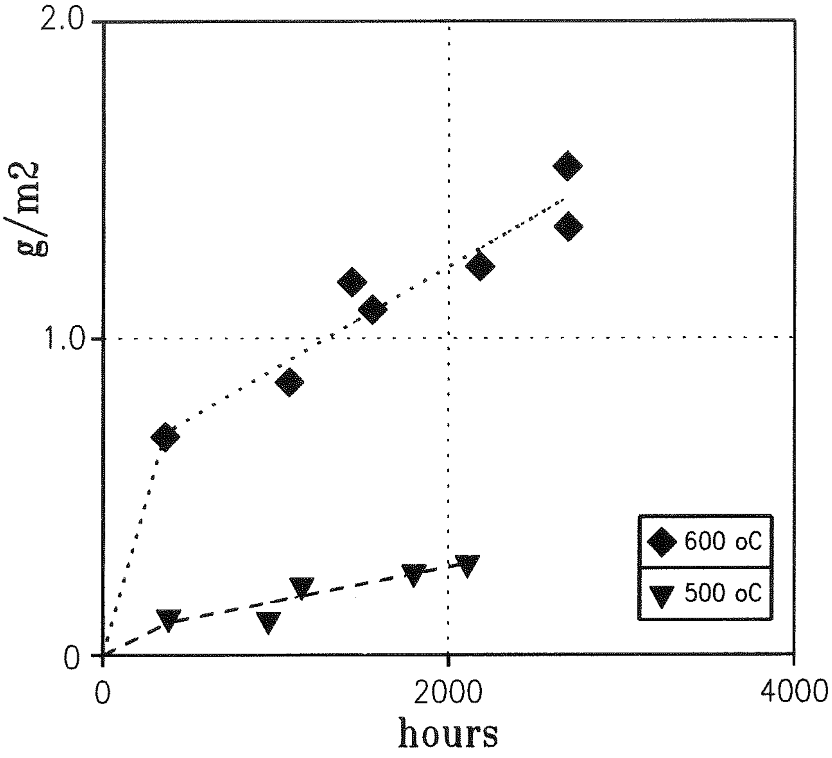


Fig. Fe-2

Steady state dissolution rate of iron

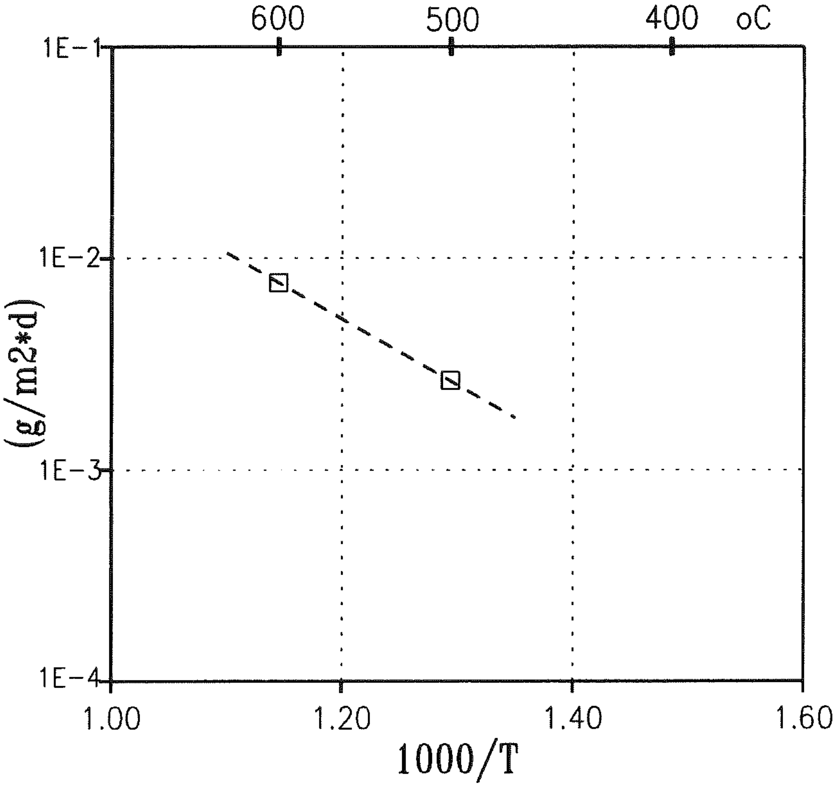


Fig. Fe-3

Solubility of iron in Pb-17Li

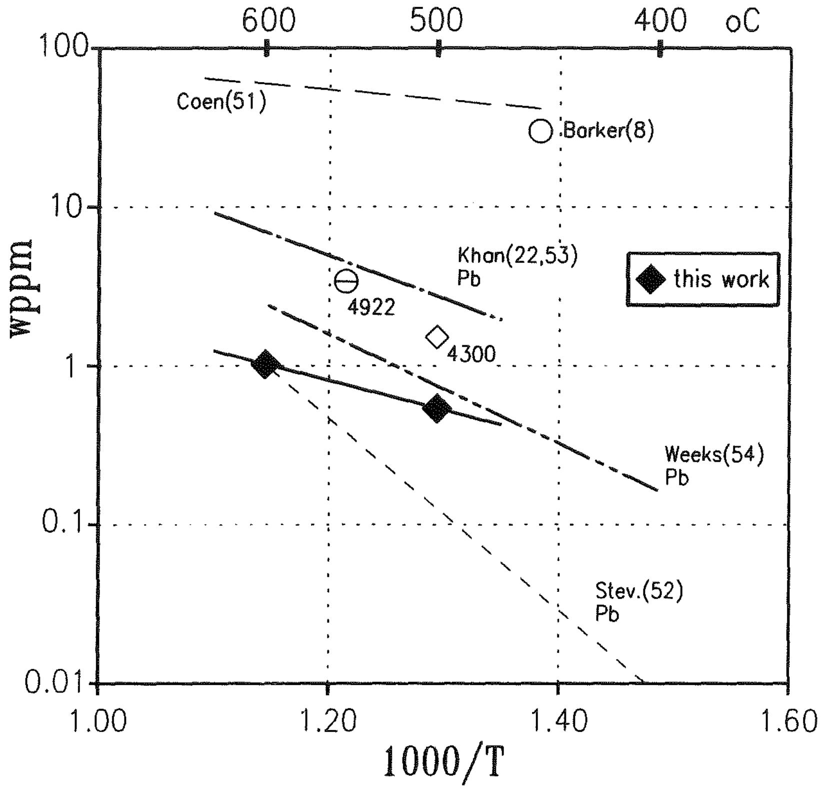


Fig.Fe-4

Diffusion coefficients of iron in Pb-17Li

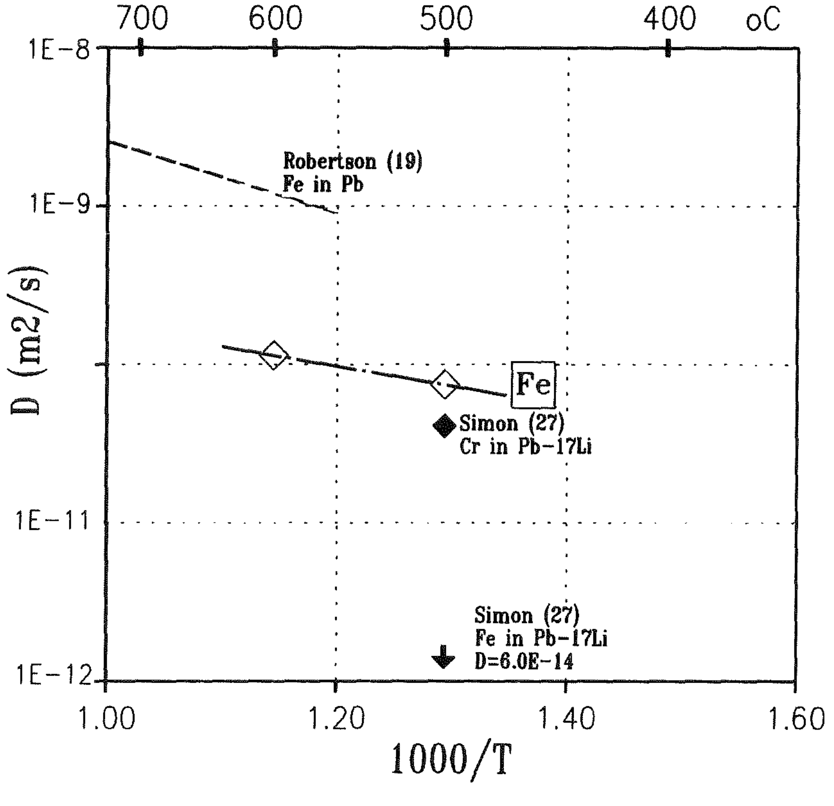
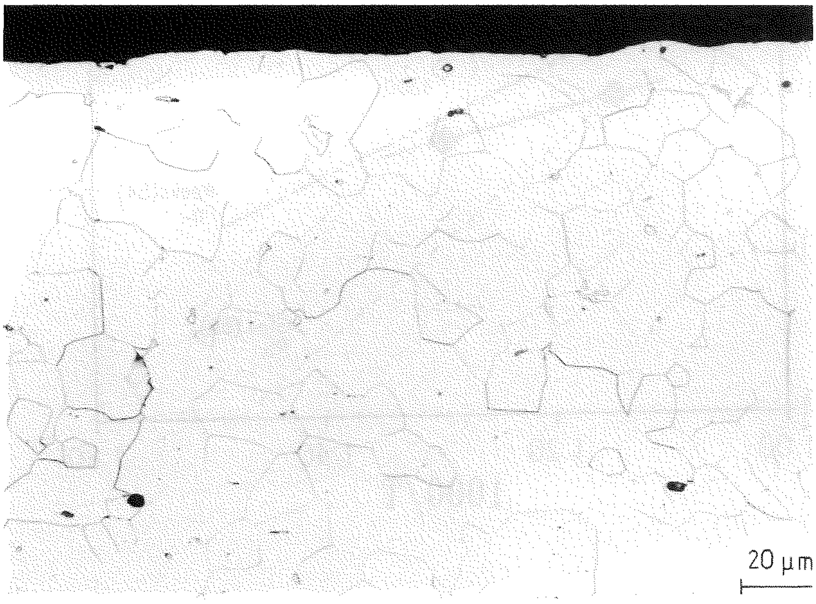


Fig.Fe-5

Fe metal after 1776 hours at 500 °C in Pb-17Li.
2 positions.
(etching 2% HNO_3 + ethanol)



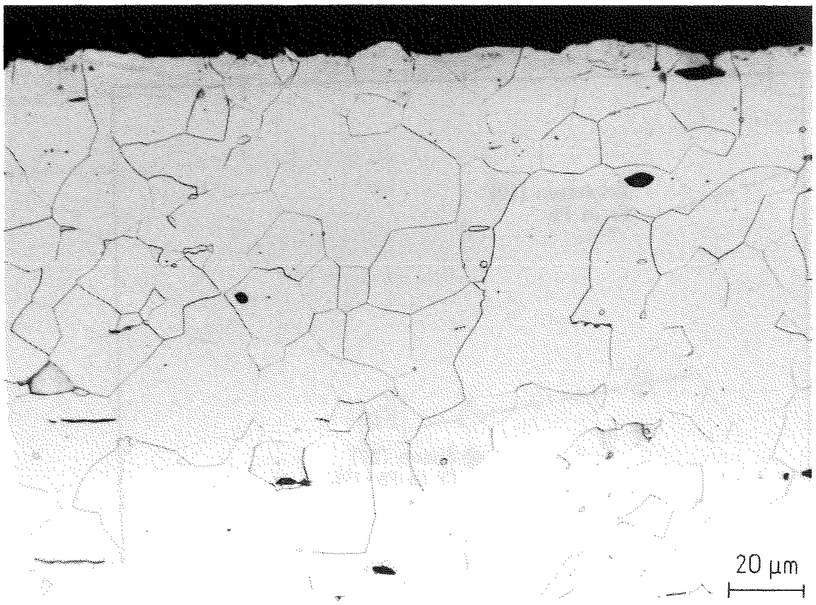
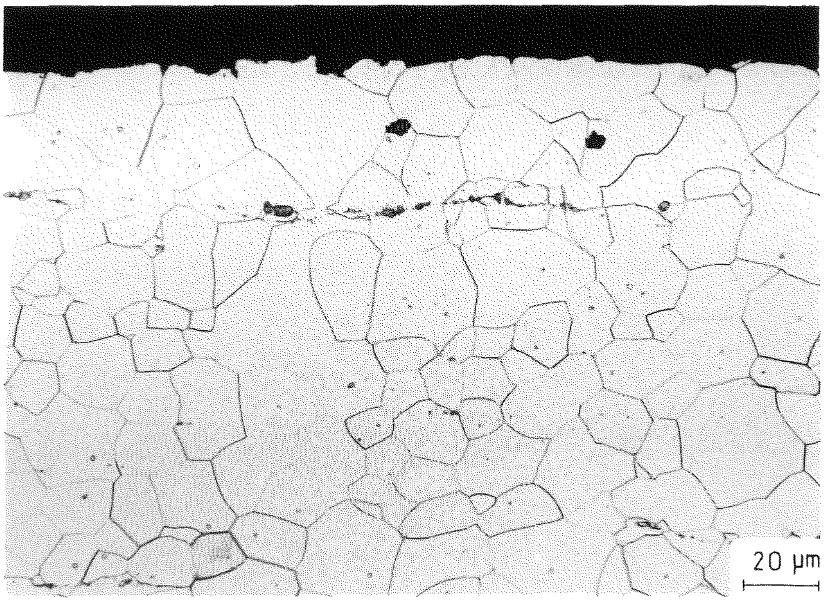
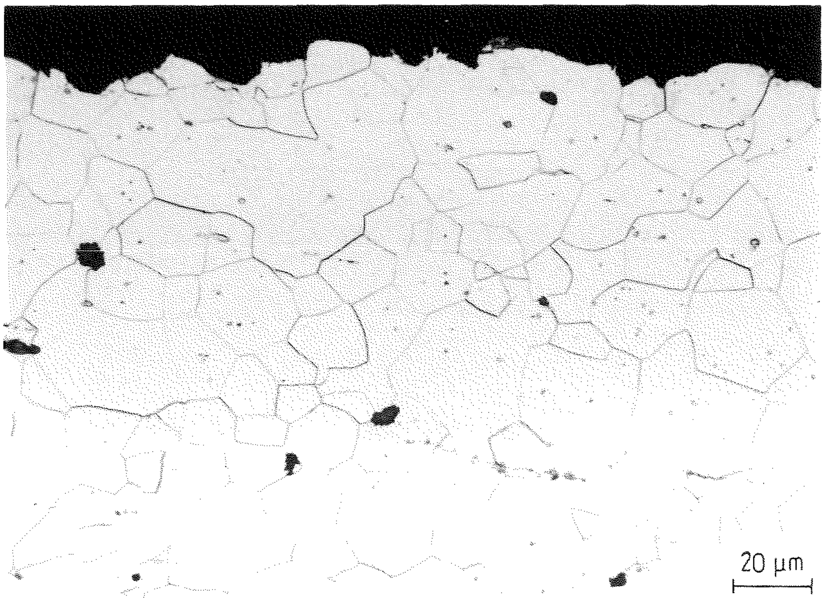


Fig.Fe-6

Fe metal after 1560 hours at 600 ^{0}C in Pb-17Li.
2 positions.
(etching as before)





Molybdenum

Because of its outstanding high temperature properties and its stability in molten metals, Mo may be considered as a structural material for liquid metal blankets. A compilation of binary Mo-systems is given by Brewer (25). Molybdenum forms intermetallic compounds with many elements and mutual inter-diffusion in the solid metals is reported . The isothermal mass transfer as observed with many metals in our experiments may be connected to this effect.

1. Experiments

All molybdenum, samples as well as crucibles, were chemically polished and vacuum annealed at 700 °C for 2-4 hours to a final pressure of 10^{-5} mbar. Using Goodfellow 99.9+% quality molybdenum in armco-iron crucibles, 11 experiments were performed. In addition, nearly all other tests were performed with Mo-crucibles. These crucibles were obtained from Plansee company, the purity was 99.95+ % . Therefore, analysis for Mo was performed in many experiments.

2. Results

Wetting was always good in experiments with temperatures of 500 °C and higher. Poor wetting was seen below 500 hours at 400 °C, no wetting in a 300 °C/66 hours experiment.

Dissolution and solubility

The analytical method was not sensitive enough to detect the solubility of Mo in Pb-17Li in experiments with iron crucibles. Also, Mo may have been covered by iron because of mass transfer (refer to chapter iron). Only upper limits can be given for dissolution rates : $<2*10^{-3}$ g/m^2*d at 600 °C and $<4*10^{-3}$ g/m^2*d at 645 °C.

With an improved technique, developed especially for Nb and Ta, values were obtained. In four experiments crucibles were heated for 5280 hours to 600 °C. 0.02 $\pm$0.005 mg Mo were dissolved. No Mo was found on the surface of Nb and Ta samples, all Mo was dissolved. Saturation can be assumed after such a long exposure time. The solubility of Mo in Pb-17Li at 600 °C is

$$0.3 \pm 0.1 \text{ wppm.}$$

Fig.Mo-1 shows solubilities of Mo in Pb-17Li and lead. The function of Coen (51) for the solubility in the eutectic was a proposal but never published again. The values are too high. For lead Shepard (55) gives 3 wppm for 816 °C, Brasunas (15) 10 wppm at 1000 °C. It can be seen in the figure that these two values and our 0.3 wppm for 600 °C in Pb-17Li fit very well an Arrhenius-slope, given by

$$\ln S \text{ (wppm)} = 10.0 - 9784/T$$

The heat of dissolution is -81 kJ/mol.
A boundary value from Alden (56) for 1200 °C fits in this function, while a value from Asher (36) for 700 °C is 10 times lower than the function. A function compiled by Brewer (25) is orders of magnitude lower and not considered to be correct.

(The solubility of Mo in Li is reported by Leavenworth (57). A wppm-function would fit well in Fig.Mo-1. Because of the large difference in the molecular weights Li-eutectic/Pb, an appm-function gives much lower values.)

Reaction zone

It is not clear from the results if there is a chemical reaction zone on Mo from reactions with the eutectic. Even if during cleaning processes more Mo was dissolved from crucible walls than from fresh Mo, results seem not to depend on temperature or exposure time. Chemical reaction zones were found e.g. below deposited Ti or Zr. In this case, however, reactions may have occured with the deposited metals.

There was never any embrittlement seen on Mo samples or crucibles. But from metallographic pictures (**Fig.Mo-2 and 3**), an attack of the surface, as well as intercrystalline penetration, is evident. The severity of the effect was a function of time and temperature. Such attack was observed for higher temperatures in lead before. Only Grassi saw no attack after 500 h at 1093 °C in lead. This was probably a problem of preparation when removing lead. He found modified mechanical properties, pointing to a reaction (24).

3. Summary

As expected Molybdenum is very stable in the eutectic. Its solubility at 600 °C could be measured, it is only 0.3 wppm. A good Arrhenius function was found together with data for lead. Inter-crystalline penetration and a modified surface structure was seen after exposure at higher temperature for a longer time.

Table: List of experiments with **molybdenum.**
in iron crucibles.
Header line temperatures °C, other numbers hours
of exposure time.

550	600	645
.	137	.
.	354	.
610	617	.
610	.	.
1308	1100	.
.	.	1880
.	.	1880
4850	.	.
4850	.	.

With only a few exceptions, tests for other metals were performed in Mo crucibles. These tests were also experiments for molybdenum.

Fig. Mo-1

Solubility of Mo in Pb−17Li and Pb

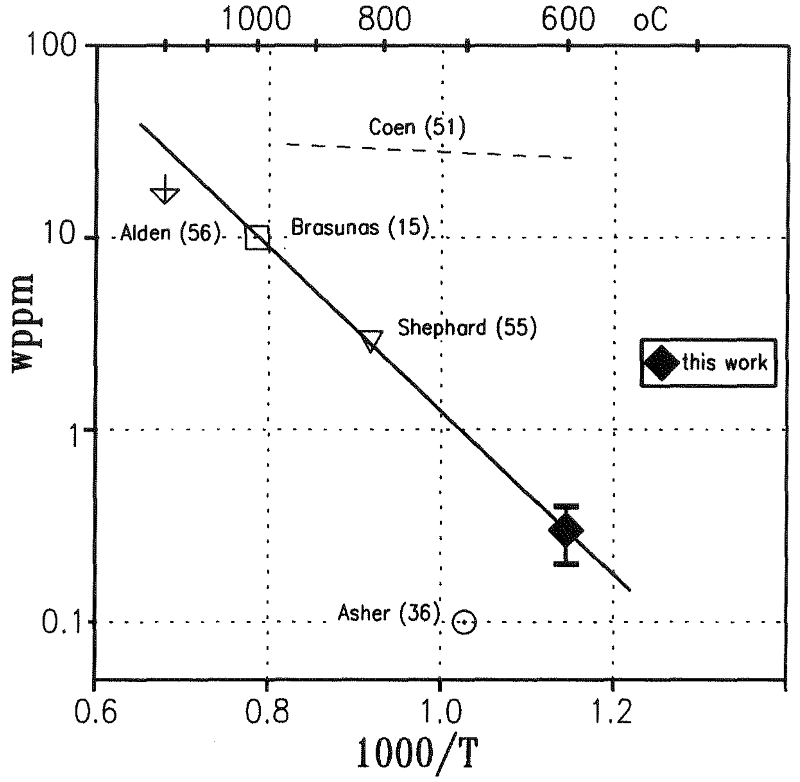


Fig.Mo-2

Mo metal after 5280 hours at 600 ^{0}C in Pb-17Li.
2 positions.

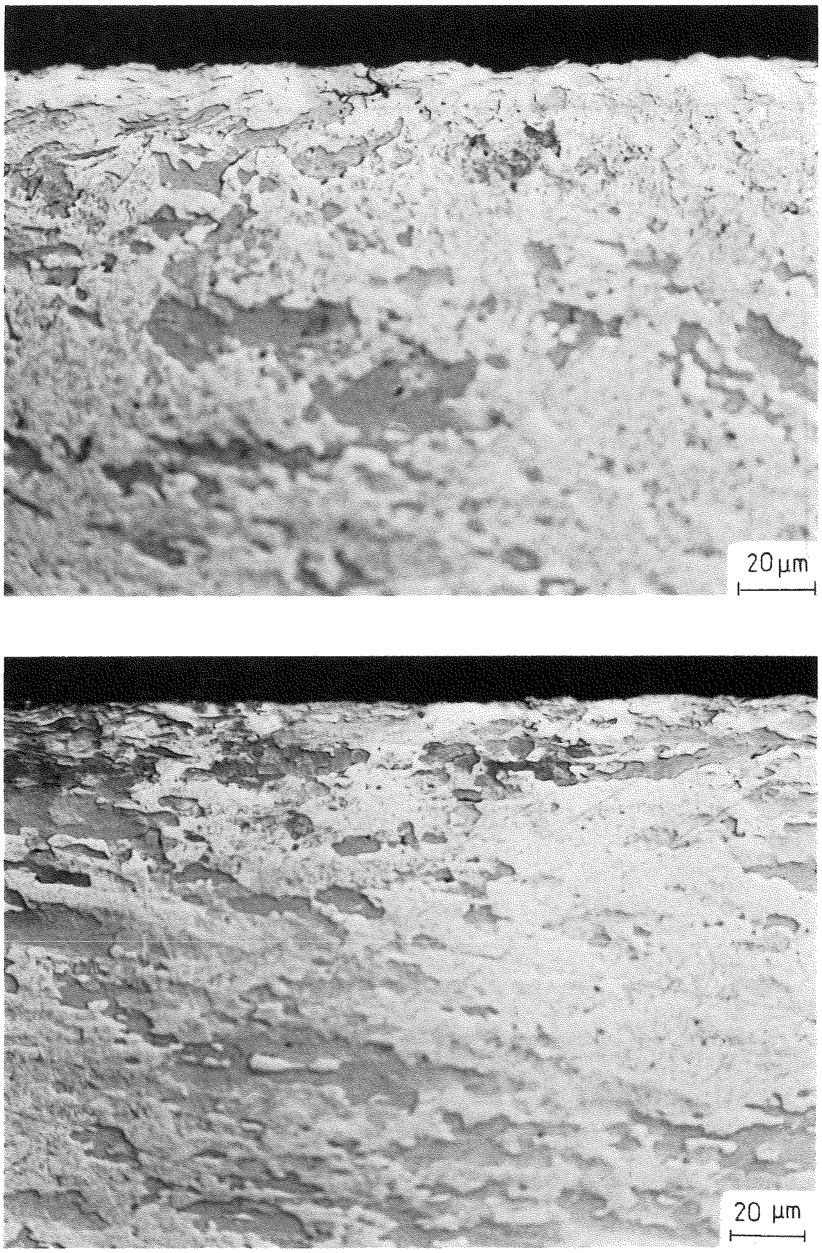
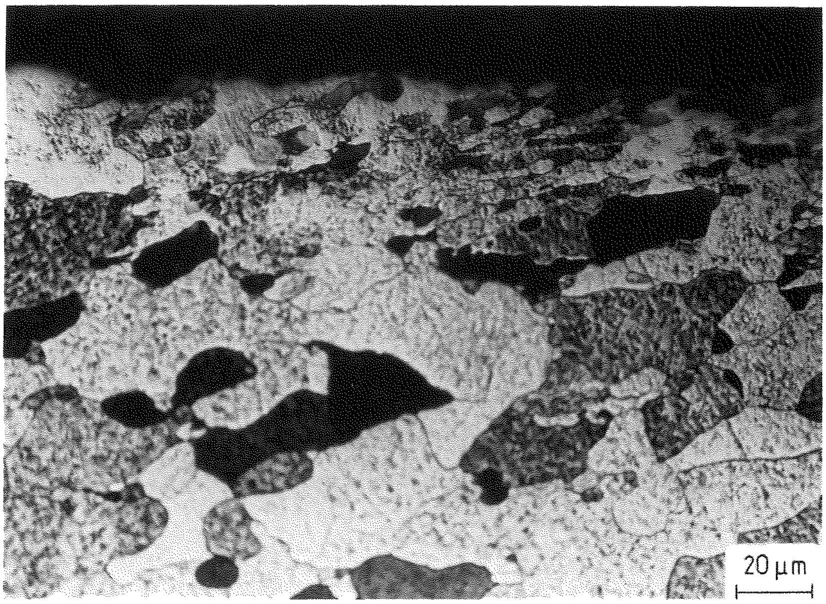
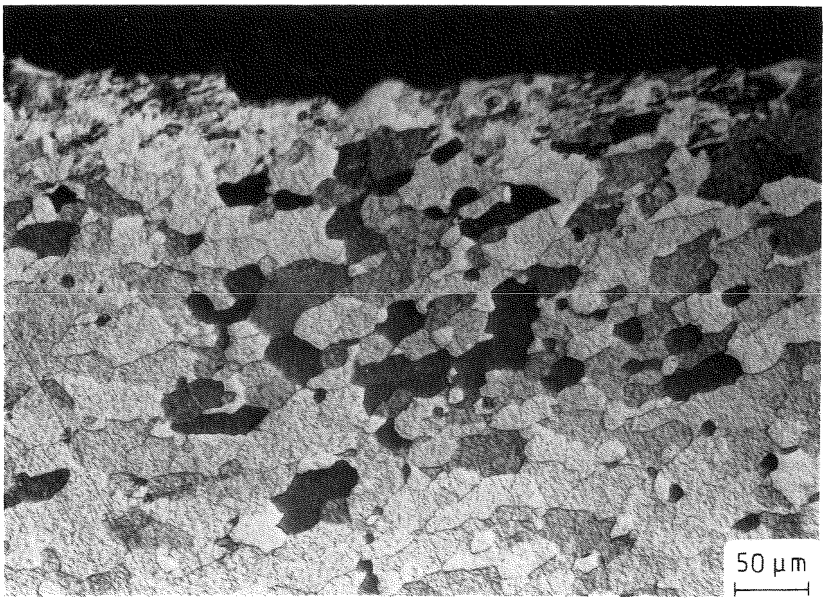


Fig.Mo-3

Mo metal after 1880 hours at 645 °C in Pb-17Li.
2 positions.





Niobium and tantalum

Metals like niobium or tantalum will be used only in special cases for fusion reactor blankets. Only a few tests were performed when looking for materials which could be used in experimental facilities. No phase diagrams were reported for Nb and Ta with Li or Pb.

1. Experiments

The tables show the performed experiments. Niobium was obtained from Goodfellow with 99.9+ % , tantalum with 99.8+ % purity from Plansee company. The metals were cleaned and vacuum degassed at 800°C for several hours. The behaviour of Nb and Ta is very sensitive against oxygen dissolved in the metals. Klueh (58) describes the penetration of lithium along grain bounderies if the oxygen concentration is as high as 1000 ppm. Rumbaut (68) mentioned preferential leaching of Nb from Nb-Mo alloys in lithium, this may have been because of nitrogen in lithium.

We assume, however, no such effect in our experiments. The oxygen content in both metals was low, it was further decreased by the process of vacuum degassing at 800°C. The solubility of oxygen and nitrogen in the eutectic is very low, no transport is expected.

2. Results

Good wetting was observed in all 500 and 600°C experiments. Both elements are extremely stable in the eutectic. In most tests neither dissolution rates nor solubilities were obtained. The only values were from the longest experiment : 5280 hours at 600°C. As averages from two crucibles only $6.2*10^{-4}$ mg/cm^2 Nb and $2.2*10^{-3}$ mg/cm^2 Ta were dissolved. Assuming these are values for saturation, the solubilities at 600°C are:

Nb	0.053 wppm
Ta	0.19 wppm

The values are shown in **Fig.NbTa-1.** But even to get these values, the extractor technique for bulk Pb-17Li dissolution had to be modified : Pb was precipitated as $Pb(NO_3)_2$ and removed from the solutions. All values were near detection limits. There were a few older experiments with Nb and Ta in lead. The results are compiled by Ali Khan (22). All tests were done at temperatures around 1000 °C. Even if the results are not consistent, corrosion of both metals at this temperature was evident. Ali Khans own measurements gave 0.001 ppm Ta in lead at 1000 °C, a value much lower than our value at 600 °C.

No mass transfer to the crucible wall was seen. No chemical reaction zone was detected (less than 0.01 microns). Metallographic examinations showed no attack or reaction zone. Only at a few spots at a Nb sample, week intercrystalline reaction was seen. **Fig.Nb-1, Fig. Ta-1** .

3. Summary

Both Nb and Ta are stable in the eutectic. Solubilities at 600 °C could be determined, they are very low. No reaction zones were identified.

Table: List of experiments with **niobium**.
Header line temperatures °C, other numbers hours of exposure time.

400	460	500	600
.	137	.	192
.	.	644	.
.	.	644	.
.	.	.	826
1138	.	.	.
1138	.	.	.
.	.	.	5280
.	.	.	5280
.	.	.	5280

Table: List of experiments with **tantalum**.
Header line temperatures °C, other numbers hours of exposure time.

460	500	600
137	.	192
.	644	.
.	644	.
.	.	826
.	.	5280
.	.	5280
.	.	5280

Fig. Nb,Ta-1

Solubility of Nb and Ta in Pb-17Li

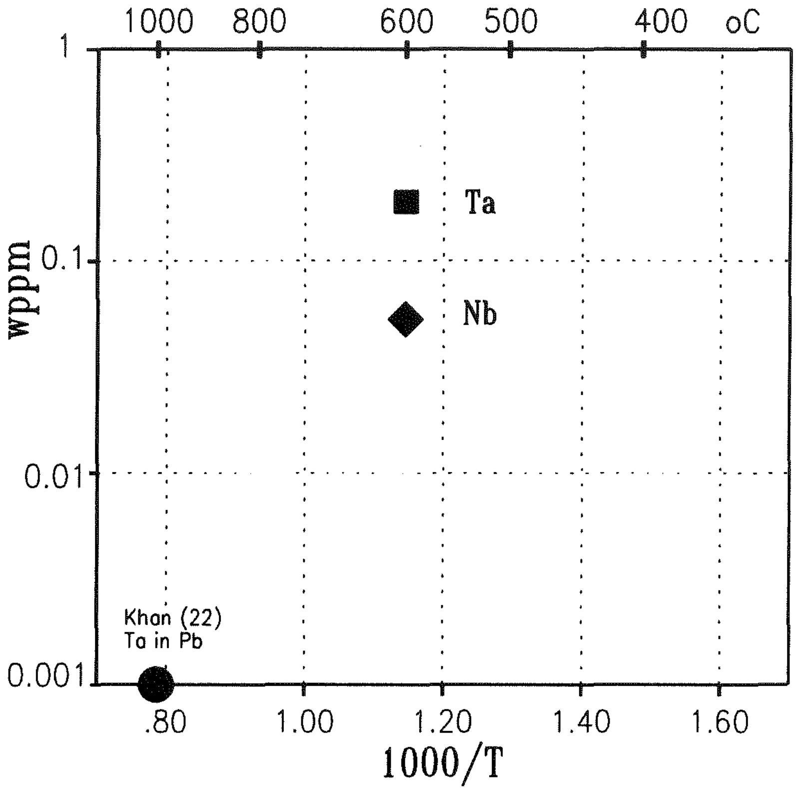


Fig.Nb-1

Nb metal after 5280 hours at 600 °C in Pb-17Li.
2 positions.
(etching glycerol/HF/HNO_3 1:1:1)

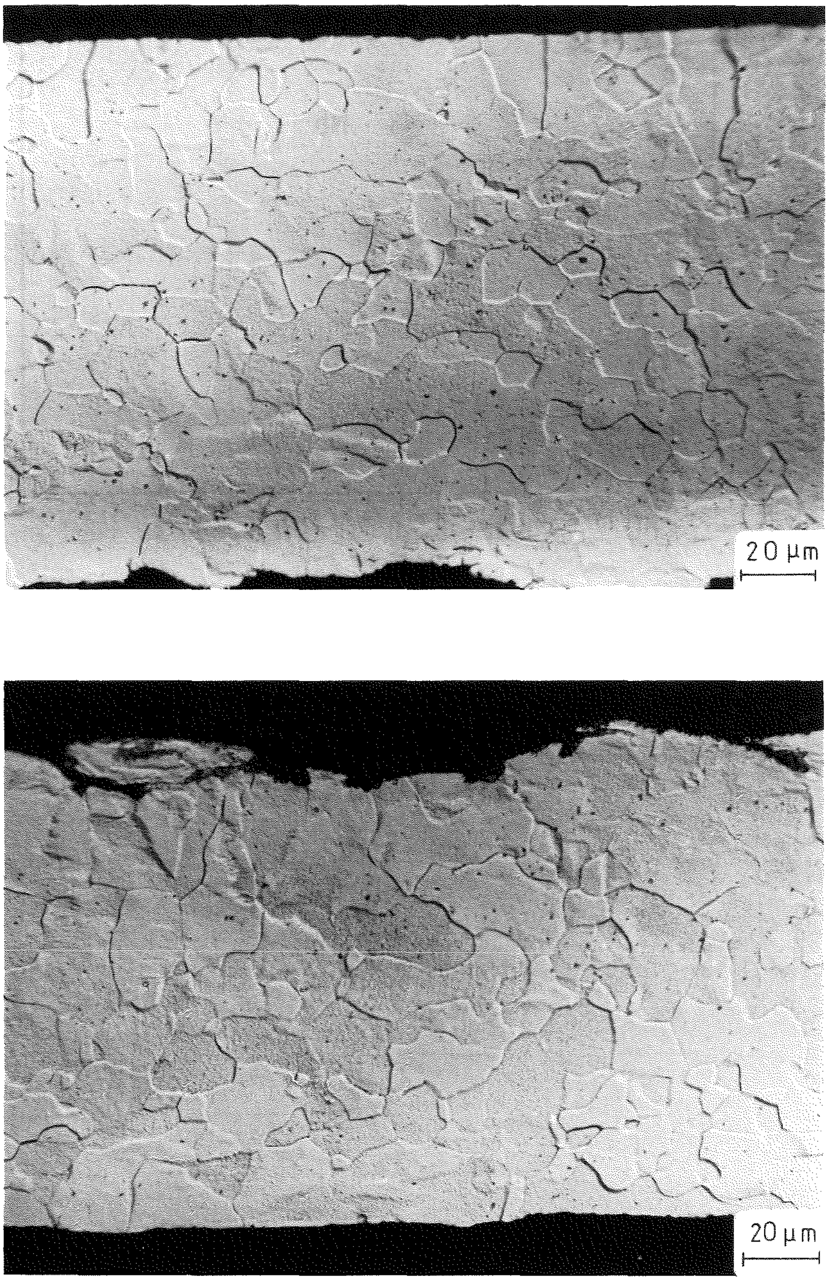
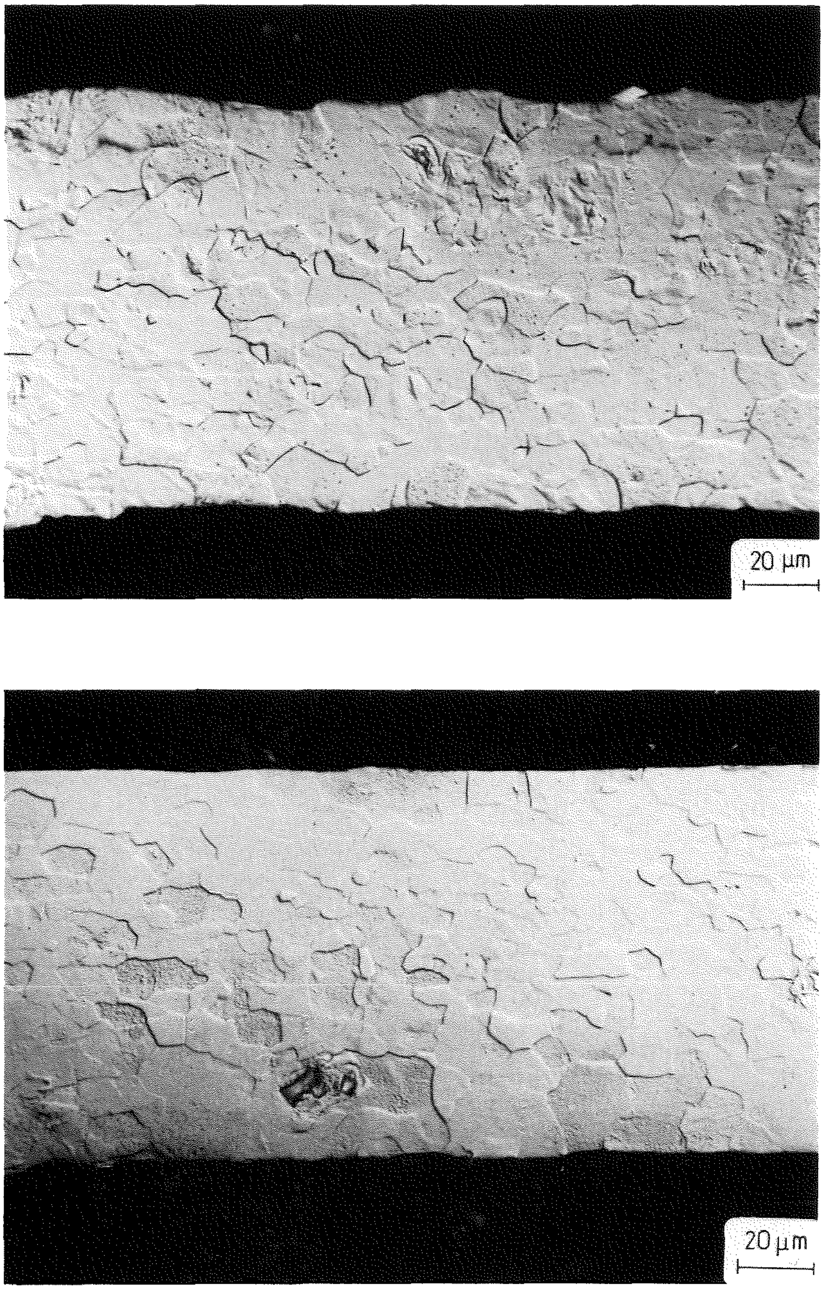


Fig.Ta-1

Nb metal after 5280 hours at 600 °C in Pb-17Li.
2 positions.
(etching as Nb)



Rhenium

Actually there were no experiments with pure Re metal. The alloys Mo5Re and Mo41Re were treated in the eutectic at 450 and 500 °C up to 2750 hours. Because of Mo in this alloys, most of the tests were done in crucibles from alumina. The table shows the performed experiments.

As expected, the alloys were very stable. Neither dissolution rates nor solubility values were obtained. The **solubility of Re at 500 °C is below 1 wppm.** In agreement with results for Mo as given above, also the solubility of Mo is below 1 wppm. After Guminski (10) the solubility of Re in lead should be smaller than this of Mo.

No attack can be seen at the surface **Fig.Re-1** . This was expected. Allen (59) found an alloy Mo-33Re at 1600 °C more stable in liquid tin than pure Mo.[8]

3. Summary

Rhenium is very stable in the eutectic mixture. Its solubility at 500 °C is below 1 wppm. Alloys with Mo are probably even more stable than pure Mo. No attack of the surface was observed.

Table: List of experiments with **Mo-Re alloys.**
Header line temperatures °C, other numbers hours of exposure time.

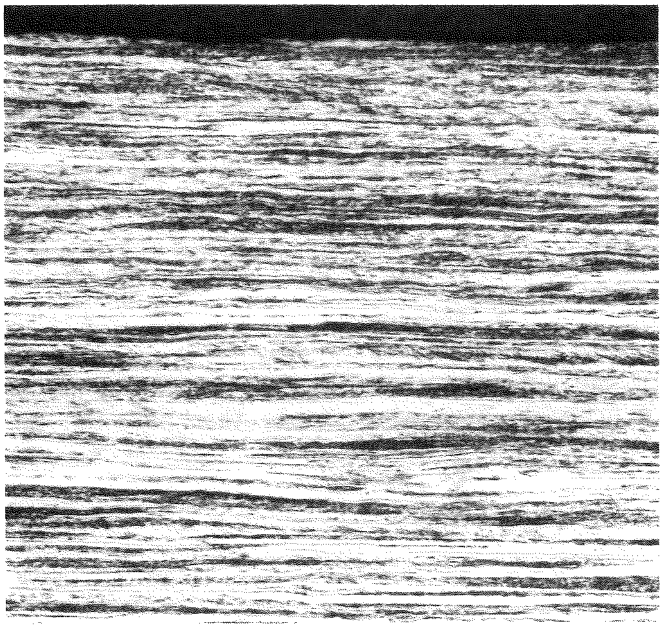
Mo5Re		Mo-41Re	
450	500	450	500
.	330	.	330
.	1176	.	1176
.	1270	.	1270
1584	.	1584	.
1992	.	1992	.
.	2760	.	2760

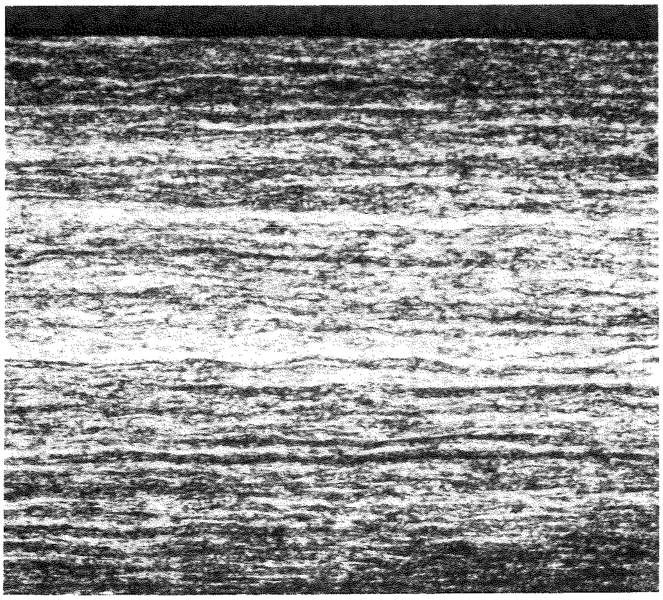
---

[8] The pictures in **Fig.Re-1** were kindly prepared by Plansee Company, Reuthe (Austria).

Fig.Re-1

Upper picture :
Mo5Re metal after 1600 hours at 450 ^{0}C in Pb-17Li.
(magn.100x)
Lower picture :
Mo41Re metal after 2760 hours at 500 ^{0}C in Pb-17Li.
(magn.100x)





Titanium

Titanium was proposed as a tritium getter and studied as one of the first metals (60). Most of the results have been published (23). For completeness, the results are given with more details in this report. The phase diagram Ti-Pb is investigated in detail (12,61). A number of intermetallic compounds are identified, but not all compounds were found by all authors.

1. Experiments

The table shows the performed experiments. Only experiments are included which were used for data evaluations. In addition, 6 experiments at 550 °C were performed with pure lead instead of Pb-17Li. The titanium was obtained from Goodfellow with 99.6+% quality. The metal was chemically cleaned and degassed at 700 °C for at least 2 hours at a final pressure of 10^{-5} mbar.

2. Results

There was only a minor isothermal mass transfer observed to the crucible wall. Different to most other metals, however, the behaviour of Ti in lead or the eutectic is controlled by the formation of intermetallic Ti-Pb compounds (23). Lead reacts with titanium, forming a surface layer of reaction products. After longer time at temperatures above 450 °C well shaped crystals are growing on the Ti surface.

Dissolution

Steady state dissolution was seen after an 'incubcation time'. The weight of formed crystals was added to find the 'total dissolved amount'. Unfortunately this weight was often not determined and not too many data points exist. The formed reaction zone is not included. The so defined steady state dissolution rate should not be compared with those for other metals. It is given by (23)

$$\ln R = 11.6 - 9260/T$$

(R in g/m^2*d). The heat of activation for the process is -77 kJ/mol. The function is included in **Fig.Zr-1.** Data, however, are widely scattered, the function may be considered only as an approximation.

Solubility of Ti in Pb-17Li

Fig.Ti-1 gives the solubility of Ti in Pb-17Li. Actually the function corresponds to the **solubility of Pb-Ti compounds**. As discussed below with alloys the chemical activity of Ti in Ti_2Pb, the compound of the reaction zone, determines the solubility function found in this work.

The function is given by

$$\ln S(\mathrm{wppm}) = 21.3 - 13600/T$$

The heat of dissolution is -113 kJ/mol.

Weeks (54) has extrapolated a value of 6 wppm Ti in lead for 500 °C from Bi-Pb data. This value may be only a rough estimation, it was derived from only two data points with a solubility of 1400 ppm for pure Bi. Our function would give 41 wppm. Higher solubilities in Pb-17Li than in lead can often be expected as discussed in Part-I of this report. However, our lead values for 550 °C fits into the function for the eutectic. Nevertheless, our solubility function is assumed to be reliable because derived from many data points.

From solubilities and the steady state dissolution rates **diffusion coefficients** were calculated, **Fig.Ti-2**. The values are in an expected range. The Arrhenius function is given by

$$\ln D = -27.7 + 4348/T,$$

the heat of diffusion is +36 kJ/mol.

Solubility of Pb in Ti

After removing reaction layers from the surface the solubility of Pb in solid Ti could be determined by dissolving the remaining metal. **Fig.Ti-3** shows the results. The function is given by

$$\ln S(\mathrm{wt.\%}) = 19.9 - 15980/T$$

(S in wt.% !!). The heat of dissolution is -133 kJ/mol. The solubilities are rather high, but fit well with a proposed line of the phase diagram (61), **Fig.Ti-4**. There is a homogenious distribution of this dissolved Pb over the cross section of the sample, as can be seen in the normalized microprobe picture, **Fig.Ti-5**.

Reaction zone, the compound Ti_2Pb

Metallographic examination of samples shows reaction zones at the surface. Examples are given in **Fig.Ti-6** and **Fig.Ti-7**. The reaction zone is less stable than Ti metal. It can be dissolved in nitric acid, but it remains intact during the electrolytic purification. The reaction zone grow thicker at higher temperature and with longer exposure time, but the maximum thickness found was 20 mikrons. Because of dissolution and formation of crystals, the sound metal gets thinner and is finally destroyed. The same kind of reaction zone was found in experiments with Pb-17Li as well as with pure lead. Brasunas (15) found no reaction zone at 1000 °C in lead. Probably the dissolution rate of Ti or formed compounds is too high at this temperature.

Chemical and microprobe analysis (Fig. Ti-5) shows that the reaction zone consists of a Pb-Ti compound with homogenious composition : 65 ± 3 at.% Ti and 35 ±3 at.% Pb. We assume that Ti_2Pb is formed, a compound proposed by Farrar (62) for the Ti-Pb system, but identified for the first time in our work(23).

Formation of crystals

As was mentioned before, well shaped crystals were growing or deposited on the Ti surface. In some experiments crystals were also seen at the crucible wall. These crystals remain at the surface during treatment with acetic acid/peroxid or electrolytic cleaning and are even stable in hot 2m nitric acid. They are also stable in fresh Pb-17Li at 720 °C for more than one day. However, the crystals can easily be scraped off. **Fig.Ti-8** shows some of the crystals. The amount of formed crystals as a function of temperature is given in **Fig.Ti-9**. The crystals have a homogenious composition (Fig.Ti-5). Independent on temperature and exposure time, they contain in experiments with pure lead 56 at.% Ti and 44 at.% Pb - with a very narrow range of only ± 1 at.% ! In experiments with Pb-17Li the composition was 57 at.% Ti, 42.6 at.% Pb and 0.4 at.% Li.

The intermetallic compound Ti_3Pb_2

In the literature no compounds are reported with more than 33 at.% Pb. The found composition of the crystals would give Ti_3Pb_2 or a more complex compound. With some selected crystals, crystallographic parameters were determined : space group $P6_3/mmm$, with a=0.93 and c=0.58 nm spacing.

In this new compound, Pb and/or Ti can be replaced by other metals. There was no systematic investigation of this effect. Other elements were found only when using Ti-alloys as discussed below. The crystals contained in our experiments the following elements:

Zr	up to	14	at.%
Al		40.6	at.%
V		0.27	at.%
Mo		0.27	at.%
Sn		0.63	at.%

A partly replacement of Ti by Zr over the whole concentration range was found e.g. for the intermetallic compound Ti/Zr_5Pb_3 (63,64). The very high concentration of Al, however, points to a replacement of lead. More tests would be needed to quantify these effects.

Experiments with pure lead

The rate of reaction as well as the formation rate of crystals were slightly smaller compared to experiments with the eutectic. All other results were identical, as can be seen in the figures.

3. Summary

Except at lower temperatures Ti cannot be used to extract tritium from the molten mixture. Because of reactions between the metals, the compound *Ti_2Pb* is formed at the surface in a reaction zone, destroying the sound metal. Also, problably by an dissolution-precipitation process, crystals of an other intermetallic compound, *Ti_3Pb_2*, deposit on the Ti surface. **Both compounds have not been reported in the literature.** Also solubilities of Ti in lead respectively Pb-17Li and of Pb in solid Ti could be determined, improving the knowledge of the Ti-Pb system.

List of experiments with **titanium.**
Header line temperatures °C, other numbers hours
of exposure time.

400	450	475	500	535	550	600	645
.	62	.	.	.	.	.	.
.	140	.			167	.	.
.		.	235	262	261	.	.
	.	.	476	.	490	450	450
	.	.	476	.	490	.	450
550	.	.	650	.	634	.	.
.	835	.	907	792	.	.	.
1176	.	1032	.	.	.	1100	.
2016	.	2080	.	.	2415	.	.
3048	.	.	.	.	.	.	.
.	.	3790	.	.	.	.	.
.	6200	.	.	.	.	.	.

Fig. Ti-1

Solubility of Ti in Pb−17Li

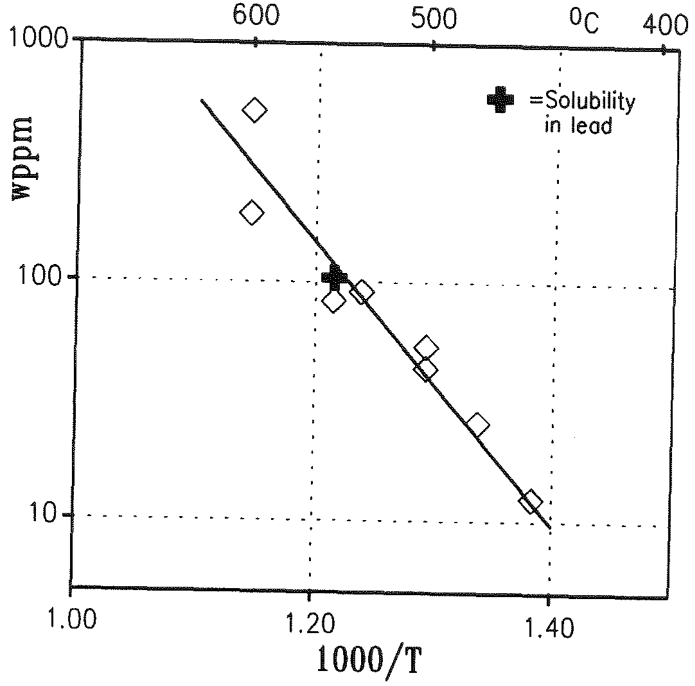


Fig. Ti-2

Difussion coefficient

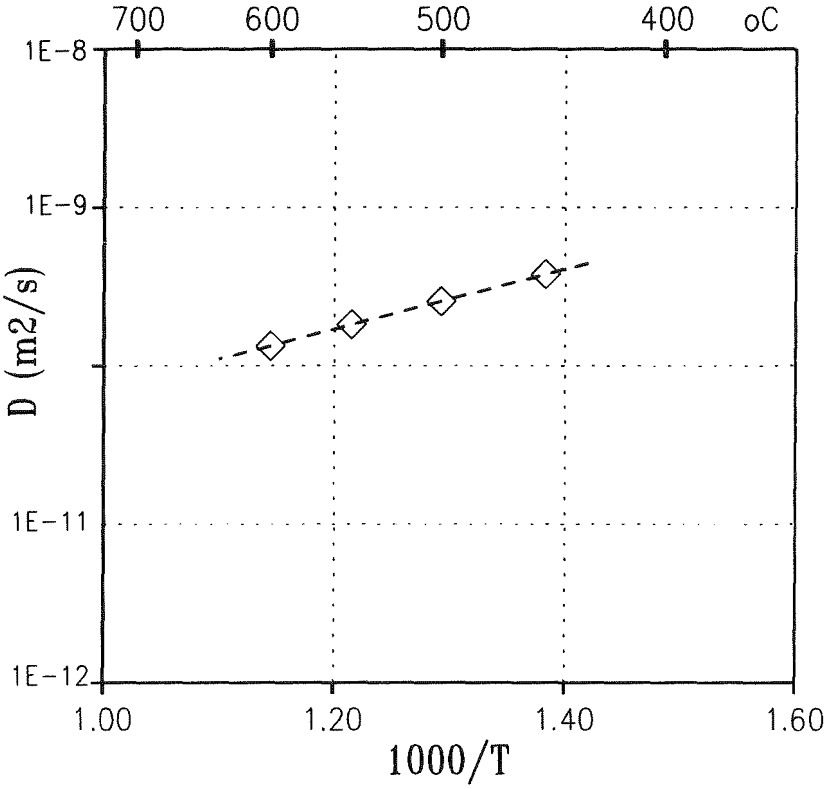


Fig. Ti-3

Solubility of Pb in Titanium

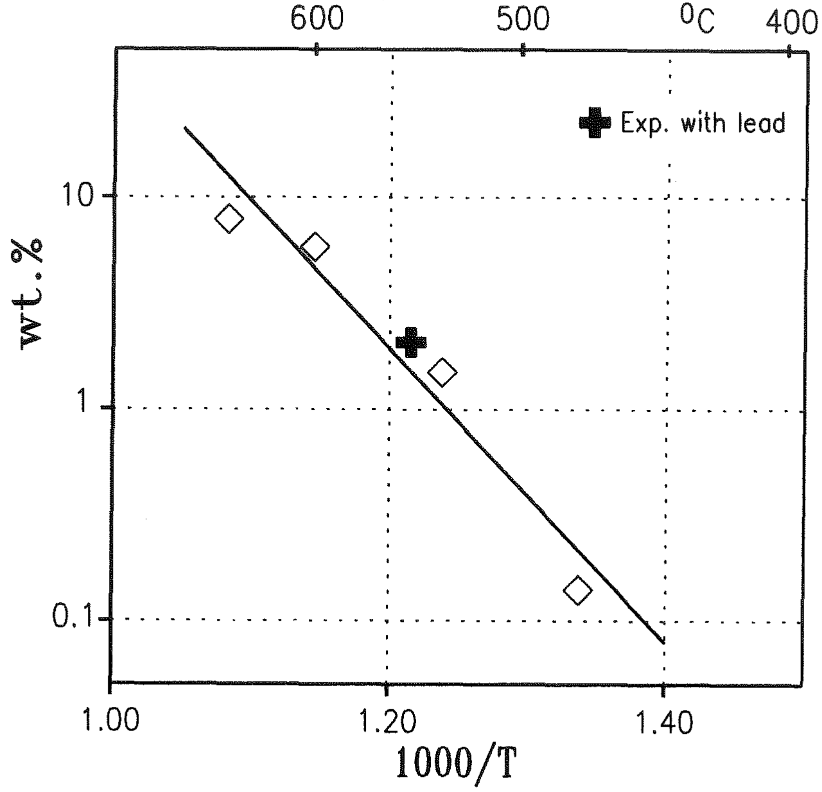


Fig. Ti-4

Phase diagram Ti-Pb from ref.(61)

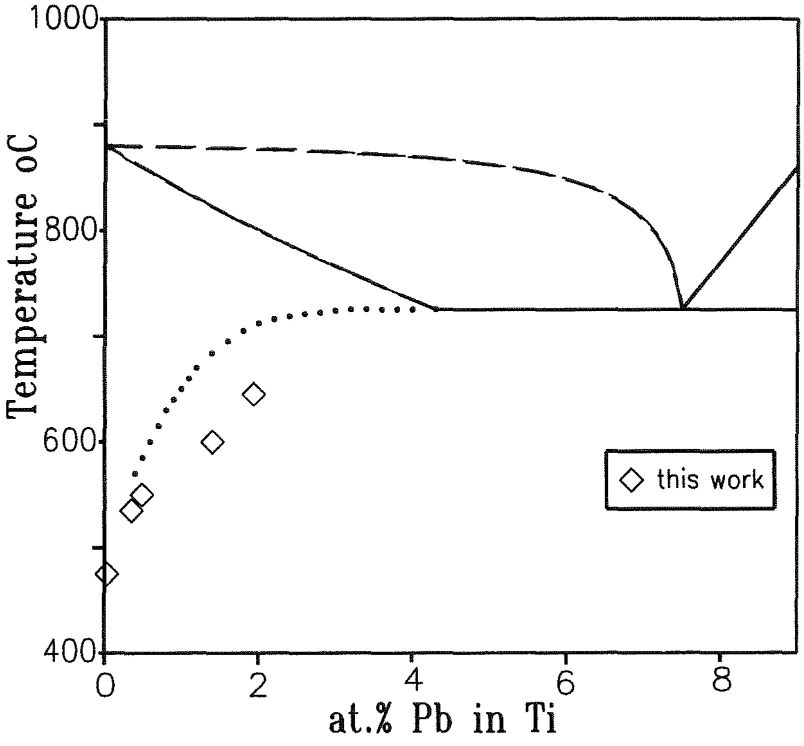


Fig. Ti-5

Microprobe scan of the sample Fig.Ti-7, cut A-B.
(1+3 = reaction zones, 2 = Ti foil, 4 = crystal)

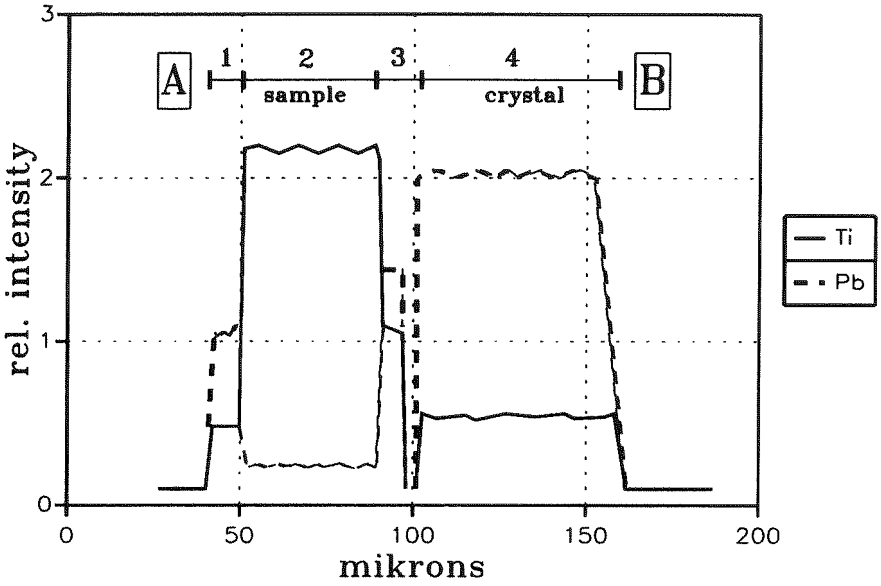


Fig.Ti-6

Ti metal.
Upper picture : without exposure to Pb-17Li.
Lower picture : after 476 hours at 500 ^{0}C in Pb-17Li.
Reaction zone only.

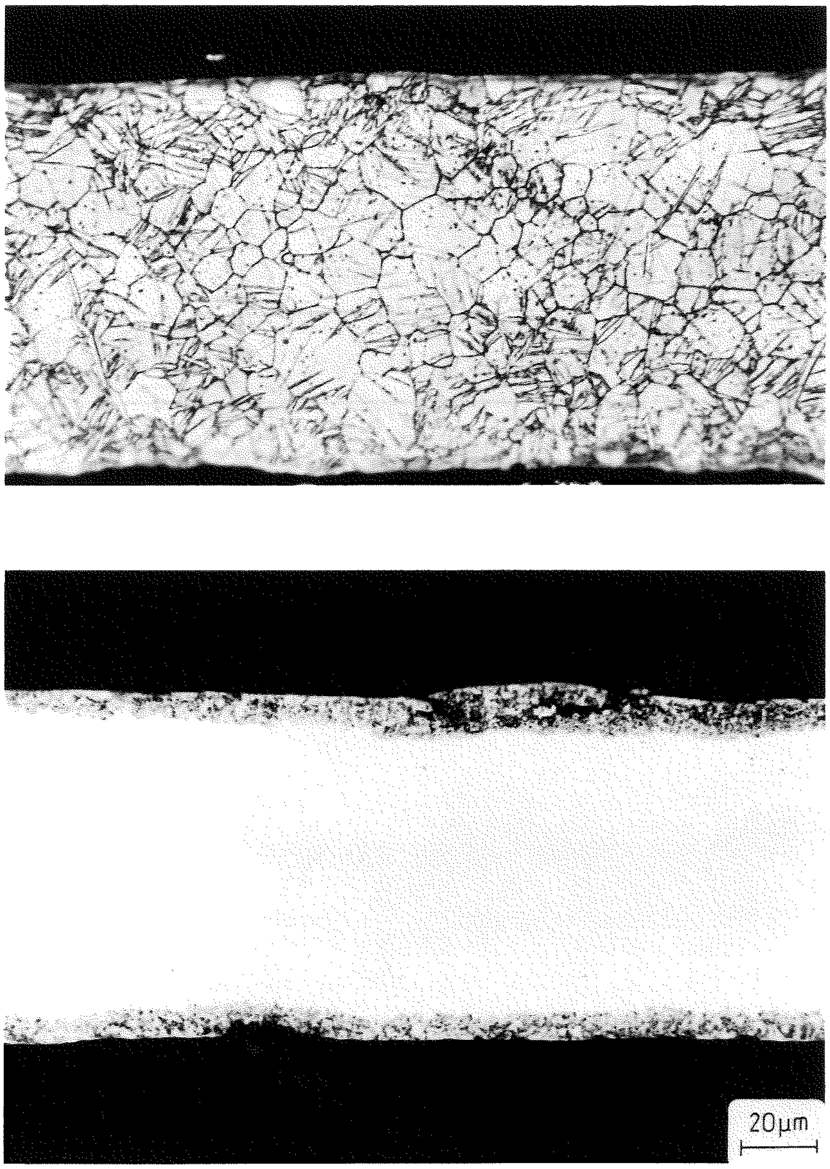
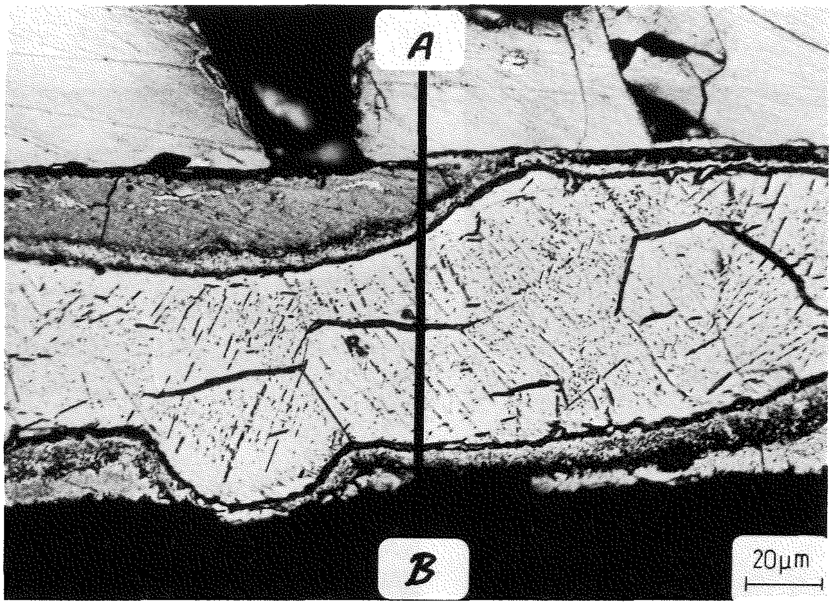


Fig.Ti-7

Ti metal after 634 hours at 550 °C in Pb-17Li.
Reaction zone and formed crystals.



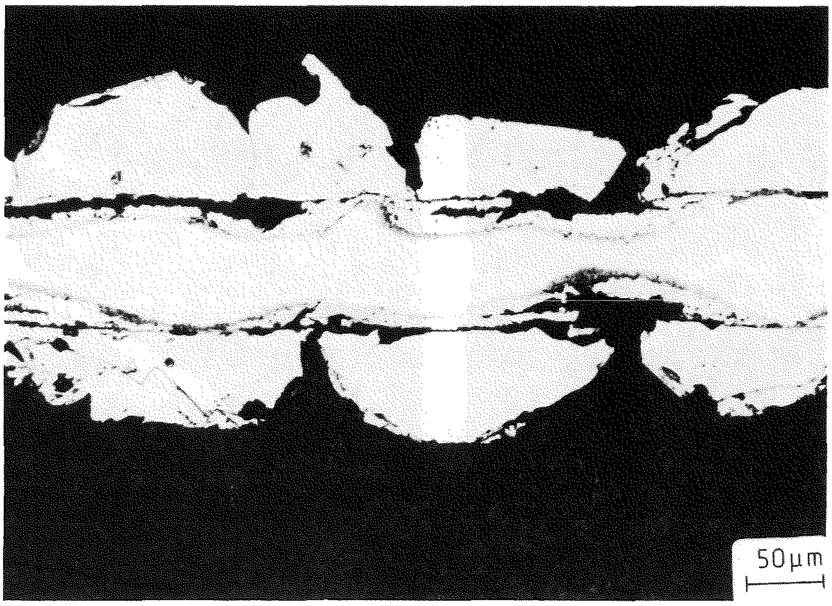


Fig.Ti-8

Crystals of Ti_3Pb_2,
deposited at the Ti surface after exposure to Pb-17Li.

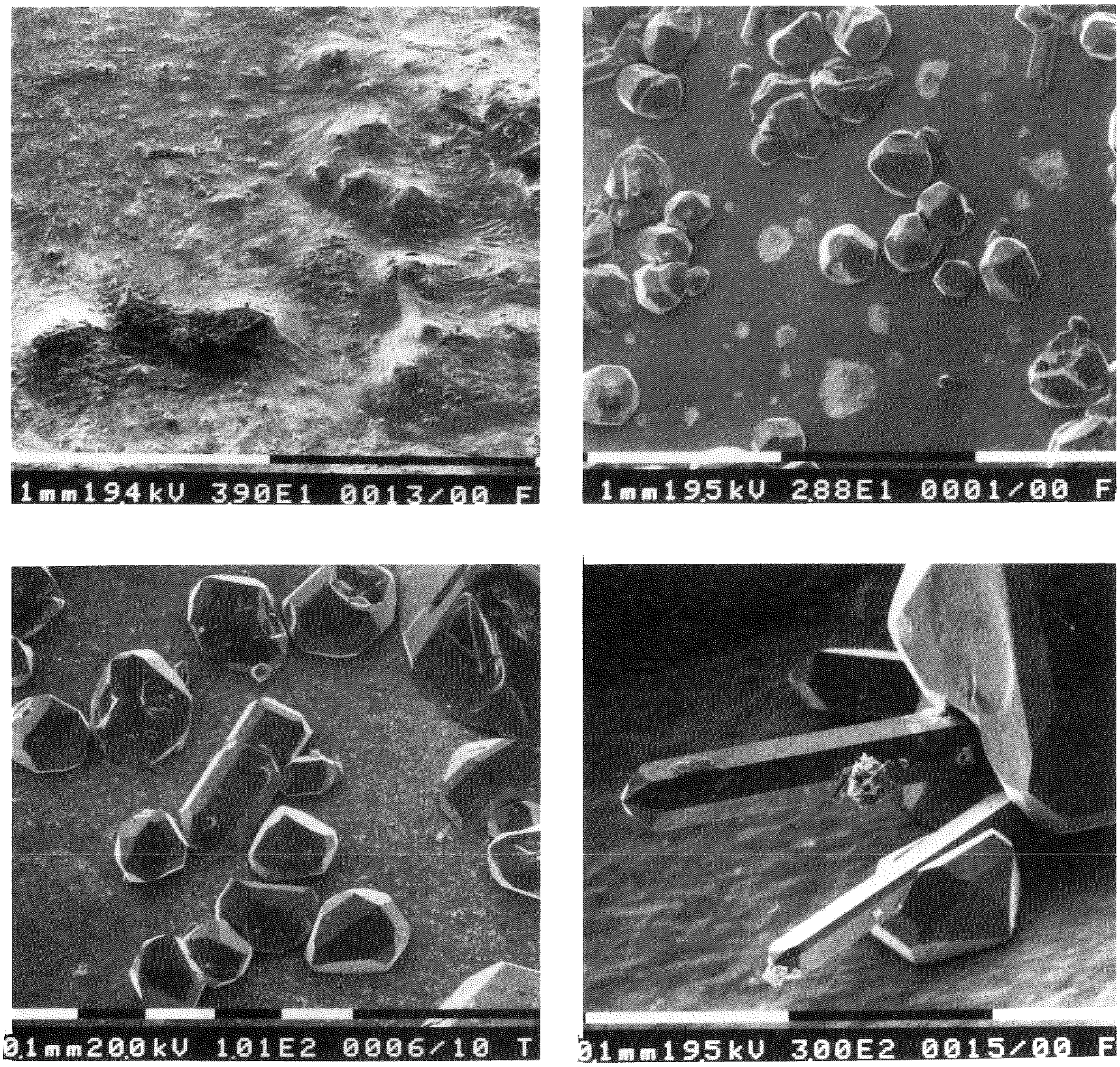
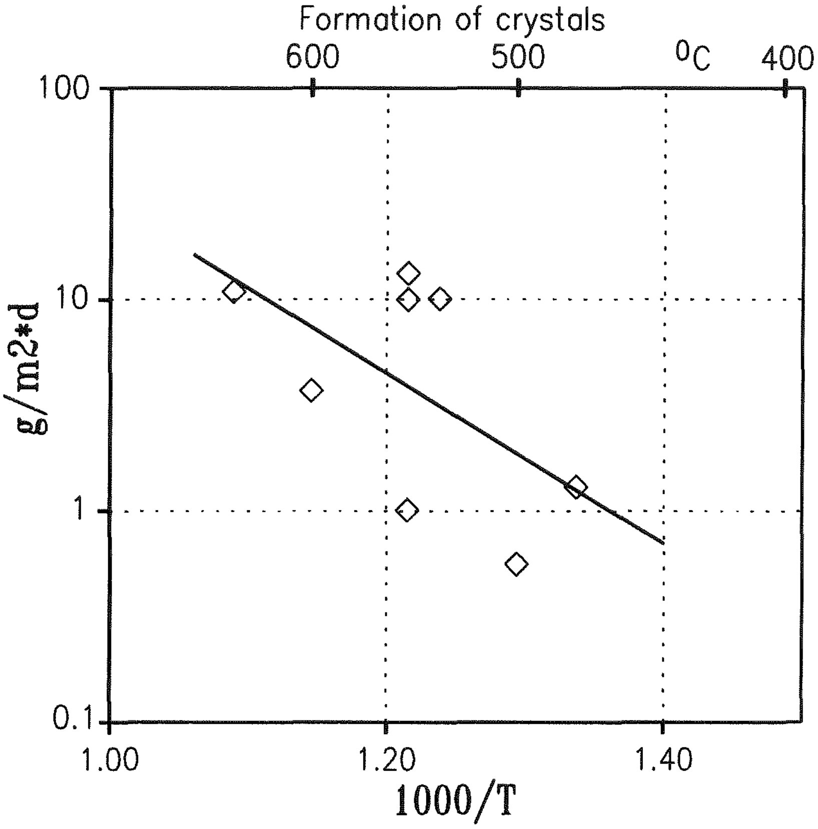


Fig. Ti-9


Formation of crystals
600
500
0C
400
100
10
1
0.1
g/m2*d
1.00
1.20
1.40
1000/T

Uranium

Uranium, yttrium, titanium, zirconium and other metals are often used for hydrogen gettering from a gas phase. The phase diagram Pb-U (14) shows PbU and Pb_3U as intermetallic compounds. Brasunas reports completely dissolution of a sample after 40 hours at 1000 °C (15).

1. Experiments

The table shows the performed experiments. Uranium was obtained from Goodfellow with 99.9% purity. It was chemically cleaned and vacuum annealed.

2. Results

An incubation time before the dissolution starts was found at 300 °C with more than 1000 hours, at 400 °C with less than 20 hours. The incubation time was **not a wetting effekt** : samples were wetted at 300 °C after 350 hours. A chemical reaction between U and Pb (below) causes fast dissolution.

Dissolution

Fig.U-1 shows the dissolution of uranium in Pb-17Li. After the initial incubation time, dissolution of U in the eutectic is fast and isothermal mass transfer to the crucible wall strong. Samples were completely dissolved at 400 °C after 400 hours, at 500 °C after 136 hours. Steady state dissolution rates could be derived only from the data points of Fig.U-1. It is given by

$$\ln R = 23.6 - 12970/T$$

(R in g/m^2*d). The heat of activation for the process is -108 kJ/mol (**Fig.U-2**).

Solubility of U

In **Fig.U-3** , best possible solubilities from our experiments are plotted together with values from the literature for uranium in lead and lithium.

$$\ln S\ (\text{wppm}) = 25.8 - 12153/T$$

The heat of dissolution is -102 kJ/mol. Solubilities in lead are only reported in Hansen (83). Our values are 100 times higher, probably because of the formation of intermetallic compounds. Solubilities in lithium are even lower (12).

From constant dissolution rates at two temperatures and solubilities **diffusion coefficients** were calculated (**Fig.U-4**). The temperature dependence can be expressed by

$$\ln D = -32.1 + 6302/T$$

(D in m^2/s). The heat of diffusion is +52 kJ/mol. This value is higher than expected for a diffusion process. It is probably influenced by the formation of compounds.

Reaction zone

There was a strong reaction between uranium and lead. The immersed part of the sample foils could not be investigated because of extreme embrittlement. Lead dissolved also in the not-immersed part of the solid U, causing there embrittlement too. Sections from about 2 cm above the liquid metal surface were not any more uranium metal. In 500 °C experiments, this part contained up to 80 at.% (!) lead and up to 9 at.% lithium. If **UPb_3** (12) was formed in this area, then some of the eutectic was 'creeping up'. Otherwise the compound **UPb_4** has to be assumed. This compound is not reported in the literature. In 400 °C experiments after 600 h exposure time, only 1.3 at.% Pb was found in the non-immersed part, no lead was detected there in 300 °C experiments.

UPb_3 was deposited at the crucible wall. Remaining eutectic after drain contained (average) 24 at.% Uranium.

3. Summary

Wetting was found at temperatures as low as 300 °C. After an incubation time uranium reacts very strongly with lead. Intermetallic compounds were found even outside of the liquid phase. Even if there the lead concentration was higher, probably **UPb_3** was formed. This compound was identified at the crucible wall. High dissolution rates were probably caused by this reaction. Pb-U compounds pretend very high solubilities of uranium in the eutectic.

Table : List of experiments with **uranium**.
Header line temperatures °C, other numbers hours of exposure time.

300	400	500
.	20	.
	61	.
143	112	136
.	.	136
.	184	
.	256	.
348	400	.
494	.	.
.	607	.
696	.	.
1200	.	.
1300	.	.

Fig. U-1

Dissolution of Uranium in Pb−17Li

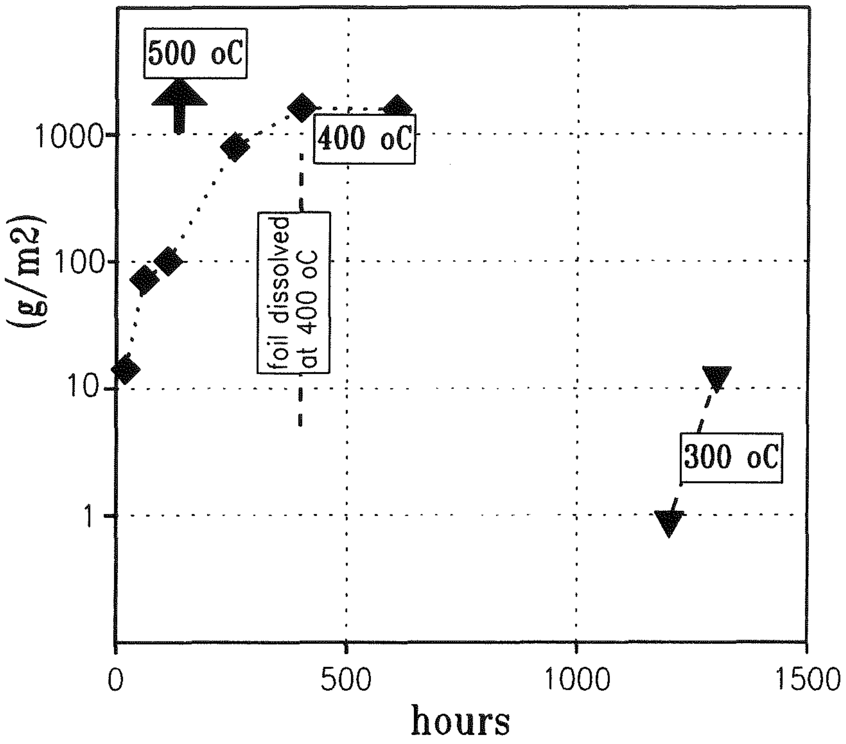


Fig.U-2

Steady state dissolution rates

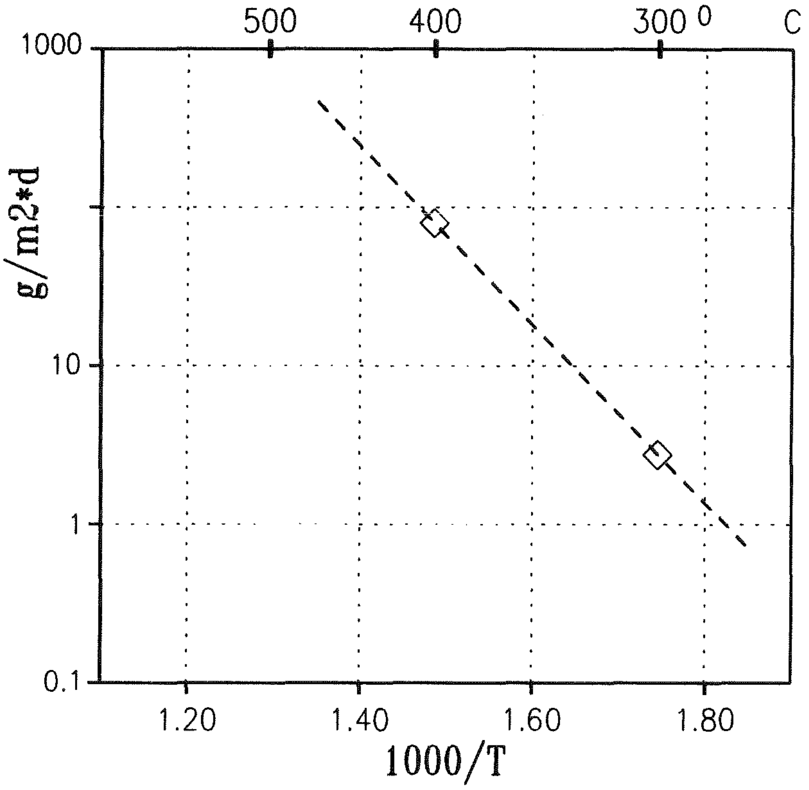


Fig. U-3

Solubility of uranium in Li , Pb and Pb−17Li

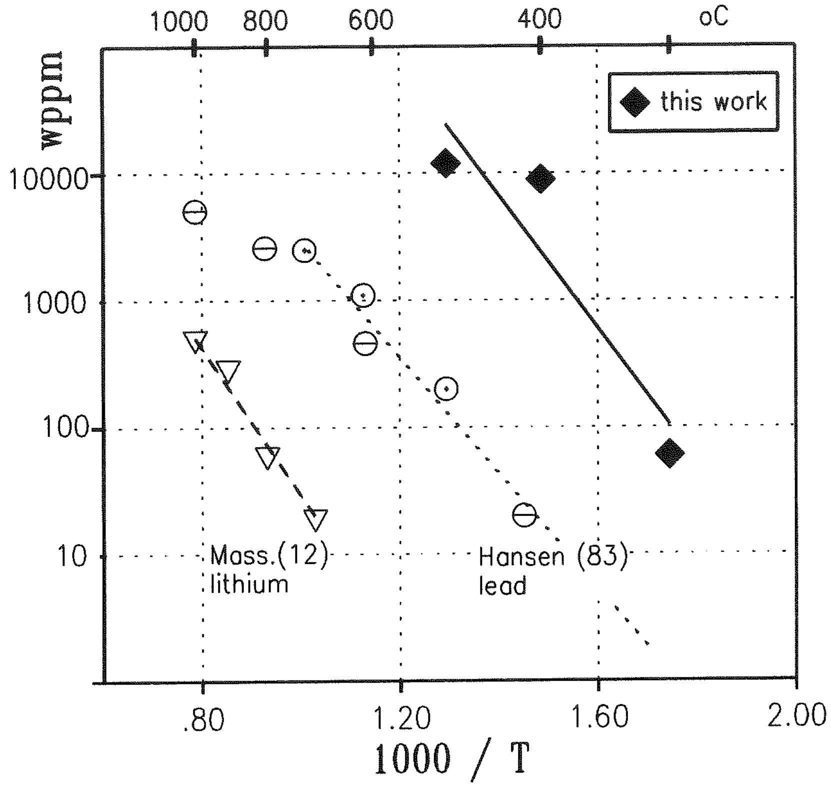
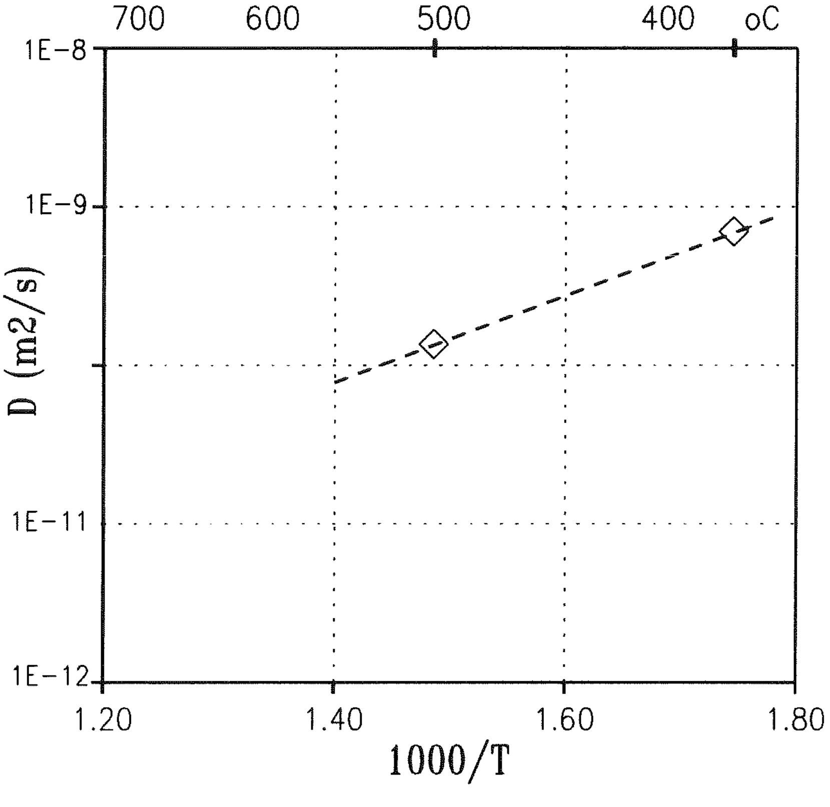


Fig. U-4

Difussion coefficient



Vanadium

Vanadium and its alloys were proposed as structural material for fusion reactor blankets (16). Vanadium was also proposed as a getter metal for tritium extraction from the eutectic (65). A large number of tests were performed with this metal.

Not much has been published for the systems V-Li or V-Pb (66). No phase diagrams are available from experimental data. A calculated Li-V phase diagram shows no reaction products.

1. Experiments

The table shows the performed experiments. Vanadium was obtained from Goodfellow with 99.8+ % and from Kelpin (Leimen, Germany) with 99.7% quality. The metal was cleaned and vacuum annealed at 800 °C for several hours. There were some experiments in alumina crucibles. But in this report only results obtained with Mo crucibles are used.

2. Results

First results on vanadium were already reported in 1988 (60). There were no remarks about **wetting** of vanadium in laboratory notes. We assume therefore wetting in all experiments. This would be in agreement with observations for hydrogen extraction where no incubation time was found after immersing the vanadium into the molten liquid (65).

Dissolution

Fig.V-1 shows the results of all experiments. It can be seen from **Fig.V-2** that the dissolution does not stop after the initial period. Mass transfer to the crucible wall is observed. The steady state dissolution rate after the initial period, **Fig.V-3** , is given by

$$\ln R = 2.37 - 5431/T$$

(R in g/m^2*d). The heat of activation for the dissolution process is -45 kJ/mol, smaller than found for most other metals.

From Fig.V-3 it is clear that corrosion experiments can not find a weight loss with small samples, even if dissolution rates in non-static systems are higher. On the contrary, Borgstedt (16) found in the Pb-17Li-loop PICOLO a weight gain because of iron deposition. Brasunas (15) found no attack of lead on vanadium after 100 hours at 760 °C. Ali Khan (22) observed a reaction between vanadium and lead at 950 and 1100 °C after 100 respectively 40 hours.

From constant dissolution rates and solubilities (below) **diffusion coefficients** were calculated (**Fig.V-4**). The temperature dependence can be expressed by

$$\ln D = -25.7 + 2300/T$$

(D in m^2/s). The heat of diffusion is +19 kJ/mol. Such a small value is expected for a diffusion process. But the value is positive as in case of beryllium. Probably the used model is too simple. The average value between 400 and 600 °C is $1.5*10^{-10}$ m^2/s.

Solubility of V in Pb-17Li

As with other metals most of the dissolved V was transported by isothermal mass transfer to the Mo-crucible wall, the concentration in the bulk Pb-17Li remained constant. **Fig.V-5** shows the solubility of V in Pb-17Li. The function is given by

$$\ln S\ (\text{wppm}) = 10.1 - 7730/T$$

The heat of dissolution is -64 kJ/mol.

Only a few values are reported in the literature. They are included in Fig.V-5. Ali-Khan (22) gives a limit of the solubility in lead with less than 10 wppm at 1000 °C. But there was clearly dissolution as could be seen from metallographic investigations. A theoretical calculation of the solubility of V in Pb gives 72 wppm at 600 °C (10). But such calculated solubilities are very questionable (Part-I). Very low solubilities in lithium of less than 1 wppm at 727 °C and less than 3 wppm at 1004 °C (66) are considered as not reliable. (The authors assume that the data given in ref.(66) are mixed by mistake). Beskorovainyi (67) gives a solubility of V in Li with less than or equal to (?) 30 wppm at 1000 °C. Rumbaut (68) mentioned strong corrosion of V-Cr alloys in Li at 700 °C and preferential leaching of V. Therefore, solubility of V should be higher than that of Cr. However, no Cr values were reported (6,8).

Solubility of Pb in V

The solubility of lead in vanadium was found to be less than 0.02 wt.% at all temperatures. Also Li could not be detected in vanadium samples. Because some informations are lost, no solubility limits can be given.

Reaction zone

A very thin chemical reaction zone was found during the electrolytical purification process of samples from 550 to 650 °C experiments. **Fig.V-6** shows that the thickness is proportional to the exposure time. The growth of this zone can be described by

$$d = 1.4 * 10^{-5} * t + 0.001$$

(d in microns, t in hours exposure time). That means the reaction zone thickness is only 0.01 microns after 1000 hours.

Samples exposed up to 500 °C. show a surface layer if examined by metallography. These layers are not seen in experiments at higher temperature. (**Fig.V-7:**, **Fig.V-8**). Such surface layers were described e.g. by Borgstedt for V-3Ti-Si in flowing Pb-17Li after 1058 hours at 550 °C (16). The layer in his experiment was 55 microns thick and very hard. It was formed because of pick up of non-metallic elements from the molten metal. A similar very hard layer was found by Brasunas (15) after 100 hours at 1000 °C in lead. The layer formed in our static experiments may have been formed by the same mechanism. But this layer was very thin and **did not prevent the dissolution** of vanadium. (A thin hard surface layer was observed on vanadium, exposed for 2500 hours at 450 °C in flowing Pb-17Li in loop TRITEX (69)).

Corrosion, visible by metallography, starts at 600 °C, **Fig.V-8** . But only unetched samples show this. Ali Khan (22) found strong corrosion of vanadium in lead at 950 (100h) and 1110 °C (20h) and the formation of large grains. This was not observed in our experiments with lower temperatures. He also observed the formation of a reaction layer on vanadium.

3. Summary

Vanadium dissolves in molten Pb-17Li, but the solubility is low. Also, dissolution rates are low. Because of isothermal mass transfer to Mo, dissolution does not stop at saturation. Solubilities of vanadium in molten Pb-17Li and diffusion coefficients were determined. Besides a surface layer at lower temperatures, probably caused by pick up of non-metallic elements from the eutectic and/or atmosphere, a very thin chemical reaction zone was found at higher temperatures.

Table: List of experiments with **vanadium.**
Header line temperatures °C, other numbers hours of exposure time.

400	460	505	550	600	645
.	.	.	167	.	.
.	.	.	261	252	.
.	319	.	.	.	.
.	319	.	.	.	.
.	476	476	.	450	.
.	.	.	668	.	.
.	.	907	.	.	.
.	.	907	852	.	.
.	.	.	.	1130	1190
.	.	.	.	1220	.
.	.	.	.	1250	.
1460	.	.	.	1250	.
.	.	.	.	2000	2086
.	.	.	.	2000	.
.	.	.	.	2300	.
.	.	.	2720	.	.

Fig. V-1
Dissolution of vanadium in Pb-17Li
(wld=weight loss data)

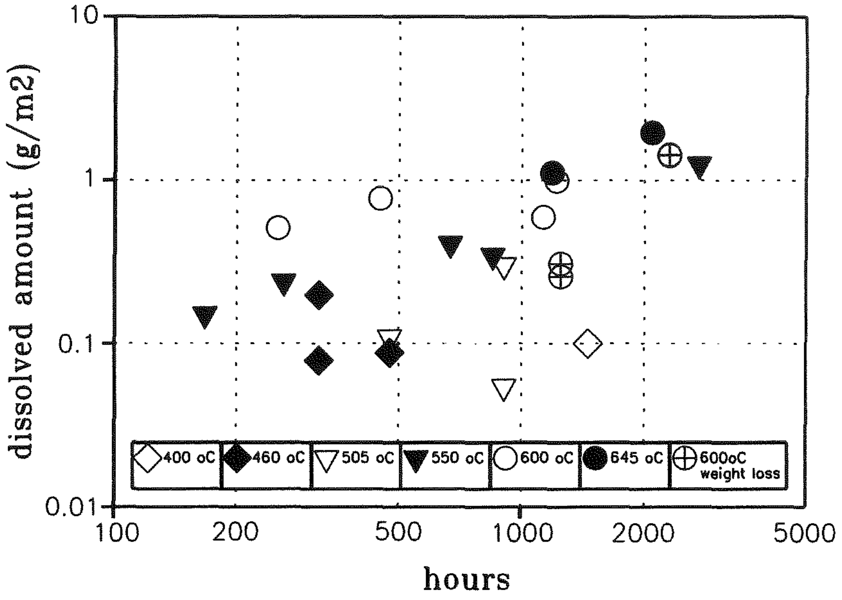


Fig. V-2
Dissolution of vanadium in Pb-17Li

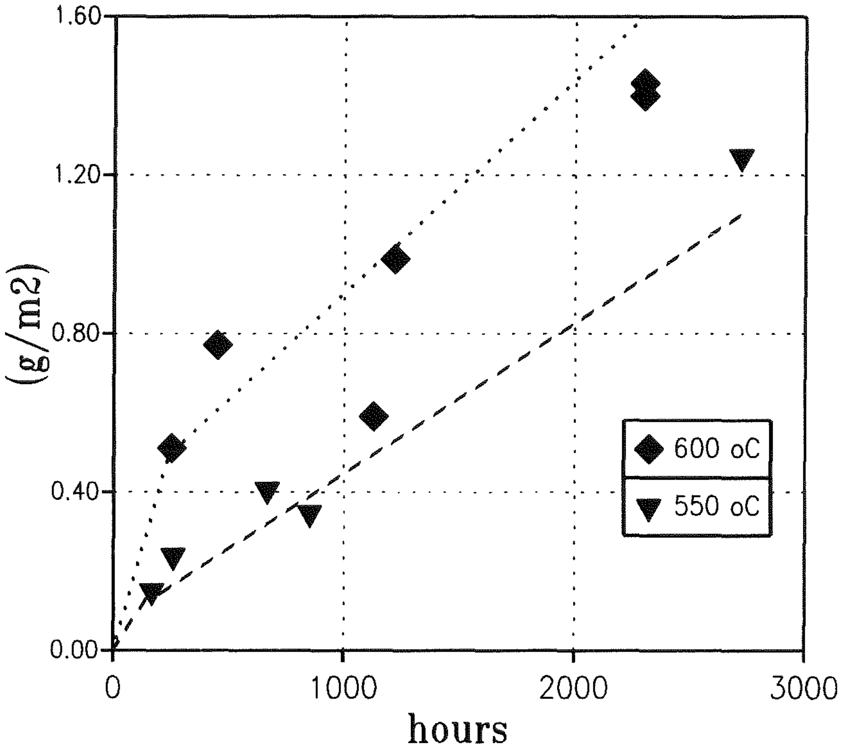


Fig. V-3

Steady state dissolution rate of vanadium

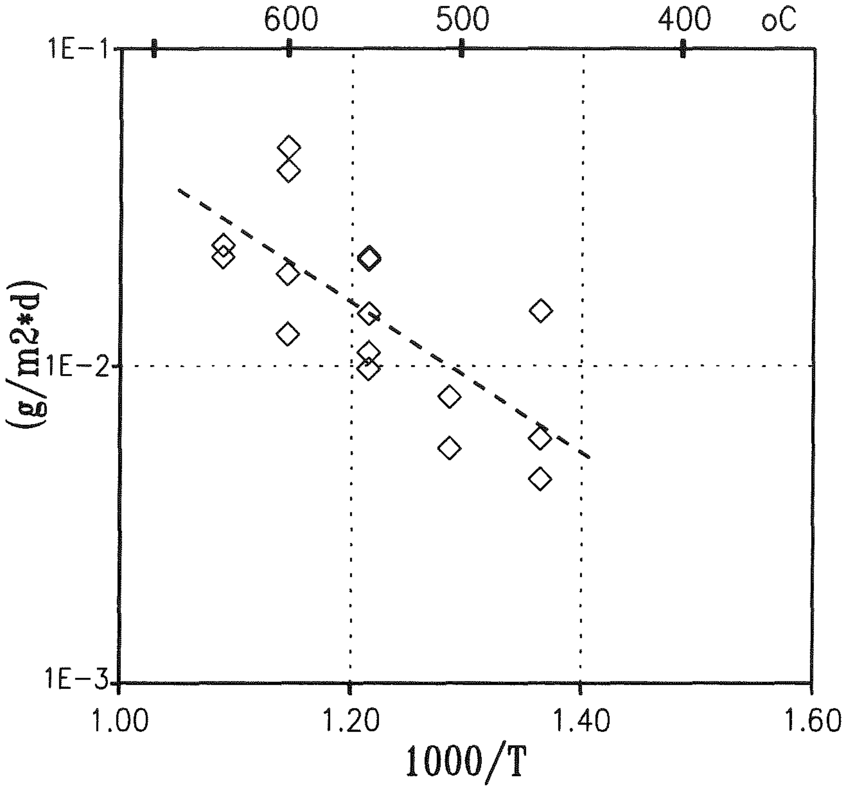


Fig. V-4

Difussion coefficient

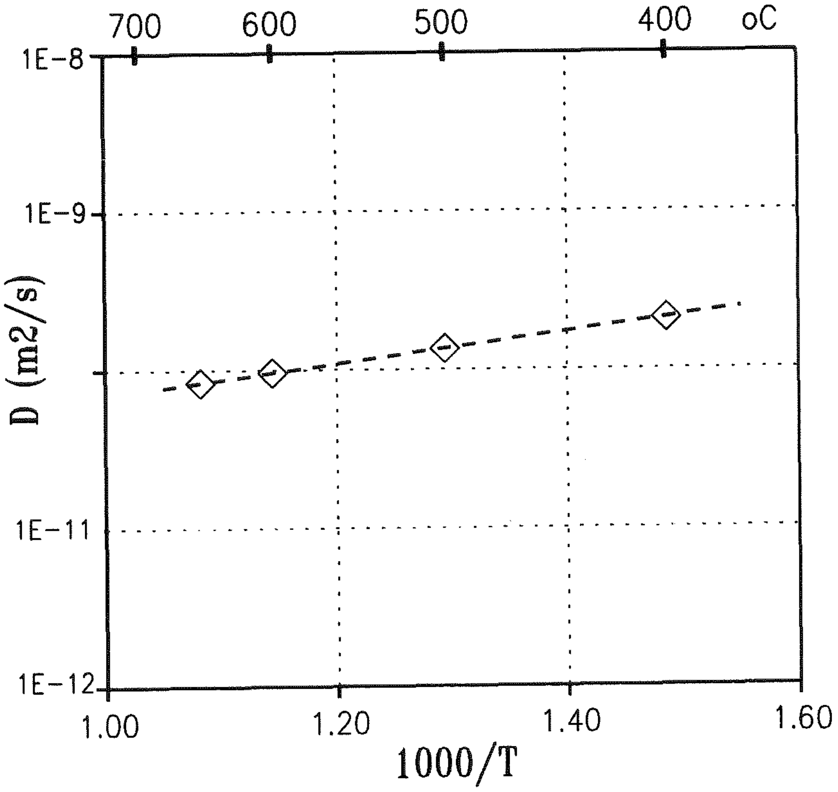


Fig. V-5

Solubility of vanadium in Pb−17Li

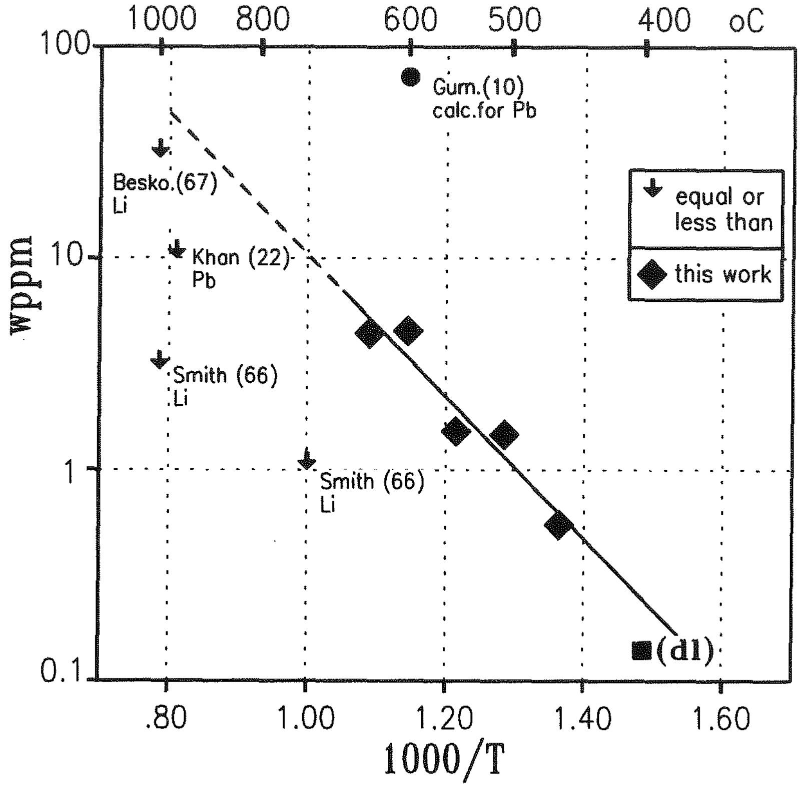


Fig. V-6

Chemical reaction zone on vanadium 550 to 650 oC

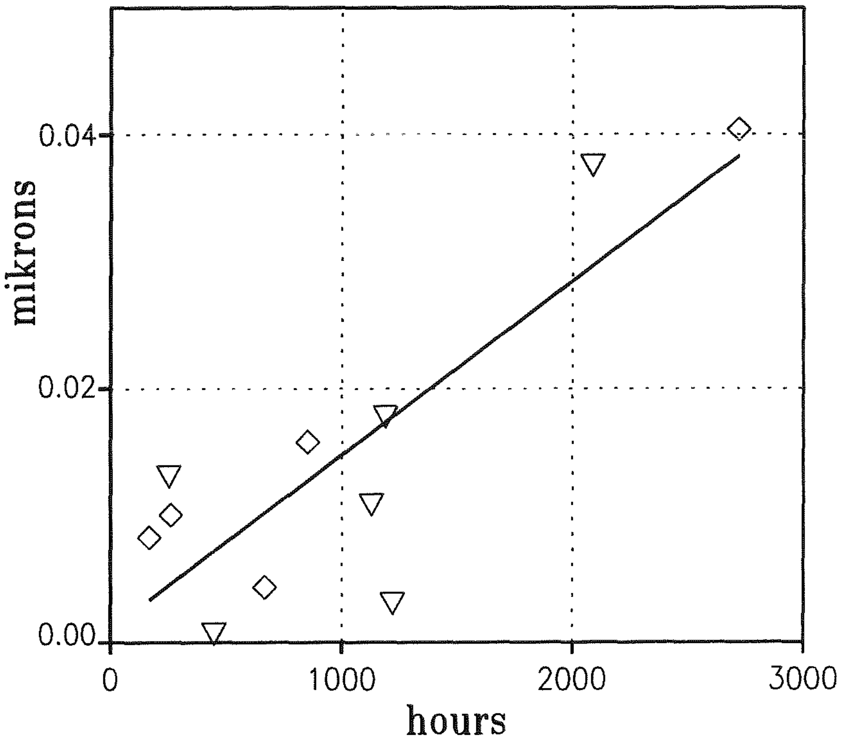
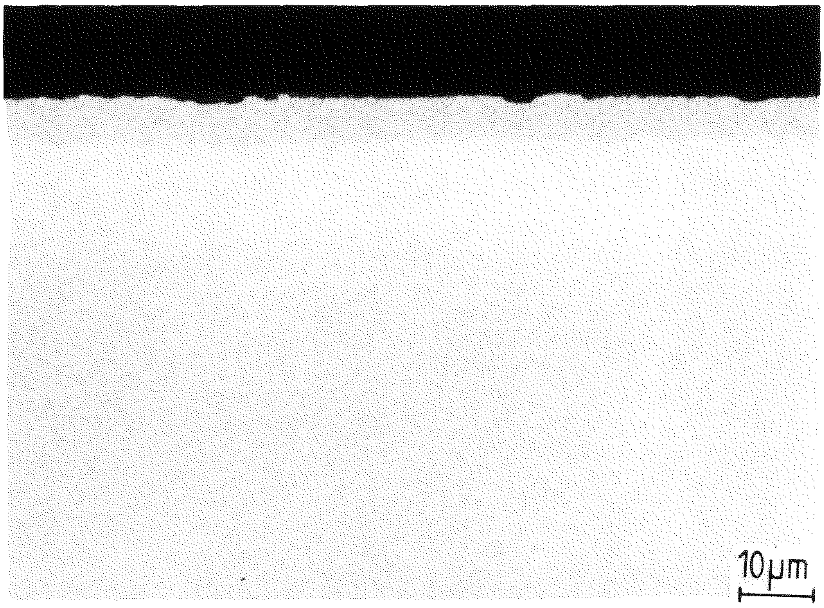


Fig.V-7

Vanadium after 907 hours at 500 °C in Pb-17Li.
Thin gray surface layer in upper picture of an unetched sample. After etching (as Nb), this layer is lost (lower picture).



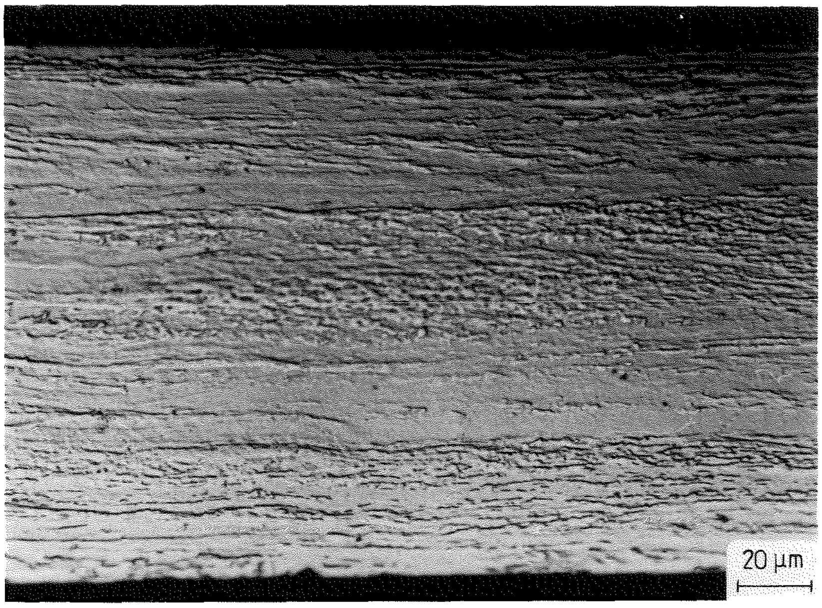
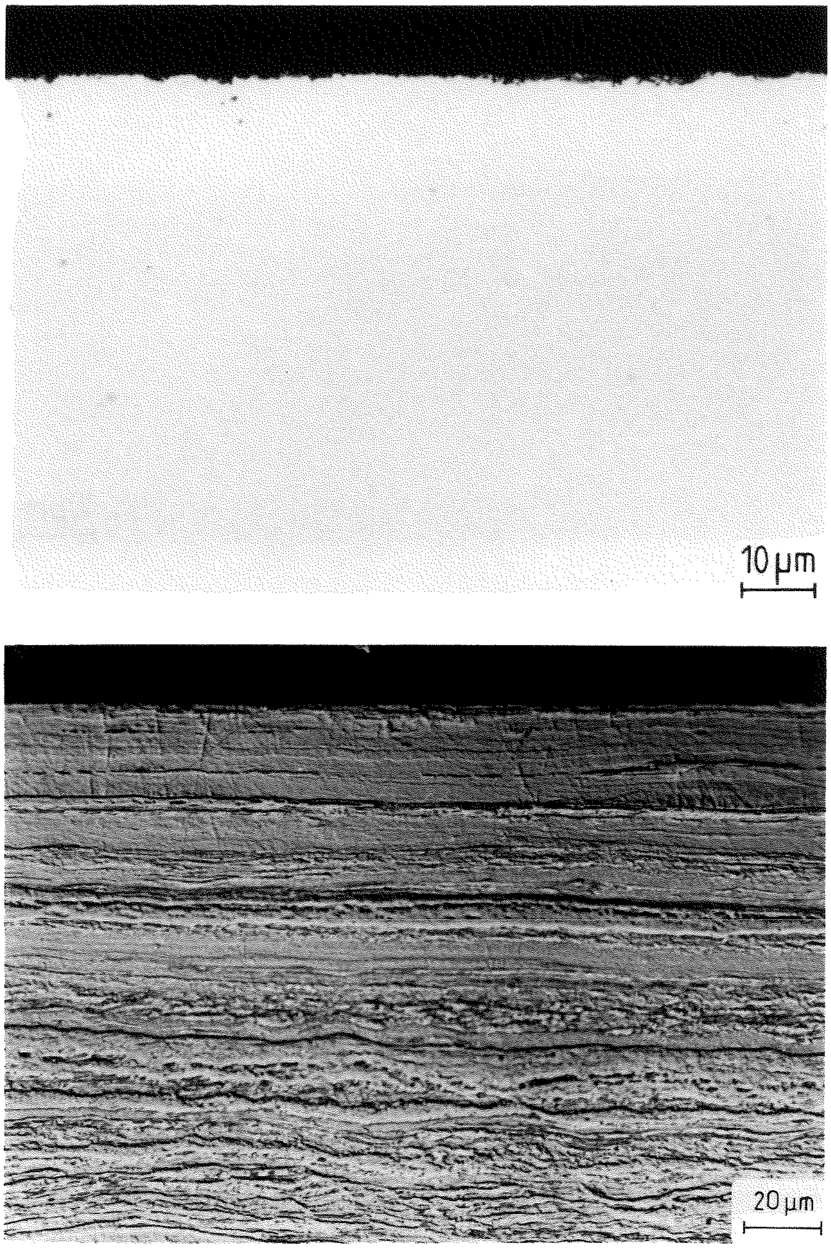


Fig.V-8

Vanadium after1220 hours at 600 °C in Pb-17Li. No surface layer. Week corrosion attack seen in etched sample (lower picture).



Tungsten

Tungsten will not be considered as a structural material for liquid metal blankets. A few experiments were performed with W-crucibles. From the analysis of Pb-17Li it can be concluded that the solubility of W in the eutectic is less than 1 wppm at 600 °C.

Alden (56) reports a solubility below 23 wppm at 1200 °C. Ali Khan (22) found no attack at 950 °C after 306 hours in lead, Brasunas (15) no attack at 1000 °C after 100 hours. Tungsten is like molybdenum very stable in the eutectic.

Our boundary value, as well as the value of Alden, would fit well in our function for Mo. Because the values are upper limits, actually solubilities are lower than expected from ref.(10).

Yttrium

Yttrium was proposed as a getter metal to extract tritium from molten lithium (70). For the high temperature range the phase diagram Pb-Y is well investigated (12). Several intermetallic compounds exist with lead concentrations between 40 and 75 at.%. Bhat (71) used Y metal to getter oxygen from Pb-17Li. He found high dissolution rates. At temperatures of 235 to 450 °C, the Y-foils were dissolved completely. Only a few experiments were performed in our study.

1. Experiments

The table shows the performed experiments. Y was obtained from Goodfellow company with 99.5% purity. It was chemically cleaned and vacuum annealed to dissolve remaining oxides from the surface.

2. Results

Many similarities were found to the behaviour of uranium. There is an incubation time of about 60 hours at 400 °C before the dissolution starts. But even at 300 °C **wetting** was observed after 66 hours. This is caused by a reaction between Y and Pb (below).

Dissolution

After the initial incubation time, dissolution of Y in the eutectic is fast (**Fig.Y-1**). Often samples were completely dissolved. No real dissolution rates were determined, but in any case at 300 and 400 °C more than 50 g/m^2*d get dissolved. Isothermal mass transfer to the crucible wall is strong.

Solubility of Y

Only for 400 °C a solubility can be given:

$$S\ (400\ ^0C) = 1100\ \text{wppm}.$$

This value is similar high as for uranium. It may be not too high. Smith(9) measured the solubility of samarium in Pb-Li mixtures. From his data a solubility of 450 wppm Sm in Pb-17Li can be derived for 400 °C. Wet chemistry of Y and Sm is similar, the radii of ions of the two metals comparable. Therefore, a similar solubility is expected.

Reaction zone

Obviously there is a strong reaction between yttrium and lead. The immersed part of the sample foils could not be investigated because of extreme embrittlement. But as for uranium, lead dissolved in the not-immersed part of the solid Y, causing there embrittlement too. Fractions from about 2 cm above the liquid metal surface contained 80 to 85 at.% lead (!) , but less than 1 at.% Li. This lead concentration corresponds to an intermetallic compound YPb_4 . In the phase diagram (12) only compounds up to YPb_3 are reported.

3. Summary

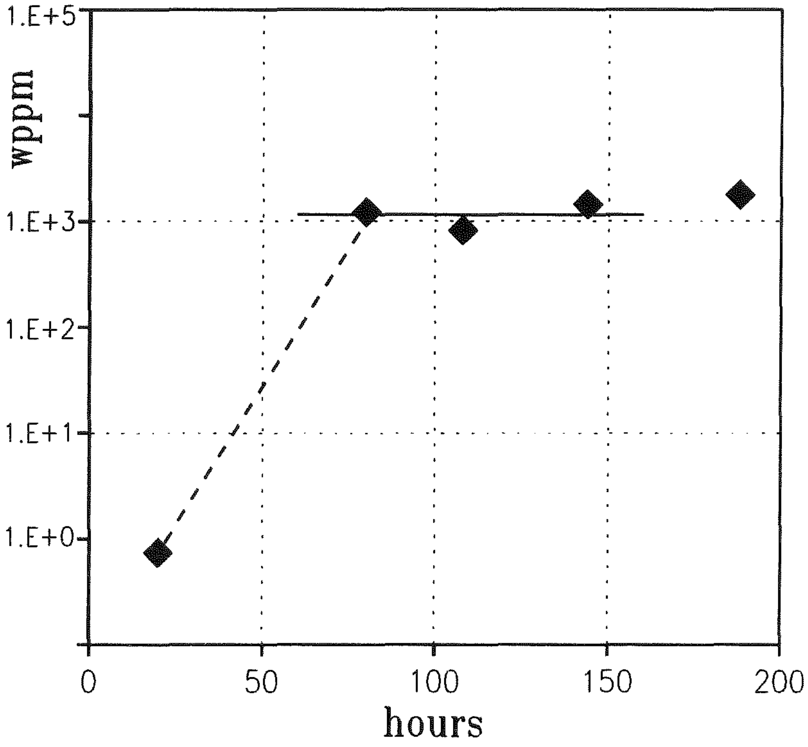
The behaviour of Y is comparable to that of Uranium. Y reacts very strongly with lead from the eutectic, forming intermetallic compounds even outside of the liquid phase. YPb_4 was identified. Wetting at temperatures as low as 300 °C and a high dissolution rate is probably caused by this reaction.

Table : List of experiments with **yttrium.**
Header line temperatures °C, other numbers hours
of exposure time.

300	400
.	20
66	.
66	.
	80
.	108
.	144
.	188

Fig. Y-1

Concentration of Y in Pb-17Li
at 400 oC



Zirconium

Besides Ti, U and Y, zirconium was studied as a possible tritium getter (60). A similar behaviour was expected as found for titanium.

1. Experiments

The table shows performed experiments. In addition some tests were done with pure lead instead of Pb-17Li. Because there was no difference in the results these tests are not mentioned separately. The zirconium was obtained from Goodfellow with 99.8+ % quality. The metal was chemically cleaned and degassed at 700 ^{0}C for at least 2 hours at a final pressure of 10^{-5} mbar.

2. Results

As found with Ti (23) lead reacts also with zirconium, forming a surface layer of reaction products. The most remarkable effect with Ti, however, the formation of an intermetallic compound in form of crystals, was never seen.

Isothermal mass transfer to the crucible wall was observed. Similar to titanium the effect was smaller than for other metals. Even after 3500 hours at 450 ^{0}C, only 15 % of the dissolved metal were deposited.

Dissolution

Excluding the formed reaction zone the steady state dissolution rate is given by

$$\ln R = 11.7 - 8858/T$$

(R in g/m^2*d). The heat of activation for the process is -74 kJ/mol. In **Fig.Zr-1** the corresponding function for Ti is included. Both metals show the same slope, dissolution rates for Zr are a factor of two higher.

There is a possibility to calculate **reaction rates** from remaining sound metal from metallographic pictures. These 'loss of sound metal' values are also included in Fig.Zr-1. Reaction rates are higher than dissolution rates.

Solubility of Zr in Pb-17Li

Fig.Zr-2 shows solubilities of Zr in Pb-17Li. The function is given by

$$\ln S(\text{wppm}) = 11.2 - 3423/T$$

The heat of dissolution is only -28.5 kJ/mol. Zr solubilities are remarkably high if compared to titanium, but the heat of dissolution is small. There is only one value published for the solubility of Zr in Pb : 12 wppm at 500 °C (54), extrapolated from solubilities in Bi-Pb. Our value from the function would be 873 wppm. Weeks (54) found for the same temperature in Bi a solubility of 1200 wppm. Different behaviour in Pb and Bi was also found in the system with Ti. But with Ti Weeks and our solubility values are not so much different.

Experiments with Ti-Zr alloys (below) showed proportionality between the mole fraction X(Zr) in the alloy and the equilibrium concentration in Pb-17Li. That means chemical activities in the metal determine solubilities, and not a formed compound as in case of titanium.[9] A value of 250 wppm for 500 °C can be evaluated from these experiments for X(Zr)=1. This is 3.5 times lower than calculated from the function, but still much higher than expected from (54).

From solubilities and steady state dissolution rates **diffusion coefficients** were calculated. They are shown in **Fig.Zr-3** The values are in an expected range. The Arrhenius function is given by

$$\ln D = -17.6 - 5220/T.$$

The heat of diffusion is -43 kJ/mol, rather high for a diffusion process.

Reaction zone

Metallographic examination of samples shows reaction zones at the surface. Examples are given in **Fig.Zr-4** and **Fig.Zr-5.** As with Ti, reaction zones grow thicker at higher temperature and with longer exposure time. The chemical analysis gives 18.8 ±1 at.% Pb. This would correspond to an intermetallic compound Zr_4Pb. Two intermetallic compounds are listed in the phase diagram (12) : Zr_5Pb_3 and Zr_5Pb, the latter with a question mark. We do not know if, as for the Ti reaction zone that on Zr has a homogenious composition. No microprobe analysis was done. Therefore, Zr_5Pb may also be possible.

Solubility of Pb in zirconium

There was no determiniation of the concentration of Pb in sound Zr. But as in case of titanium, there is clearly a dissolution of Pb in Zr. The remaining metal after removing the layer of reaction products was very brittle. The effect is described in the literature (12) but not investigated in our work.

---

[9] Otherwise a compound at the surface would have also Zr concentrations proportional to X(Zr). This, however, was not seen.

3. Summary

Like Ti, Zr cannot be used to extract tritium from the molten mixture. Reaction zones of intermetallic Pb-Zr compound(s), probably ***Zr_4Pb***, are formed on the surface until the whole sample is destroyed. The solubility of Zr in the eutectic was found very high, with a low value for the heat of solution. From experiments with Ti-Zr alloys, much lower 'solubility'-values were derived than for pure zirconium. The effect will be discussed below with alloys. Diffusion coefficients were in an expected range.

List of experiments with **zirconium**
Header line temperatures °C, other numbers hours exposure time.

400	450	500	535	550	600	645
.	62	.	.	.	.	.
.	140	.	.		.	.
.		.	262	.	252	.
.	476	496	.	.	450	.
.	476	.	.	.	.	.
.	.	.	.	610	.	.
.	.	821	792	.	826	.
1110	1006	.	.	.	1100	1150
.	1320	1514	.	.	1100	.
2110	1700	1826	.	.	.	.
2470	2320	2000	.	.	.	.
.	3013	.	.	.	.	.
.	3466	.	.	.	.	.
.	.	.	.	.	.	.
.	6200	.	.	.	.	.

Fig.Zr-1

Steady state dissolution rate of Zirconium

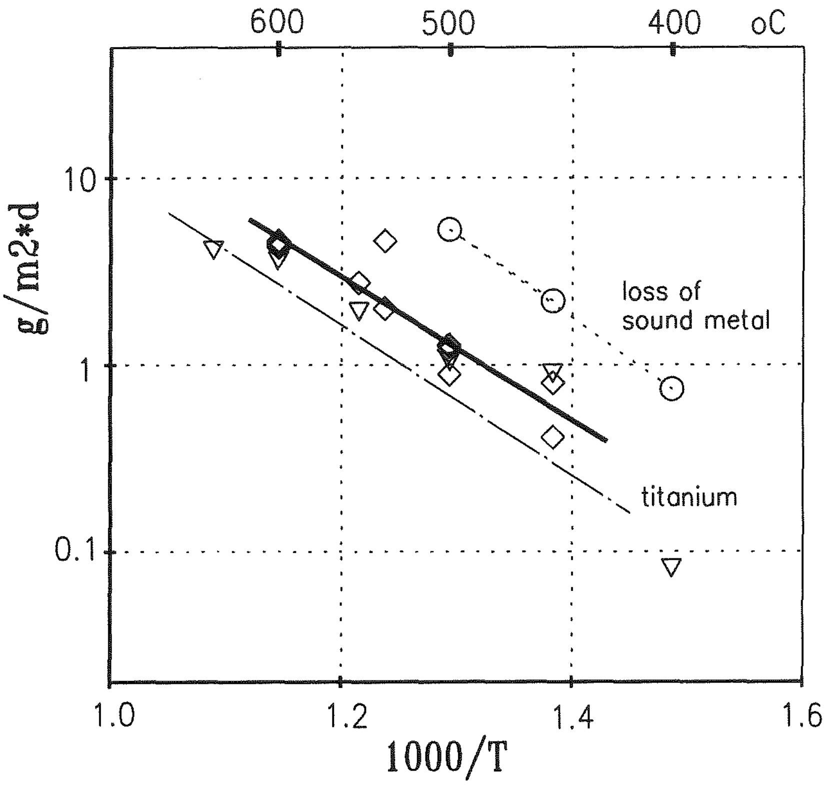


Fig. Zr-2

Solubility of Zr in Pb-17Li

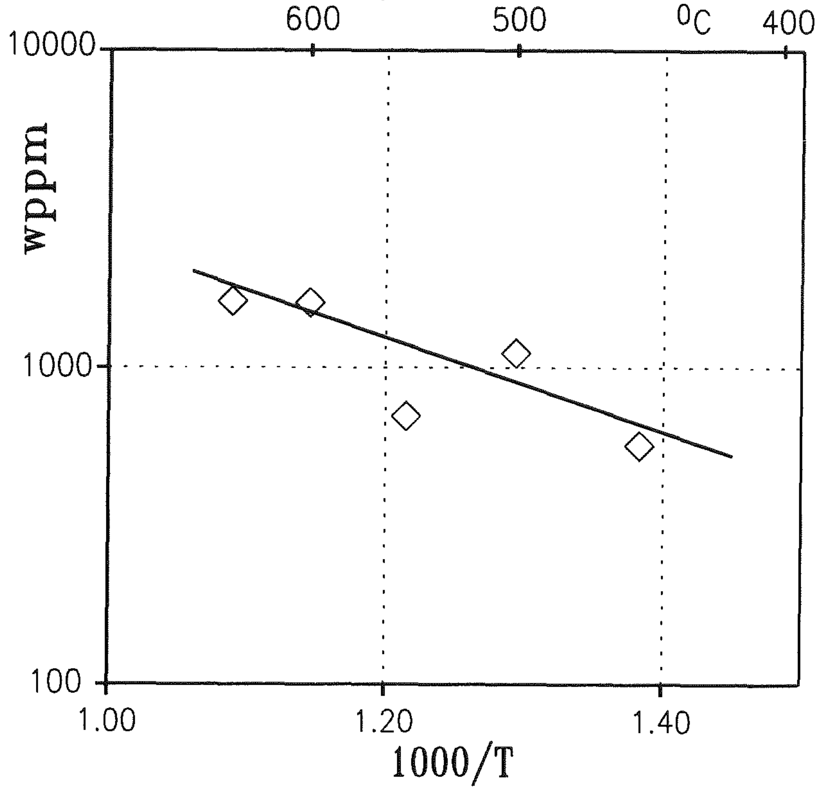


Fig. Zr-3

Difussion coefficient

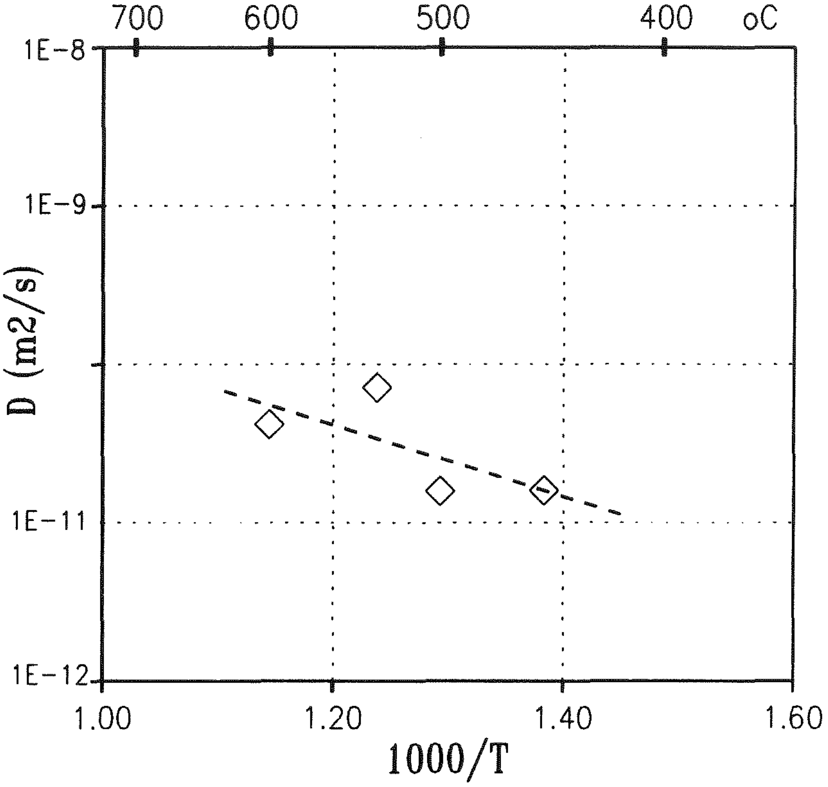
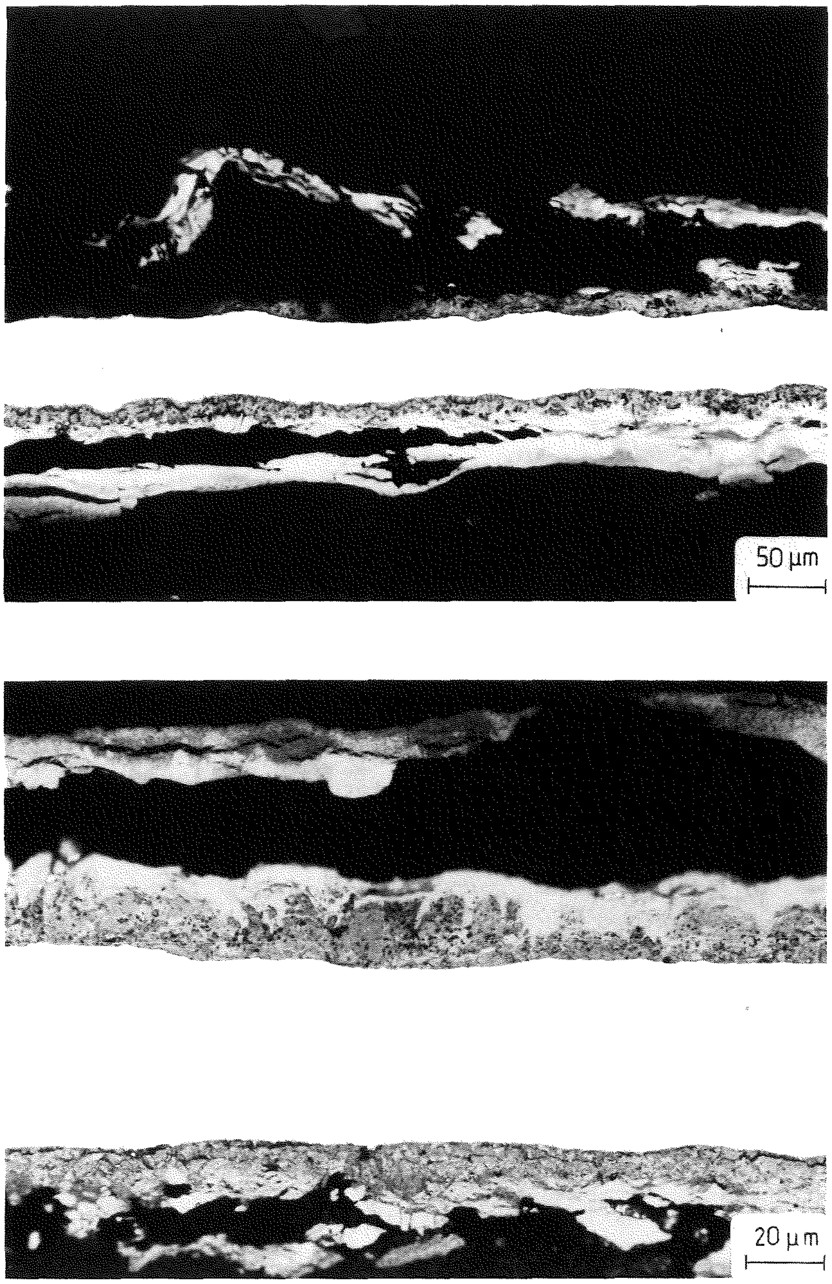


Fig.Zr-4

Zr metal after 1320 hours at 450 °C in Pb-17Li.
Lower picture:
Reaction zone removed by etching with
|21ml H_2O + 21ml HNO_3+ 6ml HF|.

Fig.Zr-5

Zr metal after 1514 hours at 500 °C in Pb-17Li.
Contact between reaction zone and sound metal partly lost.



Ti - Zr -alloys

Ti and Zr form mixed crystals over the whole concentration range at all temperatures (12). It was reported that also the ternary compound $(Ti/Zr)_5Pb_3$ exists over the entire concentration range of Ti/Zr (63,64). A new intermetallic compound Ti_3Pb_2 was identified in our work in experiments with Ti (23). To investigate if a replacement of Ti atoms is also possible in this compound, Ti-Zr alloys were tested.

1. Experiments

Ti/Zr alloys with 11, 26, 33 and 75 at.% Zr were fabricated by arc melting the components under vacuum. The alloys were degassed and annealed at 700 °C at a final pressure of 10^{-5} mbar for 2 hours. Only experiments at 500 °C were performed.

2. Results

The **table** summarizes some results.

Dissolution rates were similar to those of the pure metals. Crystals, as in case with pure titanium, were formed only with Ti concentrations in the alloy higher than 66 at.%. It is clearly visible from Ti/Zr ratios that in these crystals Ti was replaced by Zr, equivalent to the atomic fraction in the alloy. The compound can be written $(Ti/Zr)_3Pb_2$ with X(Ti) higher than 0.66.

An other point of investigation was the equilibrium concentration of Ti and Zr in Pb-17Li as a function of mole fractions in the alloy. The results are included in the table.

Ti concentrations are independent on X(Ti). The average value of 54 wppm Ti is only slightly higher than the value for Ti metal (41 wppm). The concentration is controlled by a formed Ti-Pb compound rather than by the composition of the alloy. This compound can not be that of the crystals because of different Ti concentrations with different alloys. Also this compound is not formed with lower Ti concentrations in the alloy (s.table), while the equilibrium concentration is the same. Even if not investigated we think that the compound of the surface reaction zone has always the composition Ti_2Pb. This compound is controlling the concentration in solution.

Concentrations of Zr, however, are clearly a function of X(Zr) in the alloy, **Fig.TiZr-1** .[10] Dividing appm Zr by X(Zr) would give the solubility for 100 % Zr. The average value for this solubility is 480 appm or 250 wppm. This is 3.5 times lower than found with Zr metal. X(Zr) determines the equilibrium concentration of Zr in the eutectic. Otherwise, if the same assumptions as for Ti are made, the reaction layer on Zr should have different compositions. This, however, was not seen by chemical analysis. Therefore we assume that the chemical activity of Zr in the alloys is lower than X(Zr).

---

[10] In this figure appm were used to be compared with X(Zr).

3. Summary

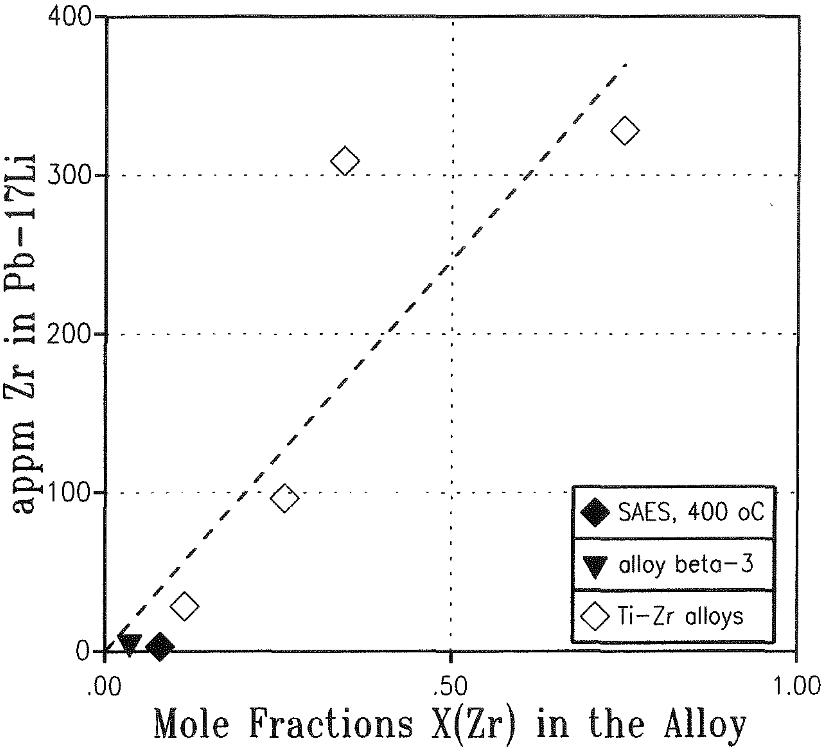
Generally, the behaviour of Ti-Zr alloys in eutectic Pb-17Li is similar to the behaviour of the two metals. In the crystals, up to 30 at.% of Ti atoms can be replaced by Zr. The intermetallic compound can be written $(Ti/Zr)_3Pb_2$. The compound $\mathbf{Ti_2Pb}$ at the sample surface is controlling the equilibrium concentration of Ti in solution. It should have a constant composition independent on Ti concentrations in the alloy. The saturation concentration of Zr on the other hand is proportional to X(Zr). From this, a solubility for Zr at 500 °C in the eutectic of 250 wppm is calculated, 3.5 times smaller than found with pure Zr-metal.

Results from experiments with titanium alloys at 500 °C.

alloy at.%	 ratio Ti/Zr	Composition of crystals (at.%) Ti	 Zr	 Li	 Pb	 ratio Ti/Zr	Conc.in Pb-17Li (wppm) Ti	 Zr
Ti								
100	-	57	-	0.4	42.6	-	41	-
88.7	7.85	47	7.2	0.4	46	6.5	32	15
74	2.85	41	14	0.4	45	2.9	75	50
67	2.03	-	no crystals formed		-	-	63	160
25	0.33	-	"		-	-	58	170
0	(Zr)	-	"		-	-	-	870
Alloy beta-3								
Ti-87.6 Zr- 3.6 and Mo- 6.8 Sn- 2.0	24.6	53	2.8	0.4	43	19	51	3
		There are also 0.27 at.% Mo and 0.63 at.% Sn in the crystals.						
TiVAl alloy-1			Al	V			Ti	Al
Ti 86.2 V 3.6 Al 10.2		35.7	40.6	0.27	23.4		47	5

Fig. TiZr-1

Zr in Pb-17Li (500 oC)



Alloy Beta-3

A higher stability in Pb-17Li was expected from alloy Beta-3 (Goodfellow) because of its molybdenum content. The composition of the alloy, used in our experiments, was

Ti	77.5 wt.%	=	87.6 at.%
Mo	12 wt.%	=	6.78 at.%
Zr	6 wt.%	=	3.56 at.%
Sn	4.5 wt.%	=	2.05 at.%

This alloy was tested in many experiments over a wide range of temperature and exposure time.

Results

The behaviour of this alloy was nearly identical to the behaviour of pure titanium. The incubation time before dissolution started seemed to be longer, exact data are lost. Steady state dissolution rates as well as equilibrium concentrations of Ti in the eutectic, were identical. The concentrations are shown in **Fig.Beta-1** together with the solubility function for pure titanium. The equlibrium concentration for Zr fits into **Fig.TiZr-1.**

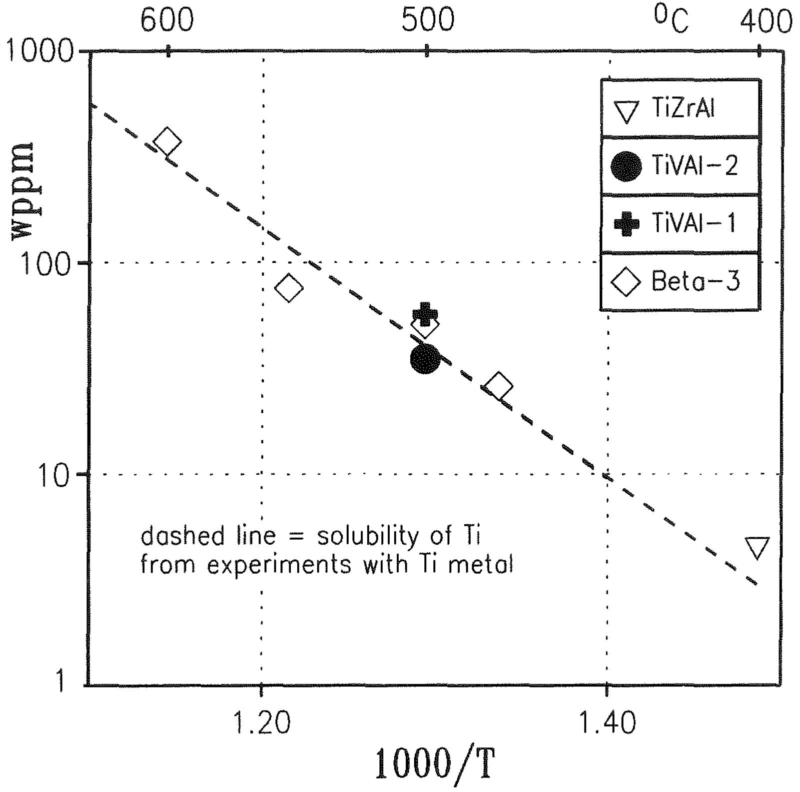
Crystals were formed on surfaces with the same rate as in case with pure titanium. In the table, given with Ti-Zr- alloys before, crystals from Beta-3 metal are included. From this it is evident that Ti can be replaced not only by Zr but also by Mo and Sn. Metallographic and microprobe investigations show a reaction zone at the surface and below crystals. In this zone Mo and Sn are enriched, probably an effect of Ti and Zr leaching.

Summary

In spite of the Mo content, the behaviour of alloy Beta-3 is not better than the behaviour of titanium metal. Also this alloy cannot be used as a tritium getter in the eutectic. Ti atoms in the crystals can be replaced not only by Zr but also by Mo and Sn. In a reaction zone at the surface and below crystals, Mo and Sn are enriched because of Ti and Zr leaching from the alloy.

Fig. Beta-1

Equilibrium concentration of Ti in Pb-17Li



dashed line = solubility of Ti from experiments with Ti metal

Alloys of Ti-V-Al

Ti-V-Al alloys are often used for hydrogen gettering from a gas phase. Two of these alloys were investigated. The compositions were

	alloy-1 (MBH)	alloy-2 (Goodfellow)
Ti	90 wt.% = 86.2 at.%	76 wt.% = 70.5 at.%
V	4 wt.% = 3.61 at.%	13 wt.% = 11.3 at.%
Al	6 wt.% = 10.2 at.%	11 wt.% = 18.1 at.%

Experiments were performed at 400 and 500 °C, with exposure times up to 2900 hours.

2. Results

Some results are included in the table given wit Ti-Zr alloys before. Also the behaviour of these alloys in the eutectic was controlled by dissolution of Ti and the formation of reaction zones and crystals. In addition **aluminium** was leached from the alloys.

Typically with alloy-2 the following amounts were dissolved from a sample :

at 400 °C. , 3000 h : 1.4 mg Ti and 1.6 mg Al
at 500 °C. , 850 h : 2.0 mg Ti and 1.8 mg Al

A large fraction of this Al was accumulated in the crystals. The concentration in Pb-17Li at 500 °C was only 5 wppm Al, much lower than expected from Al-solubilities and mole fractions. Alloy-1 and alloy-2 gave the same concentration. Mass transfer of Al to the crucible wall was also detected.

The titanium concentration in Pb-17Li was the same as for Ti metal. The 500 °C values are included in **Fig. Beta-1** and in the table. In fact, all titanium alloys as well as Ti metal gave the same Ti concentration in the eutectic. This was discussed before with Ti-Zr alloys.

Because of its low solubility no **vanadium** was detected in the molten eutectic.

Fig. TiVAl-1 and **Fig. TiVAl-2** show metallographic cross sections of the alloys after exposure to Pb-17Li. Reaction layers at the surface as well as crystals were formed with about the same rates as in case with pure titanium. In the table, the composition for an example is included. It is evident that not only Ti but also Pb can be replaced by other metals. Amazing is the high Al concentration.

3. Summary

Also these alloys cannot be used as a tritium getter in the eutectic. Besides titanium also aluminium is leached from the alloys. The Al concentration in the eutectic, however, is low. This metal is bound in the intermetallic compound of the crystals and transported to the crucible wall. With all alloys and with Ti metal, the same Ti concentrations were found.

Fig.TiVAl-1

Alloy TiVAl-1
after 1060 hours at 500 °C in Pb-17Li.
Lower picture:
Reaction zone removed by etching with
|100ml H_2O + 5ml HCl+ 5ml HF|.

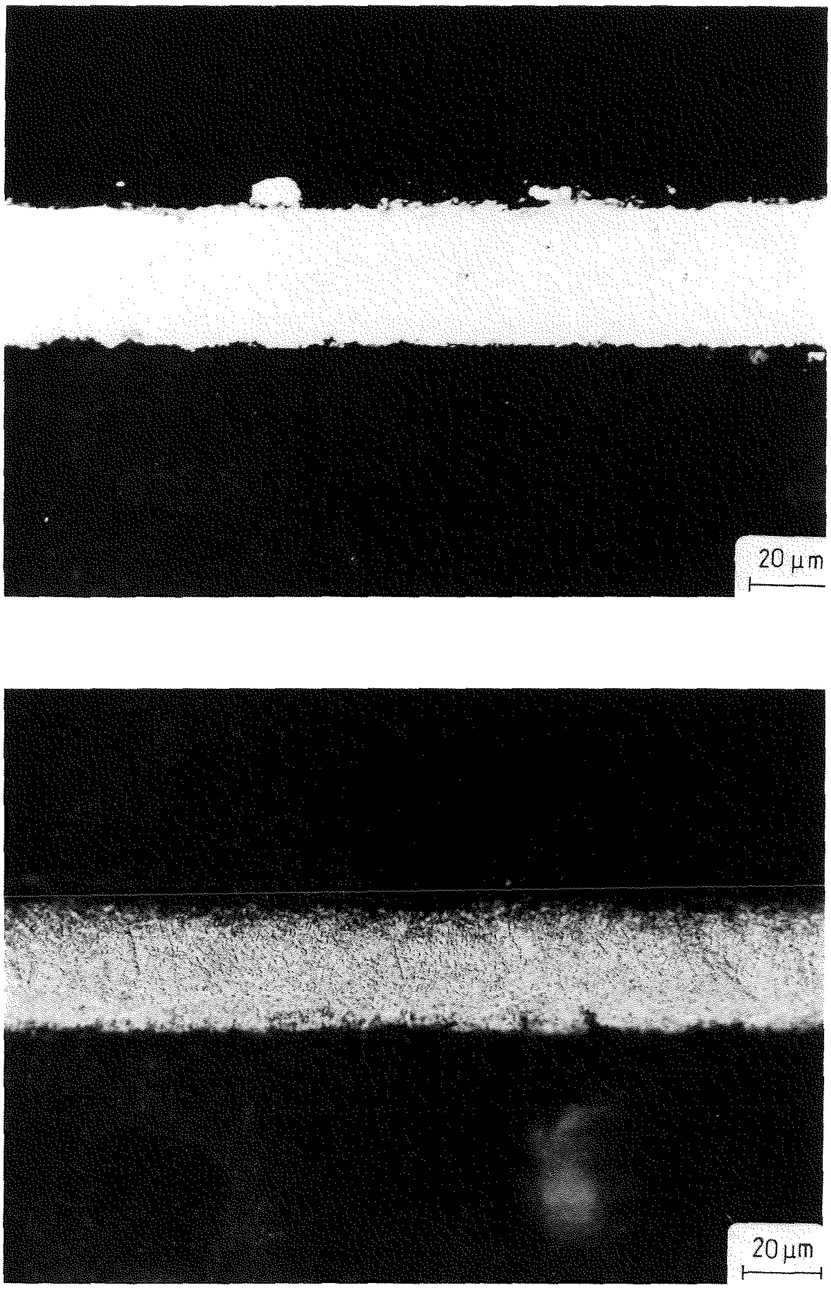
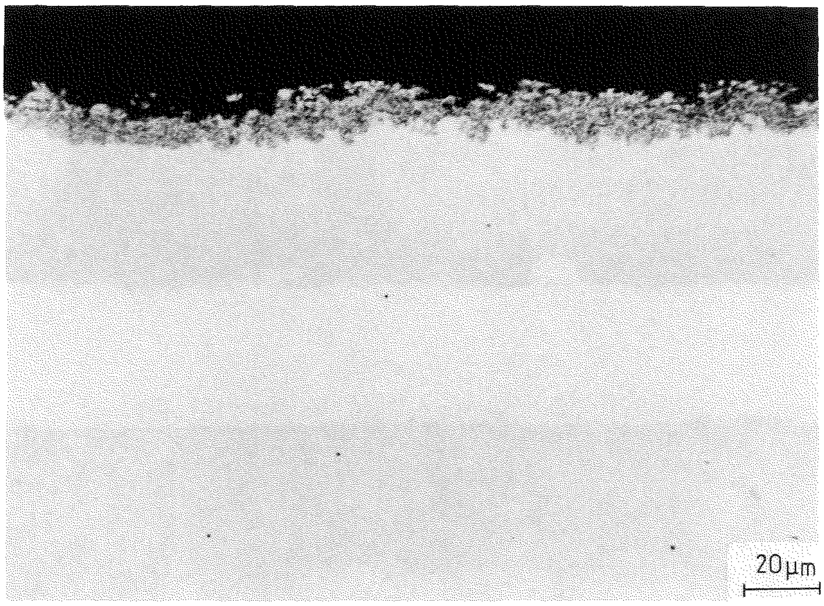
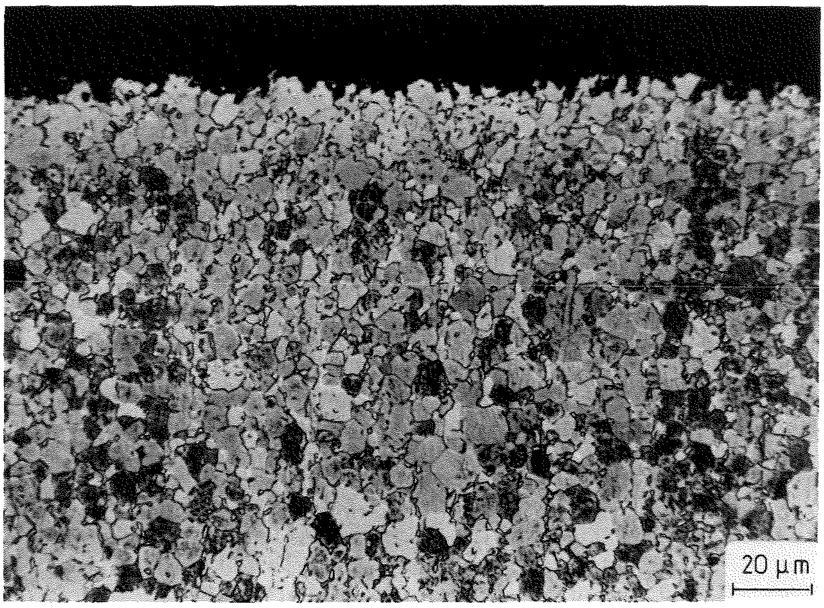


Fig.TiVAl-2

Alloy TiVAl-2
after 840 hours at 500 °C in Pb-17Li.
Lower picture:
Etching as before.





Alloy of Ti-Zr-Al

Probably the best getter materials for extraction of hydrogen from gases are alloys of Ti-Zr-Al. These alloys are fabricated from SAES, Milano. They are delivered in form of sintered material on a substrate metal, have a very large active surface and are used at temperatures below 100 °C. Type SAES-121 was used in our experiments, it was in form of an 0.1 mm thick layer on Mo metal.

The compositions of the alloy was

	SAES-121		
Ti	82.8 wt.%	=	86.9 at.%
Zr	14.5 wt.%	=	8.0 at.%
Al	2.8 wt.%	=	5.1 at.%

Activation was done by heating for 10 minutes to 500 °C. Experiments with Pb-17Li were performed only at 400 °C with exposure times up to 3000 hours.

2. Results

As with the alloys described before, the dissolution rate is nearly identical to pure titanium : Ti-metal = 0.12 , SAES-121 = 0.20 g/m^2*d. Ti is leached from this alloy with 0.10 g/m^2*d. Of course, the actual dissolution rate for the alloy will be smaller if using the 'active surface' instead of the geometrical one. But this 'active surface' in contact with Pb-17Li is not known. Therefore, the geometrical surface is used.

Also the behaviour of this alloy in the eutectic was controlled by the dissolution of Ti. Even if no reaction zone or crystals were seen in these tests, the concentration of Ti in the eutectic was 4.5 wppm, a value expected for pure Ti **(Fig.Beta-1)**. The Zr concentration was only 1.5 wppm, very low if compared with Zr metal. But even this value would fit into **Fig.TiZr-1**, keeping in mind that it was obtained for 400 °C.

Aluminium was leached out with a rate of 0.07 g/m^2*d, nearly that of Ti. Similar as in the case with Ti-V-Al alloys, the concentration was found with only 4 wppm, much lower than expected for pure Al metal. Al was mainly deposited at the crucible wall.

The getter layer remained intact until about 1000 hours. The sintered particles, however, are growing. **Fig.TiZrAl-1** and **Fig.TiZrAl-2** show this effect. After longer exposure times the sintered getter alloy gets dispatched from the Mo-substrate. No more investigations were done.

3. Summary

Also SAES-121 cannot be used as a tritium getter in the eutectic. The adherence is lost after longer exposure time at 400 °C.

Again the Ti dissolution is controlled by the Ti-Pb compound. No crystals were found (too low temperature), this may be caused by the low temperature (s.chapter titanium).

Besides Ti also Al is leached from the alloy. The Al concentration in Pb-17Li, however, is as low as in the case with TiVAl alloys.

Fig.TiZrAl-1

SAES-121 on Mo
after 2016 hours at 400 ^{0}C in the gas phase
above Pb-17Li.
Structure identical to 'as received' material.
Getter particles removed during etching.

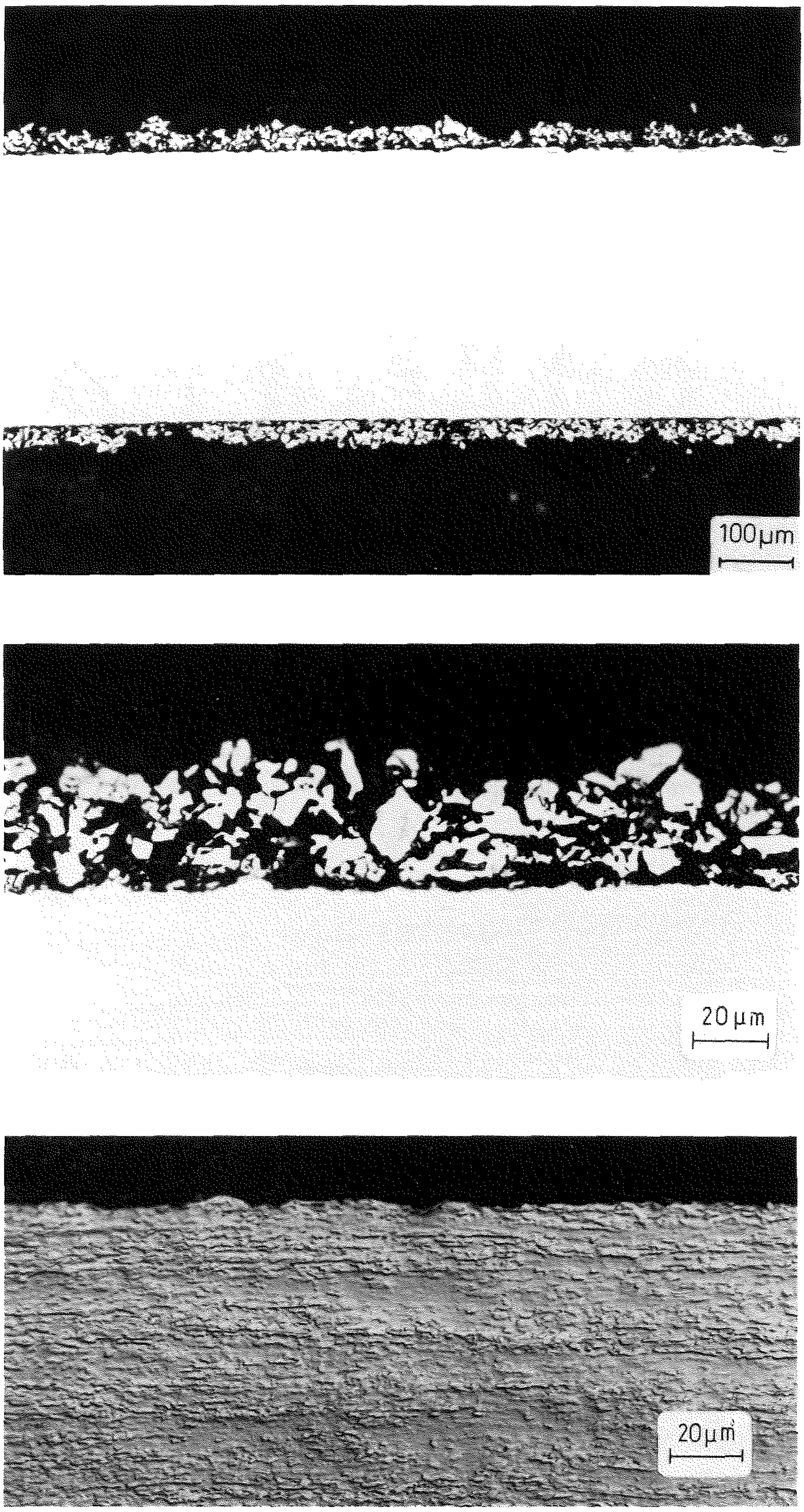
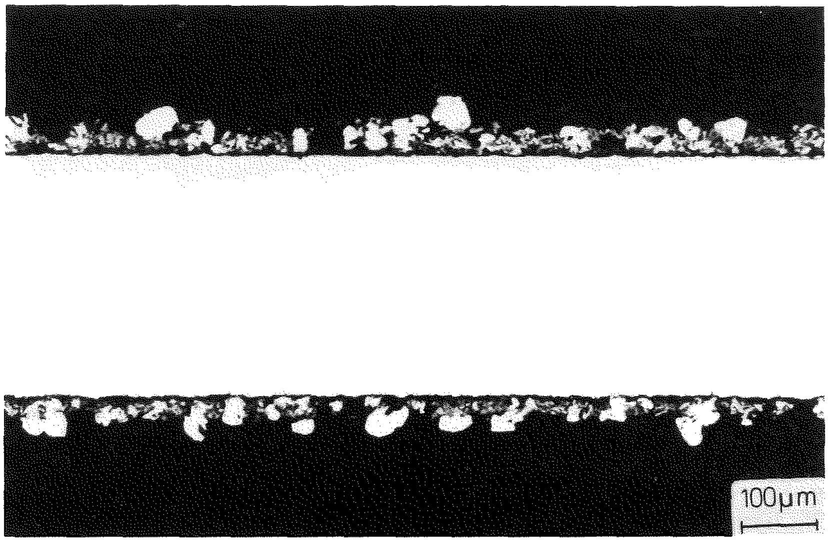
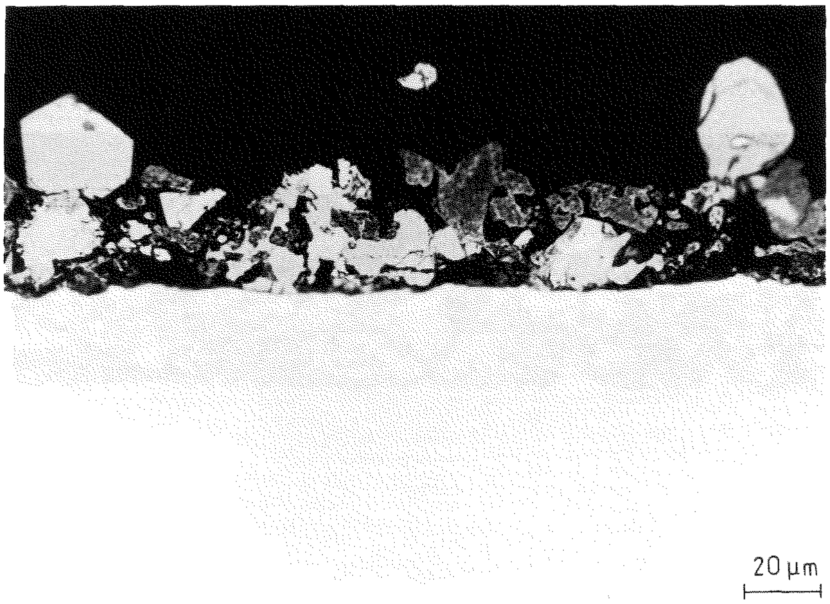
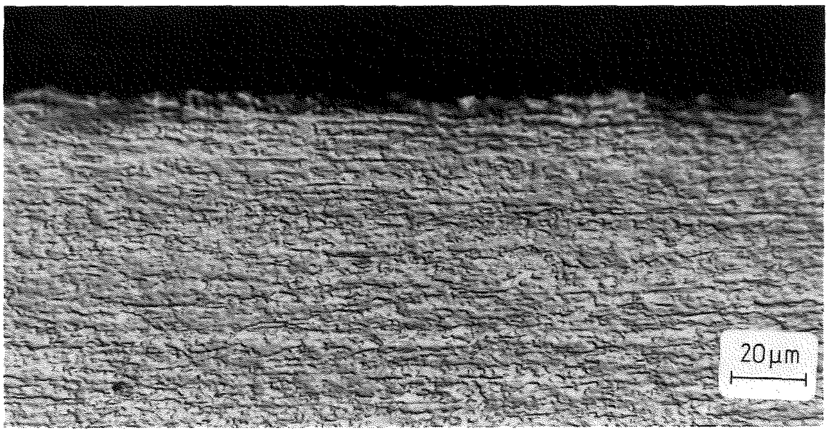


Fig.TiZrAl-2

SAES-121 on Mo
after 2016 hours at 400 °C in Pb-17Li.
Getter particles removed during etching.







Other alloys, steels

Mo-Re alloys

These alloys were described before in chapter Rhenium. They are probably more stable than Mo-metal (59).

TZM

TZM (Plansee) is often used instead of pure Mo because of its better workability. It contains 0.5 wt.% Ti and 0.1 wt.% Zr in Mo. It was found as stable as Mo metal. After 1000 hours at 600 °C Ti and Zr could be detected in the eutectic, but the values were only 0.1 wppm Ti and 6 wppm Zr. Because of the low dissolution rate, these elements were assumed not to be in equilibrium with the solution. There was no reaction zone visible.

TZM can be used for Pb-17Li systems like Mo metal.

Austenitic stainless steels

Austenitic stainless steels with different composition (steel 4571, 4300 and others) were tested at the beginning of the experimental program. Many corrosion experiments were performed with austenitic steels. Ref.(72) is given as an example. All effects, especially leaching of Ni and the formation of a ferritic surface layer, were also found in our experiments. We have reported at a workshop (33) about a compound **MnNi**, found in thermal convection loops at the spot with lowest temperature. In the meantime this compound was identified in other facilities und proposed to remove manganese from the eutectic (35). The compound could not be seen in isothermal compatibility tests. That means the solubility of this compound at experimental temperatures is high.

Because there were no new effects no results will be given in this report.

Ferritic steel 4922

This is the steel of the TRITEX facility in our laboratory (38). The steel contains 12 % Cr, 0.5 % Mn, 0.3 % Ni, it is stabilized by 1 % Mo and 0.3 % V. First results from static compatibility tests were published in 1988 (60).

Results

A too long time passed since the investigation of this steel, not all data are now understandable any more. Generally observations are in agreement with the literature for ferritic steels.

A two step dissolution is shown in **Fig. 4922-1** with a higher dissolution rate at the beginning as found for most metals in our experiments. The steady state dissolution rate is given by

$$\ln R = 4.06 - 5195/T$$

(R in $g/m^2 * d$). The heat of activation is -43 kJ/mol.

Chopra (74) found also for ferritic steels a faster dissolution at the beginning, but the mechanism may be different. Tortorelli (11) found only a linear weight loss with time while Borgstedt observed a long incubation time with much lower disslolution rate than under steady state conditions (50).

Inspite of such odds, steady state dissolution rates are compared with corrosion rates of ferritic steels in flowing and static Pb-17Li (**Fig. 4922-2**). Tas (72) found 1988 that all data fit between 2 lines, a factor of 28 apart. Newer values from Sannier (76) and Borgstedt (77) fit also between these lines. As expected for static tests our values are lower. A few values from Tortorelli (78) for static corrosion of HT-9 fit better to our function (values taken from ref.(6)).

In equilibrium at 550 ^{0}C the eutectic contained 3 wppm Fe, 2 wppm Cr, 0.8 wppm Mn and 15 wppm Ni.

The equilibrium concentration for iron is higher than obtained with alpha-iron metal (see Fig. Fe-3), but still in the range of values from the literature. Also, dissolution rates are higher than for pure iron. In loop TRITEX (69) particles with different Fe : Cr ratios were found. Therefore we assume that in case of steel 4922 not iron but **Fe-Cr compounds** are dissolved.

Using mole fractions X for chemical activities of the elements in steel and solubility functions from Barker(8), 8 wppm Mn and 12 wppm Ni are expected in solution. The Ni value was found. **Nickel** is in an ideal solution in the steel, it is clearly leached out. A nickel depleted zone should exist at the surface, but this was not seen (**Fig. 4922-3 and 4**). The Mn value is too low, pointing to non-ideal behaviour of this element in steel. No solubility function is reported for chromium. Sample (6) and Barker (8) found widely scattered data between 2 and 18 wppm, corresponding to 0.3 to 2.5 wppm are expected for experiments with steel 4922. The found value is in this range.

No 'metallographical' reaction zone is seen (**Fig. 4922-3 and 4**). At higher temperature and longer exposure time, the roughness of the surface increases. This process probably continues with more dissolution, as seen by Borgstedt (50) for steel X18CrMoVNb 12 1 in PICOLO loop.

However, a 'chemical reaction zone' was found. During the eletrolytical purification process, more material is dissolved than from fresh (and equally heat treated) steel. Such an effect was described before for pure iron and other metals. Typically 0.05 microns were removed from a sample after 2000 hours at 550°C. This reaction zone is proportional to exposure time and thicker at higher temperatures.

Summary

The ferritic steel 1.4922 gets dissolved by an even dissolution process. The dissolution rates are lower than seen with flowing Pb-17Li, but higher than those of pure iron. Also iron 'solubilities' from 4922 experiments are higher than obtained with pure iron.

No reaction zone can be seen with metallographical examinations. A thin chemical reaction zone is identified. There is clear leaching of Ni from the alloy. Nickel is in ideal solution in the steel, while manganese is not.[11]

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[11] More investigations were done from TRITEX samples. The results will be published in an other paper (69).

Fig. 4922-1

Dissolution of steel 4922 at 550 oC

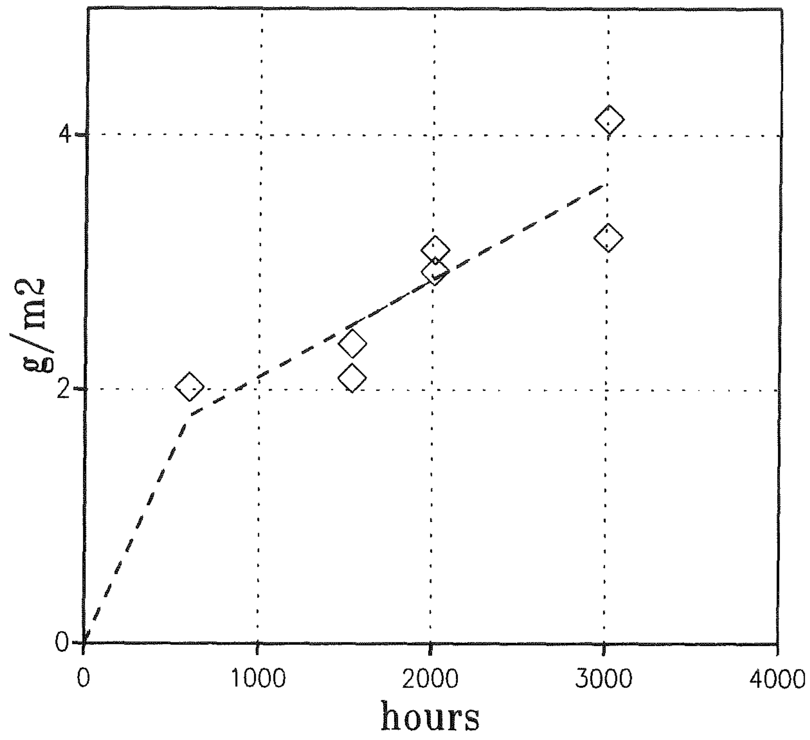


Fig.4922-2

Corrosion of ferritic steels in Pb-17Li

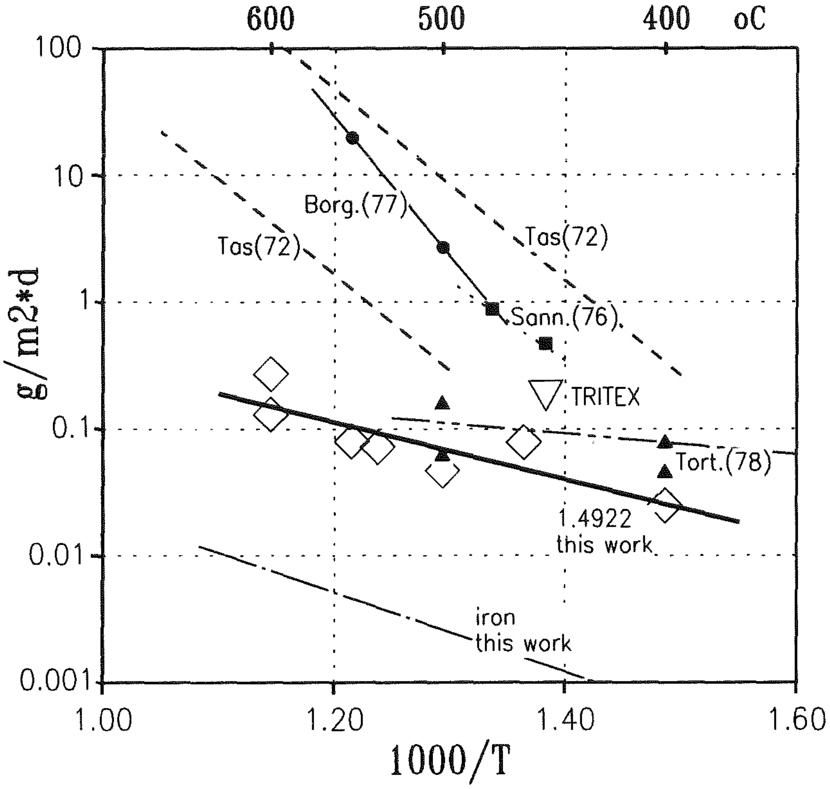


Fig.4922-3

Steel 4922
after 1138 hours at 400 °C in Pb-17Li.
Two positions.
Etching with
|100ml ethanol + 4g picric acid + 1ml HCl|.

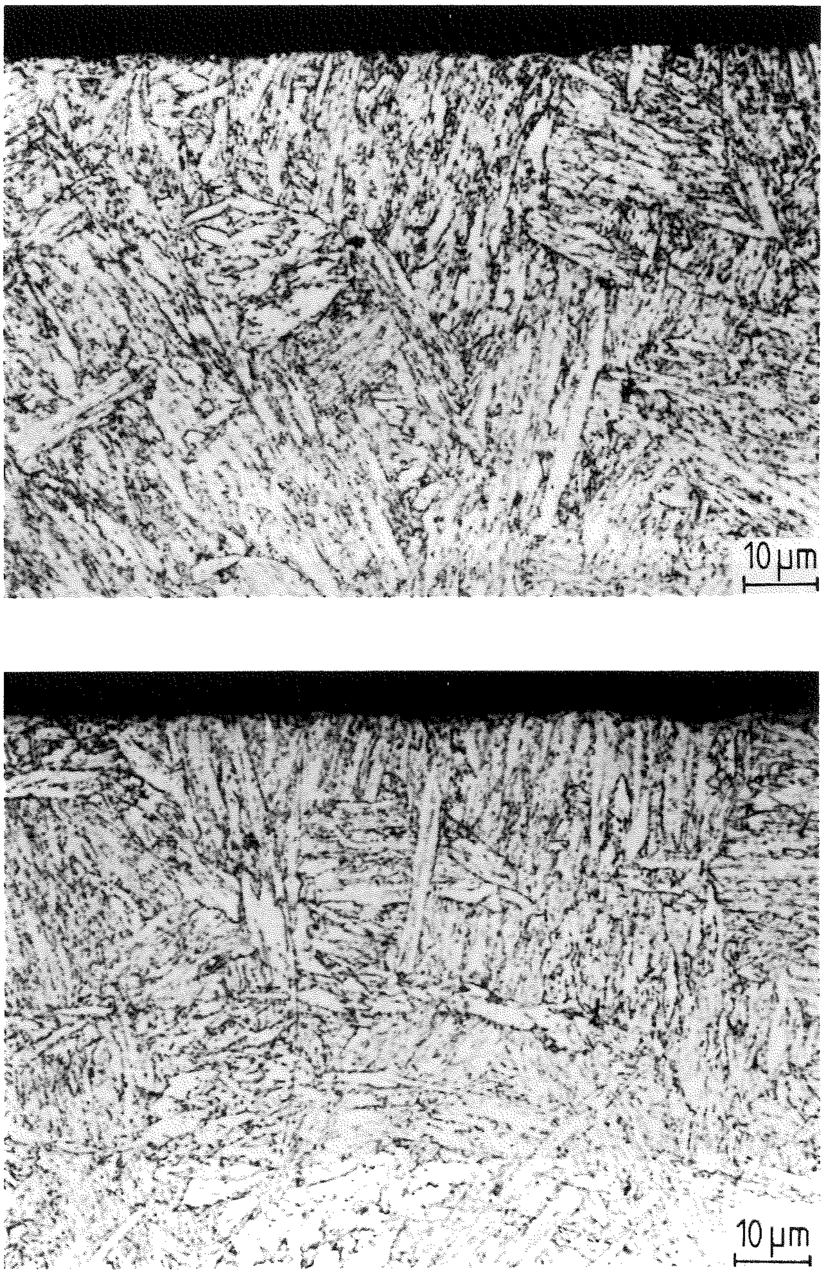
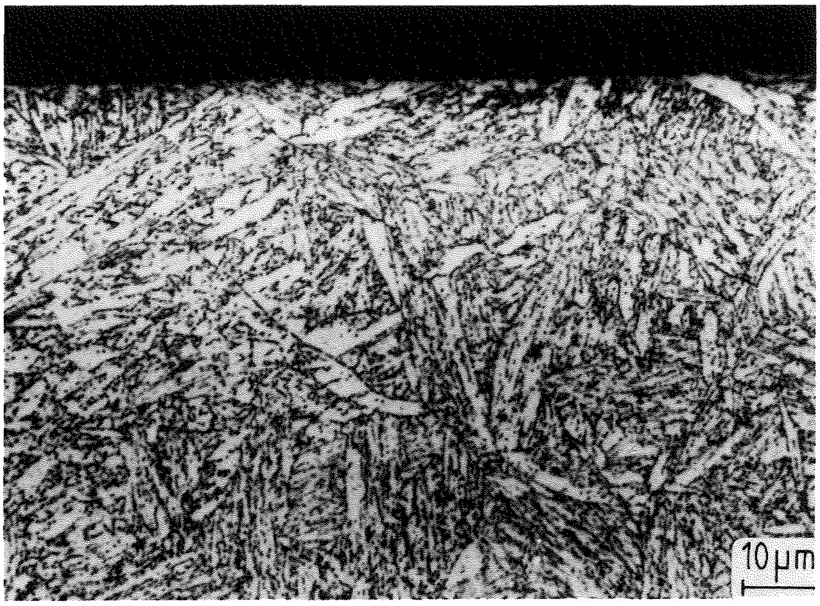
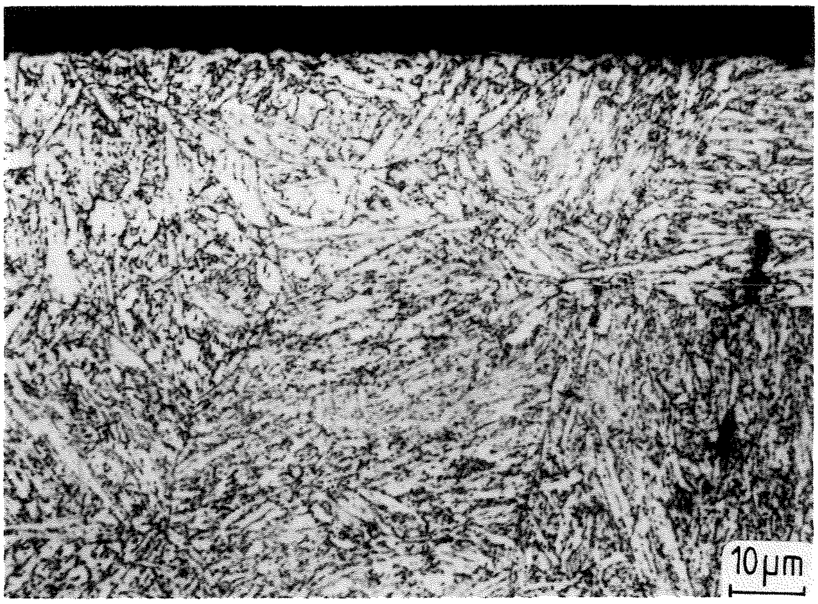


Fig.4922-4

Steel 4922
after 1536 hours at 550 ^{0}C in Pb-17Li.
Two positions.
Etching as before.





Mo coatings

Metallic coatings are widely used to protect less noble metals against corrosion in atmosphere or aqueous solutions. In liquid metal systems coatings are of limited value. Instead of easy to understand electrochemistry, more complicated dissolution processes and solubilities are important. Furthermore, because of the usually applied high temperatures, mutual diffusion of the metals has to be considered.

Mo coatings on stainless steel 316 were studied in connection with sodium cooled reactors (75). While the corrosion rate of steels in sodium at 700 °C was reduced, poor adherency of the Mo layer was found. Blisters were formed and the coating peeled off.

Asher (36) has tested Mo and other coatings on steels at 700 °C in liquid lead. With the exception of Al, no coating was successful to protect the steel against corrosion. There was always an 'uptake of lead' by the samples, the authors describe the effect of 'lifting, spalling and flaking' of the coating.

In liquid lead systems at high temperatures, Mo coatings on stainless steel were studied by Block (37). The main problem besides adherency was the diffusion of nickel trough the Mo layer. This is not only caused by the high solubilty of Ni in lead. With high Ni concentration in the steel, well formed crystals of Ni grow at the surface after only 100 h at 1100 °C.

1. Experiments

In spite of this discouraging results from the literature, some Mo-coated getter metals were investigated. As discussed before, Metals like Y, Ti or Zr cannot be used directly to extract tritium from the molten mixture. The metals were coated by 5 mikron Mo by different companys: Pansee, Goodfellow, Kammerer, mostly by PVD techniques. The goal was to protect the metals against corrosion, but keep the resistance against tritium permeation low. The results with different coating techniques were identical. This is in agreement with observations by Asher (36). Therefore, companys or coating techniques are not mentioned any more in this report.

Experiments were performed mainly at 500 and 550 °C with exposure times up to 5200 hours.

2. Results

Yttrium - 5 mikron Mo

It was not possible to obtain good quality Mo coating on Y metal. Always the Mo skin was loose after cutting or bending of sample pieces. The problem is caused probably by an oxide layer at the Y surface. Therefore, not many experiments were performed. Mo did not protect Y, dissolution rates were very high and comparable with uncoated metal. e.g. samples were completely dissolved after only 100 hours at 500 °C, leaving the Mo-skin behind.

Titanium - 5 mikron Mo

Fig.Ti/Mo-1 gives an example for the dissolution of titanium without and with a Mo coating. In the figure, the formed crystals are not included. It can be seen that Ti is protected at 500 °C for nearly 1000 hours. But then the dissolution rate is the same as without coating. A metallographic examination, **Fig.Ti/Mo-2** , shows that after extended exposure time the Mo is partly detached, the Ti metal shows a reaction zone as seen on pure Ti and the same kind of crystals are formed on the surface of Mo as before on Ti.

Discussion

Mo is protecting Ti only for a short time. Then Ti is diffusing through the Mo coating, dissolution rate and formation rate of crystals are the same as for uncoated Ti. The protecting time may be long enough at lower temperature for using coated Ti in Pb-17Li. It can however not be used as a tritium getter because the tritium recovery from the getter metal has to be done at least at 600 °C . At this temperature, however, Ti with or without coating is destroyed within a short time because also lead is diffusing through molybdenum.

Alloy Beta-3 - 5 mikron Mo

The behaviour of Mo-coated alloy Beta-3 was identical to the behaviour of Mo-coated titanium. Therefore, no results are given in this report

Zirconium - 5 mikron Mo

Fig.Zr/Mo-1 shows the dissolution of Zr without and with a Mo coating at 500 °C, **Fig.Zr/Mo-2** at 550 °C. There is clearly a protection effect at the lower temperature. But at 550 °C the behaviour is similar to titanium : Zr is protected only for a short time; then the dissolution rate is the same as without coating. A metallographic examination was done for one sample. **Fig.Zr/Mo-3** shows only a thin Mo layer remaining. We do not know where the missing Mo was gone, e.g. if it was dissolved in the Zr metal. No more investigations were done.

Discussion

At 500 °C, Zr can be protected for some time by coating with Mo. The behaviour at higher temperatures is similar to titanium : after an initial time the same dissolution rate is found as for uncoated Zr. Zr can not be used as a tritium getter because the tritium recovery has to be done above at 600 °C . At this temperature Zr with or without coating is destroyed within a short time.

3. Summary

The investigated thin Mo coatings protect Ti and Zr only for a short time against corrosion. As the uncoated metals also the coated metals cannot be used as getters for tritium extraction because the tritium recovery has to be done at too high temperatures.

Fig. Ti/Mo-1

Dissolution of titanium at 500 oC
without and with Mo–coating

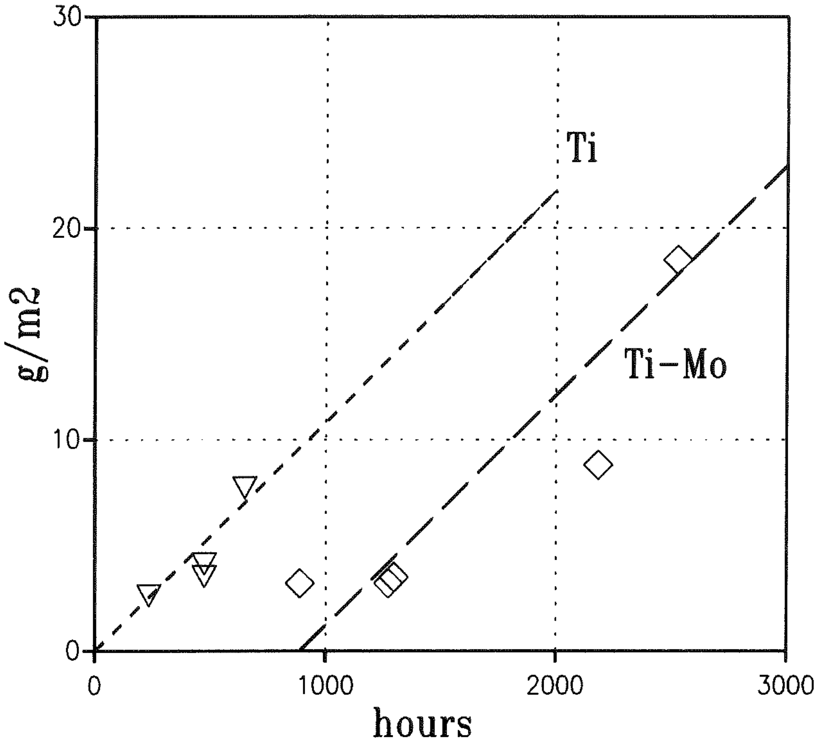
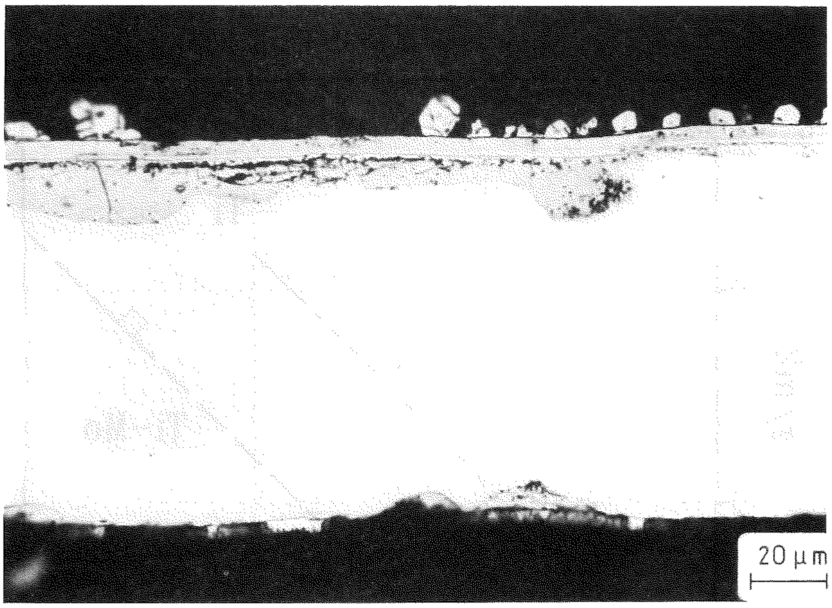


Fig.Ti/Mo-2

Mo coating on Ti after
1000 hours at 500 ^{0}C in Pb-17Li.
Two positions.



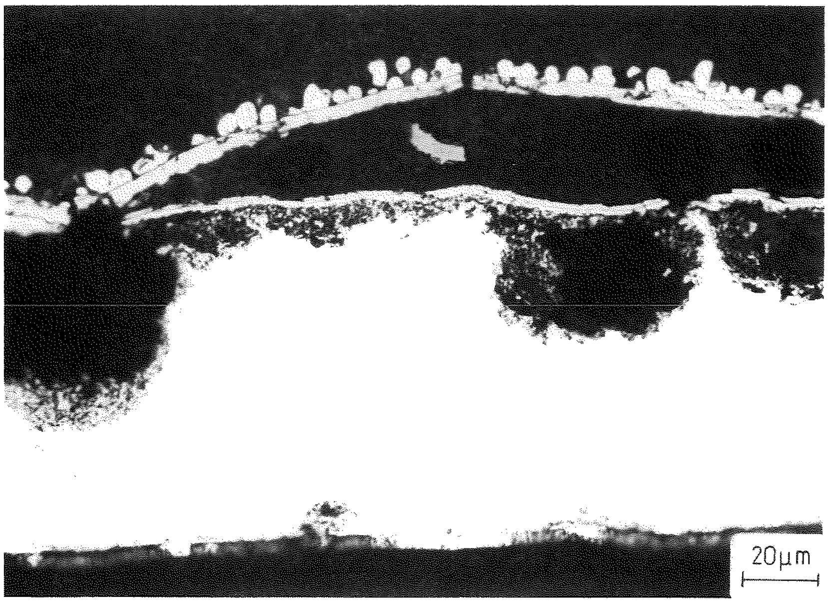


Fig. Zr/Mo-1
Dissolution of zirconium at 500 oC
without and with Mo-coating

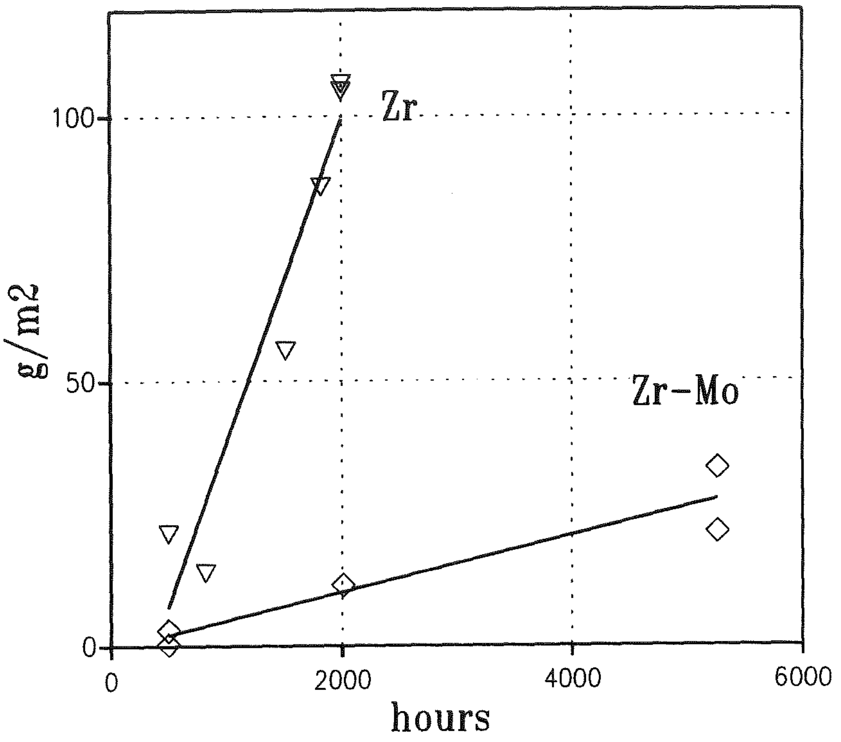


Fig. Zr/Mo-2
Dissolution of zirconium at 550 oC
without and with Mo-coating

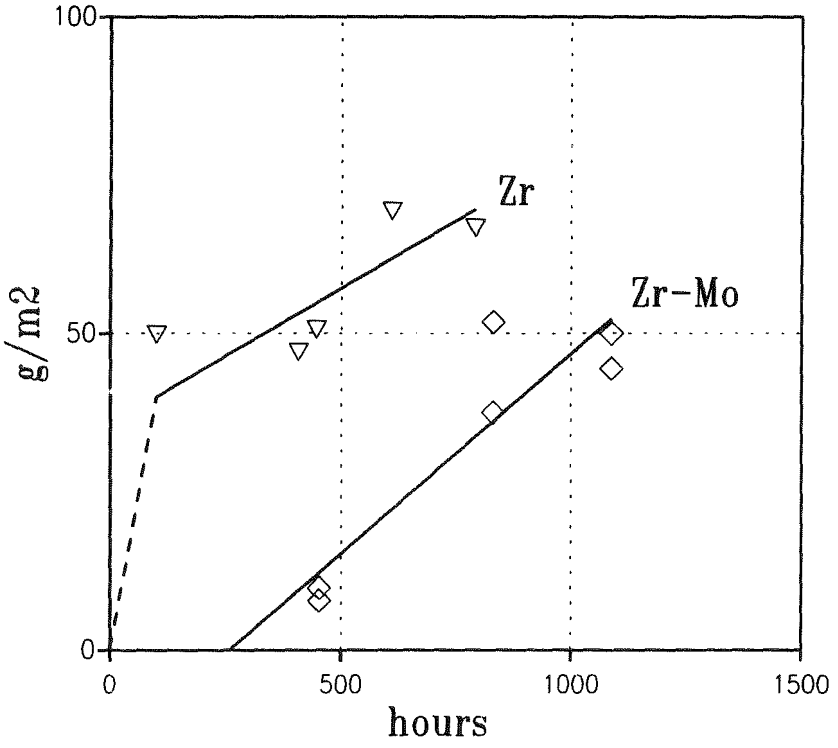
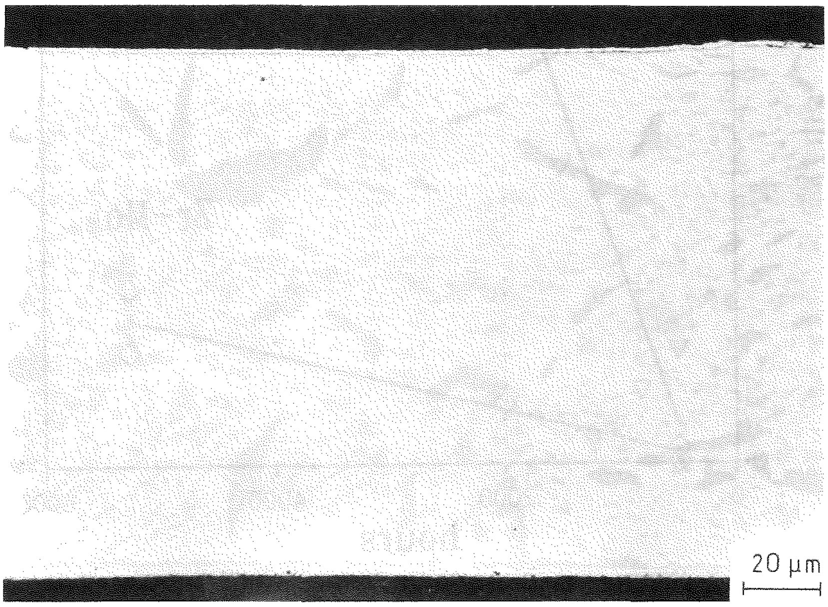
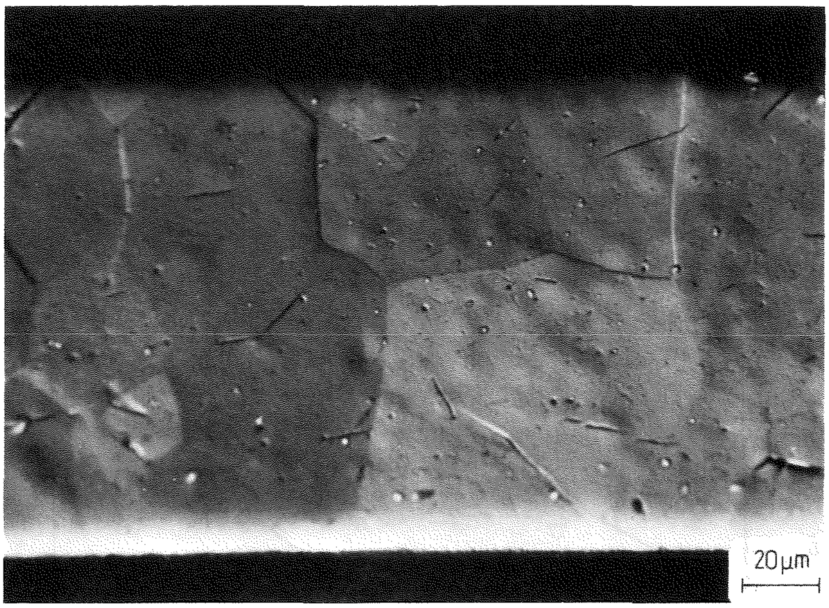


Fig.Zr/Mo-3

Mo coating on Zr after
500 hours at 500 ^{0}C in Pb-17Li.
Lower picture etched as zirconium.





Part-III : Description of experiments

1. Used Materials and preparation

1.1 Eutectic mixture Pb-17Li

The eutectic mixture Pb-17Li was obtained in 1986 from Metallgesellschaft, Frankfurt. It was shipped in a very coarse way, the surface of the ingots had to be removed mechanically. After this all handling of the eutectic was done inside of an argon filled glove box. Oxygen and humidity concentrations in the box atmosphere were measured contineously and kept below 1ppm. Nitrogen was measured occasionally and found up to 500 ppm.

Further purification of the eutectic was done by several times remelting, always removing floating crusts. There was no knowledge of the problem of segregation (7) at the time of this treatment. Therefore, the Li concentration was different in each experiment. However, analyzing the results in respect of Li concentrations showed no influence within the error range of data.

Chemical analysis was done mainly by ICP-AES (below). The following concentrations of elements were found :

Table 1 : Impurities in eutectic mixture Pb-17Li.
Except for Li, all values are given in wppm.

Li	0.62 to 0.77 wt.% (15.7 to 18.8 at.%)		
Na	28	Be	0.042
K	2.0	Mg	0.45
		Ca	1.55
		Sr	0.02
		Ba	0.01
B	0.88 (?)	Sn	0.07
Al	0.34 (?)	As	<0.4
Ga	<0.5	Sb	0.06
In	<0.5	Bi	53
Tl	1.9		
---	-----	Se	<0.2
Sc	<0.5	Te	0.02
Y	<0.01		
Fe	4.3	Cu	0.22
Cr	0.25	Ag	6.1
Ni	0.18	Zn	0.52
Mn	0.042	Cd	1.5
Co	< 0.5	Hg	<0.4
Mo	<0.05		
V	0.01		

Other elements were not determined. After crust removal during remelting, the eutectic was probably saturated with **oxygen** and **nitrogen**. Solubilities of these elements are very low (71,82) and further reduced during vacuum degassing (below). Also some used sample metals were getters for these gases.[12]

Brewer (25) points to a special problem when using molybdenum : the formation of very stable Mo-carbides. **Carbon** could be transported e.g. from iron samples to Mo. The role of carbon in Pb-17Li systems is not yet studied. Borgstedt assumes a very low solubility and, therefore, only negligible transport (3).

1.2 Crucibles and boats

Most experiments were done with Mo-crucibles. They were obtained from Plansee, pure Mo with <0.5 % impurities. The size was 25 mm diameter, 40 mm high with 0.5 mm wall. Crucibles were chemically etched and vacuum degassed at 700 °C for several hours at a final pressure below 10^{-4} mbar.

Only a few tests were done with crucibles of iron, tungsten or alumina. The metals were purified as described in Part-II. Alumina crucibles (Al-23, Friedrichsfeld) were cleaned with boiling HNO_3, heated in air to 900 °C to remove all organic material and vacuum degassed at 1000 °C for 10 hours to a final pressure below 10^{-4} mbar. They were cooled under purified argon.

Al_2O_3 boats were used at the end of exposure (below). Boats (Friedrichsfeld) were treated as crucibles.[13]

1.3 Sample materials

Sample materials were obtained from different companies. They were chemically cleaned and vacuum degassed for several hours until a final pressure below 10^{-4} mbar. Chemistry as well as the temperature of the vacuum treatment, was different for each metal. Details are given in Part-II. Some informations are lost. All volatile impurities were removed by this treatment. Furthermore for most of the investigated metals oxygen and nitrogen from the surface dissolved in the metal, leaving the best possible surface for the experiments. Beryllium metal was mechanically polished in some tests.

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[12] The color of samples and the appearence of the eutectic after exposure was an indication for trace amounts of O and N in an experiment.

[13] Because in some tests alumina reacted with Li from the eutectic, only a few experiments were done with alumina crucibles. The results are not included in this report.

2. Facility and experiments

Mo-crucibles with stripes of sample metals in Pb-17Li were heated in stainless steel capsules. **Figure 1** shows a drawing of a capsule, **Figure 2** a photo of the arrangement of crucibles. Because of heat reflectors and radiation shields the temperature across the crucible chamber was constant within ± 0.5°C. This should be good enough to avoid convection flows.[14]

2.1 Initial Setup

All handling of the eutectic was done inside of the argon filled glove box.

Crucibles were filled with Pb-17Li up to 20 mm high. The wetted Mo-surface was about 15 cm^2, 60 to 90 grams of eutectic were used.

Then sheets of sample were fixed in the molten metal with stripes of Mo as seen in **Figure 2.** The sample surface in contact with the eutectic was 3 to 8 cm^2. The surface to volume ratio, therefore, was similar to the crucible. Any contact between sample metal and crucible below the liquid metal surface was avoided. Otherwise often a reaction between the two metals caused a failure of the crucible. Such an effect is well known from sodium systems and observed by Khan (84) with steels and high melting metals in lead.

Still inside of the glove box and after solidificaton of the eutectic, crucibles were set into the holder and the capsule was closed. Up to 6 crucibles were placed in one capsule, often with different metals to be studied. The capsule was taken from the box to the laboratory.

The next step after a He-leak test was the degassing of the Pb-17Li. The capsule was evacuated and heated to the experimental temperature. Heating up had to be done very slowly to avoid bubble release of gases and splashing of the eutectic. The capsule was kept for several hours at a pressure below 10^{-4} mbar. Then the capsule was filled with Ar-6.0, further purified near the entrance by Oxisorb-S (Messer Griesheim). The procedure of vacuum degassing should also help wetting of samples, but there are no observations reported in laboratory notes.

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[14] Brasunas (15) mentioned that in crucibles with lead thermal convection can be expected at temperature differences of ± 2°C.

Figure 1: Facility for static compatibility tests

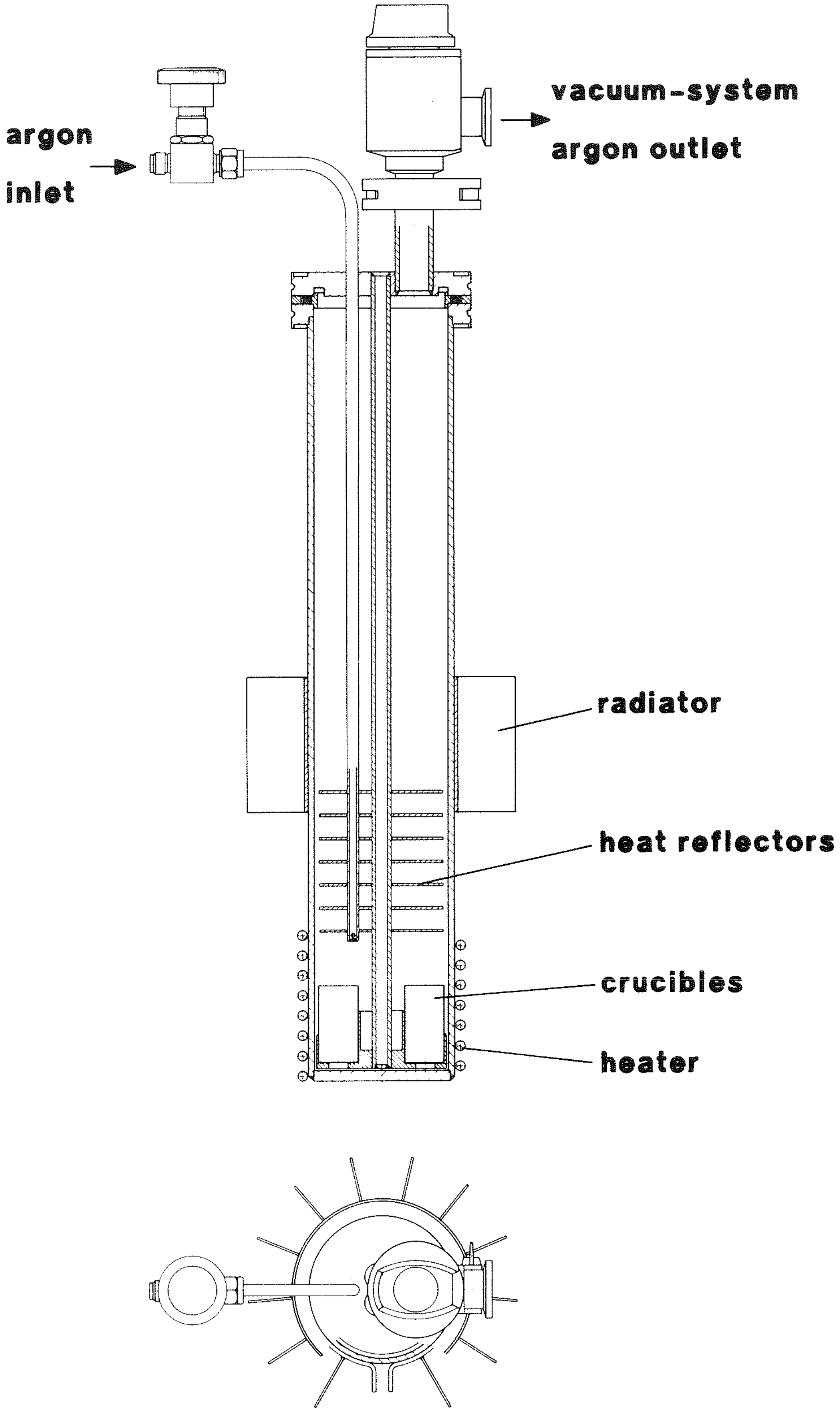
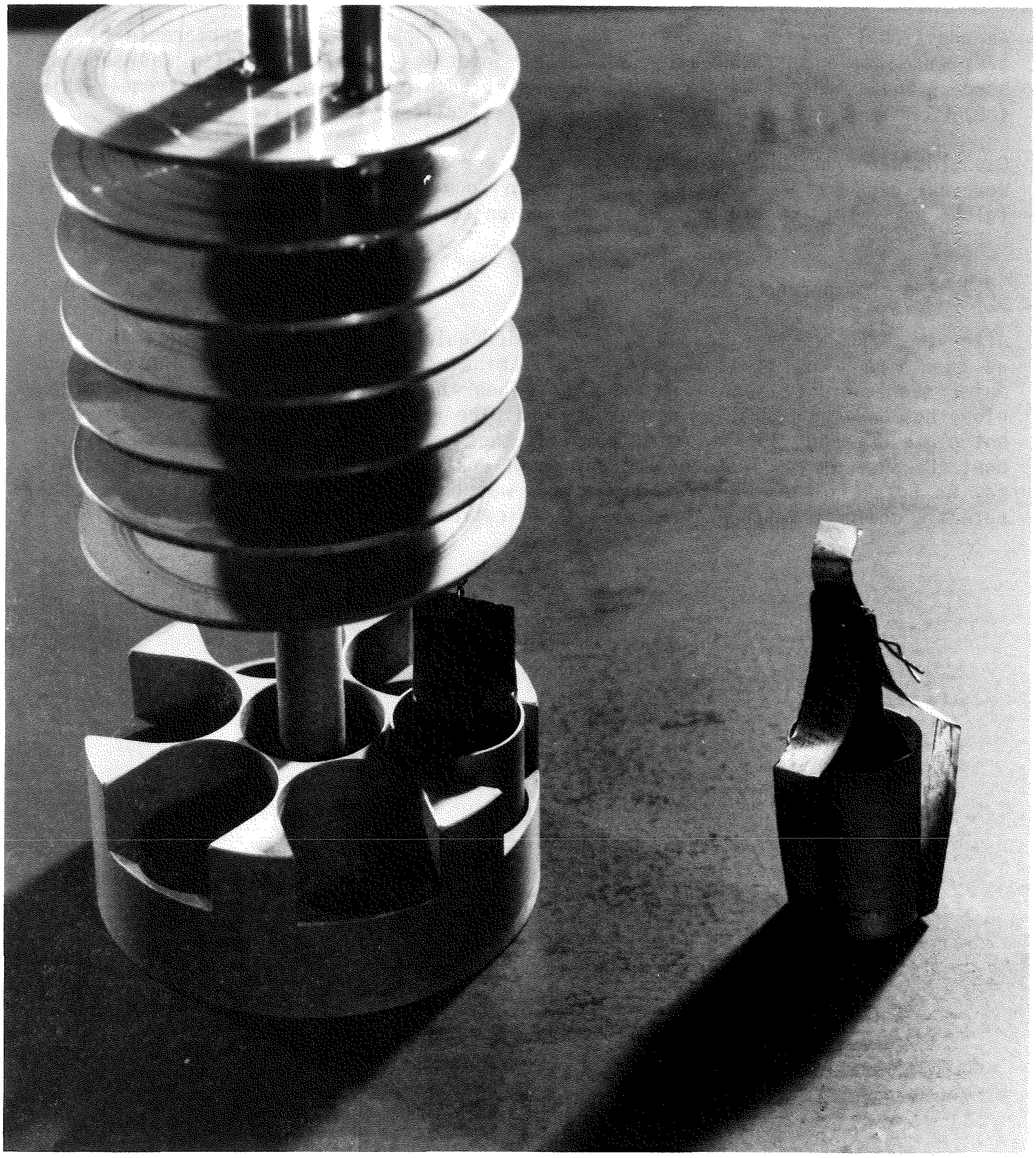


Figure 2: Arrangement of crucibles



2.2 Exposure

A number of investigated metals and alloys are getters for oxygen und nitrogen. The atmosphere in the capsule was therefore strictly controlled. It was found better to have an argon flow of 10 to 20 cm^3/min at an overpressure of 100 mbar than a sealed capsule. The gas leaving the capsule was analyzed from time to time with an electrochemical oxygen meter. The oxygen concentration was always below 1 ppm. Also humidity and nitrogen concentrations were below 1ppm.

An additional control for the purity of the atmosphere was the appearance of Pb-17Li and sample surfaces after exposure. Sometimes a slight tarnish was seen at samples and a haze of oxides at the eutectic. Such oxide layers were extremely thin (86).[15] In most cases, however, samples and eutectic were metallic clean.

Capsules were kept during exposure time at **one** temperature, constant within ± 1°C. However, capsules were cooled sometimes to room temperature to exchange crucibles (glove box). This should have no influence on results.

2.3 End of exposure

After the exposure time capsules were cooled quickly to room temperature. This was no quenching but it took only about 5 minutes to solidification. Therefore no major segregation effects are expected. Then the capsule was opend in the argon glove box and the crucibles were taken out. The eutectic mixture was remolten on a hot plate at about 350 °C. After removing the sample it was poured into an alumina boat. Because of the fast cooling and short contact time of Pb-17Li with the alumina, no uptake of Li, Pb or other metals was observed. There was no wetting, the eutectic could be taken away after solidification for analysis.

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[15] Because the small total amounts of O and N, properties of sample metals were not influenced.

3. Chemistry and analysis

Samples, crucible and Pb-17Li had to be prepared for analysis.

3.1 Purification of samples and crucibles

After removing a sample from the eutectic and pouring out the crucible at 350 °C, 4 to 8 mg/cm^2 remained at sample and crucible surfaces, corresponding to a layer of 4 to 8 microns. However, there was not always a homogenious layer of Pb-17Li at the surface. Depending on wetting, small droplets could remain, making the purification difficult. In the crucible often up to one gram remained in corners. This adhering Pb-17Li had to be dissolved and analyzed for the sample metal.

The purification of samples is a problem with liquid metal corrosion experiments in liquid metals. Especially the removal of lead and Pb-17Li is difficult without attacking the sample surface.

Normal **wet chemistry**, e.g. dissolving adhering eutectic in acids, is in most cases too aggressive. Only a few metals, when the electrolysis (below) was not possible, were treated by this way : Pb-17Li was dissolved in a mixture of 2% acetic acid with less than 1% H_2O_2 at 50 to 80 °C.

Often in corrosion experiments with Pb or Pb-17Li, samples are washed with molten **sodium** (17,50) or **lithium** (11,85). In our experiments we would have to use extremely clean Na or Li and dissolve it for analysis. To avoid handling of large amounts of alkali metals, this method was not tested.

Attempts were made to remove Pb-17Li by dissolving in **mercury** (36). Hg can easily be purified by destillation. At room temperature about 400 mg/cm^2 eutectic can be dissolved within one hour in 40 ml stirred mercury. Under the same conditions less than $2*10^{-4} mg/cm^2*h$ of metals like V, Nb, Ti, Zr, Hf, Mo or stainless steel get dissolved. Metals like uranium or yttrium dissolve or disintegrate in Hg.

The mercury method is complicated. Because of lithium it must be done in an inert atmosphere. Otherwise Li is oxidized and a black foam is floating on the surface. An attack of sample surfaces cannot be excluded. And finally the determination of trace amounts of metals in mercury is difficult. This method was therefore used only at the beginning of the experimental program to get clean samples for metallography.

Electrolytic method

With a few exceptions, adhering eutectic was dissolved under extremely mild conditions by an electrolytic method:

> The sample was used as anode, Cu-covered platinum as cathode. In most cases the electrolyte was a 10 % solution of ammonium-acetate. The potential of the cell was kept as low as possible, usually between 0.1 to 0.3 Volt. The cell current was measured to get information about the progress of dissolution and a possible attack to the base metal. The potential was high enough at the anode to dissolve lithium and lead. Standard potentials of the other metals are much higher.

A special technique had to be applied for the **cathode.** Lead was mainly deposited at the cathode, together with dissolved sample metal. It reacted there with platinum and could not be dissolved for analysis. Therefore Cu-plated Pt was used, the Cu dissolved after the electrolysis in nitric acid, the solution analyzed.

Figure 3 shows a typical time-current curve for steel 4922. The first sharp drop in the curve indicates the end of Pb-17Li dissolution. Then the **'chemical reaction zone'** is dissolved, followed again by a sharp drop of the current to values below 0.1 mA.[16] Of course, such 'ideal' curves were only found for well wetted samples with smooth layers of eutectic at the surface. Visual control during the electrolysis was important to detect droplets or thicker layers at parts of the sample or crucible.

Sometimes problems occured because of the very low voltage and copper dissolved from the cathode ! (Reverse flow of current.) In this case results were not used for data evaluations in Part-II.

The electrolytic purification could be used for nearly all metals and alloys. U and Y could not be treated because of too high dissolution rates. Also alpha-Fe gets dissolved to a larger extent. The dissolution rate of Mo, 0.005 mg/h, was just small enough to use the method for crucible purification.

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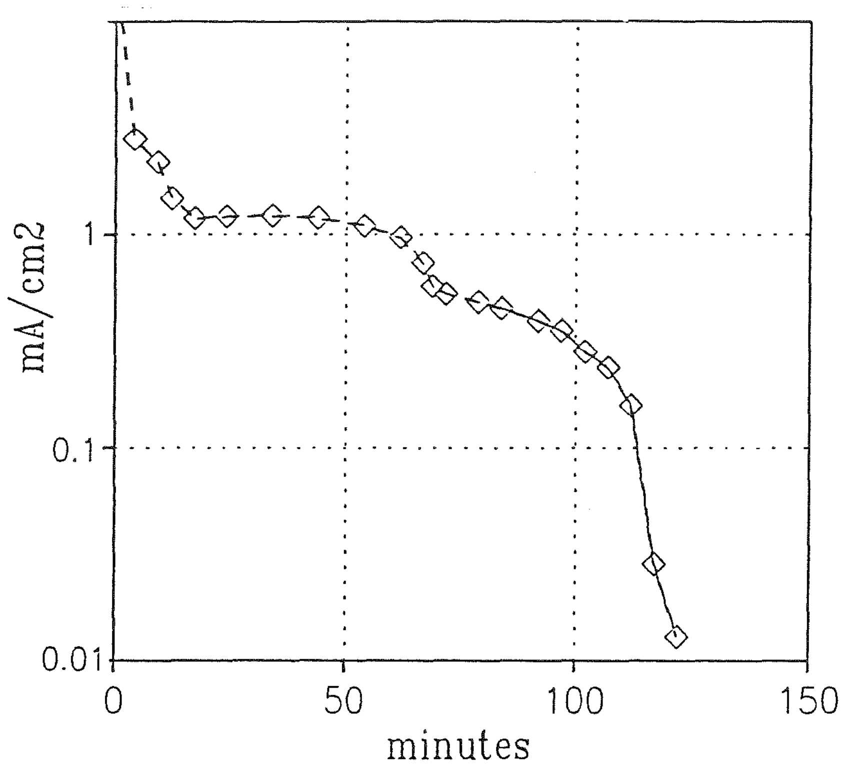
[16] In many cases, the 'chemical reaction zone' was too thin to be seen in this curves. In this cases it was identified by chemical analysis of the solutions.

Figure 3: Electrolytic purification of steel 4922.
0.1 Volt, 10% ammonium acetate solution.
Exposure of sample 3000 hours at 450°C.



3.2 Preparation for analysis

The solutions from the electrolysis could be used directly for ICP-AES analysis.

The bulk Pb-17Li, 60 to 90 grams, taken from the alumina boat, was dissolved in nitric acid. For this a special extraction technique was developed, allowing to use nearly **stoichiometric amounts of acid**. This was an important item because the acid contains trace amounts of metals. To minimize the amount of acid, therefore, means to minimize background effects.

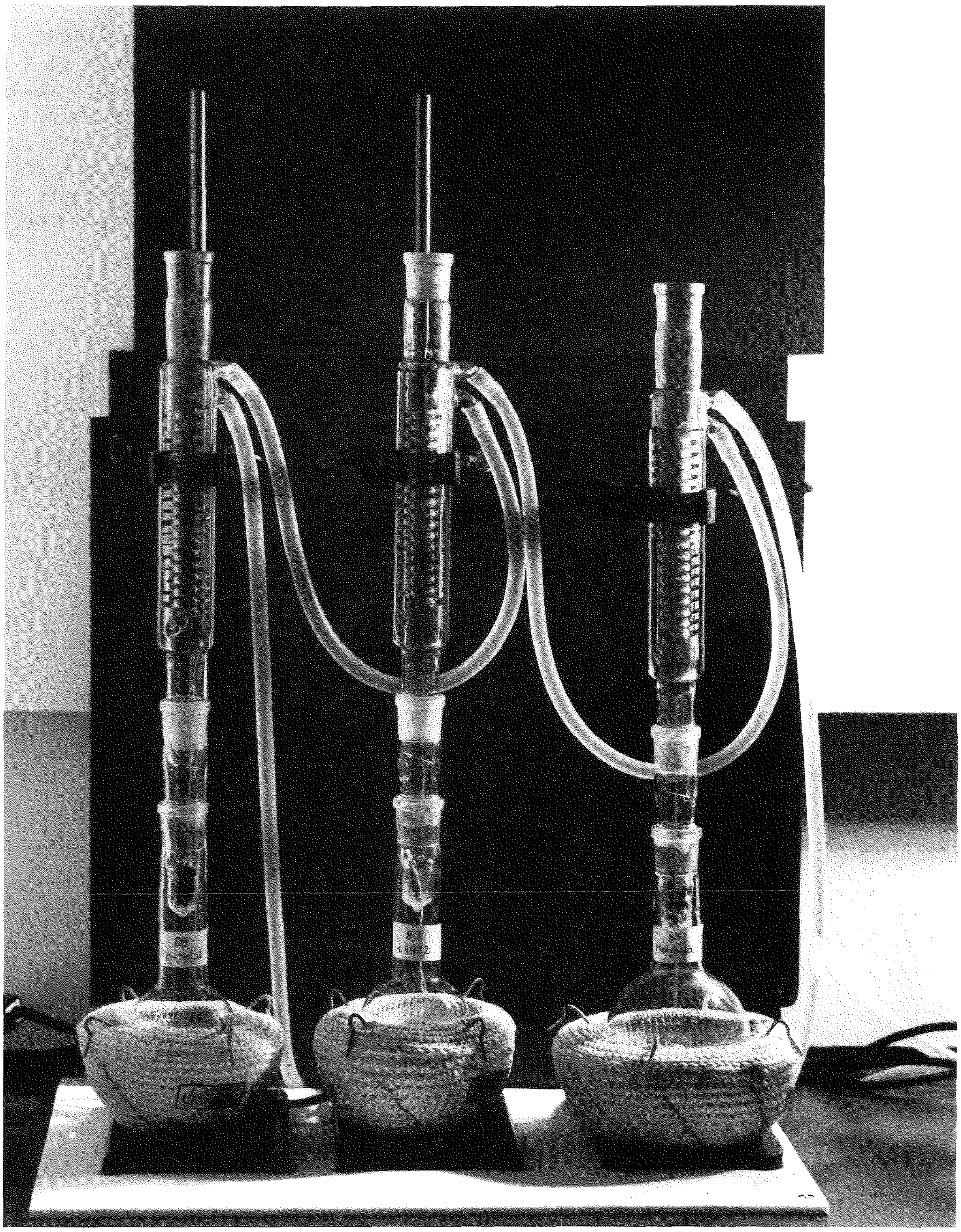
Extractor - Chemistry

Since about 1985 the extractor was used. **Figure 4** shows a photo of three extractors operating in parallel. While always clean recondensed nitric acid is dissolving the eutectic, lead nitrate is precipitating in the flask below. Only a small excess of acid is required. If a reaction stopped, water and/or acid could be added at the top without opening the apparatus.

Unfortunately in most experiments, excess nitric acid was evaporated after dissolution of the eutectic, $Pb(NO_3)_2$ dissolved in water, and lead precipitated as $PbSO_4$ by adding diluted sulfuric acid. Then the solution was adjusted to 1 liter. $PbSO_4$ settled within a few hours, the solution could be analyzed. No metals precipitated with $PbSO_4$ but the adjustment to 1 liter caused reduced sensitivity.

A modified lead-analysis procedure was applied in some cases to reduce detection limits: Excess acid with the dissolved elements were taken from the $Pb(NO_3)_2$ slurry, the latter washed with concentrated nitric acid. The combined acids were analyzed. By this way about 100 ml of solution could be measured instead of 1 liter, improving the detection limit by a factor of ten. (Only by this techique solubilities for Mo, Nb and Ta could be obtained.)

Figure 4: Extractors for dissolving larger amounts of Pb-17Li.



3.3 Analysis

Chemical Analysis

Analytical wet chemistry was in most cases chemistry with very low concentrations but with high concentrations of Pb and Li as matrix.

All solutions were analyzed by ICP-AES, using an ICP-6500 and later a PLASMA-2 of Perkin Elmer. The matrix of many solutions was crucial for ICP-AES : up to 30 % HNO_3 and 3 to 10 grams/liter Li and Pb each. But measurements up to 20 g/l Pb-17Li were possible without loss of sensitivity, using appropriate plasma conditions.

Blanks and standard solutions were produced by dissolving appropriate amounts of Pb-6.0 (Baker, Hereaus) by the same procedure, adding Li and desired elements from Merck or Spex ICP-standard solutions at the beginning of the dissolution process. For metals near the detection limit an addition method was applied.

Metallogaphy and other investigations

Many metallogaphic samples were prepared during the experimental program in our laboratory. The semi-automatic machines 'Planopol' with 'Pedemax' (Struers) were used. Most of the good pictures of Part-II, however, were prepared by Mrs.Echtle, 'Institut für Werkstoffkunde 1, Universität Karlsruhe.' Microprobe analysis was done in the 'Institut für Materialforschung' and the 'Institut für Mikrostrukturtechnik', both Forschungszentrum Karlsruhe.

4. Evaluation of results

For each experiment three values for the dissolved metal were obtained :

- amount of dissolved metal in the bulk Pb-17Li,
- amount of dissolved metal deposited at the crucible wall,
- amount of dissolved metal from sample cleaning.

From the first kind of data **solubilities** were derived. If the concentration in the bulk Pb-17Li was constant with time, saturation was attained. We assume that the diffusion profile across the crucible in case of isothermal mass transfer will have not much influence on results: saturation of most of the eutectic, lower concentration only near the crucible surface. There are no more informations about this profile from the experiments. From comparison with literature values for some elements, however, we think that the found solubilities are reliable values.

Dissolution rates were obtained from the amount dissolved in the eutectic and the amount from the crucible walls. This sum can be compared to **weight-loss** data from corrosion experiments. The dissolution rates became constant after an initial time. This **'steady state'** dissolution rates were used in this report to describe the behaviour of metals. Most often the dissolution was faster in the inital period. In a few cases, however, an incubation period was seen. Not many data points exist for the initial period; this period, therefore, is not discussed in this paper.

Even if steady state dissolution rates are of limited value for non-isothermal and loop systems, they allow at least to compare different metals with each other and to help in prediction of corrosion rates.

The amount dissolved during sample cleaning gives information about a **chemical reaction zone** at the surface. **'Loss of sound metal'** would be the sum of all three values, taking into account also formed reaction layers.

In the case of isothermal mass transfer the First Fick's Law is valid and **diffusion coefficients** can be calculated.This is discussed in detail in Part-I.

4.1 Units and definitions

ln	logarithm are always natural logarithm on base 'e'
temperature	centigrade ^{0}C, in Arrhenius functions K
time	hours or days
gas pressure	mbar
mole fraction	x

solubilities	wppm. Only in some cases appm are used. Because of low concentrations, appm can be approximated from wppm by **|appm = wppm * 176 /M|**. 176 is the molekular weight of the eutectic with 15.8 at.% Li, M the atomic weight of the dissolved metal.
dissolution rates	g/m^2*d. Steady state dissolution rates are obtained after an initial period. During the initial period dissolution is most often faster, but an incubation time was also seen. Dividing the values by the density in g/cm^3 gives mikrons/day. **Weight loss** as often given from corrosion experiments can be calculated, while **loss of sound metal** needs also informations about surface reaction zones.
Diffusion coefficients	m^2/s. They are derived from the First Ficks Law with the assumption of Co<<Cs at the deposition surface. Diffusion coefficients were calculated only if solubilities were measured at the same temperature.
temperature dependences	of thermodynamic data are given in form of the Arrhenius function: $\ln Y = A + B/T$ The heat of the process is given in kJ/mol.
reaction zones	Two kinds of chemical reaction zones are found for some metals. Chemical cleaning of samples gives information about a thin reactive surface layer. Metallographic examination shows thicker modified surface layers.

Abbreviations for experimental facilities

TCL = thermal convection loop
FCL = forced convection loop
BE = batch type experiment, sometimes stirred

Appendix

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