Forschungszentrum Karlsruhe
Technik und Umwelt

Wissenschaftliche Berichte
FZKA 6389

Corrosion and Oxygen Control

Minutes of the Workshop on Heavy Liquid Metal Technology

September 16 - 17, 1999
Forschungszentrum Karlsruhe, Germany

Edited by J. Konys

Accelerator Driven Systems (ADS)

KALLA
KArlsruhe Lead LAboratory

Institut für Materialforschung
Projekt Nukleare Sicherheitsforschung

Dezember 1999

Forschungszentrum Karlsruhe

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Agenda

Thursday, September 16, 1999

Time	Speaker	Topic
09:00	J. Konys	Welcome, Introduction
09:15	J. Knebel	Overview on ADS design

First session:Materials compatibility in lead and lead alloys
Chairman: G. Benamati, ENEA

09:45	H. Glasbrenner (FZK)	Behavior of different steels in stagnant lead at 600°C
10:15	H. Glasbrenner (FZK)	Corrosion investigations of steels in flowing lead at 400 and 550°C
10:45	C. Martini (Univ. Bologna)	Behavior of different steels in liquid Pb and Pb-Bi eutectic alloy
11:15-11:30	All	Coffee break
11:30	L. Soler Crespo (CIEMAT)	Behavior of martensitic steel in Pb-Bi: Preliminary results
12:00	V. Imbeni (Univ. Bologna)	Behavior of W and Mo in stagnant liquid Pb at 520°C
12:30	G. Müller (FZK)	Investigations on oxygen controlled liquid lead corrosion of surface treated steels
13:00-14:30	All	Lunch
14:30	P. Deloffre (CEA)	Corrosion studies in Pb-Bi liquid alloy
15:00	F. Balbaud (CEA)	Corrosion studies of steels in the presence of flowing liquid Pb-Bi
15:30-15:45	All	Coffee break
15:45-16:15	G. Benamati	Report of meeting on TECLA proposal for 5th F. P., Paris, September 13-14
16:15-17:15	All	General discussion: Materials compatibility problems in lead and lead alloys, identification of future activities
20:00	All	Dinner at Heinrich Hertz Gästehaus

Friday, September 17, 1999

Second session: *Analytical and technical problems with lead and lead alloys*
Chairman: *J. Konys, FZK*

Time	Speaker	Topic
09:00	C. Adelhelm (FZK)	Determination of impurities and oxygen in Pb and Pb-Bi
09:30	C. Fazio (ENEA)	Measurement of oxygen content in Pb and Pb alloys by means of laboratory technique
10:00	J. L. Courouau (CEA)	Physico-chemistry of Pb-Bi eutectic alloy characterization and on-line oxygen meter validation
10:30-11:00	All	Coffee break
11:00	L. Victori (IQS)	First steps in the development of an oxygen sensor for Pb/Bi melts
11:30	J. L. Courouau (CEA)	Studies on Pb-Bi physico-chemistry and associated technology
12:00-12:30	All	General discussion: Analytical and technical problems in lead and lead alloys
12:30-14:00	All	Lunch
14:00-15:00	All	General discussion: Analytical and technical problems in lead and lead alloys continued
15:00	All	End of workshop

Contents

1. Introduction

Forschungszentrum Karlsruhe has the great pleasure to welcome all participants to the **Workshop on Heavy Liquid Metal Technology** for use in Accelerator Driven Systems (ADS). The participants are coming from many countries throughout Europe: Italy, France, Spain, Sweden, Switzerland, Germany and the United States of America. But it is a real pity that the Russian colleagues could not attend this workshop, because of visa restrictions of the German embassy in Moscow.

Nevertheless, the objective of this workshop is to give metallurgists, chemists, physicists and engineers, working in different areas of science and technology of (heavy) liquid metals, an forum to present and to discuss the basic work and the need for future R&D in the field of ADS technology. This workshop is the 2nd event, following a workshop concentrated on thermohydraulics in heavy liquid metals, held in Brasimone, Italy, April 12-13, this year.

Many of the participants have a more or less intensive experience in the field of liquid alkali metals like sodium or lithium. The first contact with heavier liquid metals came with the beginning of experimental work within the International Nuclear Fusion Program, respectively the investigations concerning lead-lithium technology. During this work all of them have learned the differences in physical chemistry, corrosivity and safety, compared to, for instants sodium. FZK is very sorry to miss the Russian colleagues here in Karlsruhe because of their immense knowledge and experience in the area of lead and lead-bismuth technology.

First discussions between associations began to start in 1997 for a possible cooperation of future common activities in the field of lead corrosion. In 1998, together with intense discussions about Rubbia's concept for an ADS and the publication of the interim report of the technical working group on accelerator driven sub-critical systems, a strong push forward happened in the efforts to organize the R&D work in Europe within the 5th Framework Program. The area of this cooperation is titled: Hybrid systems for transmutation, and the proposal is called: TECLA, Technologies for Lead Alloys.

During the preparation of this proposal, everybody from each association who was involved in the discussions got to know about lacks in the basic knowledge and in the understanding about the behavior of materials in lead alloys. This included the fields of corrosion, structure protection, mechanical properties of structural materials in the presence of lead alloys, effects of irradiation, impurities control and thermohydraulics.

This workshop is therefore performed to exchange knowledge, experiences and to identify necessary future activities.

The workshop is organized in 2 different sessions:

- Materials compatibility in lead and lead alloys
- Analytical and technical problems with lead and lead alloys

The first session gives an overview on

- results of corrosion of steels in stagnant and flowing lead respectively lead-bismuth
- behavior of low solubility metals in lead
- oxygen control in liquid lead

The second session is focussed on

- analytical determination of impurities, especially oxygen, in lead and lead-bismuth
- development of electrochemical oxygen sensors
- physico-chemistry of lead-bismuth

Both sessions are followed by general discussions on the current results and understanding and the identification of future activities.

Despite the informal character of the workshop, all contributions are corresponding to the latest developments in research. Therefore, a "State of the Art" significance of the workshop will be guaranteed.

Forschungszentrum Karlsruhe hopes that this will be a successful meeting in a relaxed atmosphere and that all of the participants will enjoy the personal contacts, the discussions and that this workshop has an important impact on R&D in the field of heavy liquid metal technology for Accelerator Driven Systems.

2. Overview of the two sessions

2.1 First session: Materials compatibility in lead and lead alloys

Referring to the original concept of Carlo Rubbia for an Accelerator Driven System (ADS), ENEA, CNR, Ansaldo, CEA, CIEMAT, RIT, SCK and FZK have agreed to collaborate in the field of developing the technology of liquid lead and lead alloys, both used as spallation target for the proton beam or as primary coolant of the core of a future DEMO type reactor. Although different beam concepts for hybrid reactors are discussed in Europe, the decision for choosing lead or lead-bismuth as liquid metals is not affected on that:

- Lead and lead-bismuth show the lowest capture cross section for both thermal and fast neutrons
- Within the group of lead alloys, the Pb-Bi eutectic has the advantage of having the lowest melting point with 125°C. Therefore, the handling of the liquid alloy in technical loops (pumping, draining etc.) seems to be relatively uncomplicated. The high boiling point of 1670°C reduces the risk of local boiling and vaporization.
- With the eutectic lead-bismuth alloy, extensive experience in the use as coolant in Russian submarine reactors is available
- Lead-bismuth has been selected as spallation material for the second SINQ target at PSI

Besides their great advantages, problems due to their high corrosivity to most of the structural materials, especially steels, are of major concern. Their high solubility for steel elements like iron, chromium and nickel, the ability to serve as oxidizing media for metallic materials and the fact that the various corrosion phenomena's known as dissolution, mass transfer, impurity reactions, intergranular attack and liquid metal embrittlement are very much depending on the operating parameters, makes it necessary to investigate the behavior of potential structural and window materials under realistic conditions. Additionally, the corrosion by spallation products and irradiation assisted mechanical properties degradation have to be taken into account.

The establishing of experimental data in the EC is just at the beginning. Research Centers and Universities with immense experience in the technology of liquid alkali metals and the eutectic lead-lithium alloy, the latter thought as blanket material for fusion reactors, have started extensive investigations concerning the corrosion of structural materials, the corrosion protection by coatings and the oxygen measurement and control in lead and/or lead-bismuth.

The presentations of the first session are covering the corrosion behavior of ferritic and austenitic steels and low solubility elements like molybdenum and tungsten in stagnant and flowing lead or lead-bismuth. Another presentation shows the reduction of corrosion by changing the surface structure of different steels with a pulsed electron beam and by controlling the oxygen concentration in lead via gas phase. The results are gained within a longlasting cooperation between Russian colleagues at IPPE in Obninsk, at Prometey in St. Petersburg and at FZK.

G. Benamati gave an overview on the status of preparation of the final proposal TECLA (Technologies for Lead Alloys) for the 5th Framework Programme. He presented the structure of the proposal, the involved associations, the agreed budget and the necessary things to do up to closing date of October 4th.

General discussion

Important points

- Importance of environment
- Oxidation/preoxidation
- Cleaning procedure of samples
- Austenitic or ferritic steels for use in Pb or Pb-Bi
- Effect of spallation products on corrosion

L. Cinotti stated that the proposal for the 5th Framework Programme covers most of the information needed in the future. Some points which are not addressed should be part of the 6th F. P. Especially the development of an in-service inspection is strongly required, which is an open point at the moment.

G. Benamati answered, that because of budget reductions, no integration into the 5th F. P. is possible. Maybe an incorporation within the "Safety" part of the proposal could be discussed.

D. Gomez Briceno pointed out the differences in oxide layer thickness between results gained in high oxygen and low oxygen lead. In Pb-Bi under reducing conditions a dissolution of the oxide layer is obvious.

H. Glasbrenner mentioned that she has measured similar oxide layer thicknesses in her own experiments compared to the Pb-Bi results of F. Barbier, gained at IPPE.

G. Benamati stated that at low oxygen concentrations, a corrosion behavior comparable to Pb-17Li is measurable.

D. Gomez Briceno mentioned that nobody has really measured the oxygen concentration in Pb-Bi. Own experiments at 10^{-7} bar O_2 in the cover gas gave contradictory results corresponding oxide layer formation to the tests of G. Müller from FZK. The oxide layers dissoluted in the liquid metal, even in "pure" argon as cover gas.

D. Smith pointed out that the tube (stainless steel) for bubbling the oxygen into the liquid metal might have gettered the whole oxygen.

J. Konys stated that under specific experimental conditions, austenitic steels, although high in nickel, have shown better results than ferritic material.

G. Benamati added that even not GESA treated austenitic steels were better corrosion resistant than ferritic steels.

L. Cinotti mentioned Russian sources which indicated that for the temperature range of 300-400°C, austenites are the first choice.

G. Müller clarified that he meant with "high alloyed steels" in his presentation both, austenitic and high chromium steels.

D. Smith pointed out that differences in the thermal expansion between the base metal and the oxides are essential for the stability of oxide layers. Furthermore, ferritic steels show a better resistance to irradiation degradation of mechanical properties than austenites.

Y. Dai mentioned that martensitic steels show a lower tendency to swelling and He-embrittlement than austenitic steels.

J. L. Courouau mentioned the influence of silicon on the oxidation behavior of steels (thinner and more dense oxides, good adherence).

G. Müller said that the Russian colleagues have found, that Al (alumina) has a bad influence on the corrosion resistance.

L. Cinotti mentioned that oil at 290-320°C is often used as coolant in the secondary loop. What happens in the case of an accident? He added that experiments are planned for this subject.

G. Benamati asked L. Cinotti about his opinion of reaching the goals of a real hybrid reactor.

L. Cinotti answered the following:

a) The R&D of the 5th Framework Programme is very important

b) For a DEMO type reactor, low T and low ΔT were chosen $\Rightarrow$ "easy" parameters make a realization more likely

c) Conditions for safe operation have to be evaluated

d) Pb instead of Pb-Bi at higher T has to be used in the future $\Rightarrow$ new challenge

2.2 Second session: Analytical and technical problems with Pb and Pb alloys

The second session on Heavy Liquid Metal Technology was focussed on the analytical methods for measuring metallic elements and oxygen in lead and lead-bismuth. Additionally, the determination of oxygen activities (potentials) by means of solid electrolyte oxygen meters was subject of two presentations. To calibrate the oxygen meters, the availibility of an oxygen analysis is strongly required, too. Otherwise, measured EMK values have only a qualitative meaning. The session was closed by a general discussion on common future activities.

General discussion

Important points

- Total oxygen concentration $\Rightarrow$ influenced by precipitated oxides?
- Sampling methods $\Rightarrow$ pretreatment of samples!
- Accuracy and range of uncertainty of analytical methods
- Reference electrodes of oxygen sensors (Pt/air, Au/air, In/In_2O_3)
- Ceramic material for solid electrolyte (zirconia or thoria)
- Are all necessary thermodynamic data for the calculation of oxygen potentials available, respectively are they exact enough?
- What is the minimum operational temperature of oxygen sensors
- A specification for Pb-Bi has to be evaluated $\Rightarrow$ round robin analysis

G. Benamati pointed out the necessity of a common specification for lead-bismuth. This includes metallic and non-metallic impurities. Otherwise future experimental results will be difficult to understand and to discuss.

F. Hofmann asked if all necessary physical and chemical data of Pb and Pb-Bi are available.

G. Benamati answered that an ENEA report exists with some of the most relevant data. At the end of the year, a more comprehensive report compiled by ENEA together with the University of Bologna will be finished. G. Benamati will distribute this report to all associations.

C. Adelhelm reported about certifications of the analysis of oxygen in lead within the European Community. A certified value of 1.0 μg/g with an uncertainty of $\pm$0.5 μg/g was evaluated as an average of 98 accepted individual measurements obtained with 4 independent methods by 9 laboratories. Copies of the final report will be part of the minutes.
To accelerate the analytical discussions in the EC, an analytical subgroup was initiated with the following members:

C. Adelhelm, FZK (Chair)
C. Fazio, ENEA
L. Soler Crespo, CIEMAT
J. Desreumaux, CEA

This subgroup has to evaluate a common specification for impurities in lead-bismuth within the coming months. In a next step, the analytical methods have to be compared with regard to their accuracy and reproducibility. Finally they have to be adapted to the special necessities of lead-bismuth technology. Afterwards, a round robin analysis has to be performed.

G. Benamati asked who is developing oxygen sensors in the EC? At the moment: ENEA, FZK, CEA/Cardarache and IQS. A tight coordination and exchange of information of the specific R&D is required.

J. Konys asked what are the lower limits of operational temperature for solid electrolyte oxygen sensors.

D. Smith answered that from experiences at Argonne, Ca-stabilized zirconia should work even at temperatures down to 300°C.

J. Konys pointed out that this is in agreement with unpublished results of oxygen meters (Pt/air) in Pb-Bi of FZK.

L. Cinotti remarked that for safety reasons (shutdown of a reactor) oxygen sensors for T≈300°C are necessary.

G. Corsini mentioned that for the oxygen control in Pb-Bi, the humidity and the hydrogen content have to be measured. Is there accurate equipment available?

G. Schumacher answered that the estimation of hydrogen in the cover gas is not a problem because the concentration is in the percent range (typically 5 vol.-%). The measurements can be performed by means of gas chromatography.

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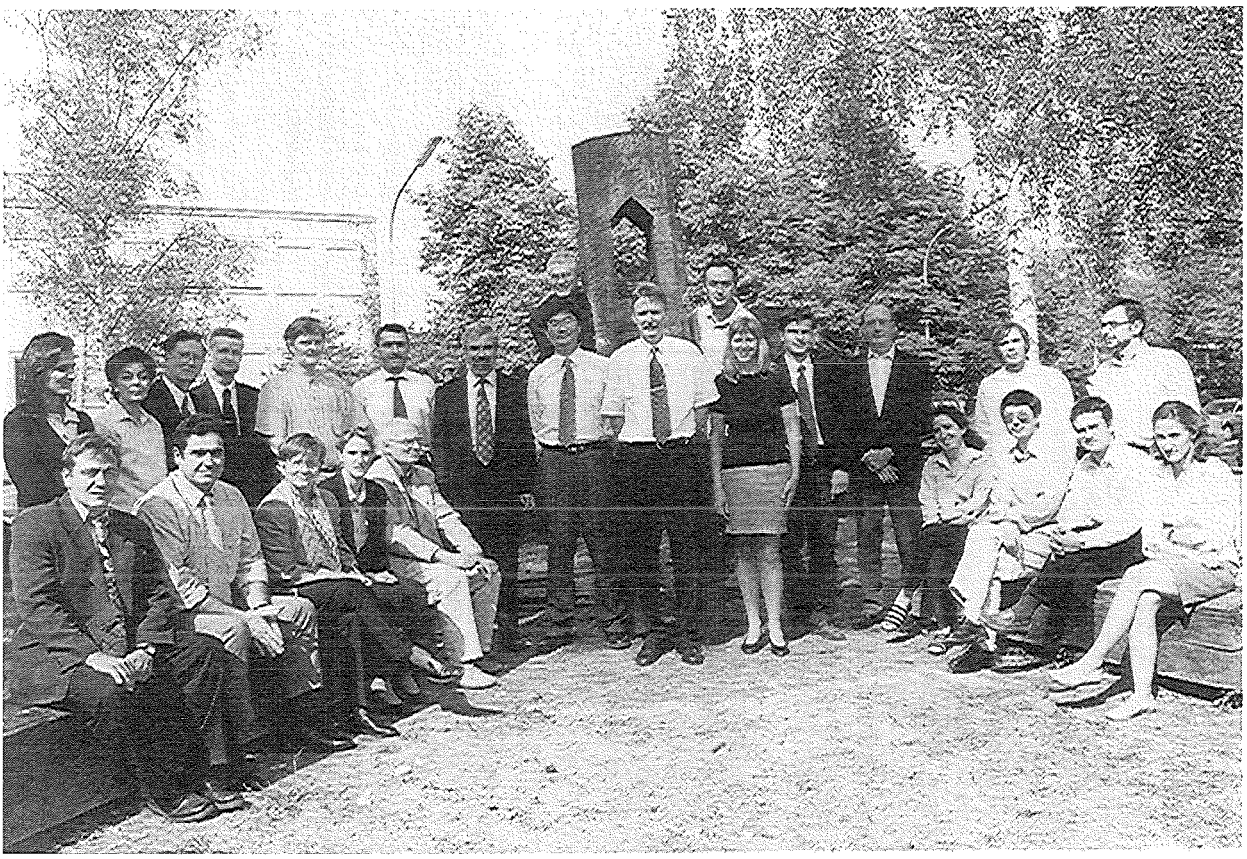
4. Photograph of the participants



(Not on the photo: V. Imbeni, C. Martini, both Univ. Bologna and
J. Knebel, F. Hofmann, both FZK)

5. Presentations

OVERVIEW ON ADS DESIGN

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ABSTRACT

An accelerator-driven subcritical reactor system (ADS) consists of three main parts (see fig. 1): an accelerator for primary particles (protons), a target in which the protons produce free nucleons (neutrons) in a spallation reaction (external neutron source), and a subcritical blanket in which the fission reaction takes place, producing fission neutrons (internal neutron source) and thermal energy. The protons are infected into the target through a vacuum beam pipe, the beam pipe being closed by a window at the end. The target is a heavy liquid metal (e.g. lead Pb or lead bismuth alloy Pb-Bi). The spallation neutrons produced in the target are completely independent of the subcritical blanket. A shut-down of the accelerator or an interruption of the proton beam immediately stops the fission reaction. Due to the subcriticality of the system advantages to safety are expected [1-2].

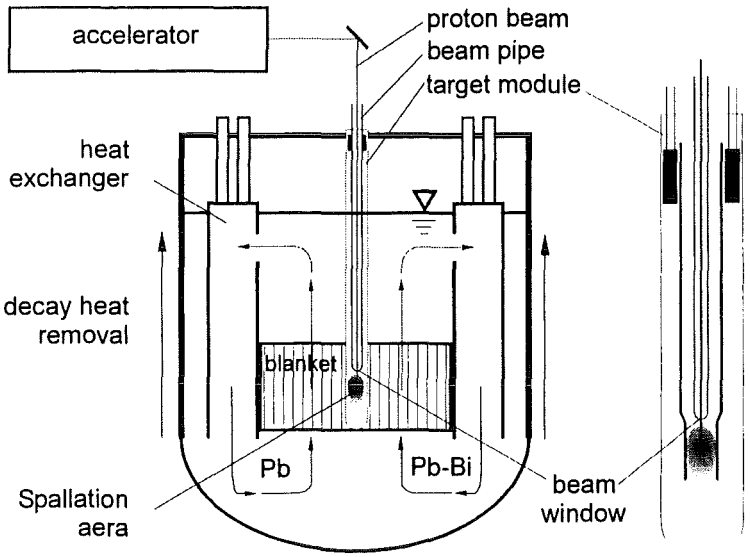

Fig. 1: Sketch of an accelerator-driven subcritical reactor system (ADS).

The main advantage of an ADS is its potential to transmute minor actinides and long-lived fission products, thus participating in closing the fuel cycle [3-6]. An ADS provides a powerful proton beam which produces a high number of neutrons, due to the spallation reaction in the heavy metal target. These neutrons are a good requirement for a transmutation machine.

Such a new reactor system involves the development of new technologies, e.g. a new reactor design using the heavy liquid metal Pb-Bi as spallation material and coolant, improved accelerators to drive the reactor, new fuel, new fuel fabrication and fuel reprocessing systems, new waste management arrangements [7].

The presentation gives a generic characterisation of the main subsystems of an ADS, mainly concentrating on three design concepts: the Energy Amplifier of Carlo Rubbia [5], the Energy Amplifier Demonstration Facility of Ansaldo [8] and the FZK Three-Beams Concept [9,10]. The pros and cons of the concepts are briefly discussed.
In order to describe the future R&D needs, the main challenges concerning the feasibility of an ADS are listed. These challenges are embedded in or closely related to major international activities, such as e.g. the Technical Working Group chaired by C. Rubbia, proposals for the 5th European Framework Programme, the 1 MW Pilot-Target MEGAPIE for SINQ, the HGF-Strategy-Fund Project 99/16 at FZK [11, 12], the ISTC Projekt 559: HLM-Target for LANSCE, the WTZ: Corrosion Behaviour of steels in liquid lead, the European Spallation Source (ESS) Programme and the European Benchmark Working Group (BWG).

Finally, the activities at FZK are outlined. Most emphasis is put on the HGF-Strategy-Fund Project 99/16: "Thermal-hydraulic and material specific investigations into the realisation of an accelerator-driven system (ADS) to transmute actinides" currently underway at FZK [11, 12]. The objectives of this work are the development of new methods and technologies to design and manufacture thermally highly-loaded surfaces which are cooled by a corrosive heavy liquid metal (lead-bismuth eutectic).

The results of this project is the basic scientific-technical tool which allows a better conception and design of a European Demonstrator of an ADS system.
The project is divided in three sub-projects:

Sub-Project 1: Thermalhydraulic Investigations:
In the field of experimental thermalhydraulics physical models for conductive and convective heat transfer along thermally highly-loaded surfaces (beam window, fuel rod) in turbulent lead-bismuth flow are developped. In parallel, a thermalhydraulic computer programme is validated for the low Prandtl number fluid lead-bismuth.

Sub-Project 2: Material specific Investigations:
In the field of material science physical methods to describe corrosion mechanisms and to solve the corrosion challenge for potential structure and window materials with and without surface treatment are developped for liquid lead-bismuth.

Sub-Project 3: Oxygen control:
In the field of reaction kinetics a physical / chemical method to measure and control the oxygen potential in lead-bismuth is developped in order to prevent the corrosion of materials used.

The FZK experimental programme is performed in the KArlsruhe Lead LAboratory KALLA [12], which comprises three different experimental loops: the *Technology Loop*, the *Thermalhydraulic Loop* and the *Corrosion Loop.*

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In: Projekt Nukleare Sicherheitsforschung Jahresbericht 1998, editor: Mühl, B., Wissenschaftliche Berichte FZKA 6300, Forschungszentrum Karlsruhe, pp. 625-643, 1999

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In: Projekt Nukleare Sicherheitsforschung Jahresbericht 1998, editor: Mühl, B., Wissenschaftliche Berichte FZKA 6300, Forschungszentrum Karlsruhe, pp. 644-657, 1999

Forschungszentrum Karlsruhe
Technik und Umwelt

OVERVIEW ON ADS DESIGN

J.U. Knebel

Forschungszentrum Karlsruhe GmbH (FZK)
Institute of Nuclear and Energy Technologies (IKET)
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Concept of an ADS-System

Feasibility

International Activities

Activities at FZK

KArlsruhe Lead LAboratory KALLA

Presented at the:
Int. Workshop on Heavy Liquid Metal Technology for Use in ADS, September 16-17, 1999, FZK Karlsruhe Germany

The author thanks the following colleagues and friends to make available some of their results for this presentation.

Special thanks are to Xu Cheng for his thermalhydraulic calculations.

L. Cinotti, ANSALDO
G. Bauer, PSI
C. Broeders, X. Cheng, IKET – FZK
J. Konys, H. Glasbrenner, IMF III – FZK
G. Müller, G. Schumacher, IHM – FZK

INTRODUCTION

Uranium-Fuel Cycle:

- ➔ **Plutonium Pu** **104 t/y**
- ➔ **Minor Actinides MA:** **Neptunium Np** **6 t/y**
  Americium Am **1.5 t/y**
  Curium Cm **0.5 t/y**

State-of-the-art:

Pu treatment

- ➔ **Recycling in MOX fuelled LWR**
- ➔ **Intermediate and final waste storage**

MA treatment

- ➔ **Highly radioactive waste, final waste storage**
- ➔ **Very long half-life periods (>10^4 years)**

Alternative:

Transmutation of Pu and MA in an accelerator driven system (ADS).

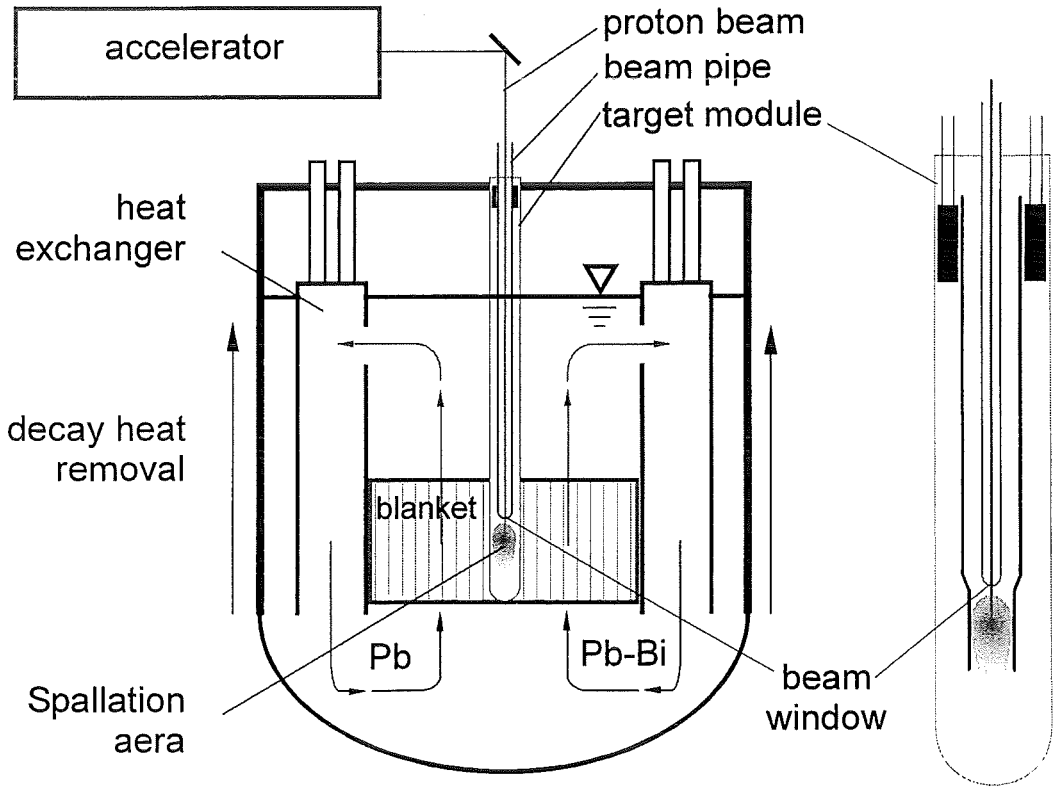
STRATEGY

Long-term and strategic objectives:

- **Reduction of the amount and the radiotoxicity of the radioactive waste.**
- **Closing of the fuel cycle.**
- **Design and construction of a Demonstrator Plant.**

BASIC CONCEPT OF AN ADS-SYSTEM

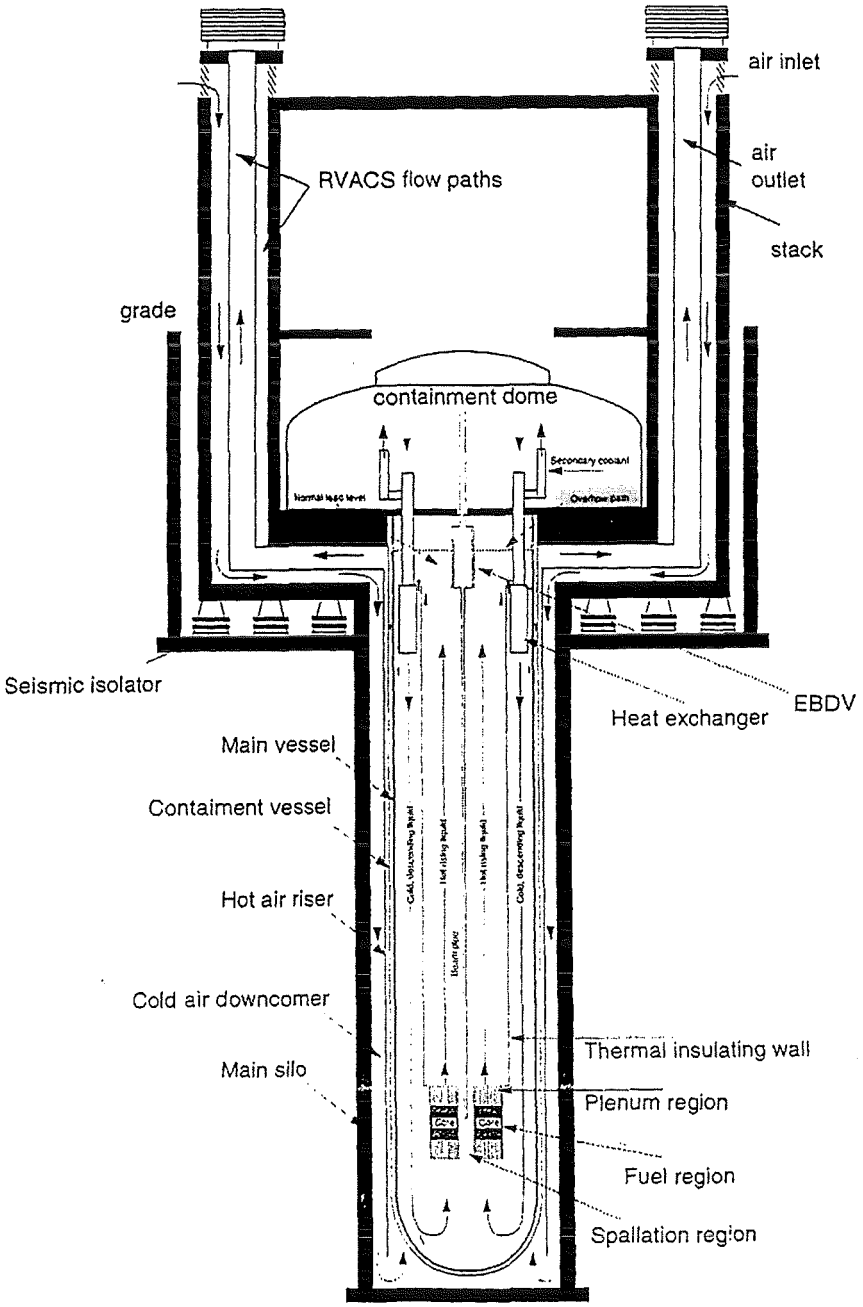
Pool type reactor and target module:



Main components:

- **Accelerator** **(high energy protons)**
- **Target module** **(fast neutrons)**
- **Blanket** **(fission, transmutation)**

GENERAL LAYOUT OF THE ENERGY AMPLIFIER



Taken from: Rubbia, C., Rubio, J.A., Buono, S., Carminati, F., Fiétier, F., Galvez, J., Gelès, C., Kadi, Y., Klapisch, R., Mandrillon, P., Revol, J.P., Roche, Ch., „Conceptual design of a fast neutron operated high power energy emplifier", *CERN/AT/95-44(ET), September 1995*

ADS design options for a 1500 MW_{th} system:

	Energy Amplifier EA (C. Rubbia)	FZK Three-Beams Concept
Type	pool reactor	pool reactor
Fluid	Pb	Pb
Cooling	natural circulation	forced convection
Height	25 m	8 m
Number of beam pipes	1, central 12.5 MW	3, decentral 4.0 MW
Beam window	solid	solid, (with grid)
Window diameter	0.2 m	0.2 m

max rod output	800 W/cm	400 W/cm
Total formfactor	2.8	2.0
excess window temperature	800 K	320 K
mean window heat flux	650 W/cm^2	110 W/cm^2
Window material	Tungsten-Rhenium	Steel

GENERAL LAYOUT OF THE

ENERGY AMPLIFIER DEMONSTRATION FACILITY

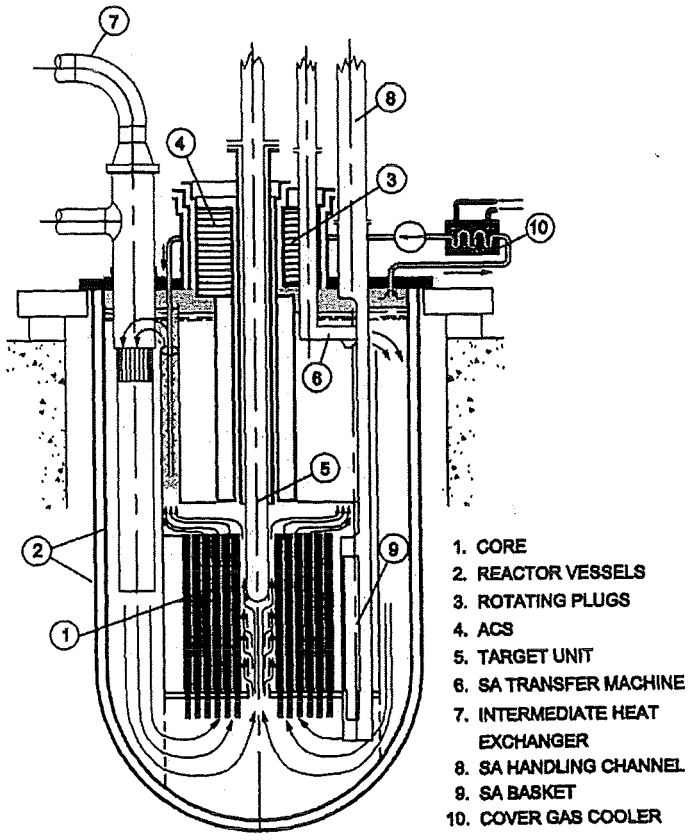


Figure 2.5-2 - Reactor System Assembly – Simplified Mechanical Scheme

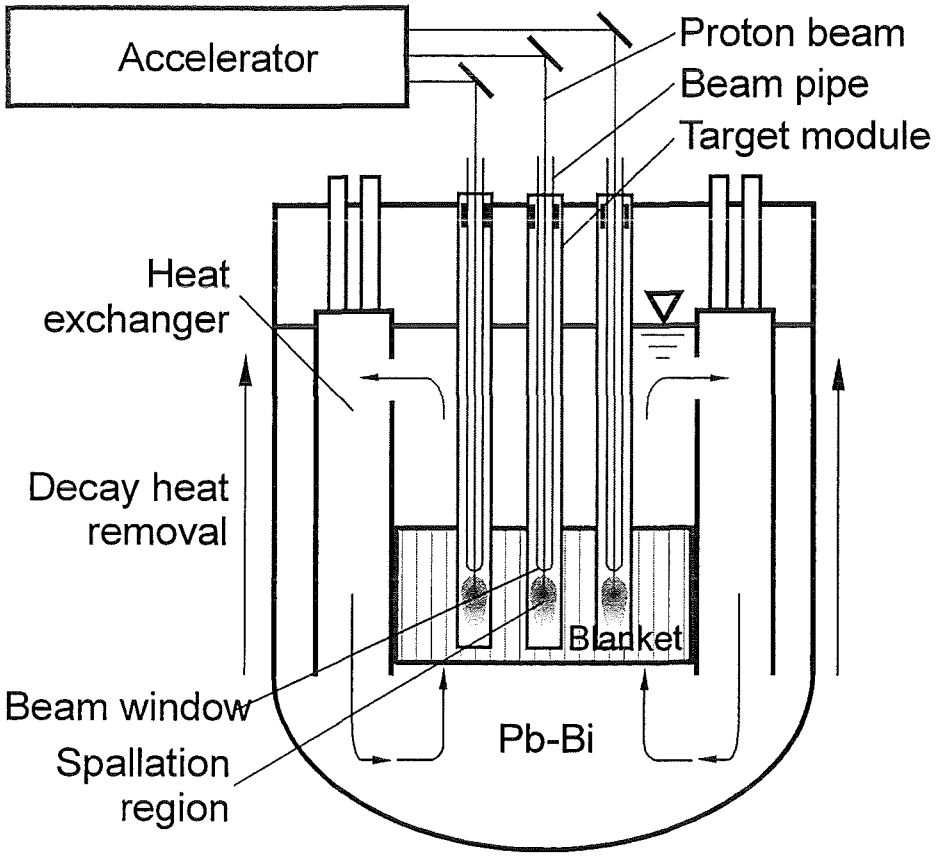
Taken from: Ansaldo Nucleare, SCR4, ENEA, INFN, „Energy Amplifier Demonstration Facility, Reference Configuration", Summary Report EA B0.001200-Rev.0 Ansaldo Nucleare Italy, January 1999

SOME ISSUES OF FEASIBILITY

(of importance for this workshop)

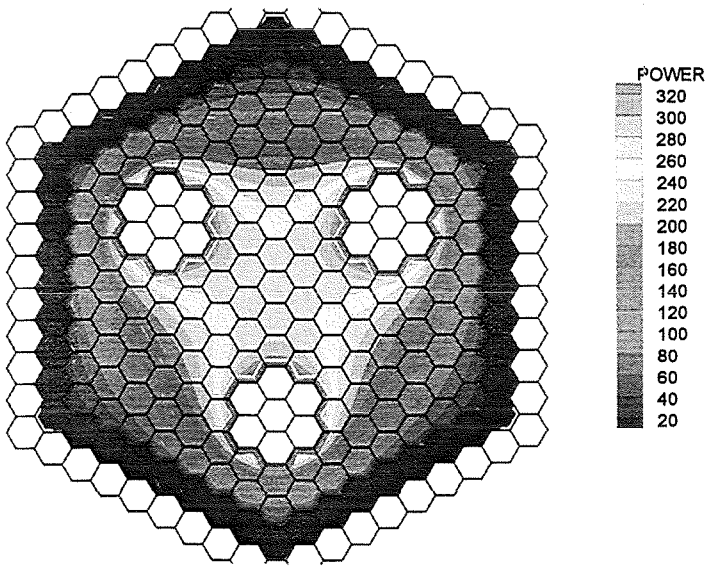
- Design of accelerator
- Design of subcritical blanket
- Design of a target module
- Cooling of the beam window
- Control of liquid metal corrosion
- Control of oxygen potential in Pb-Bi

FZK THREE-BEAMS CONCEPT



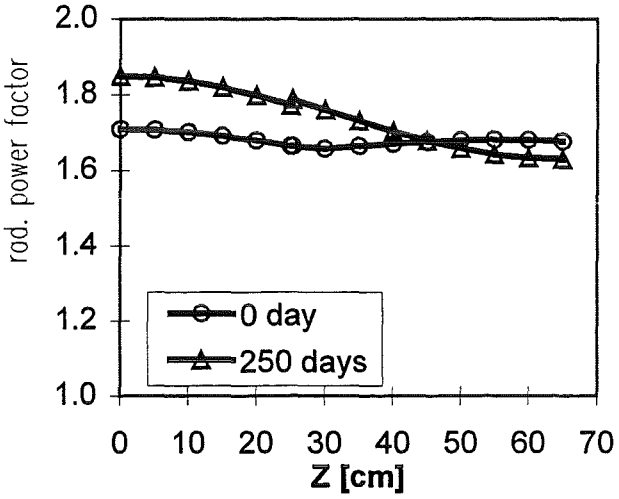
Midplane power density

(taken from C.H.M. Broeders)



FZK THREE-BEAMS CONCEPT

radial formfactor



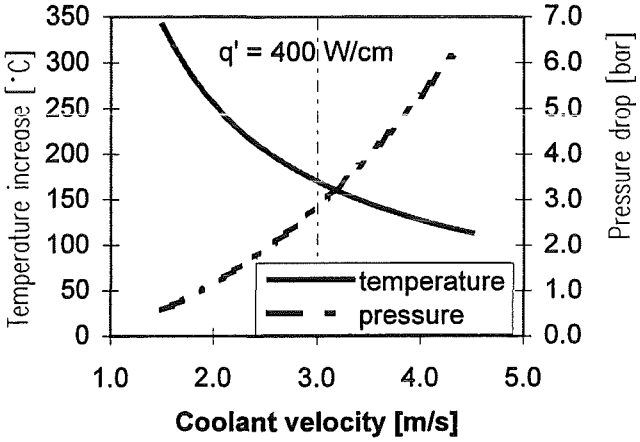
Results:

	Rubbia	FZK
• Total formfactor	2.8	2.0
• Max rod output (W/cm)	800	400

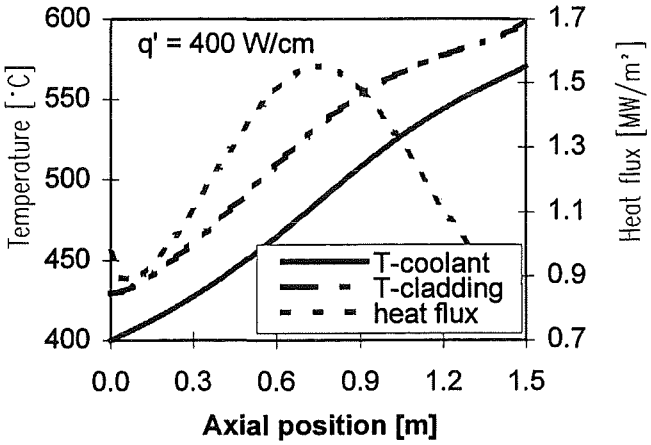
- Better power distribution within blanket
- Heat input into beam window is reduced by a factor of about 1/3
- Convective cooling of beam window seems feasible

BLANKET DESIGN:

FZK THREE-BEAMS-CONCEPT



Fluid temperature and pressure drop under forced convection.



Fluid temperature and cladding outer surface temperature under forced convection (u=3m/s).

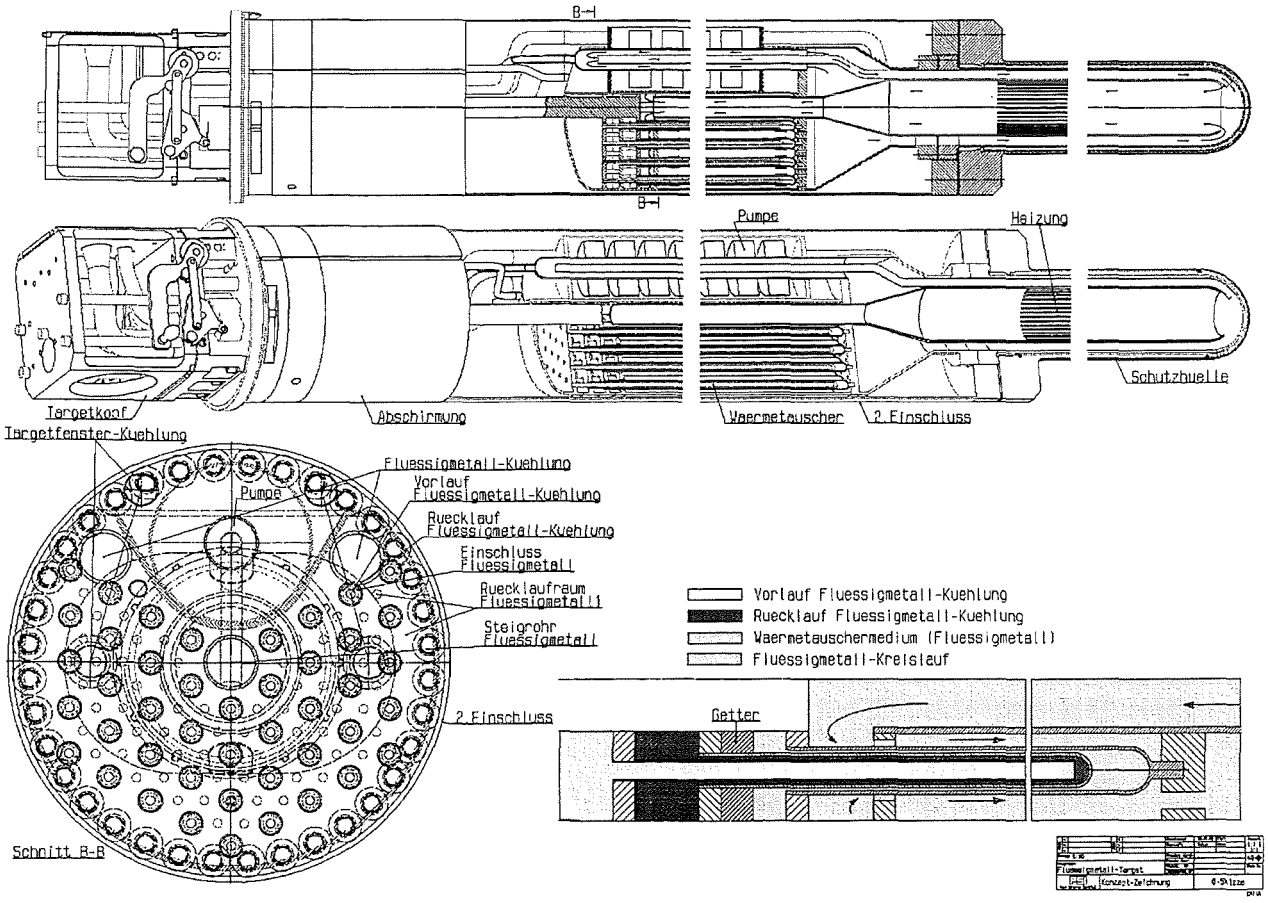
CEA
CNRS
FZK
ENEA
CRS 4
PSI
Conceptual
Design
Neutron
Physical
Data
Thermalhydraulics,
Materials,
Corrosion
FRAMA-
TOME
CIEMAT
Experimental
ADS
Demonstrator
Accelerator
Strategy
Investigations
IPPE, NIEFA
PROMETEY
FZR
MUSE
Experiment
Fuel,
Fuel Cycle
BNFL
FZJ
SCK-CEN
RIT
ECN-NRG

INTERNATIONAL ACTIVITIES

- **Technical Working Group, Chair: C. Rubbia**
- **Proposals for the 5th European Framework Programme**
- **1 MW Pilot-Target MEGAPIE for SINQ**
- **HGF-Strategy-Fund 99/16: Reduction of Radiotoxicity**
- **ISTC Projekt 559: HLM-Target for LANSCE**
- **WTZ: Corrosion Behaviour of steels in liquid lead**
- **European Spallation Source (ESS)**
- **Benchmark Working Group (BWG)**

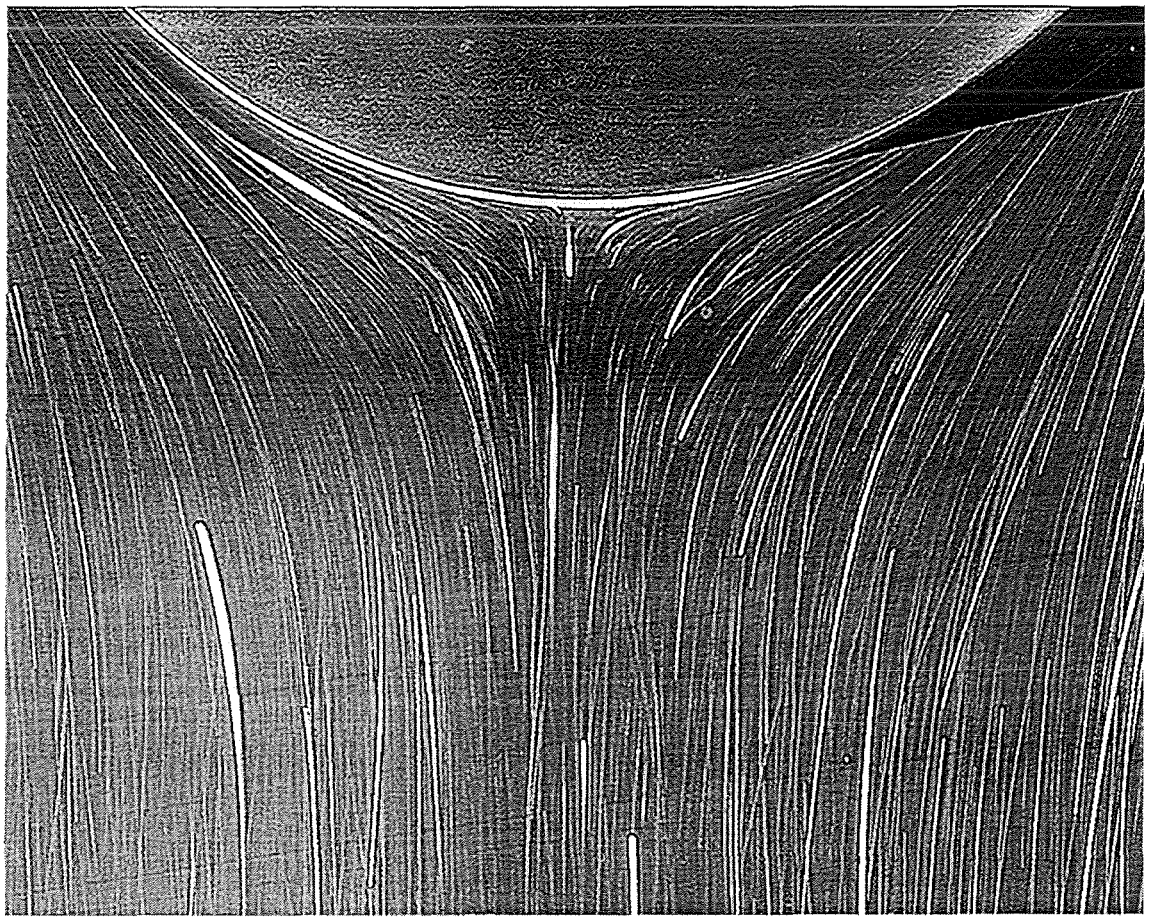
1 MW TEST TARGET MEGAPIE

AT SINQ / PSI



WATER EXPERIMENT FOR IPPE 559 TARGET

Flow around beam window (Laser Light Sheet):



ACTIVITIES AT FZK

- **Design Studies / System Analysis**
  - **Neutronics**
  - **Thermalhydraulics**
  - **Fuel behaviour**
  - **Safety studies**

- **Nuclear Data**
  - **Extension of energies above 20 MeV**
  - **Evaluation of Russian measurements**
  - **MUSE experiments**
  - **Experiments at FZK van de Graaf**

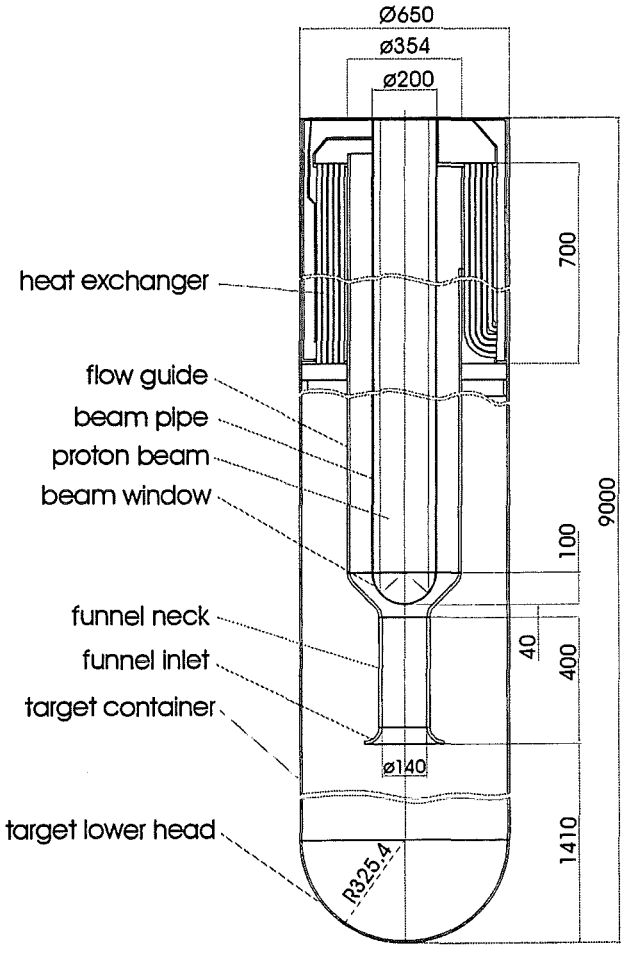
- **Materials / Corrosion Studies**
  - **Experiments at St. Petersburg / Obninsk**
  - **Experiments at FZK**

- **Pb-Bi / Pb Technology (KALLA)**
  (HGF Strategy Funds Project)
  - **Thermalhydraulics**
  - **Corrosion**
  - **Oxygen control**

OBJECTIVES OF THE HGF STRATEGY FUNDS PROJECT

Development of new methods and technologies to design and to manufacture thermally highly-loaded surfaces, which are cooled by a corrosive heavy liquid metal (eutectic Pb-Bi):

- **Beam window,**
- **Target module.**



WORK PACKAGES OF THE HGF STRATEGY FUNDS PROJECT

- **WP1: Thermalhydraulic Investigations**

  Turbulent heat transfer along thermally highly-loaded surfaces in Pb-Bi (e.g. beam window, fuel rod)

  Validated thermalhydraulic computer codes (e.g. Flutan, CFX)

- **WP2: Material Investigations**

  Physical methods to describe corrosion mechanisms in Pb-Bi

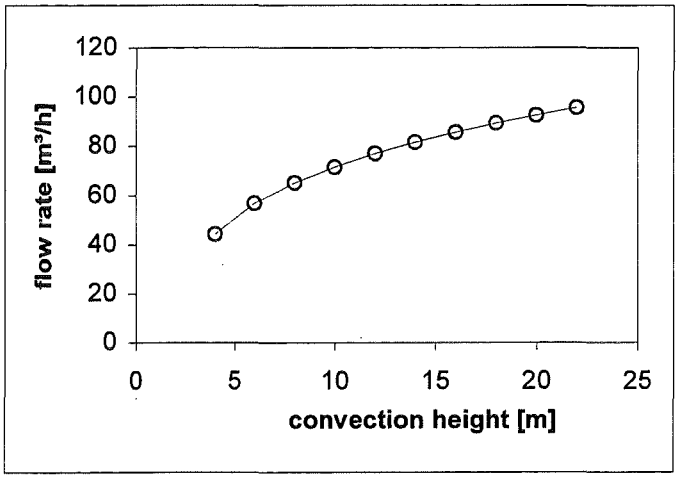
  Solution of the corrosion problem for potential window, cladding and structure materials

- **WP3: Oxygen Control**

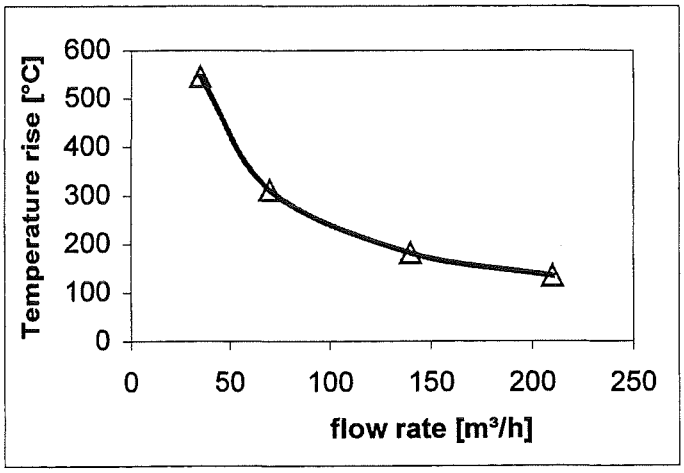
  Measurement and control device for the oxygen potential in Pb-Bi to finally control corrosion

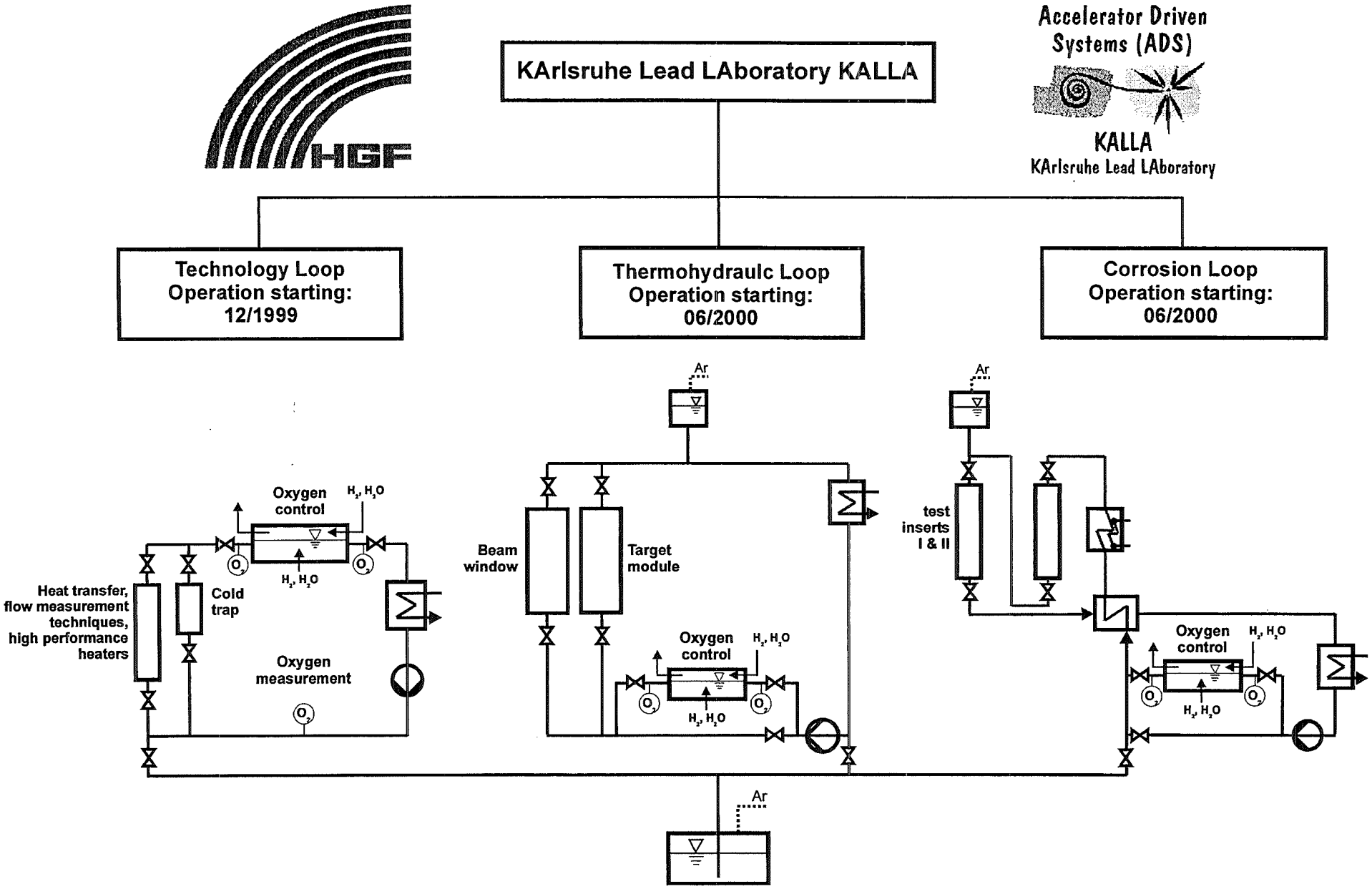
BEAM WINDOW COOLING

Natural convection height required for the target system.

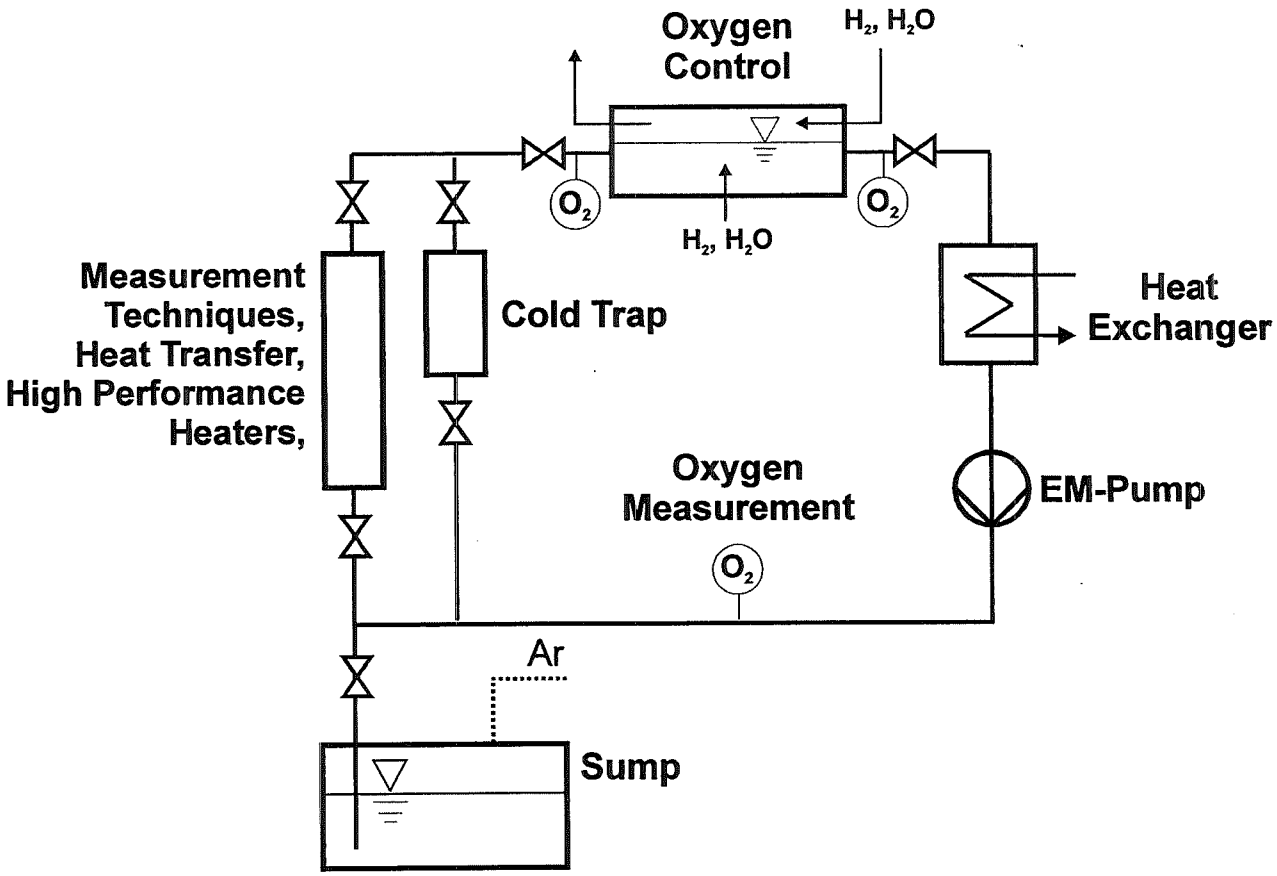


Maximum temperature rise of the beam window.




KArlsruhe Lead LAboratory KALLA
Accelerator Driven Systems (ADS)
KALLA
KArlsruhe Lead LAboratory
Technology Loop
Operation starting:
12/1999
Thermohydraulc Loop
Operation starting:
06/2000
Corrosion Loop
Operation starting:
06/2000
Ar
Oxygen control
H_2, H_2O
O_2
H_2, H_2O
Heat transfer, flow measurement techniques, high performance heaters
Cold trap
Oxygen measurement
O_2
Beam window
Target module
Oxygen control
H_2, H_2O
O_2
H_2, H_2O
test inserts I & II
Oxygen control
H_2, H_2O
O_2
H_2, H_2O
Ar

KArlsruhe Lead LAboratory KALLA



Accelerator Driven Systems (ADS)

KALLA

KArlsruhe Lead LAboratory

Technology Loop

Investigations:

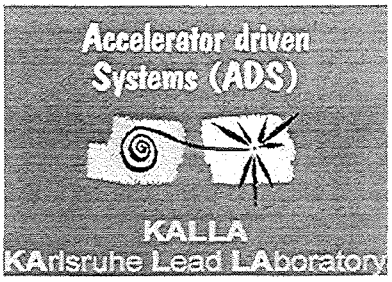
Oxygen measurement
Oxygen control
Heat transfer
High power heaters
Measurement techniques

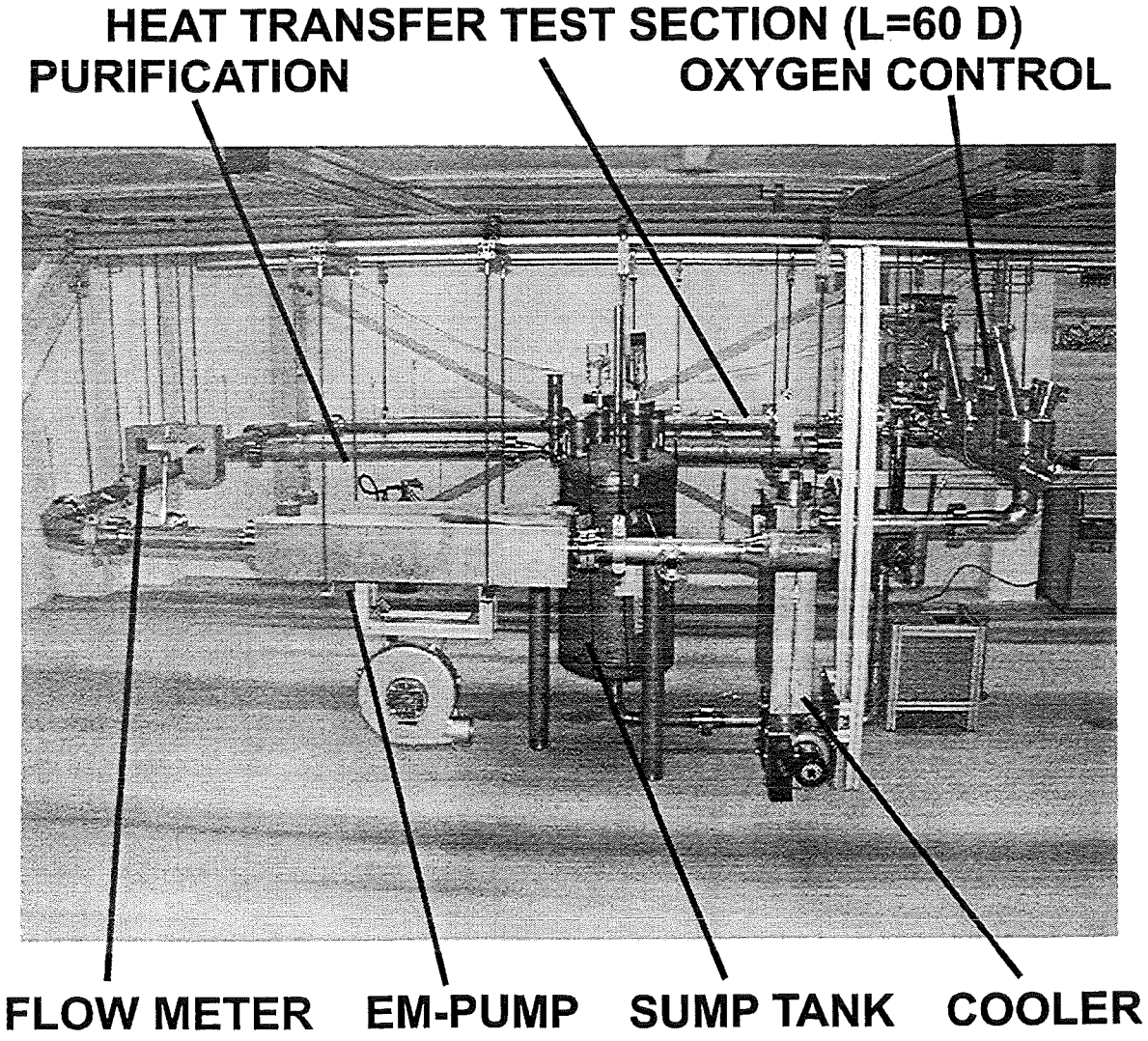
Dimension:

Volume:	0.1 m³
Temperature:	max 550°C

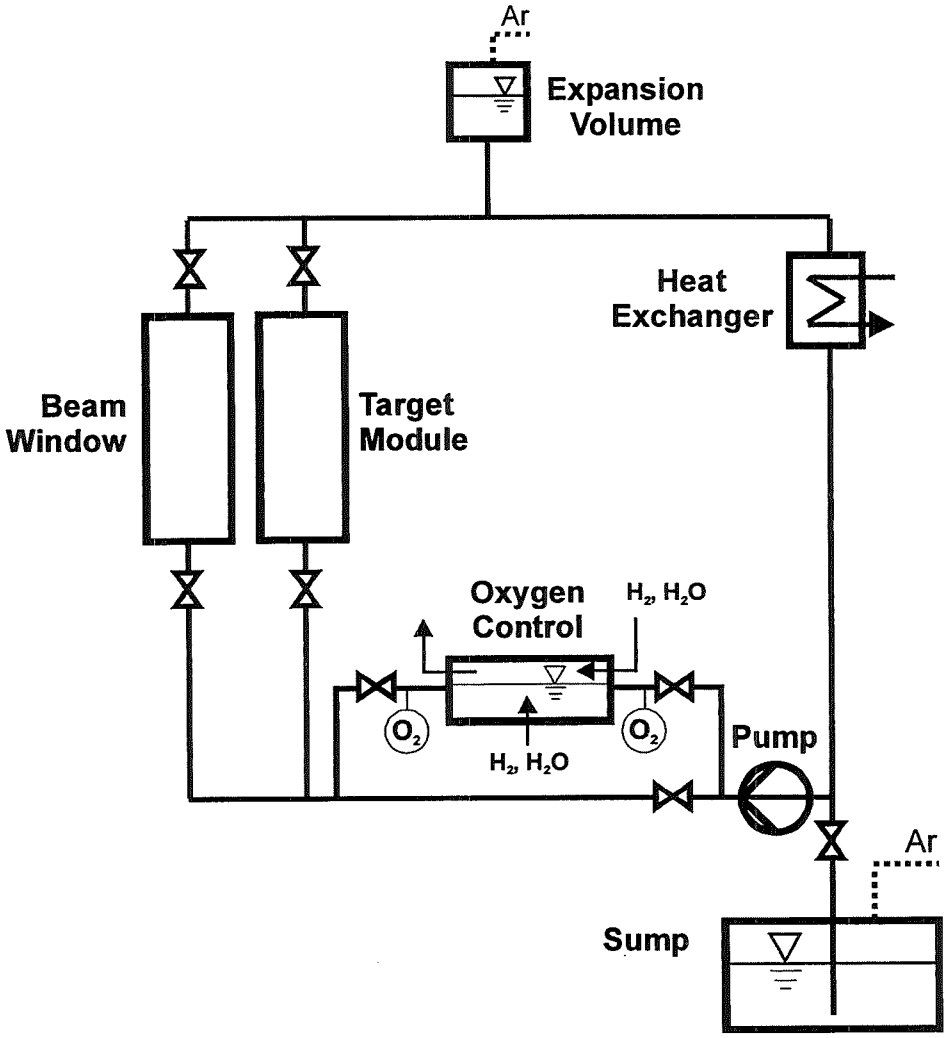
KARLSRUHE LEAD LABORATORY KALLA:

TECHNOLOGY LOOP





KArlsruhe Lead LAboratory KALLA



Thermalhydraulic Loop

Single-effect investigations:

- Beam window
- Target module
- Fuel element

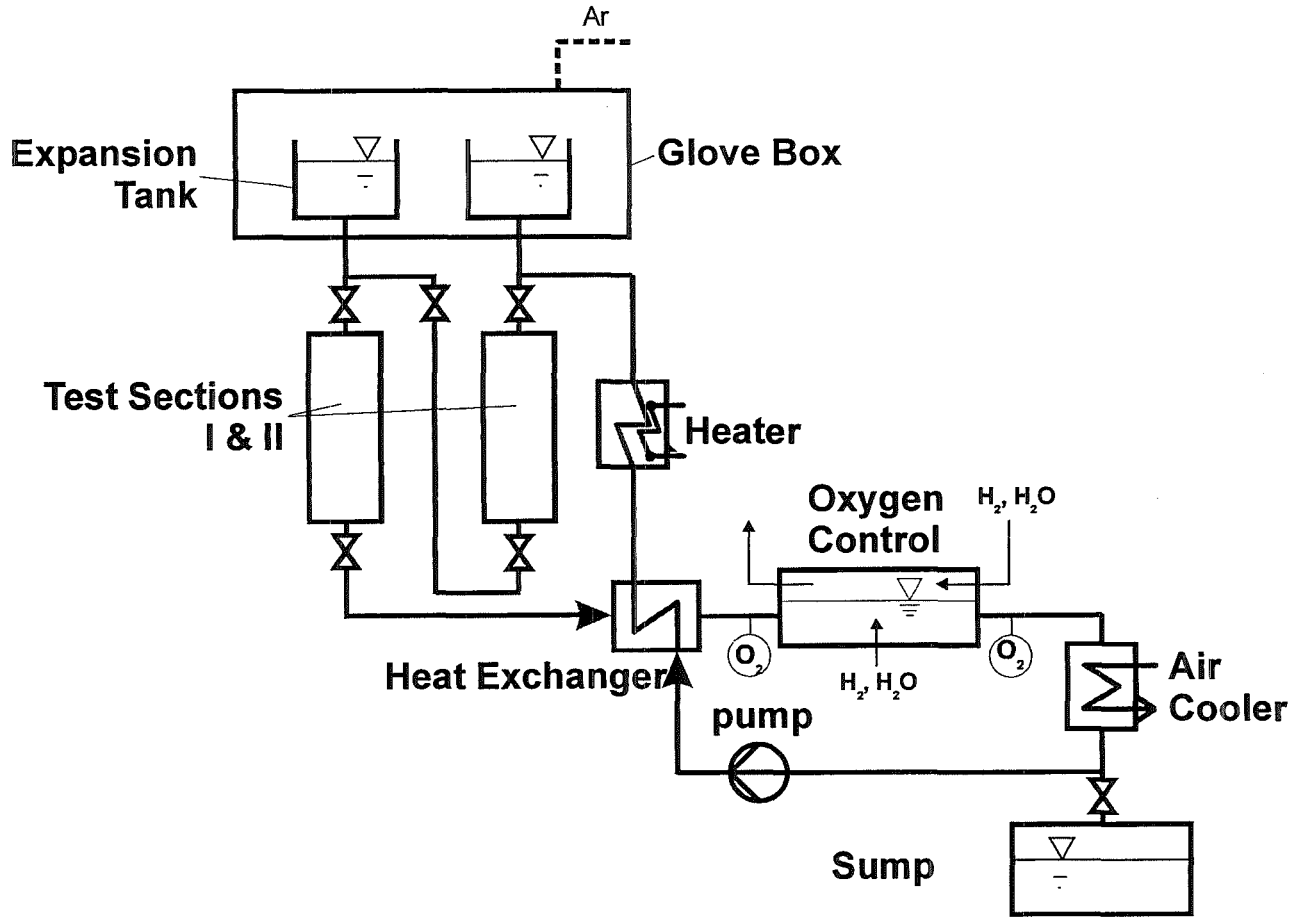
Integral investigations:

- Heat removal
- Decay heat removal

Dimension:

Volume: 4.0 m^3
Power: 0.3 MW-4.0 MW
Temperature: max 550°C
Volume flux: max 100 m^3/h

KArlsruhe Lead LAboratory KALLA



Accelerator Driven Systems (ADS)

KALLA

KArlsruhe Lead LAboratory

Corrosion Loop

Investigations:

- Corrosion mechanism
- Protection layers
- Mechanical tests

Dimension:

Volumen:	0.1 m³
Temperature:	max 550°C

SUMMARY (1)

- **An ADS is considered to be a promising system for the transmutation of MA and LLFP.**

- **An international effort is underway to develop and build a Demonstrator Plant: R+D plus industry.**

- **In the field of ADS development FZK is participating in the following research areas:**
  - **Design Studies / System Analysis**
  - **Nuclear Data**
  - **Materials / Corrosion Studies**
  - **Pb-Bi / Pb Technology (KALLA)**

SUMMARY (2)

- **FZK is developping the scientific-technical technologies to design and operate some critical components of an ADS system:**
  - **Beam window**
  - **Target module**
  - **Liquid metal corrosion**
  - **Oxygen control in Pb-Bi**

- **FZK is constructing the KArlsruhe Lead LAboratory KALLA to perform experimental investigations in the fields:**
  - **Pb-Bi technologies**
  - **Thermalhydraulics**
  - **Corrosion and materials**

Behaviour of different ferritic steels in stagnant Pb at 600 °C

H. Glasbrenner, J. Konys, Z. Voß, O. Wedemeyer, IMF III

Abstract

The behaviour of structural materials in Pb at elevated temperatures is an important issue in an accelerator driven system (ADS). Ferritic-martensitic steels show superior resistance under irradiation concerning swelling and helium embrittlement and adequate mechanical properties at high temperature. Such materials are foreseen as structural materials in a future ADS.

Therefore, eight different iron-chromium alloys are exposed to static lead at 600 °C for 3000 h, 5000 h and 12000 h. Metallographical results of specimens have shown that steels with lower chromium content were only little attacked. A more severe corrosion attack could be found in steels with higher chromium content. With longer exposure time the corrosion rate increases as well. Corrosion is probably related to the dissolution of steel components or partly leaching of elements out of the steel matrix. Further investigations are in progress.

Behaviour of different steels in stagnant Pb at 600 °C

H. Glasbrenner, J. Konys, Z. Voß, O. Wedemeyer

Outline

- Introdution
- Experimental
- Results
- Discussion
- Conclusions
- Outlook

Introduction

Pb or Pb-Bi as spallation target?

Pb: less corrosive than **Pb-Bi** but higher melting point

T_m (Pb) = 327.5 °C

T_m (Pb-Bi) =125.5 °C

Planning

- ⇨ corrosion tests in flowing Pb
  (a loop for corrosion tests is under construction)
- ⇨ first experiments under static conditions
- ⇨ investigation of the influence of Cr content to the corrosion behaviour (Ni should be avoided)
- ⇨ screening tests of various Fe-Cr materials in Pb

Experimental

- corrosion tests in static in Pb
- 8 different Cr-Fe materials (Ni content: low or free)
- T = 600 °C
- t = 3000 h, 5000 h and 10,000 h
- no oxygen control system
- Pb was analysed after the exposure
- no cleaning of the specimens after exposure

Chemical composition [wt%] of the steels investigated

Steel	Fe	Cr	Mn	Others
1.4713	87.98-92.17	6-8	0-1	Al, V, W
Optifer IVa	89.20	8.5	0.57	Ta, V, W
Optifer IVc	89.16	9.05	0.52	Mo, Ta, W, Si
MANET II	86.75	10.37	0.76	Al, Mo, Ni, Si, V
1.4923	83.54-87.25	11-12.5	0.3-0.8	Mo, Ni, Si, V
1.4742	77.21-81.6	17-19	0-1	Al, Si
PM 2000	74.5	19	-	Al, Ti, Y2O3
Ducrolloy	44.14	50.4	-	Al, Ti, Y2O3

Results

some specimens were not completely immeresed into the melt but float on the surface:

⇨ no total wetting of the samples!

specimens were not weighed before and after the tests

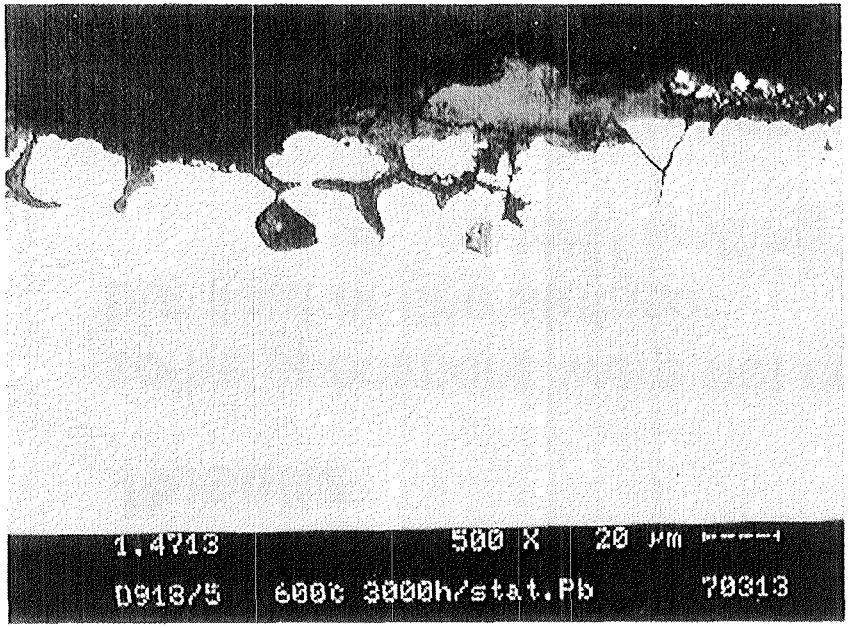
⇨ no weight change could determined!

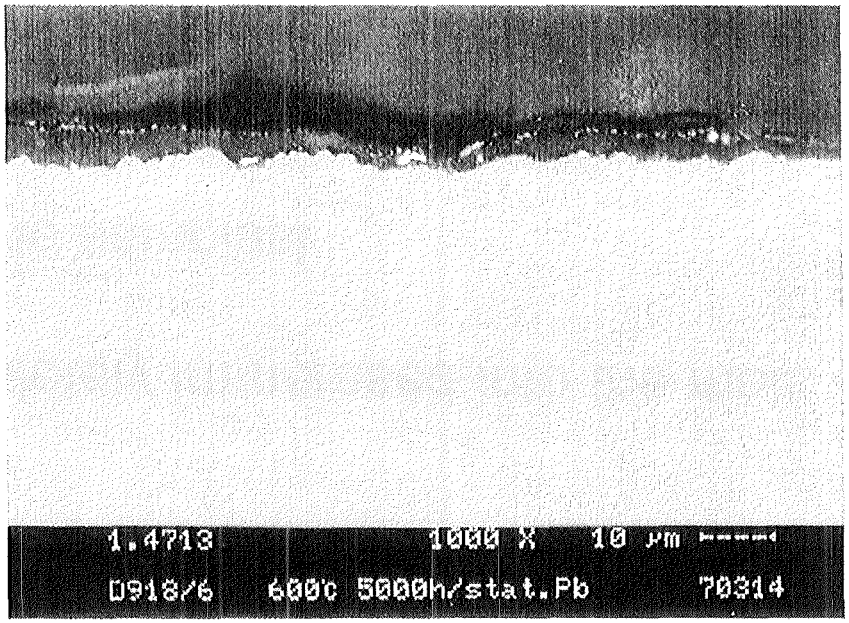
Pb analysis

after 3000 h: no difference compared to the values obtained for original lead

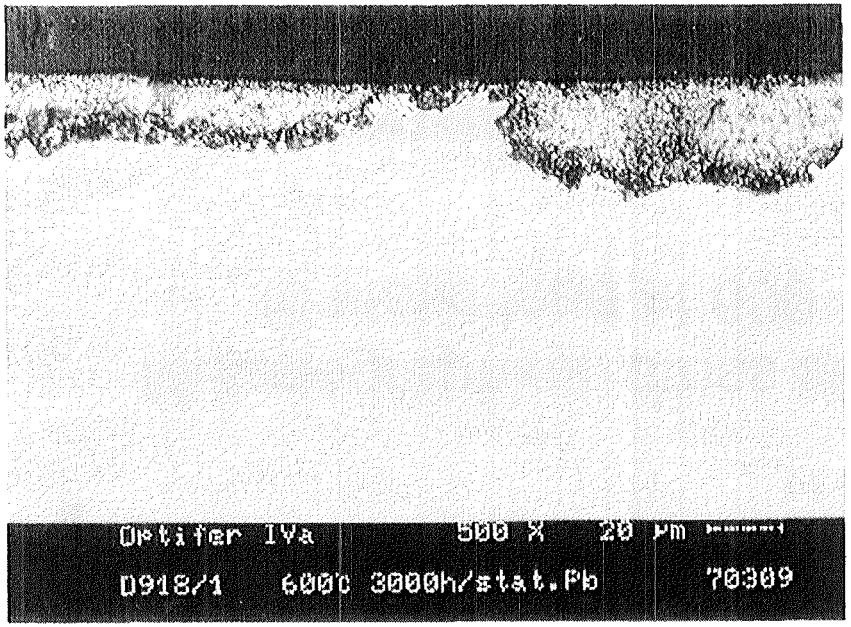
after 5000 h: slightly increase of the iron content

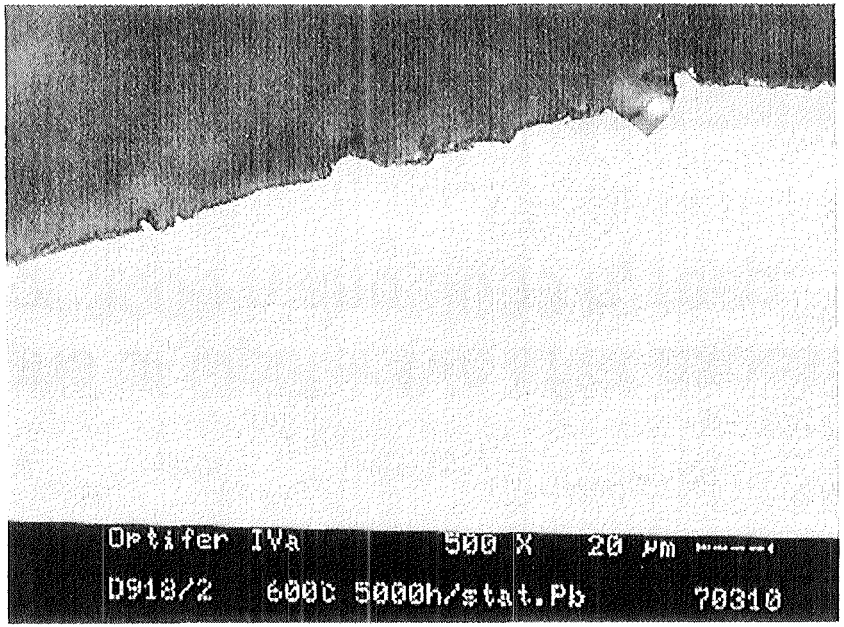
Metallographical cross sections of 1.4713 after exposure to static lead at 600 °C for 3000 h and 5000 h, resp.



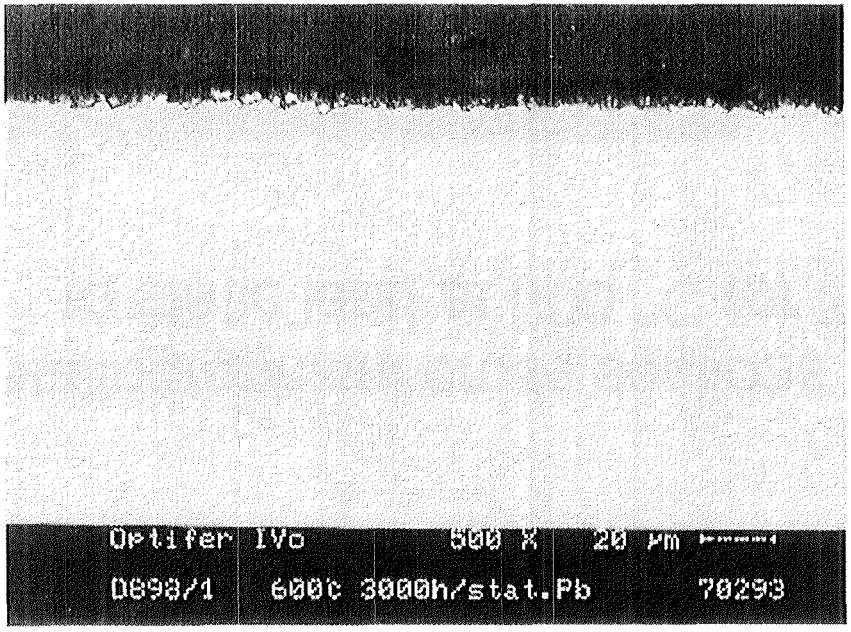


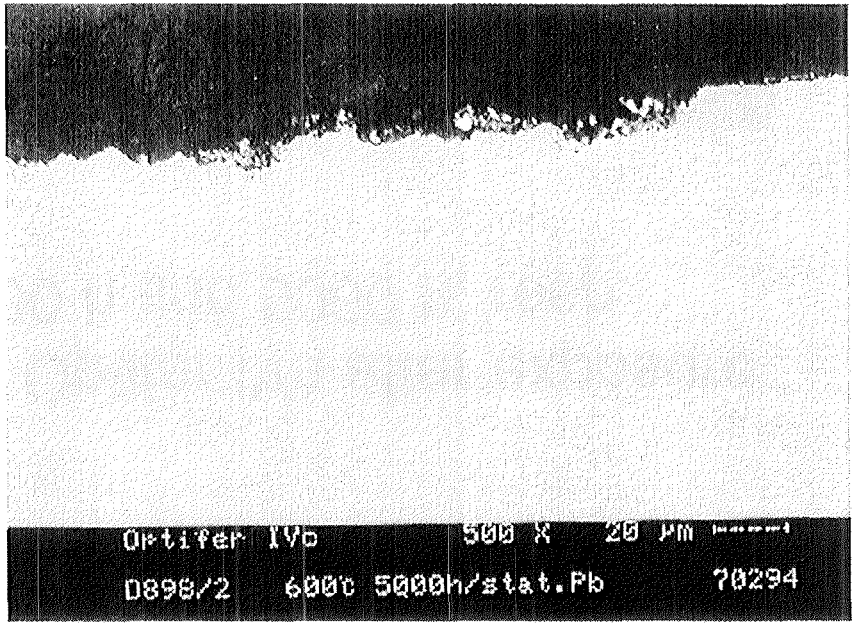
Metallographical cross sections of Optifer IVa after exposure to static lead at 600 °C for 3000 h and 5000 h, resp.



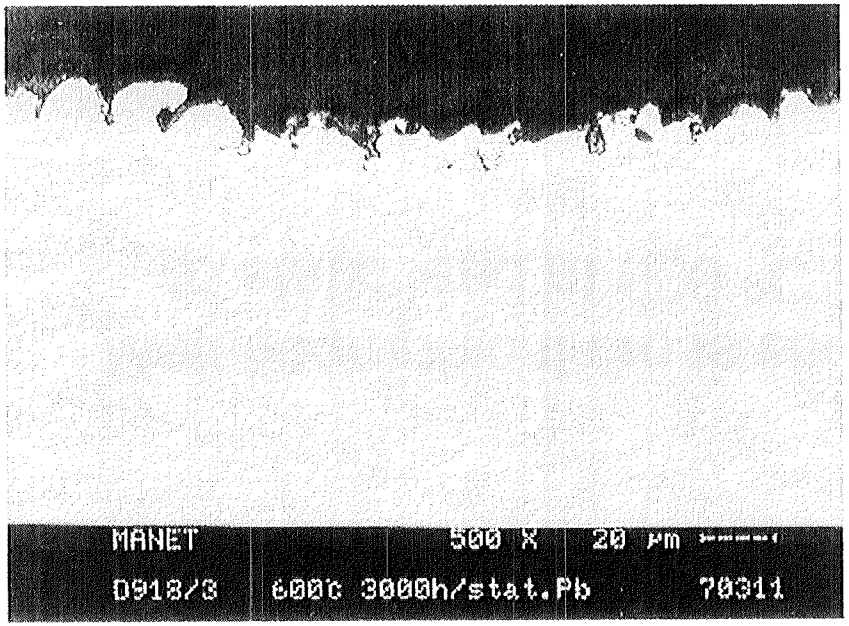


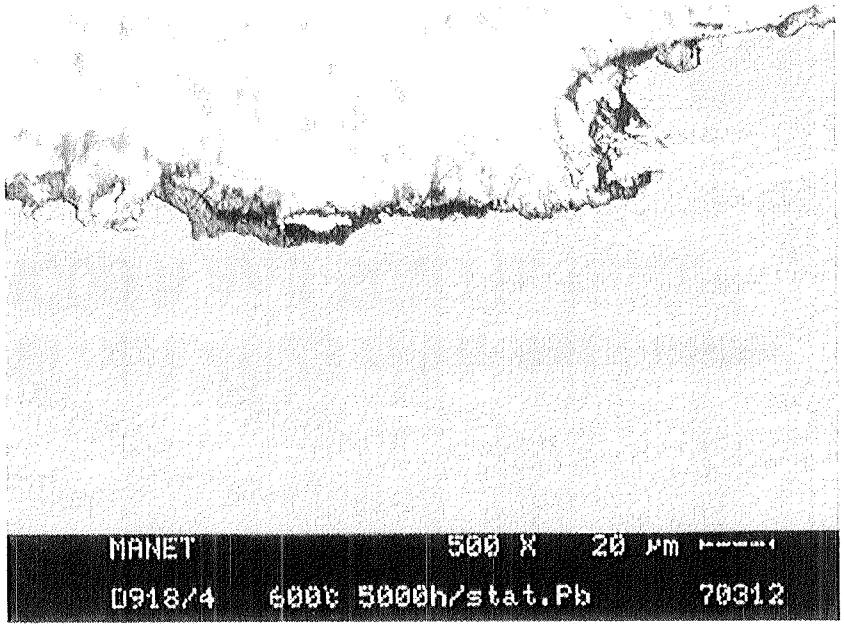
Metallographical cross sections of Optifer IVc after exposure to static lead at 600 °C for 3000 h and 5000 h, resp.



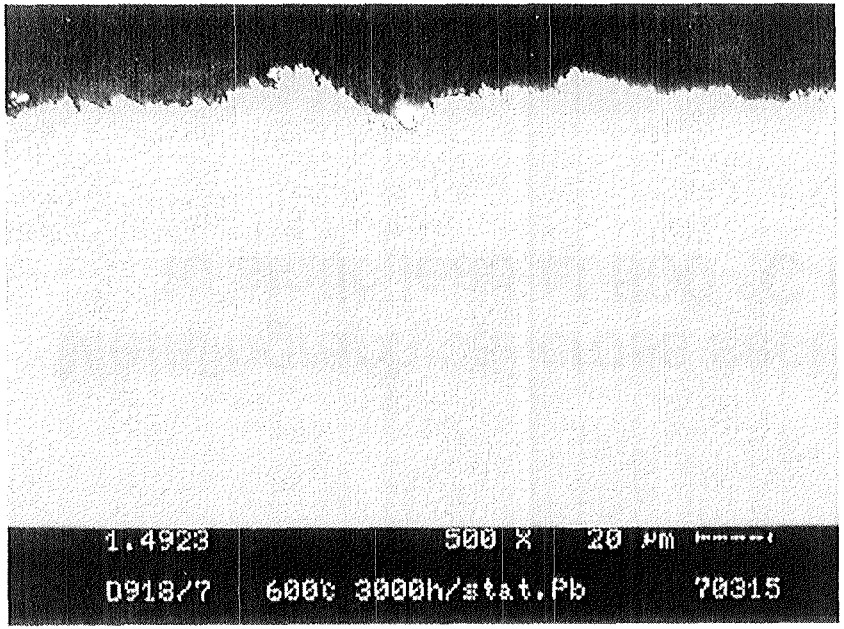


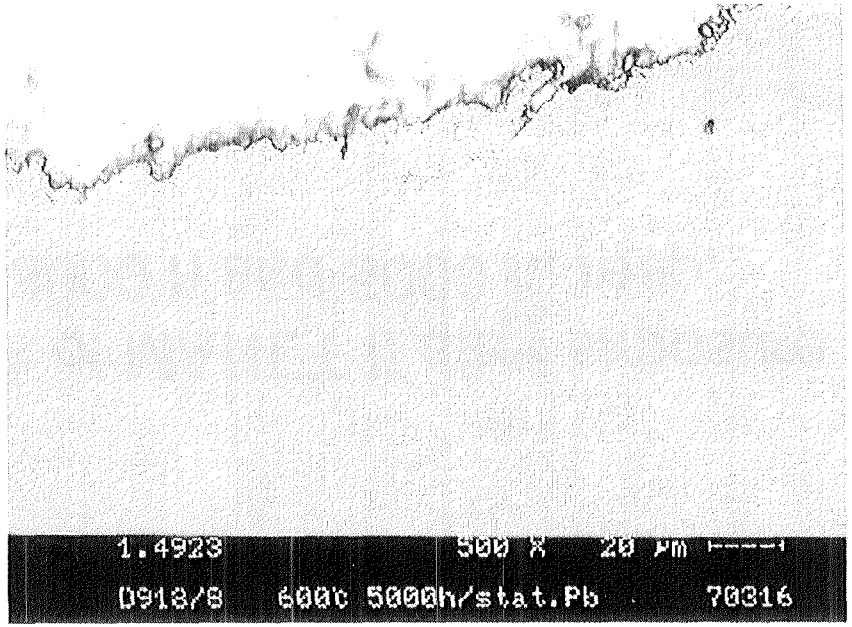
Metallographical cross sections of MANET II after exposure to static lead at 600 °C for 3000 h and 5000 h, resp.



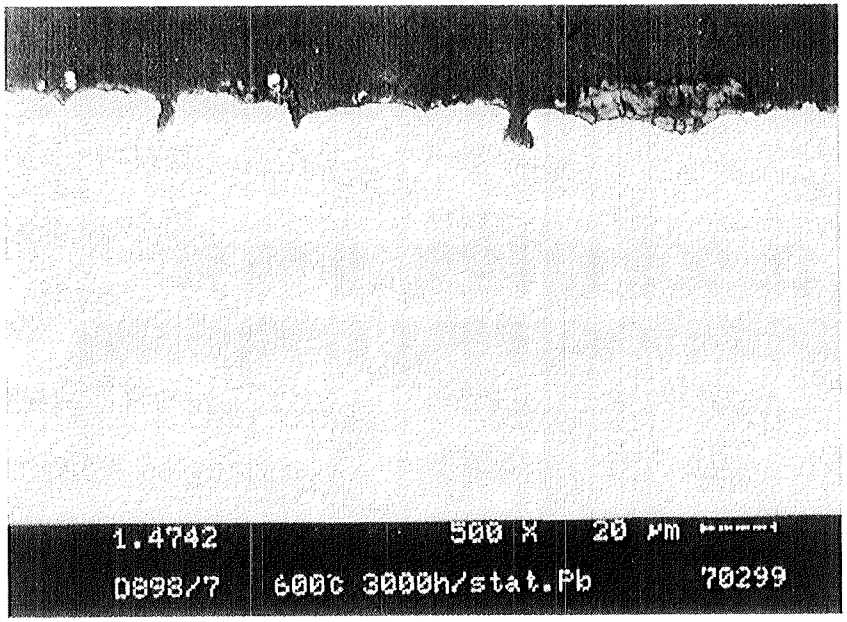


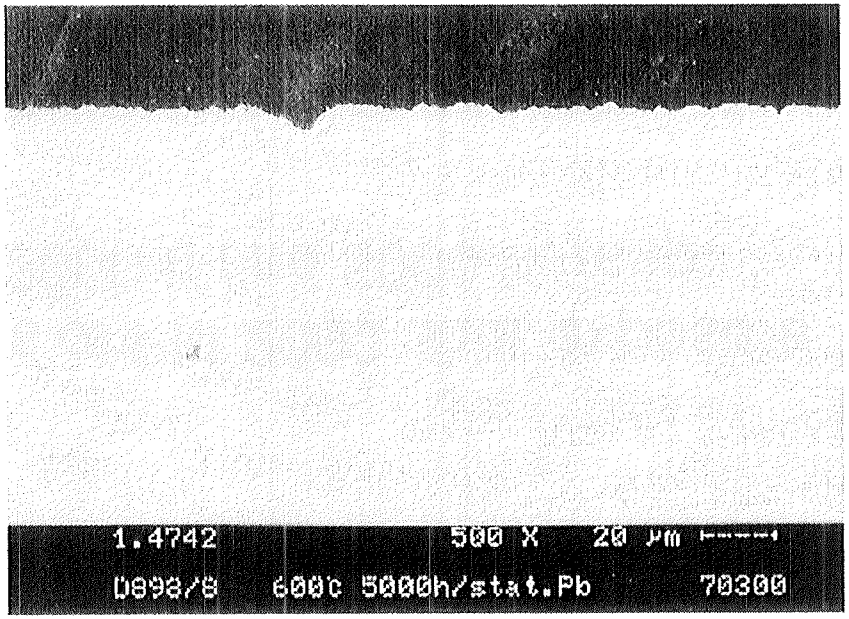
Metallographical cross sections of 1.4923 after exposure to static lead at 600 °C for 3000 h and 5000 h, resp.



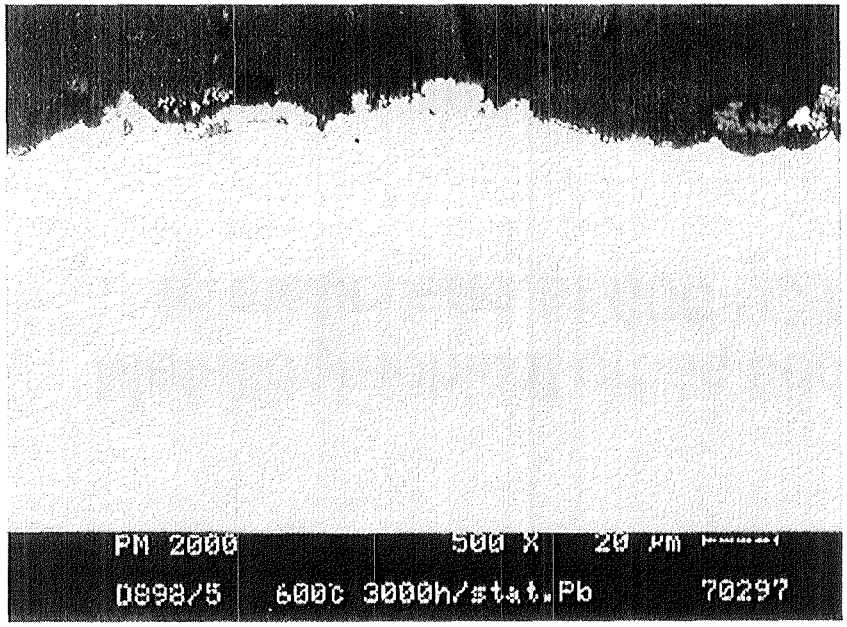


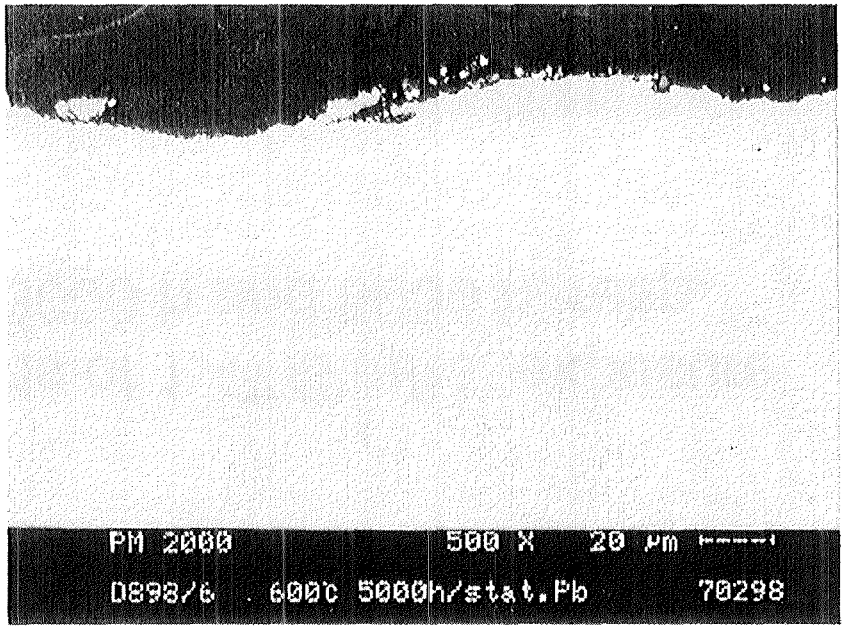
Metallographical cross sections of 1.4742 after exposure to static lead at 600 °C for 3000 h and 5000 h, resp.



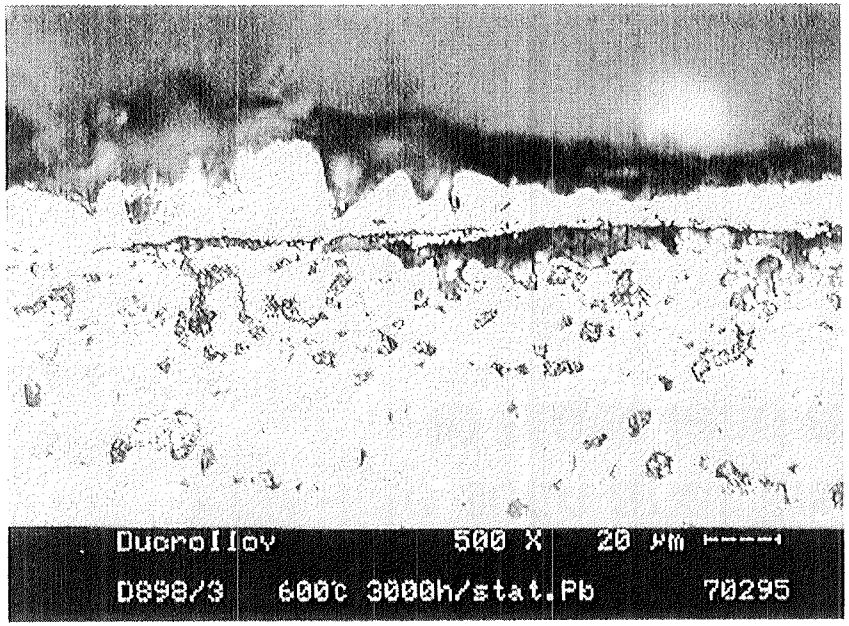


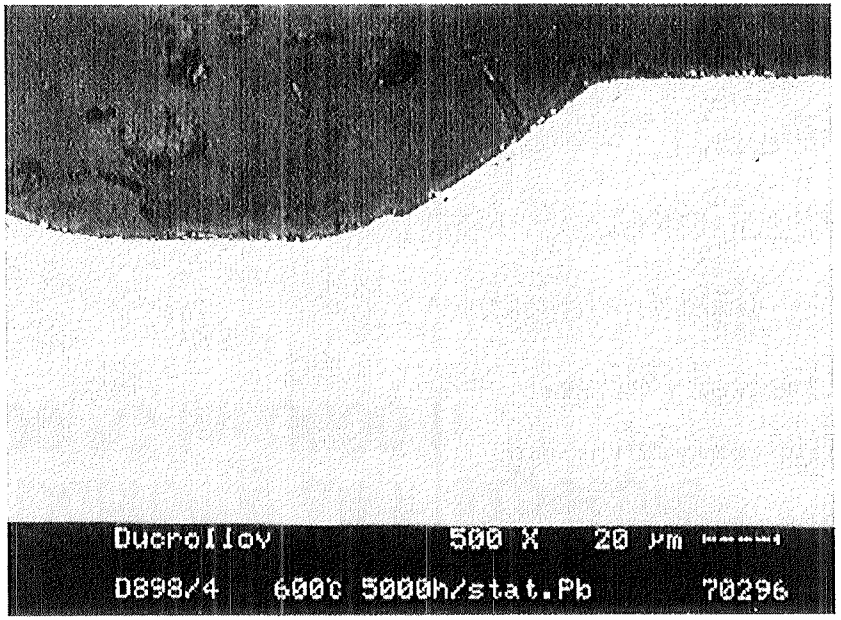
Metallographical cross sections of PM 2000 after exposure to static lead at 600 °C for 3000 h and 5000 h, resp.



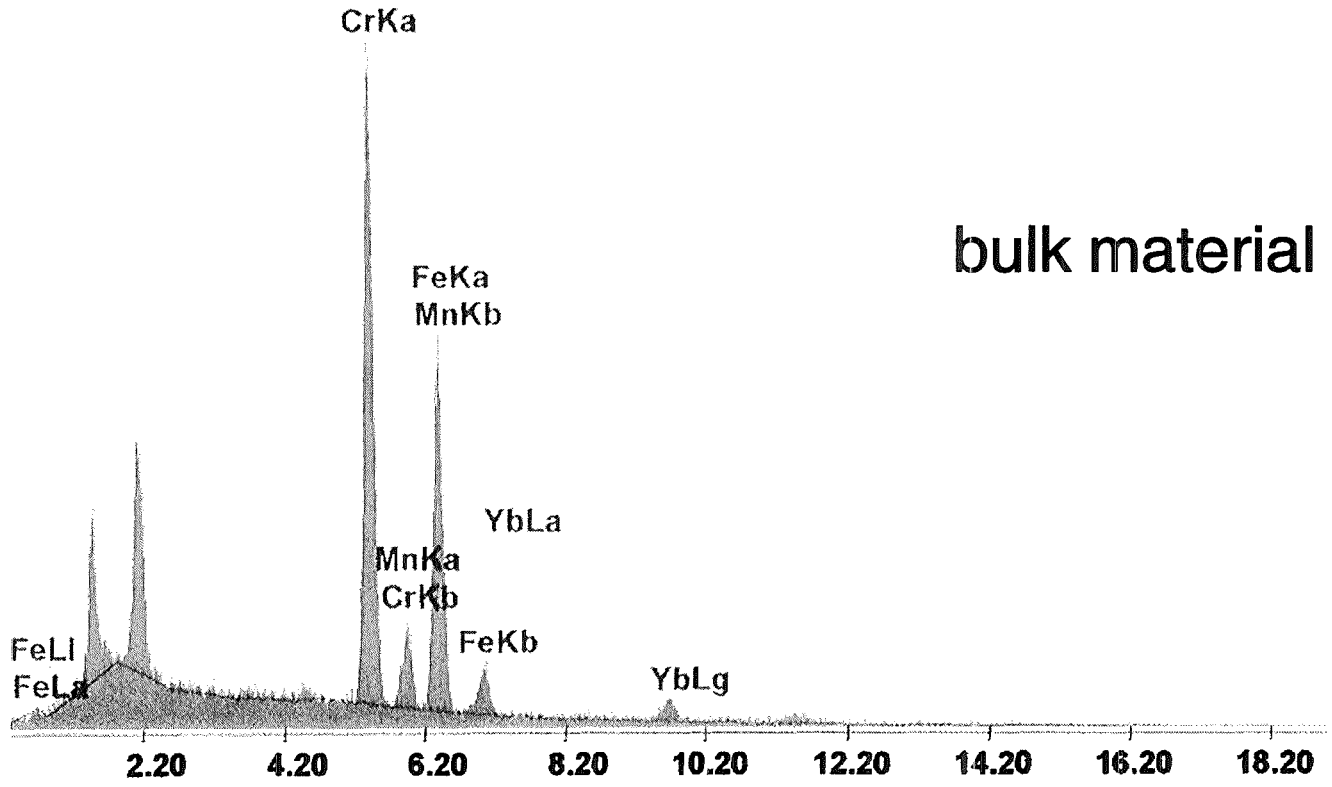


Metallographical cross sections of Ducrolloy after exposure to static lead at 600 °C for 3000 h and 5000 h, resp.



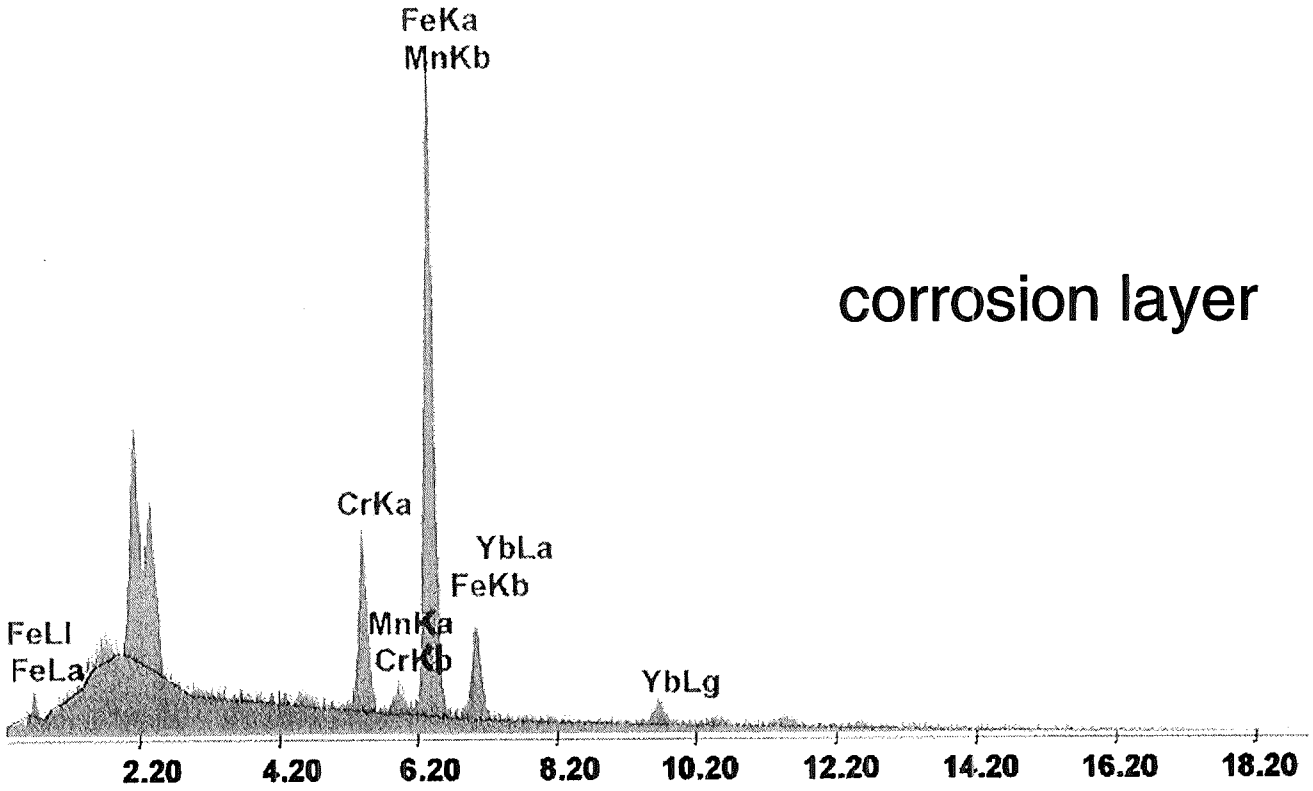


EDX-line scan analysis of Ducrolloy after exposure to static lead at 600 °C for 3000 h



bulk material

EDX-line scan analysis of Ducrolloy after exposure to static lead at 600 °C for 3000 h



corrosion layer

Observed maximum corrosive attack depth [µm] on specimens exposed to stationary lead at 600 °C

Steel	3000 h	5000 h
1.4713	about 2	about 4
Optifer IVa	about 4	about 10
Optifer IVc	about 4	about 10
MANET II	about 10	about 15
1.4923	about 12	about 16
1.4742	about 12	about 16
PM 2000	about 15	about 20
Ducrolloy	about 20	about 44

Discussion

➔ selective solution of Cr out of the alloy

higher solubility in Pb than Fe

↳ phase formation

↳ formation of subsurface voids within grains or grain boundaries

Conclusions

- ➔ the corrosion rate increases with time
- ➔ steels with low Cr content were only little attacked
- ➔ with increasing Cr content in the alloy the corrosion rate increases as well

Outlook

- investigation of 10,000 h exposed specimens in static Pb at 600 °C

- tests in circulating melt are essential
  - phenomena of erosion and mass transport

Corrosion investigations of steels in flowing lead at 400 and 550°C

H. Glasbrenner, G. Müller, A. Rusanov, FZK, IPPE

Abstract

The use of lead and lead-bismuth alloy is being considered as spallation target for the so-called hybrid reactor in which long-lived actinides should be transmuted. For the development of an accelerator driven system (ADS) the corrosion problems of structural materials in the coolant must be solved. Until now there is only little or no experience in the field of corrosion except for military application in the former USSR, but unfortunately these results are unpublished. Therefore, corrosion experiments are strongly required. The tests should be performed in a corrosion loop in which the liquid melt has a flow velocity in the order of 2 m/s and temperatures up to 550 °C. Such a loop is under design at FZK (KALLA). Beforehand some corrosion experiments have been carried out in collaboration with IPPE in Obninsk, Russia. Two ferritic-martensitic and two austenitic steels in bare condition and with a surface treatment by GESA method were exposed to Pb in a loop at 400 °C and 550 °C resp. for 1027, 2000 and 3000 h. First results of specimens exposed for 1027 h are already available.

The oxygen concentration was continuously controlled with an oxygen meter and kept constant in the Pb loop during the whole corrosion testing ($3 - 4 \times 10^{-5}$ wt%). The present oxygen in the flowing Pb was responsible for the formation of oxide layers on the surface of all steels tested during the exposure. Oxide layers on top of a steel surface can effectively protect the steel matrix for liquid metal corrosion attack. Dissolution of the steel or partly leaching out of steel elements with high solubility in lead could be successfully suppressed with this method. Generally, the oxide layers found on austenitic steels were thinner than on ferritic-martensitic steels at 550 °C and the oxide layers formed at 550 °C were thicker than the layers formed at 400 °C. The GESA treatment of the steel surfaces had no beneficial effect to the corrosion behaviour of the steel in liquid lead.

Corrosion investigations of steels in flowing lead at 400 and 550°C

H. Glasbrenner[1], J. Konys[1], G. Müller[2], A. Rusanov[3]

[1]FZK, IMF III, [2]FZK, IHM, [3]IPPE Obninsk

Outlines

- ⇨ Introduction
- ⇨ Experimental
- ⇨ Results
- ⇨ Discussion
- ⇨ Conclusions

Introduction

- corrosion behaviour of different structural materials in Pb and Pb-Bi is required
- a Pb-Bi corrosion loop is under construction in FZK (KALLA)
- corrosion experiments have been carried out in collaboration with IPPE Obninsk, Russia in a Pb loop at 400 °C and 550 °C for 1000, 2000 and 3000 h
- first results of specimens exposed for 1027 h are at hand

Experimental

The chemical composition of the steels tested in Pb

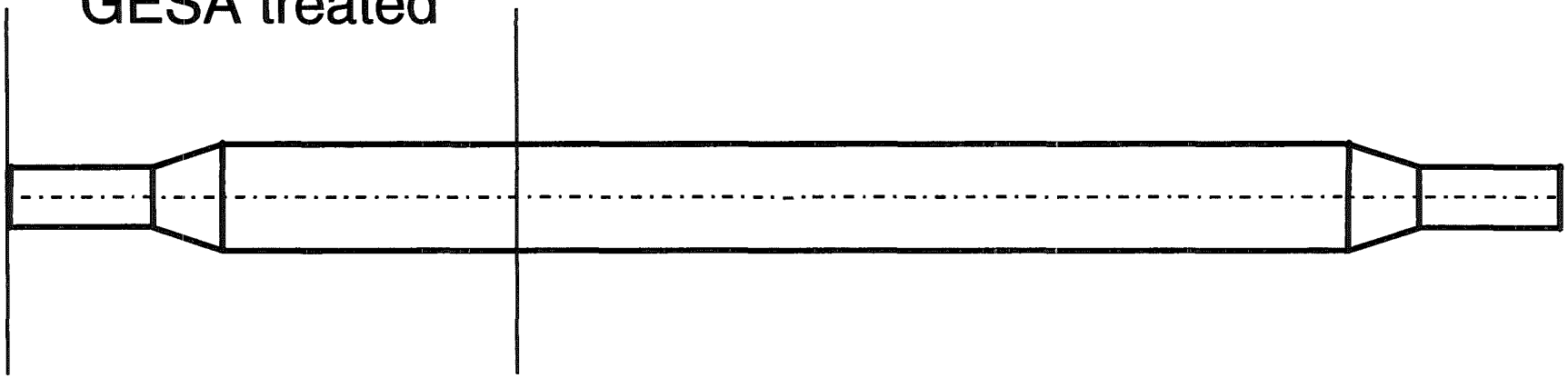
Material	C%	Mn%	Si%	Cr%	Ni%	Mo%	W%	V%	Nb%
1.4970	0.08-0.12	1.6-2.0	0.25-0.45	14.5-15.5	15-16	1.05-1.25	--	--	--
1.4948	0.04-0.08	0-2.0	0-0.75	17-19	10-12	--	--	--	--
Optifer IVc	0.13	0.52	--	9.05	--	--	1.0	0.25	--
EM 10	0.10	0.51	0.37	8.8	0.2	1.0	--	0.03	0.01

A list of the materials exposed to flowing Pb for 1027 h at 400 °C and 550 °C, resp. oxygen concentration in the Pb loop was 3-4 x 10^{-5} wt%

Material	400 °C	550 °C
1.4970	1027 h	1027 h
1.4970 - GESA	--	1027 h
1.4948	1027 h	1027 h
1.4948 - GESA	1027 h	1027 h
Optifer IVa	1027 h	1027 h
Optifer IVa-GESA	--	1027 h
EM 10	--	1027 h

The shape of the specimens exposed to flowing lead

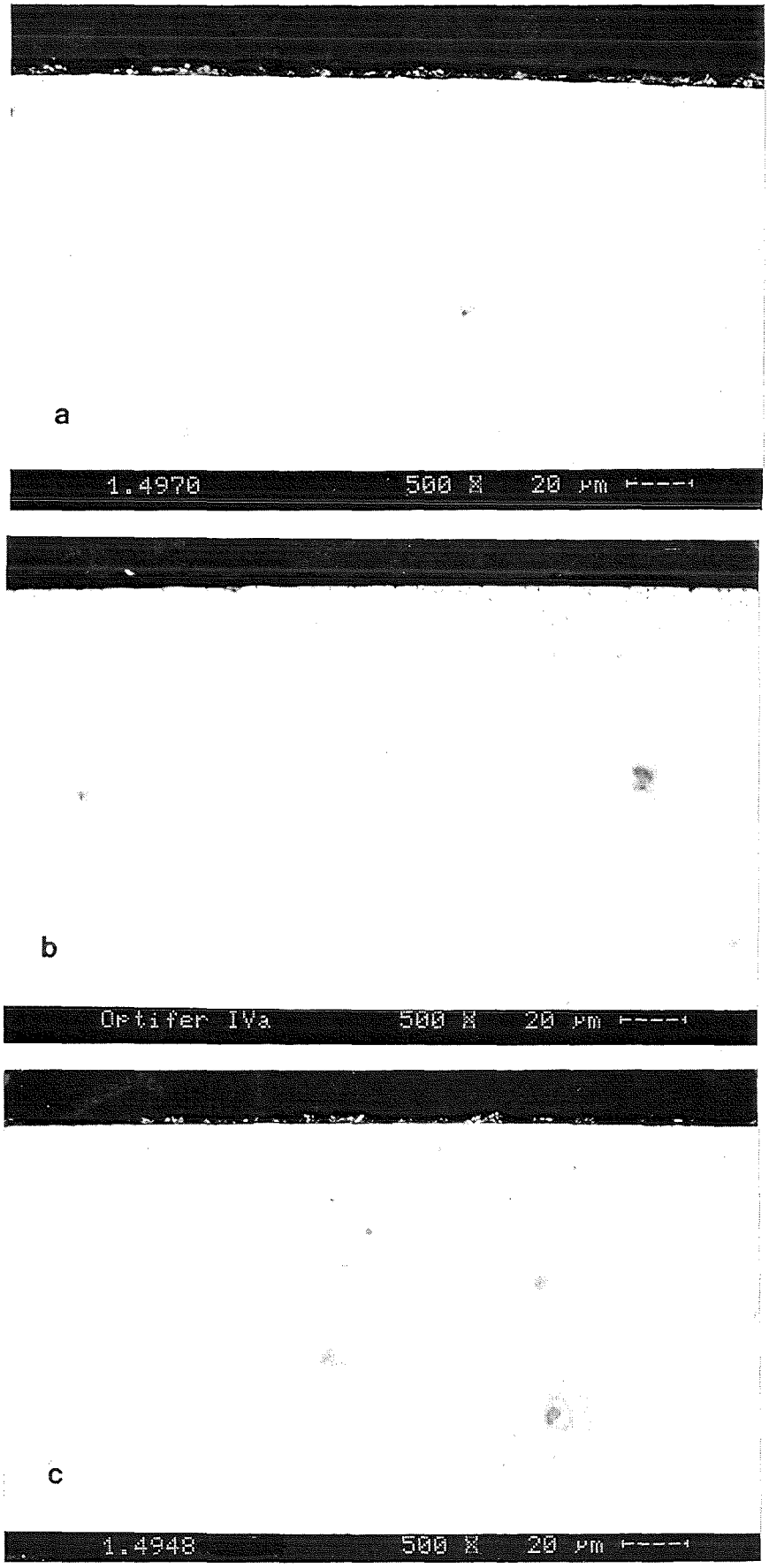
GESA treated



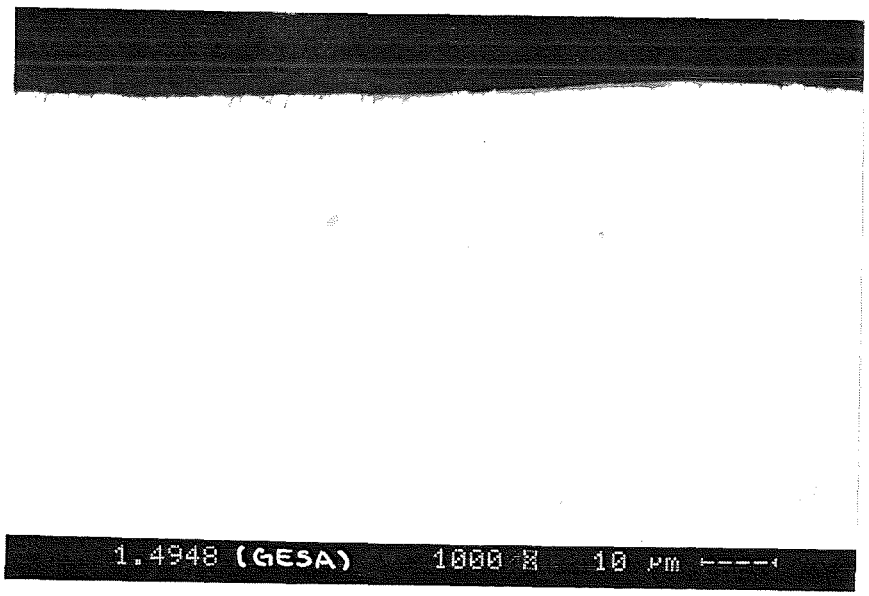
diameter 8 mm
length 110 mm

Results of weight gain measurements of bare specimens after the corrosion testing at 550 °C

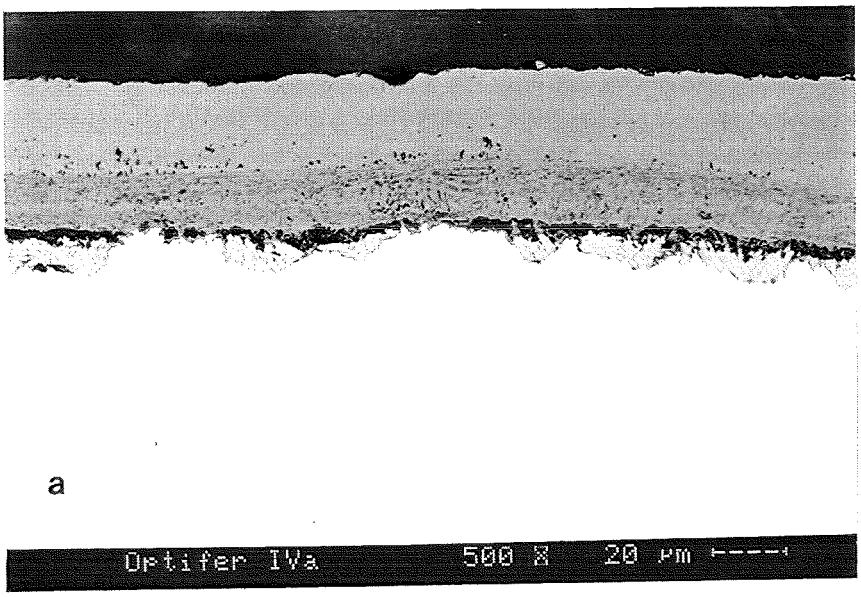
Steel	Weight before test /W_1 [g]	Weight after test /W_2 [g]	$\Delta W = W_2 - W_1$ [g]
Optifer IVc	36.0638	36.1766	1.1×10^{-1}
EM 10	35.9951	36.0678	7.3×10^{-2}
1.4970	36.7952	36.8184	2.3×10^{-2}
1.4948	36.6812	36.7016	2.0×10^{-2}



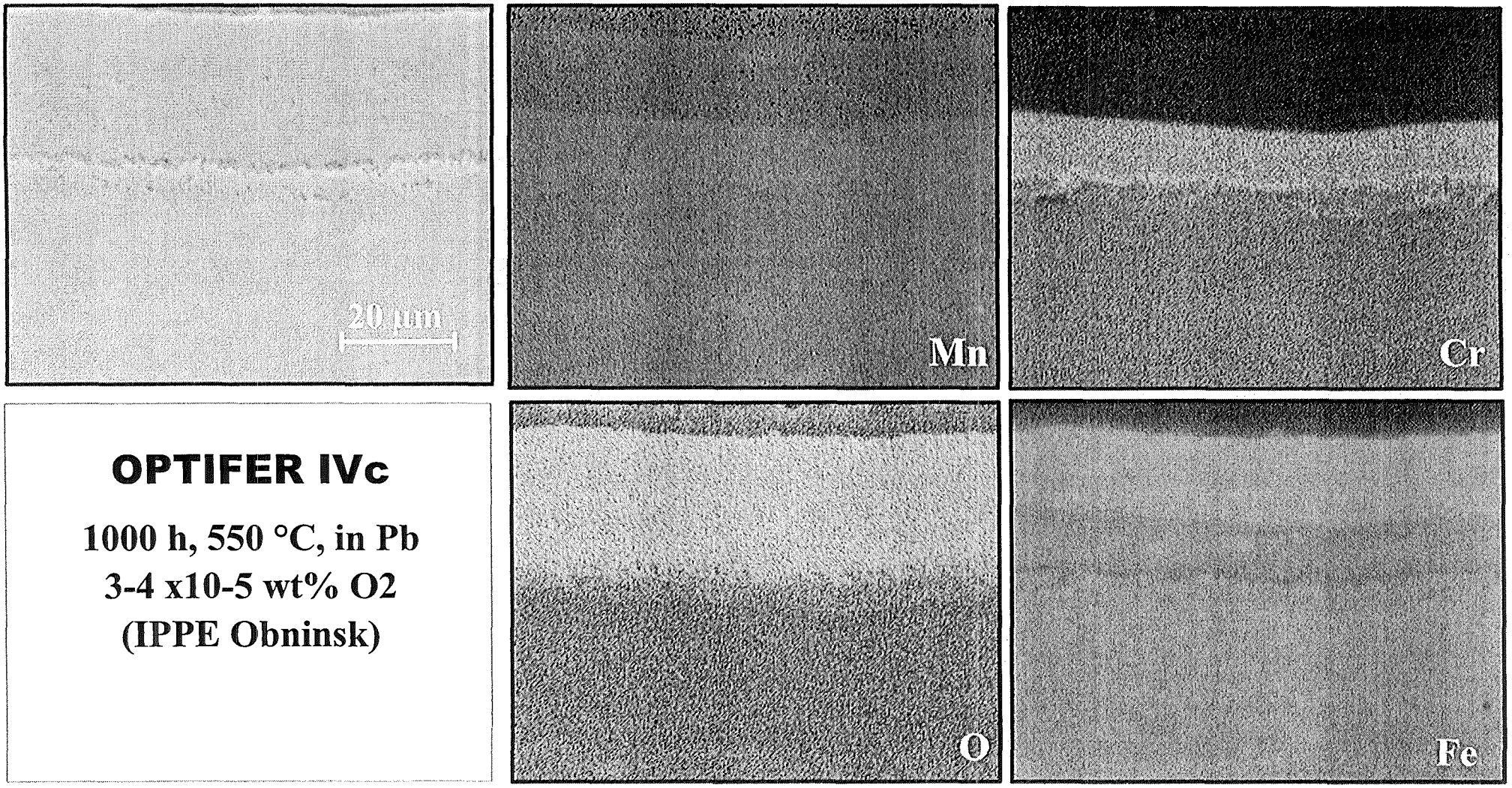
Metallographical cross sections on steel specimens exposed to flowing Pb at 400 °C for 1000 h: a) 1.4970, b) Optifer IVc and c) 1.4948.



Metallographical cross sections on steel 1.4948 GESA-treated after the exposure to flowing Pb at 400 °C for 1000 h.

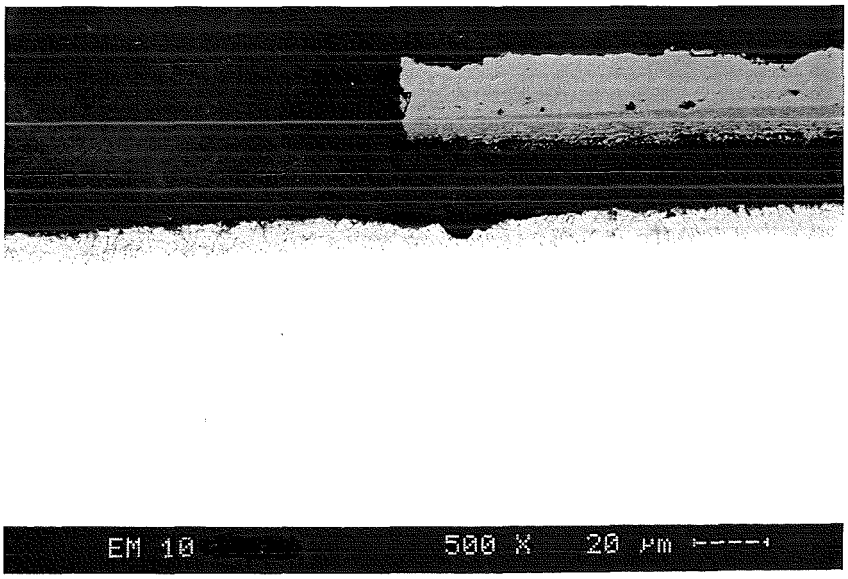


The steel Optifer IVc after the exposure to flowing Pb at 550 °C for 1000 h a) original condition and b) GESA treated surface.

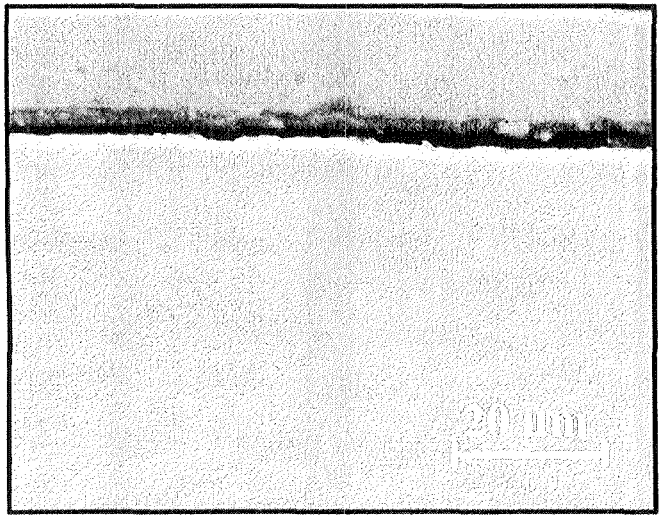


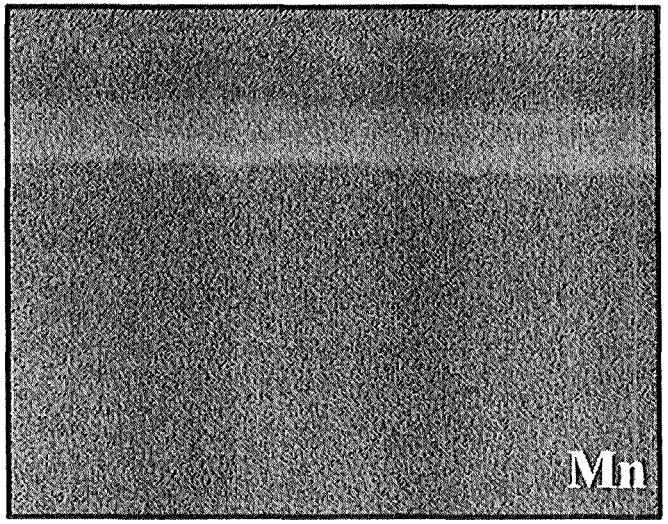
OPTIFER IVc

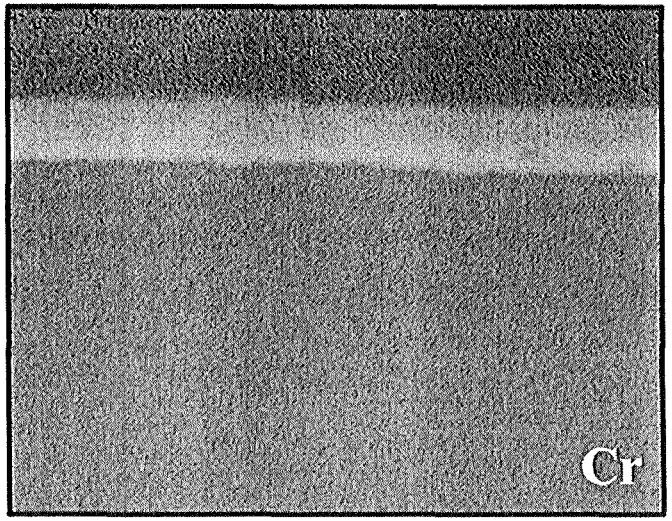
1000 h, 550 °C, in Pb
3-4 x10-5 wt% O2
(IPPE Obninsk)



The steel EM 10 after the exposure to flowing Pb at 550 °C for 1000 h in original condition.

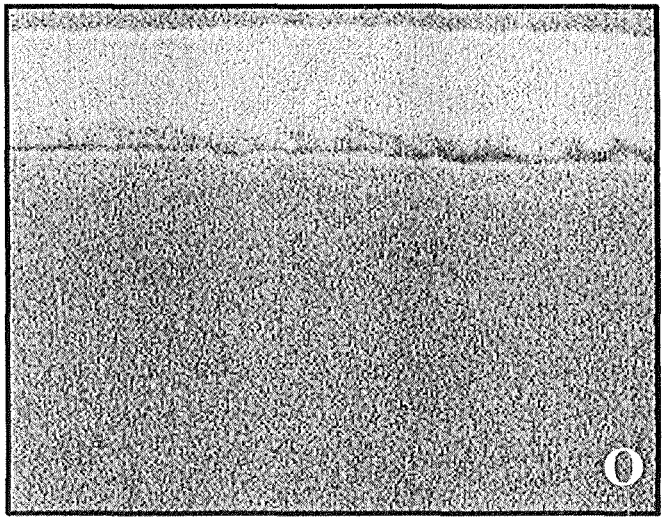


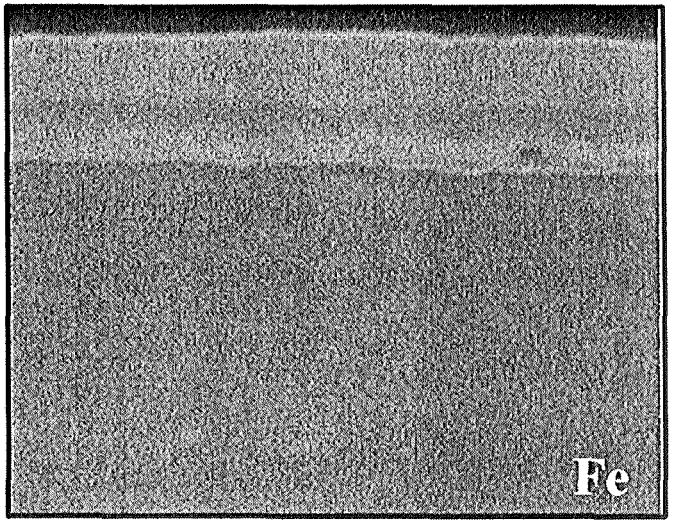


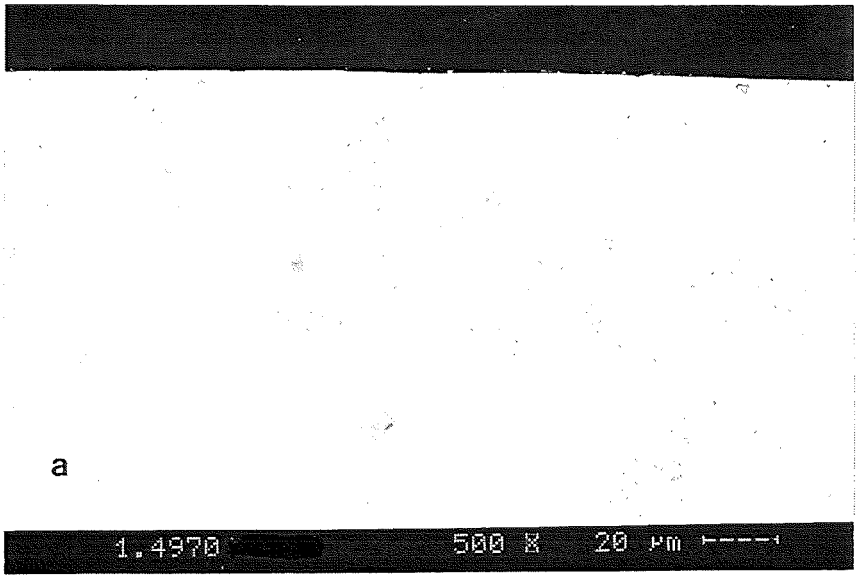


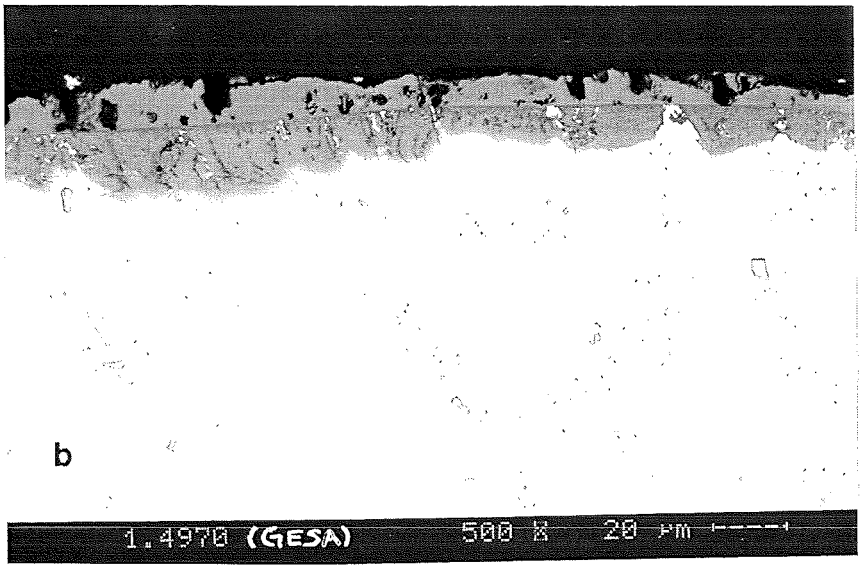
EM10

1000 h, 550 °C, in Pb
3-4 x10-5 wt% O2
(IPPE Obninsk)



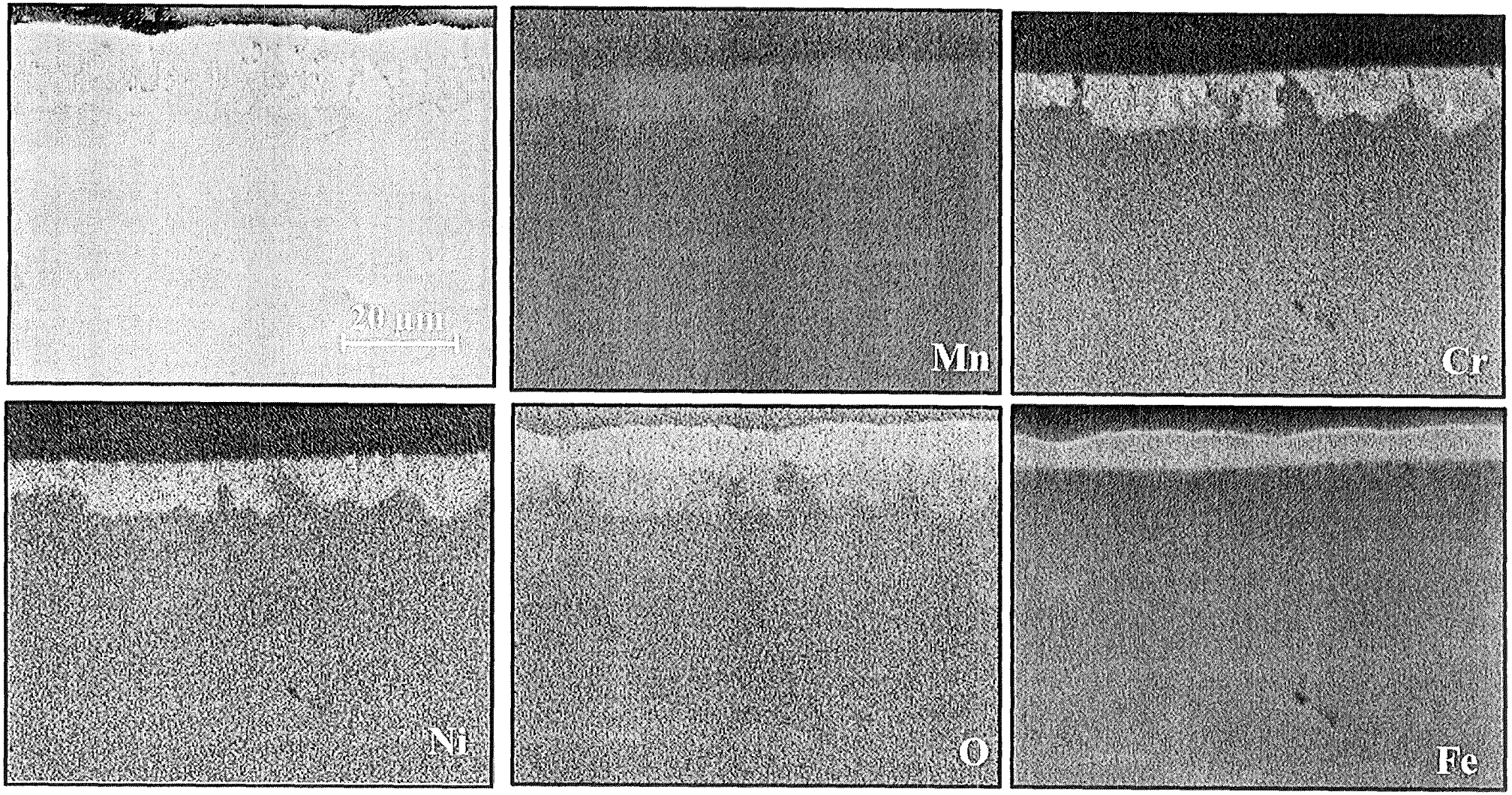


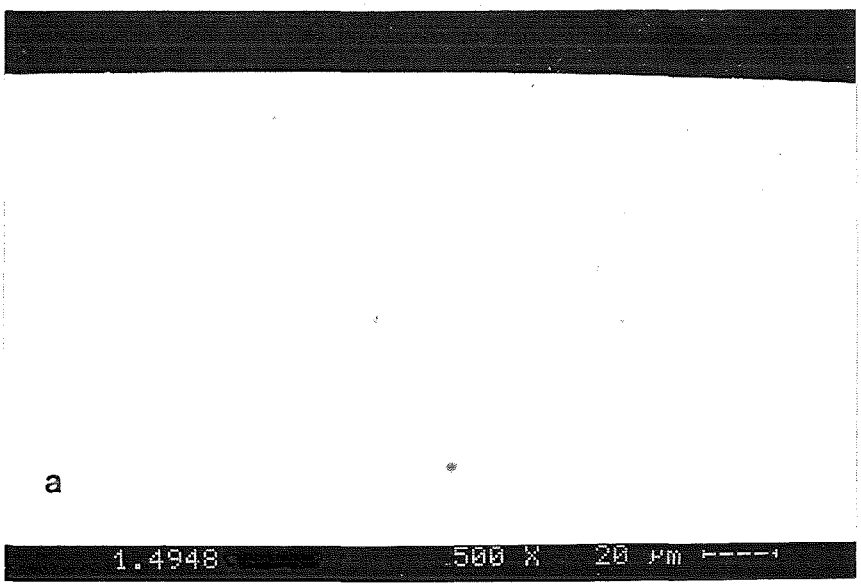


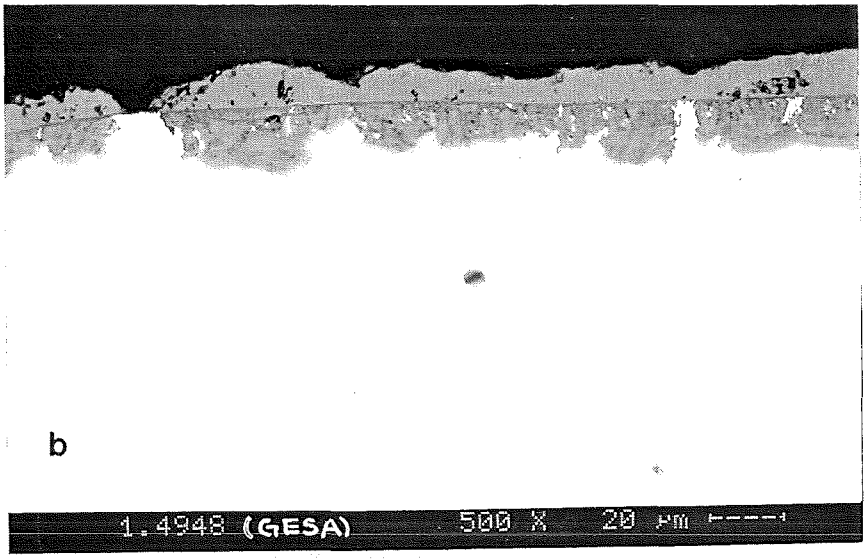


The steel 1.4970 after the exposure to flowing Pb at 550 °C for 1000 h a) original condition and b) GESA treated surface.

1.4970 1000 h, 550 °C, in Pb 3-4x10^{-5} wt% O_2 GESA (IPPE Obninsk)

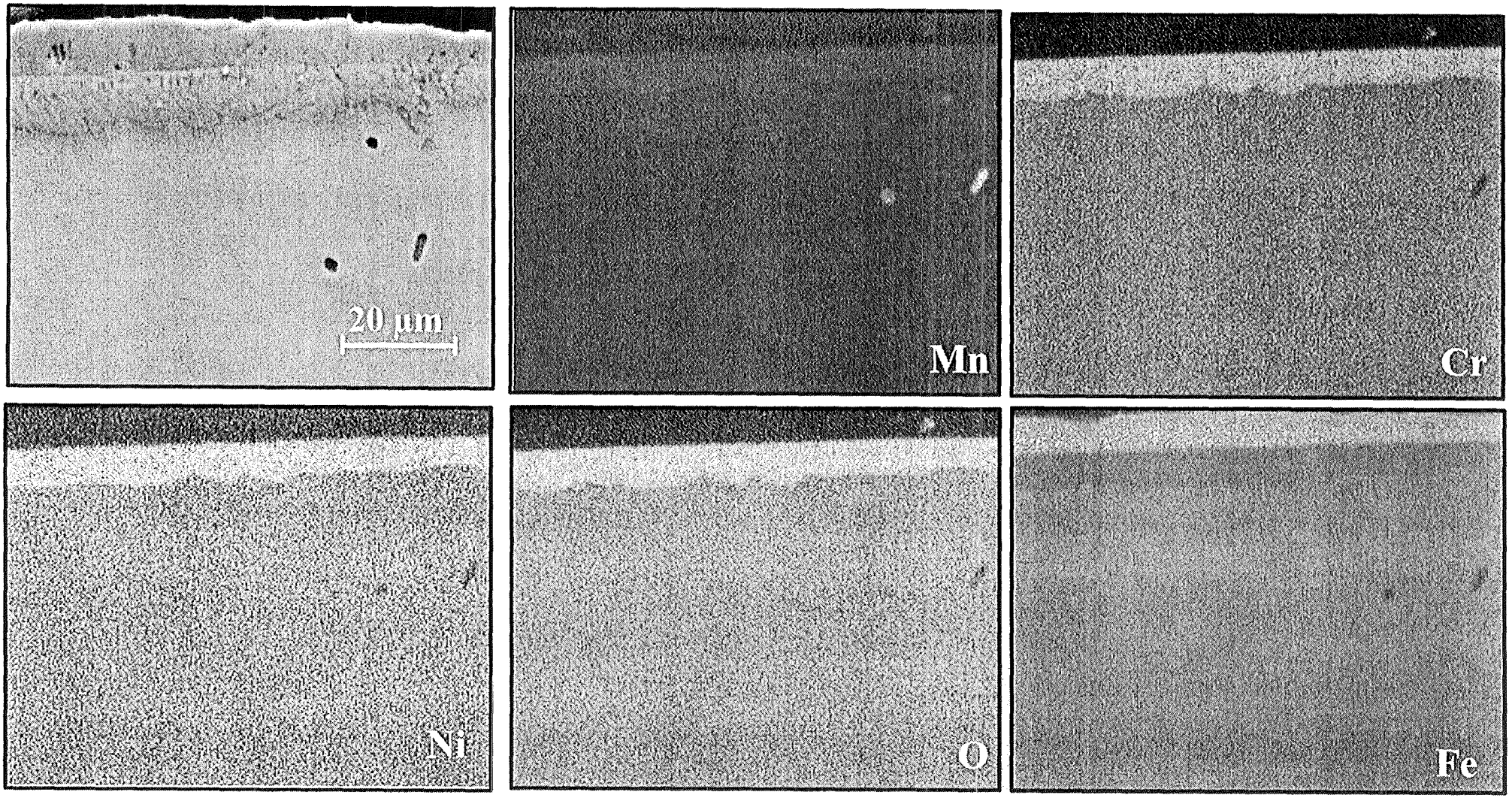






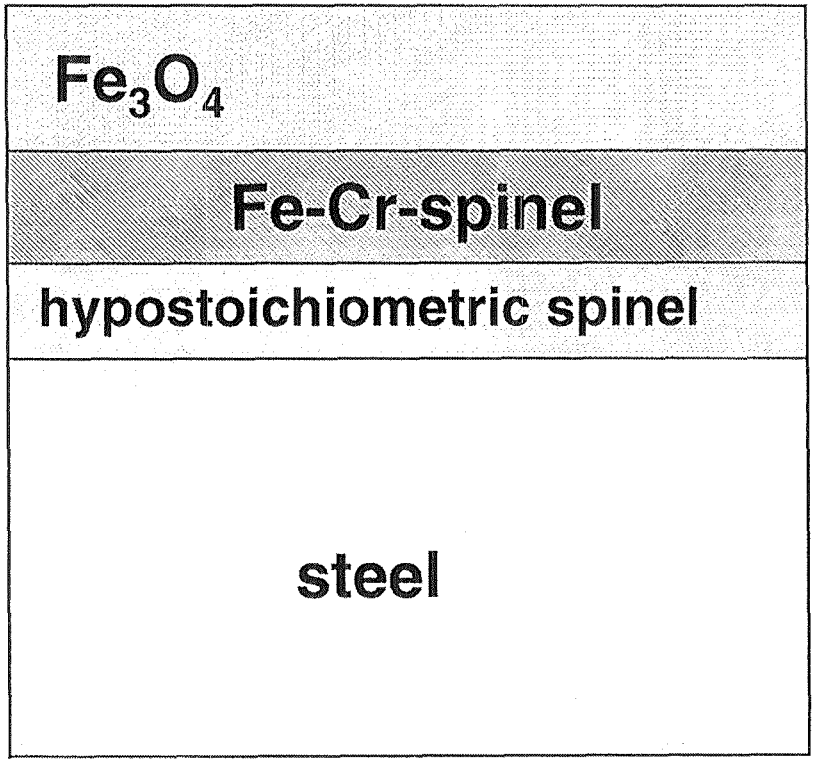
The steel 1.4948 after the exposure to flowing Pb at 550 °C for 1000 h a) original condition and b) GESA treated surface.

1.4948 1000 h, 550 °C, in Pb 3-4x10^{-5} wt% O_2 GESA (IPPE Obninsk)

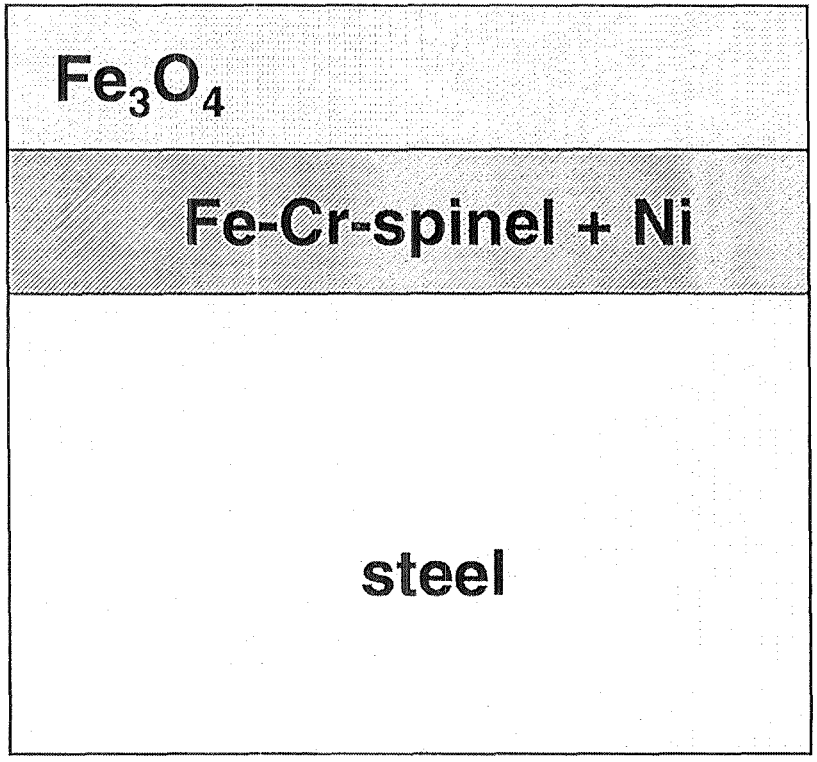


Scale structure after the exposure to Pb

ferritic-martensitic steel



austenitic steel (GESA)



Discussion

- no liquid metal corrosion attack
- passivating oxide scale on top of each steel surface

Ferritic-martensitic steels (untreated and GESA treated)

⇨ formation of a three layer system
(partially bad or no adherence)

⇨ GESA treatment has no influence to the behaviour
of the steel with lead

Austenitic steels

untreated specimens

⇨ formation of a thin oxide scale (good adherence)

GESA treated specimens

⇨ formation of a two layer system with irregular thickness (good adherence)

- ✶ treated area is irregular in thickness
- ✶ very fine grained structure
- ✶ oxygen diffusion along grain boundaries

Conclusions

high oxygen concentration in the Pb loop (3-4 x 10^{-5} wt%)

⇨ formation of thick oxide layers

GESA treatment

⇨ ferritic-martensitic steels: no improvement
⇨ austenitic steels: formation of very irregular layers

Behaviour of different steels in liquid Pb and Pb-Bi eutectic alloy

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Abstract

The interaction products on modified F82H martensitic steel immersed in stagnant, oxygen-saturated liquid lead at 793 K under an Ar atmosphere, for exposure times up to 3700 hrs, were characterised by means of SEM, EDS and XRD. Layers of Me_3O_4 consisting of an inner sublayer with Me = Fe, Cr and an outer chromium-free sublayer of Fe_3O_4, formed on the surface of the steel. Under the conditions adopted for the immersion tests, the interaction between liquid lead and the oxide layer did not lead to the formation of ternary compounds Fe-Pb-O.

The preliminary results of another set of tests carried out in stagnant, oxygen-saturated liquid Pb and Pb-Bi at 743 K under an Ar atmosphere, for exposure times up to 1200 hrs, are presented as well. The steels exposed to liquid metals were: (i) mod.F82H, (ii) Manet, (iii) AISI 316 LN. The behaviour of F82H and Manet was very similar, and can be described by the same considerations made about the behaviour of F82H in molten lead at 793 K. On the surface of AISI 316 LN a very thin (3-5 μm) Me_3O_4 (Me = Fe, Cr) layer was observed. The presence of Nickel in the oxide layer was observed as well. Further work is required to fully characterise these oxide layers.

When selecting metals to be used in contact with oxygen-containing molten lead, the solubility of alloying elements in molten lead is not the only key-parameter to be considered. The adhesion, compactness and protectiveness of the oxide layers should be also taken into account, together with their reactivity with the molten metal. Further corrosion experiments in dynamic conditions are in progress in order to fully evaluate the materials performance in the in-service conditions.

September, 16-17th 1999 - *HLM Workshop, Karlsruhe*

Behaviour of different steels in liquid Pb and Pb-Bi eutectic alloy

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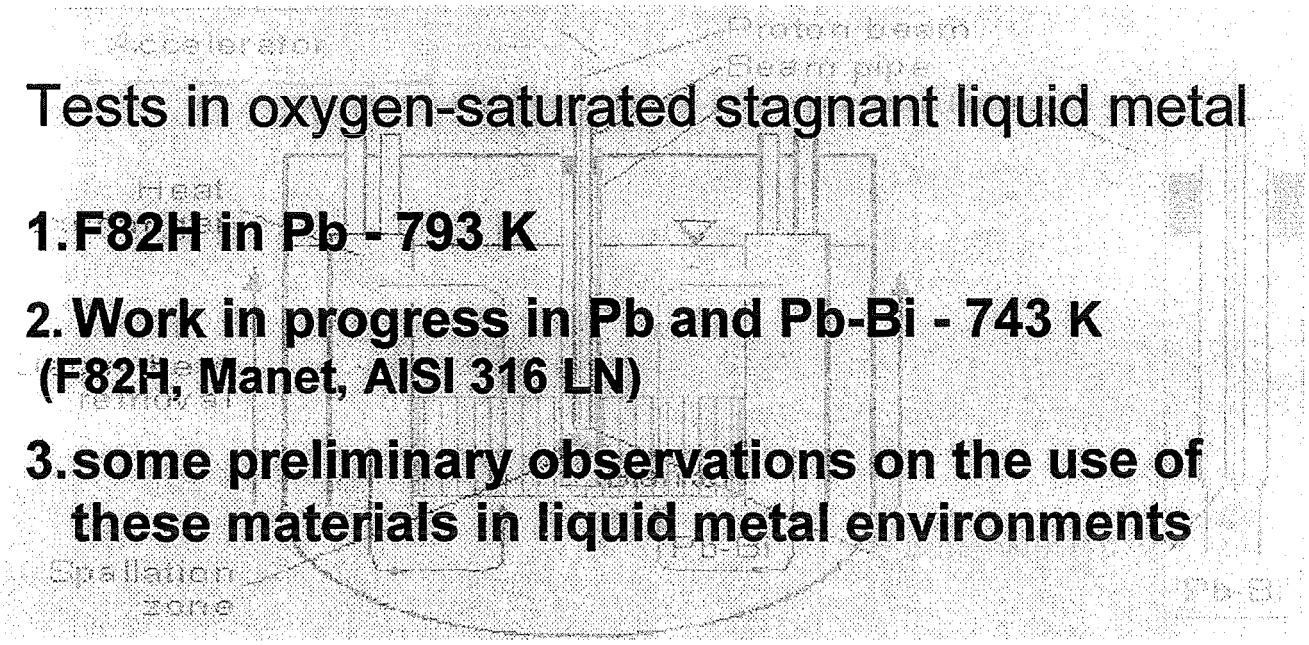
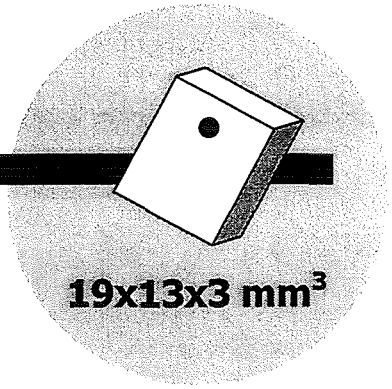


Materials



mod. F82H steel (wt.%)

C	Cr	Ni	Mo	V	Nb	Si	Mn	S
0.09	**7.8**	0.04	<0.01	0.16	<0.01	0.13	0.18	0.003
P	**B**	**N**	**Ta**	**Al**	**Cu**	**W**	**Ti**	**-**
0.004	<0.001	0.006	*0.02*	<0.01	<0.007	2	<0.02	-

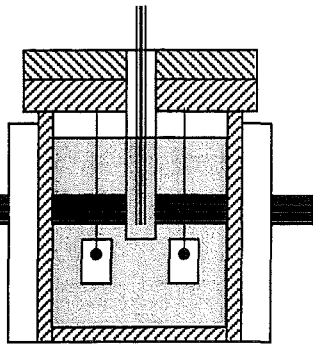
MANET steel (wt.%)

C	Cr	Ni	Mo	V	Nb	N	P	S
0.17	**10.5**	0.9	0.56	0.25	0.2	0.003	0.003	-

AISI 316 LN steel (wt.%)

C	Cr	Ni	Mo	P	N	Si	Mn	S
0.03	**16-18**	10-14	2-3	0.045	0.13	1.00	2.00	0.03

Corrosion tests



in Ar (glove box)

*Testing conditions (stagnant **Pb**, 743K)*

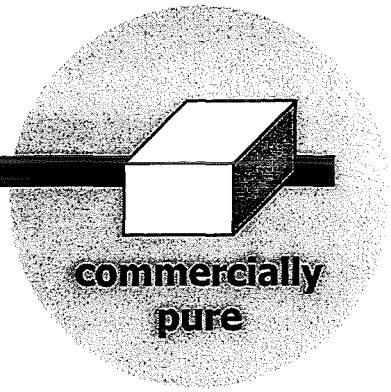
	Time of exp. I sample (h)	Time of exp. II sample (h)
mod. F82H	2000	3700

! WORK IN PROGRESS !

*Testing conditions (stagnant **Pb** and **Pb-Bi**, 743K)*

	Time of exp. I sample (h)	Time of exp. II sample (h)
mod. F82H	700	1200
MANET	700	1200
AISI 316LN	700	1200

Liquid Metals



✓ Pb

✓ Pb-55Bi (eutectic; T_m= 125.5 °C)

About 3 kg of solid metal were melted into each cylindrical crucible of alumina (d=58.5 mm, h=104 mm), in a glove-box under Ar atmosphere.

The molten metal was saturated by oxygen, as proved by the presence of floating PbO. Measurements of total oxygen content by extraction from the melt as CO_2, carried out after the tests, confirmed that lead was in all cases saturated by oxygen throughout the test.

	C_s (743 K), wppm	C_s (793 K), wppm
Pb	3.0	7.7
Pb-Bi	4.2	8.2

Orlov *et al.* 1997

Thermodynamics

The presence of oxygen in liquid metals can lead to the formation of oxide layers

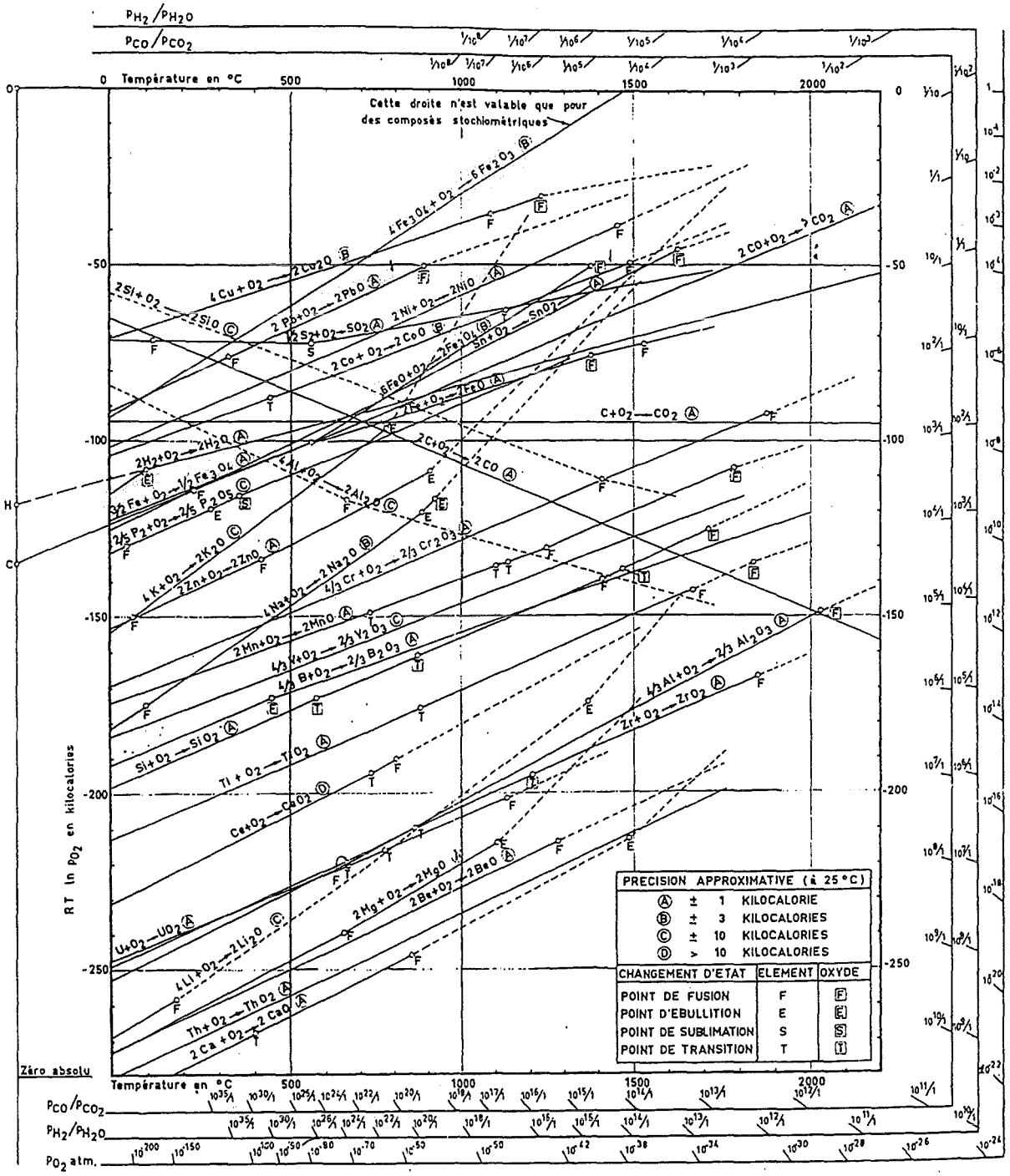
➡ **modification of the corrosion mechanism**
(eg. direct solubilisation)

Driving forces for the oxidation of the elements of the materials exposed to oxygen-containing liquid metals:

$Fe_2O_3 < PbO < NiO < Fe_3O_4 < FeO < Cr_2O_3$

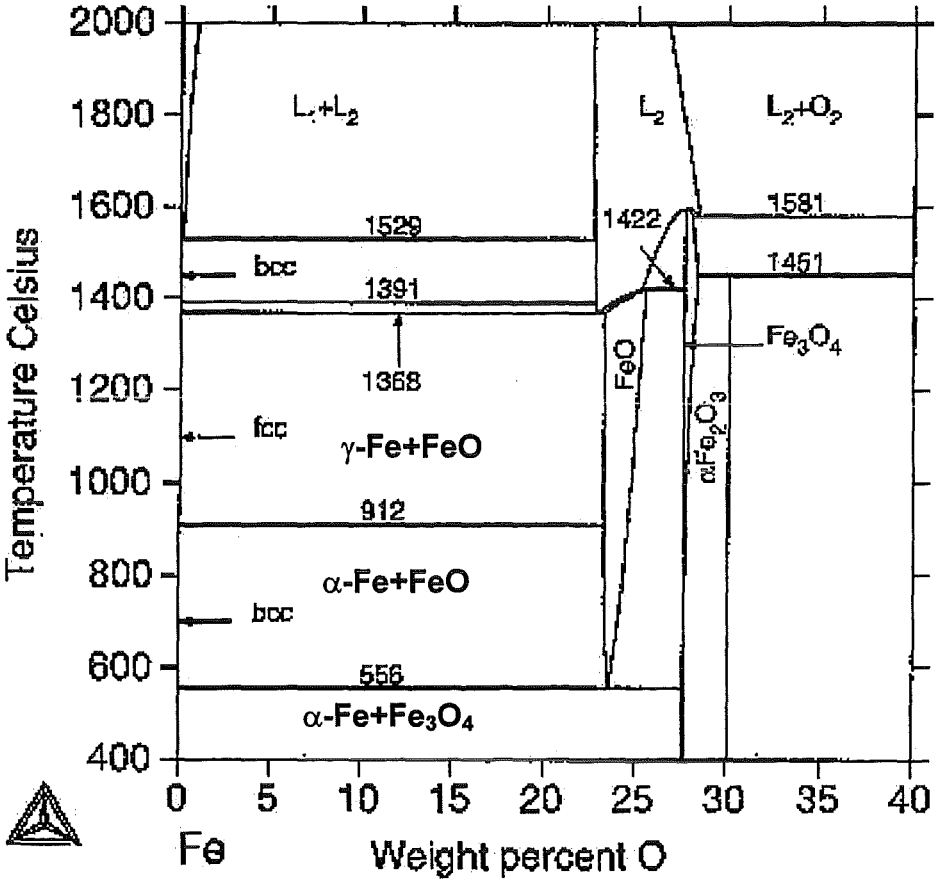
$\Delta G°_T$

Thermodynamics



(Oxidation des Métaux, J.Bénard, Gauthier-Villars Paris 1964)

Thermodynamics



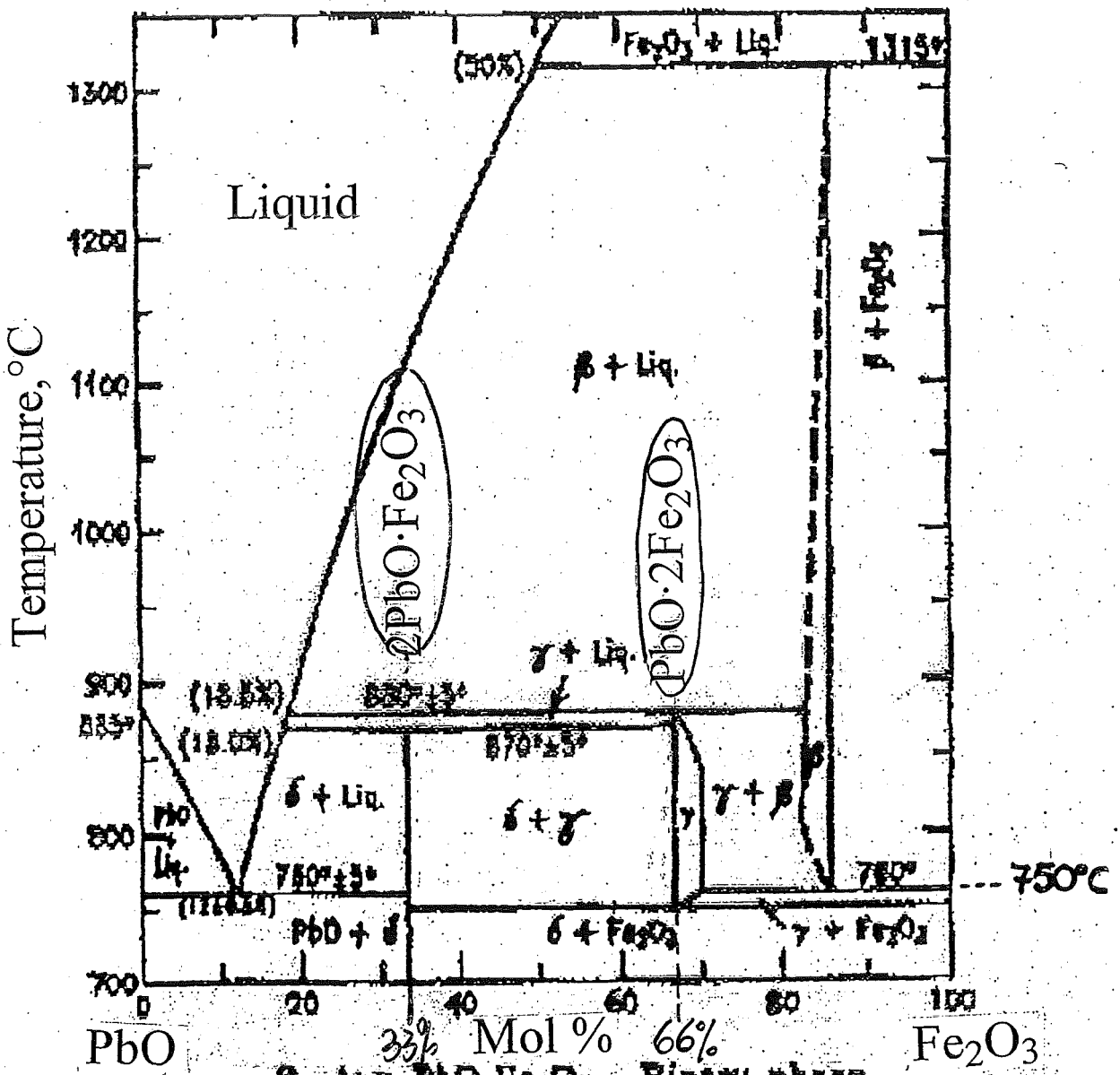
(ASM Handbook, Alloy Phase Diagrams, Vol.3 (1992), p.235)

Below 843 K, FeO decomposes to α–Fe_2O_3 (in the external layer) and Fe_3O_4 in contact with the metal.

(Oxidation des Métaux, J.Bénard, Gauthier-Villars Paris 1964)

Thermodynamics

$PbO-Fe_2O_3$



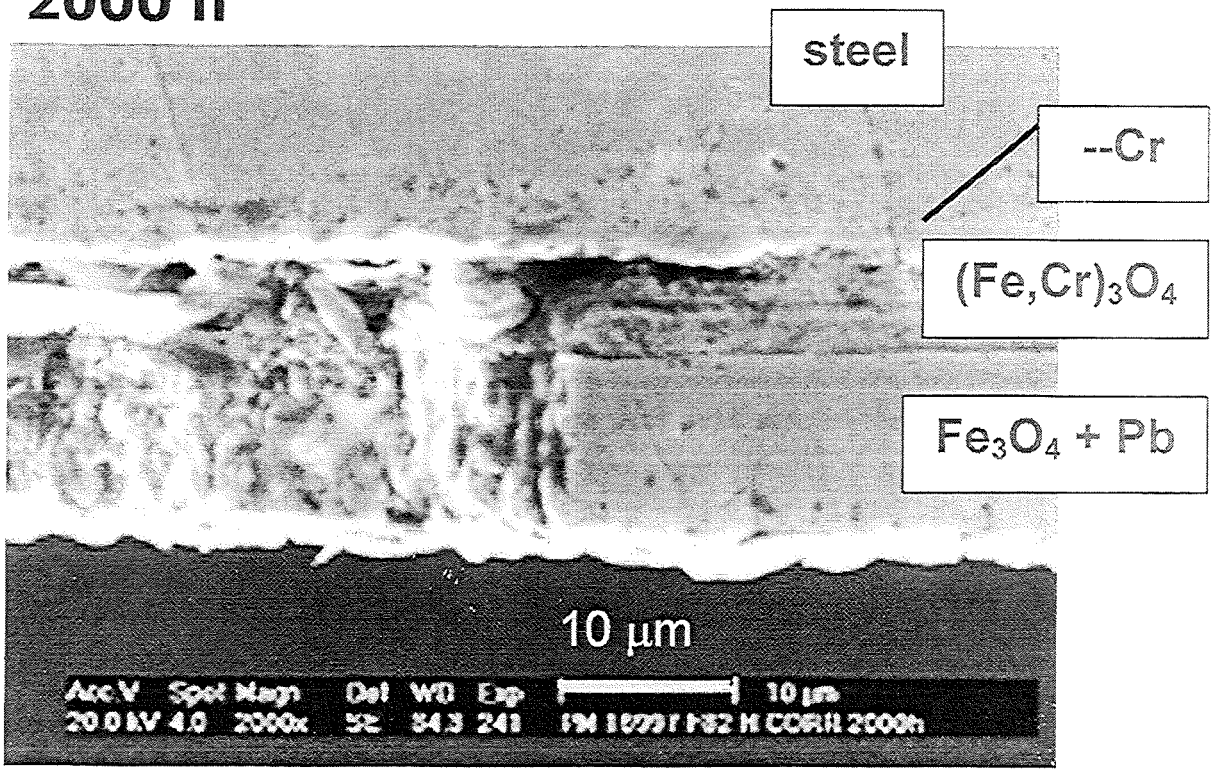
System $PbO-Fe_2O_3$. Binary phase
Relations at Fe_2O_3 > 65 mol% are from Fig. 252.

δ = $Pb_2Fe_2O_5$.

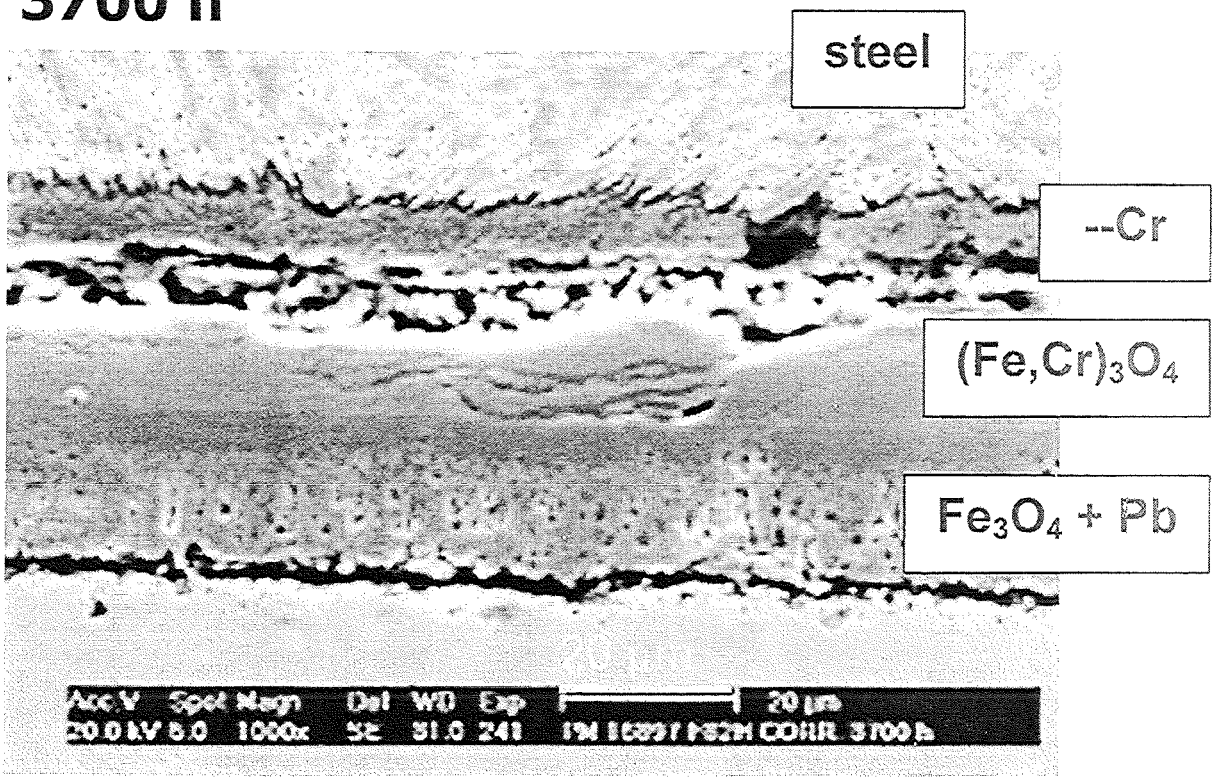
M. Nevriva and K. Fischer, *Mater. Res. Bull.*, 21 [11] 1285-1290 (1986).

F82H (793 K) - Pb

2000 h

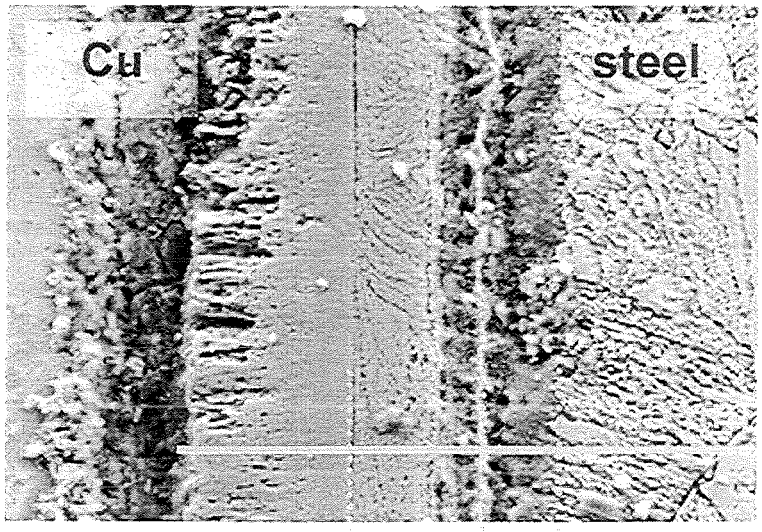


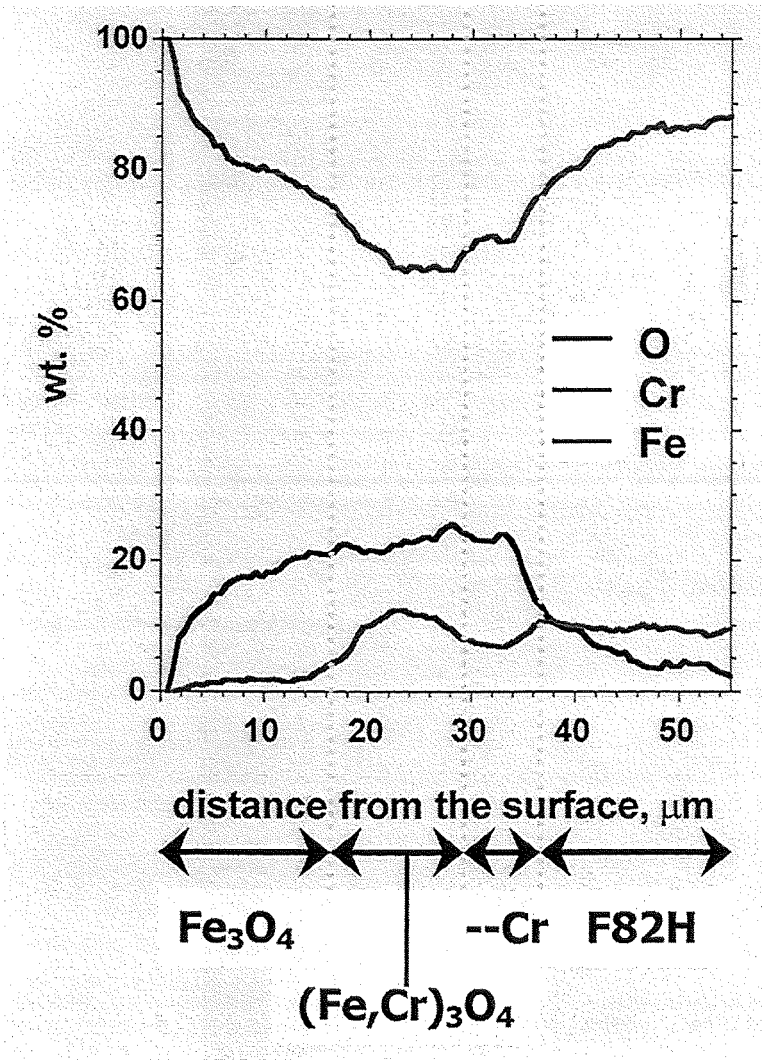
3700 h



F82H (793 K)

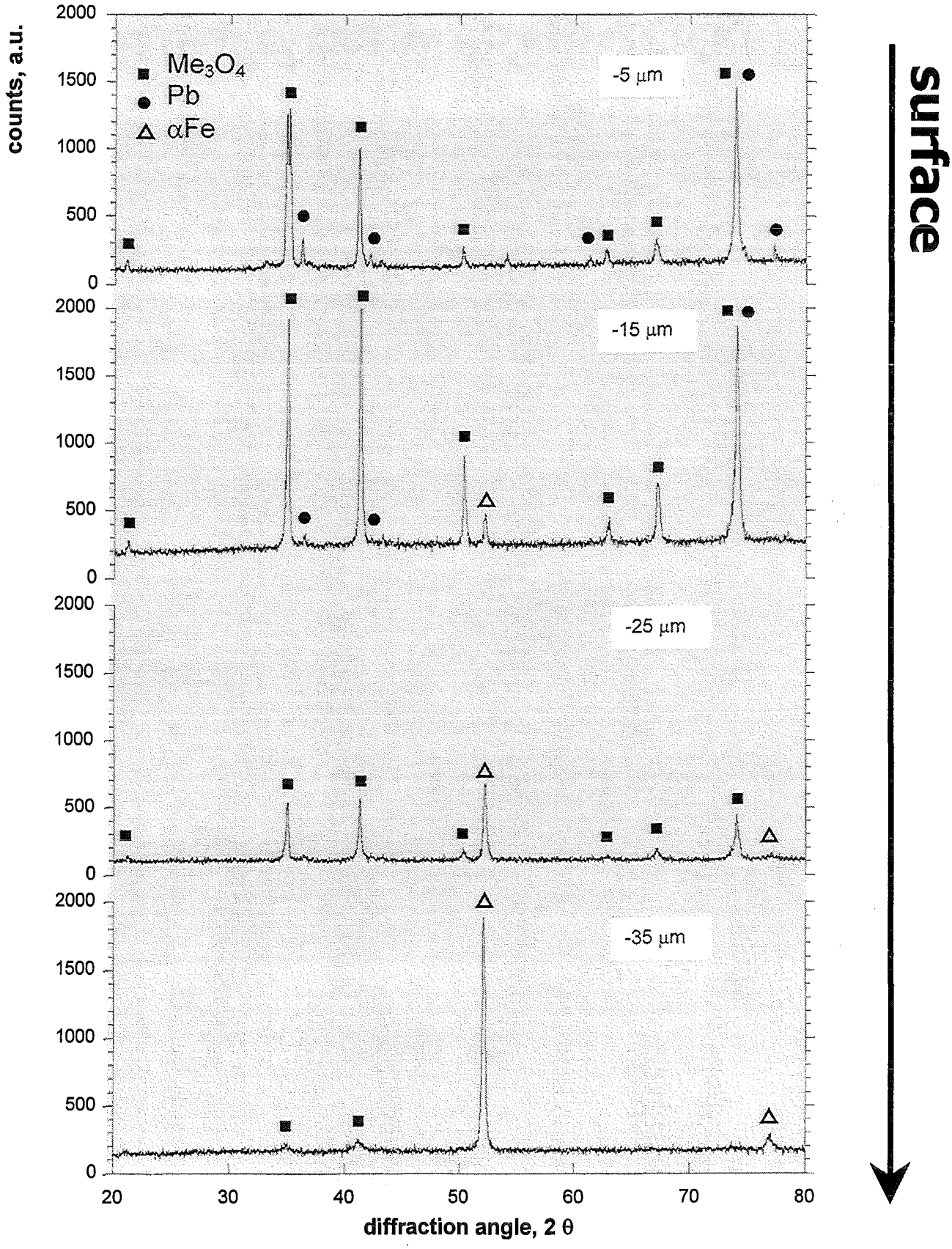
3700 h in Pb

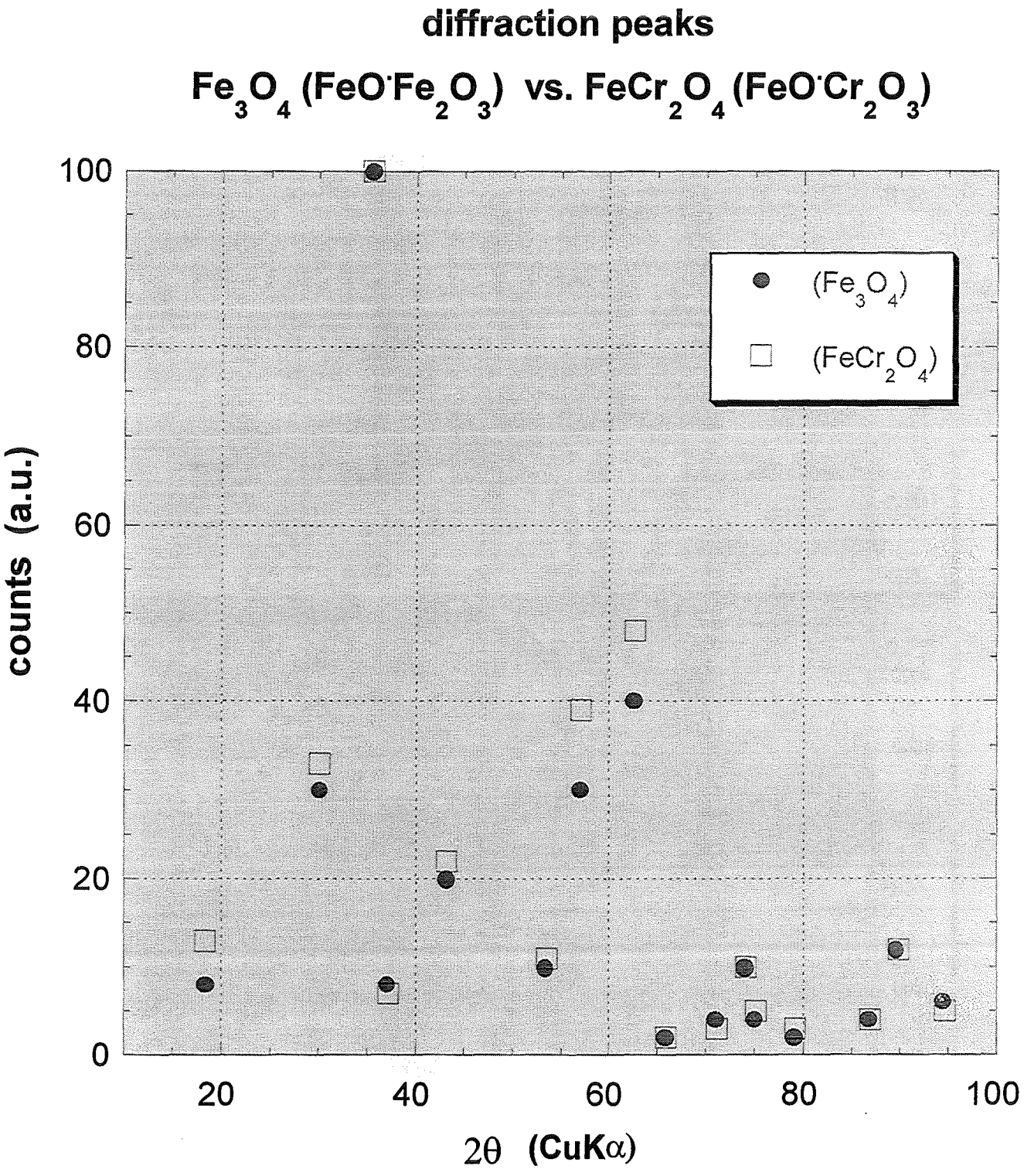




F82H (793 K)- XRD patterns (Co Kα) LBL

3700 h in Pb

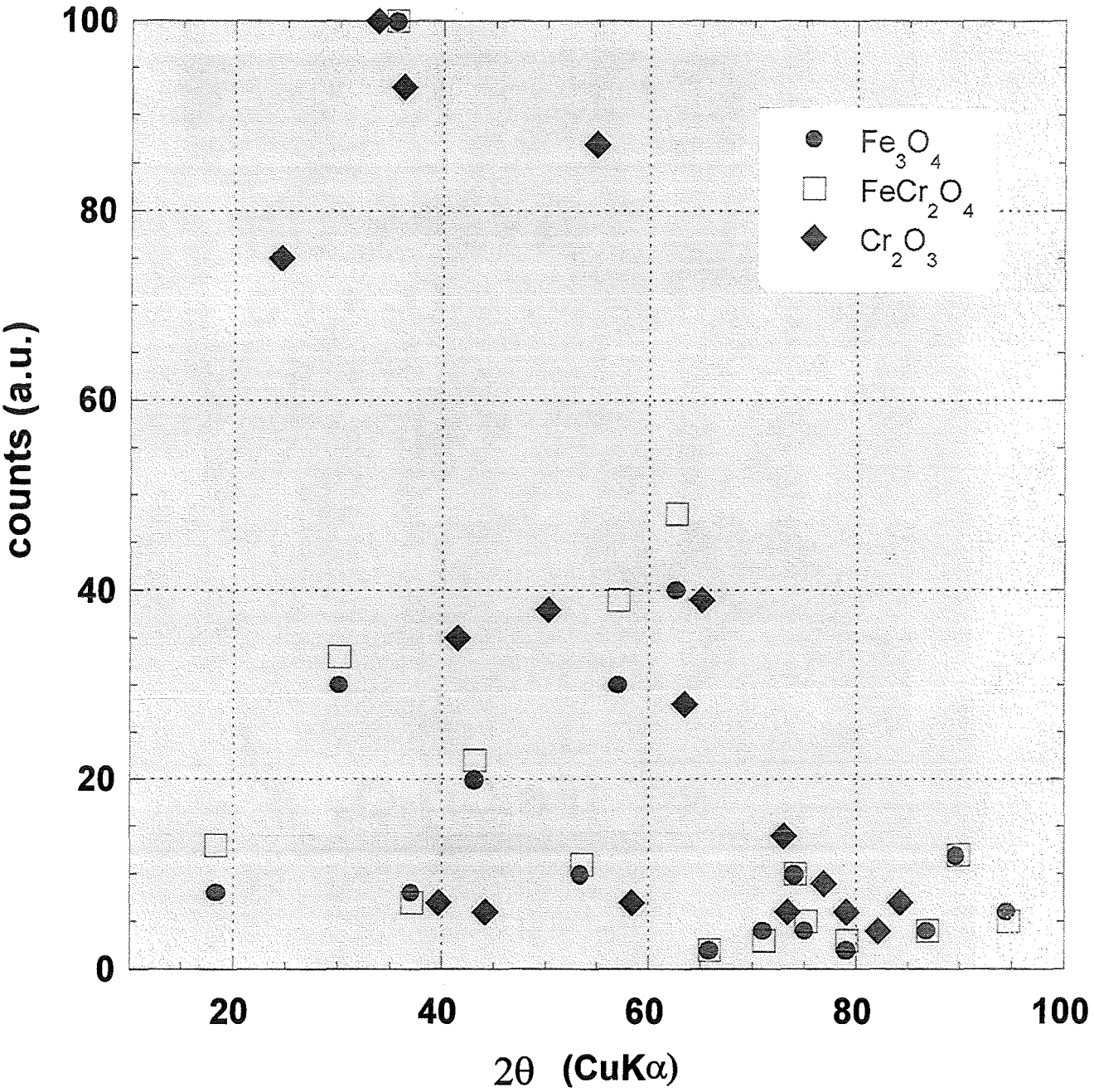




BoMet – University of Bologna, Italy

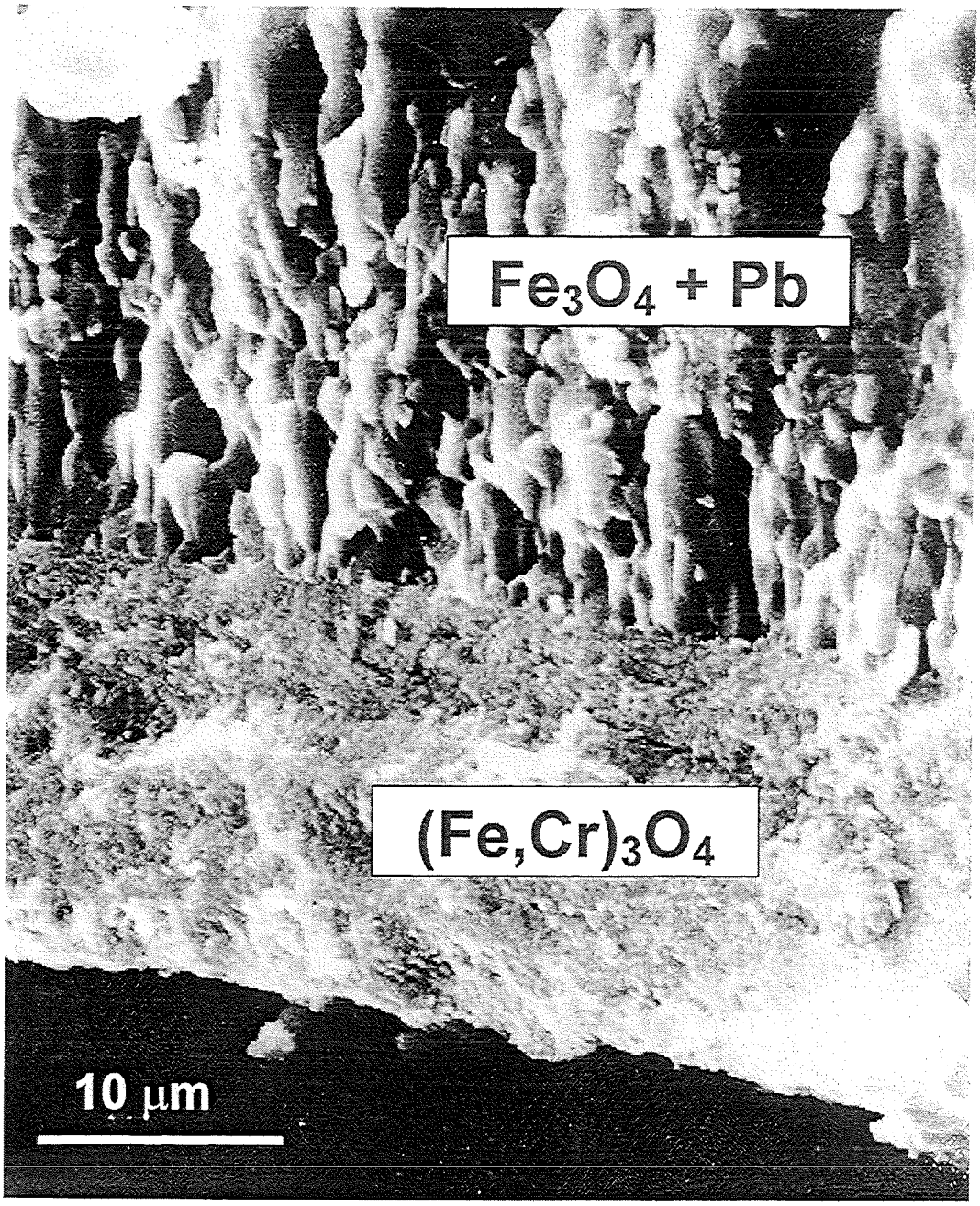
diffraction peaks

Fe_3O_4 ($FeO \cdot Fe_2O_3$) vs. $FeCr_2O_4$ ($FeO \cdot Cr_2O_3$) vs. Cr_2O_3



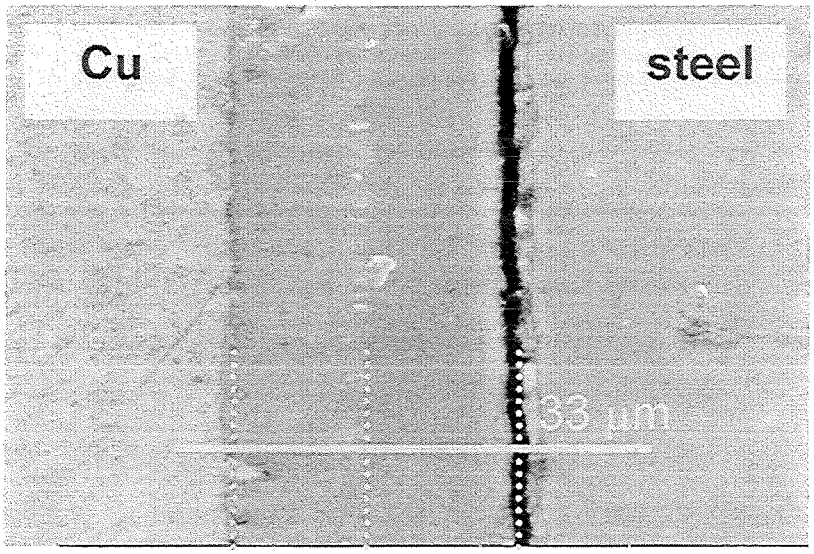
F82H (793 K) - Pb

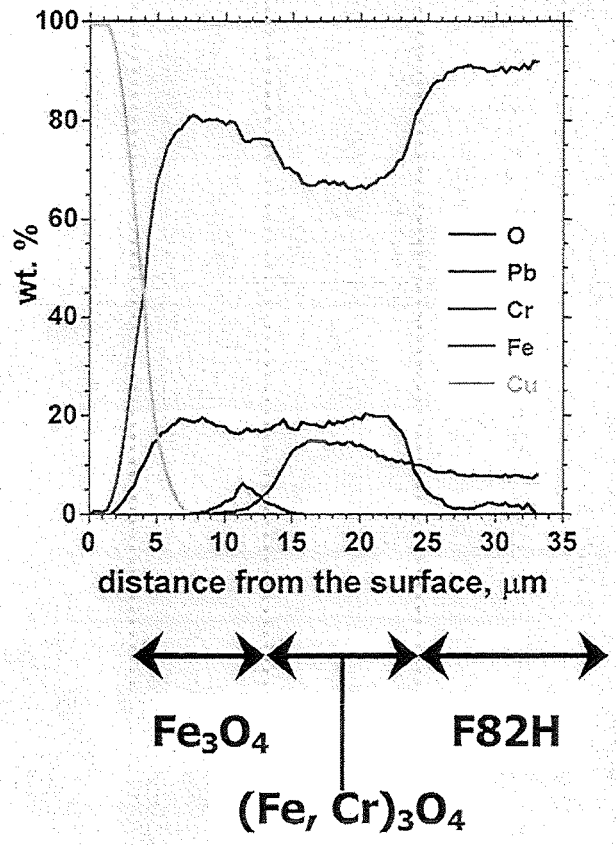
detached fragment - 3700 h



F82H (743 K)

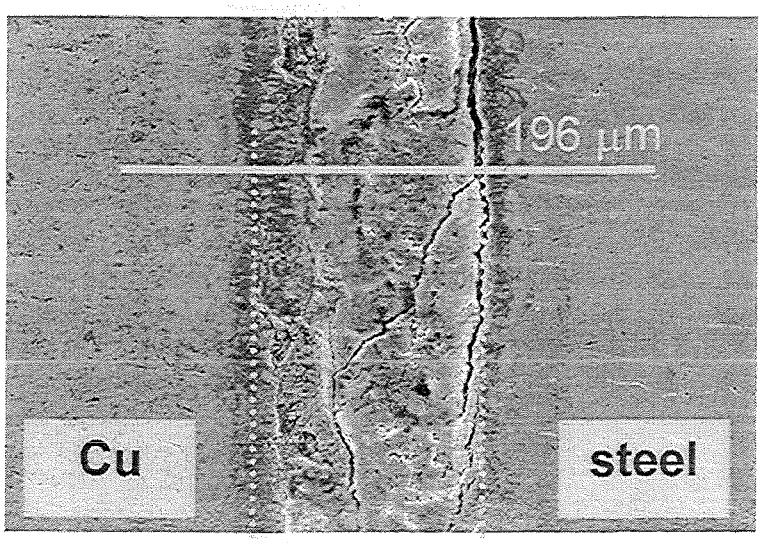
1200 h in Pb

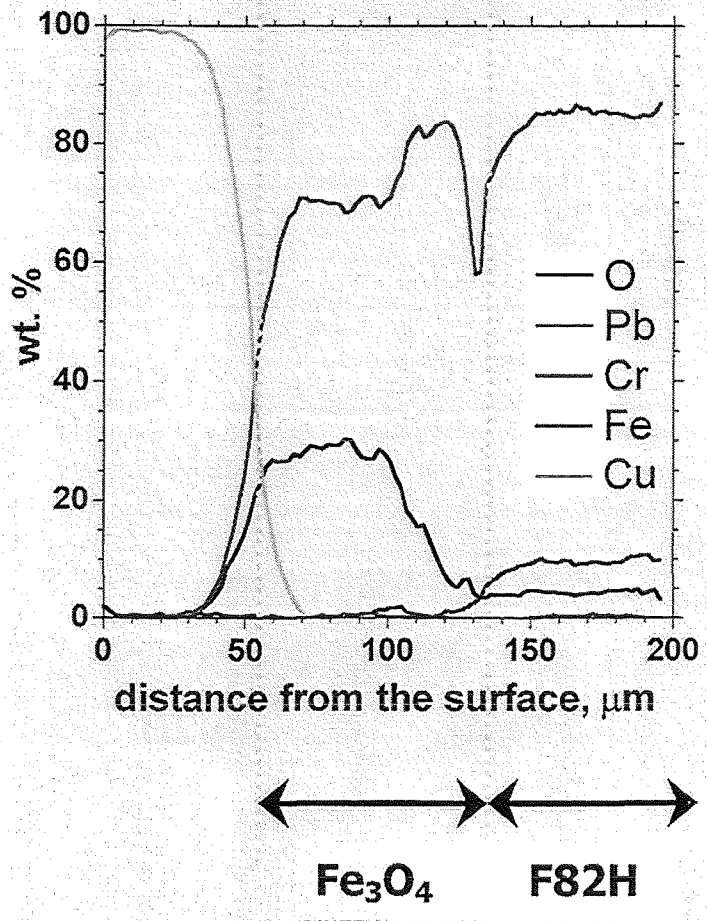




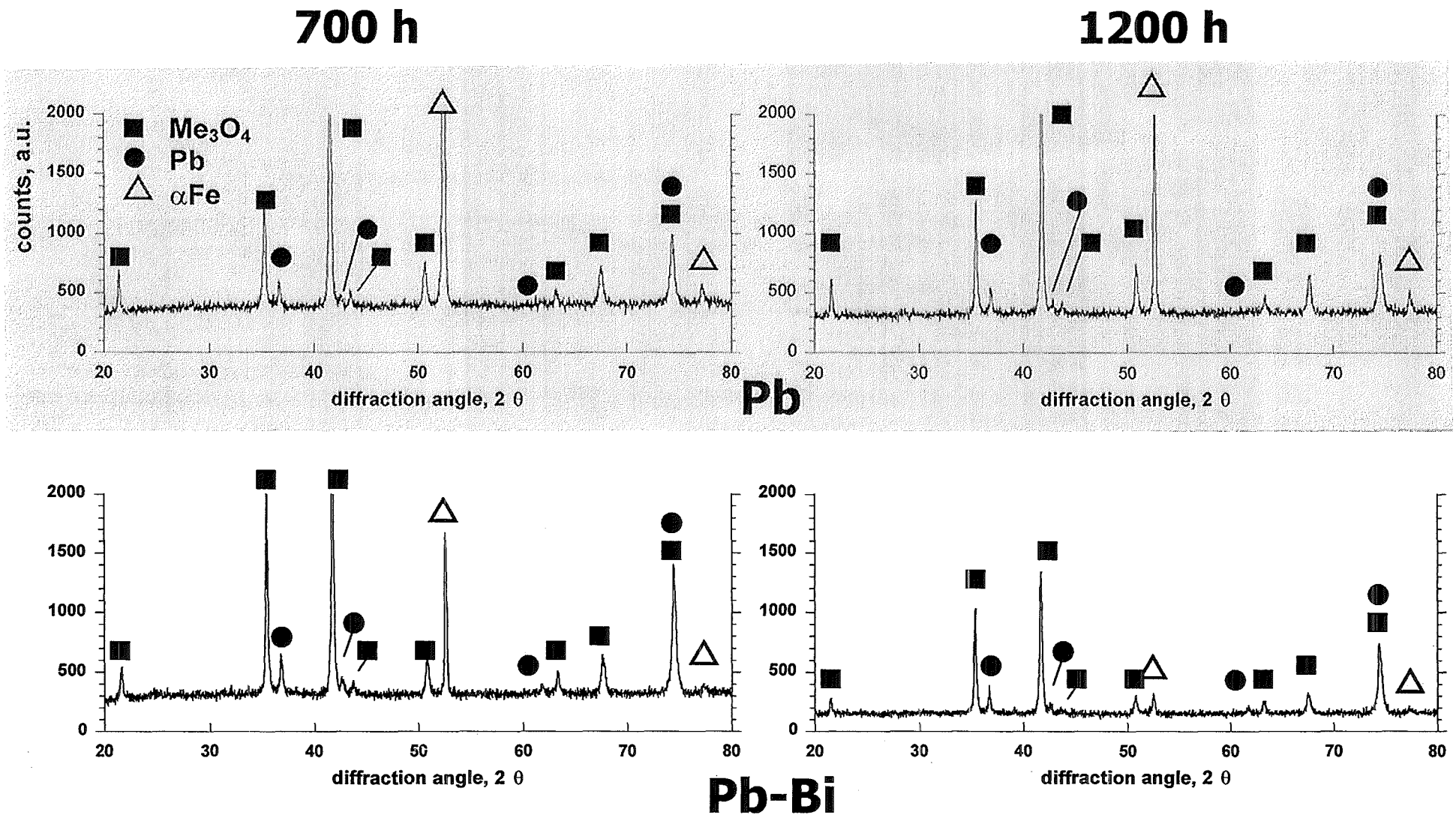
F82H (743 K)

1200 h in Pb-Bi



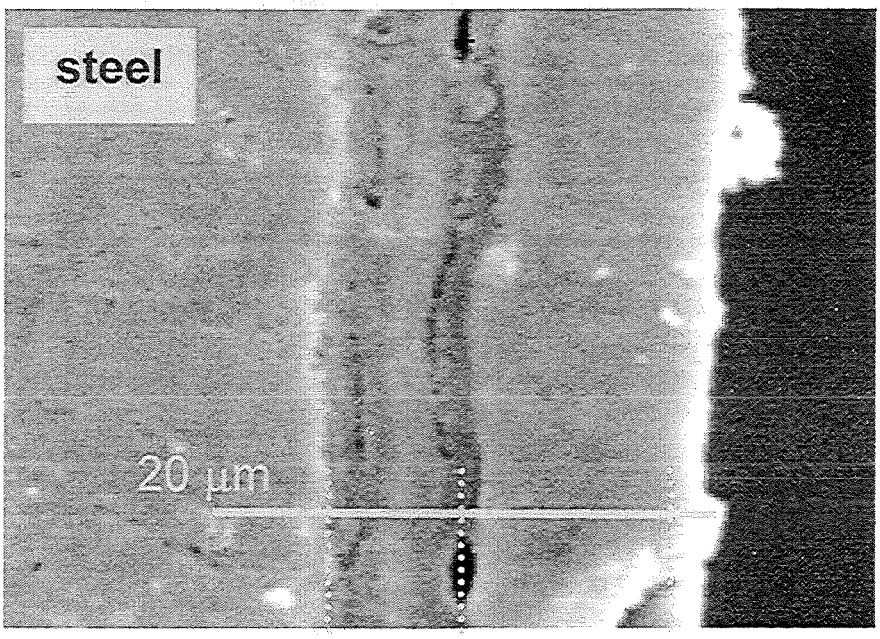


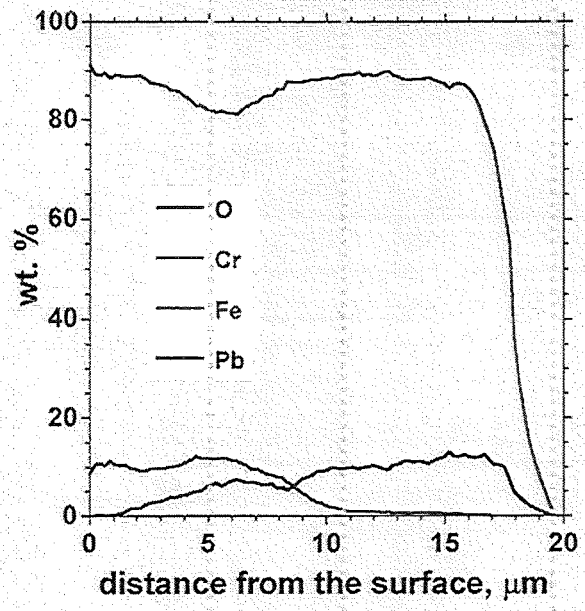
F82H (743 K)- XRD patterns (Co Kα) SURFACE



Manet (743 K)

700 h in Pb-Bi



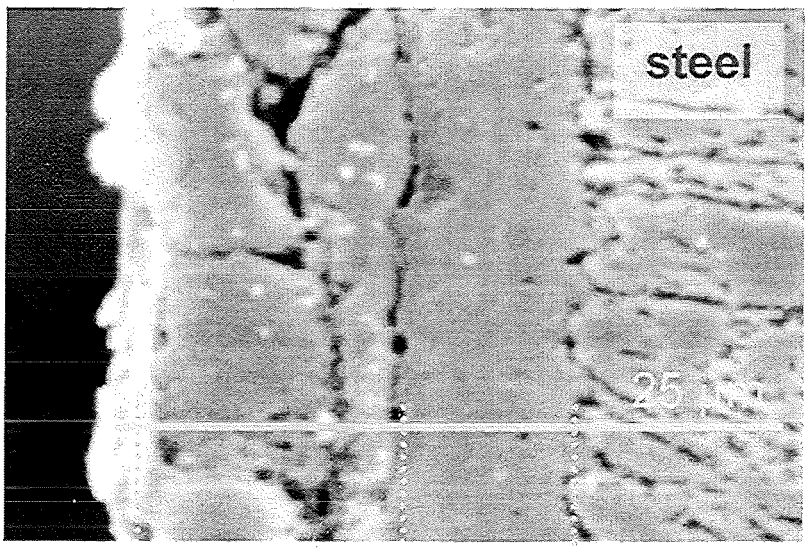


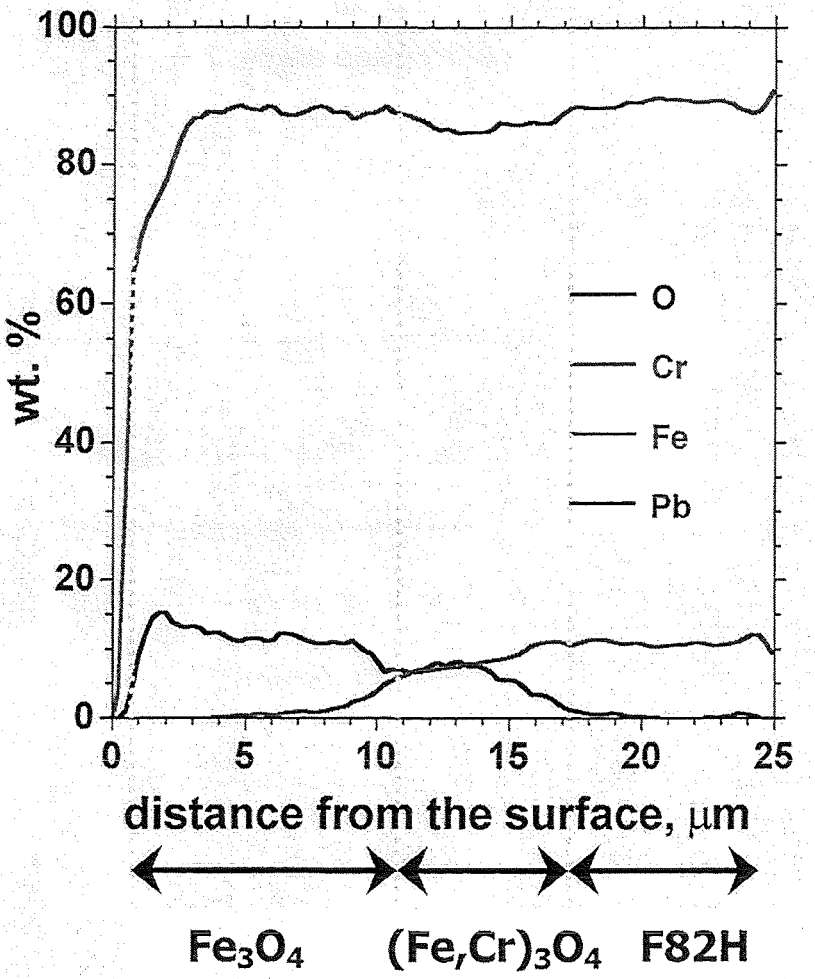
F82H Fe_3O_4

$(Fe,Cr)_3O_4$

Manet (743 K)

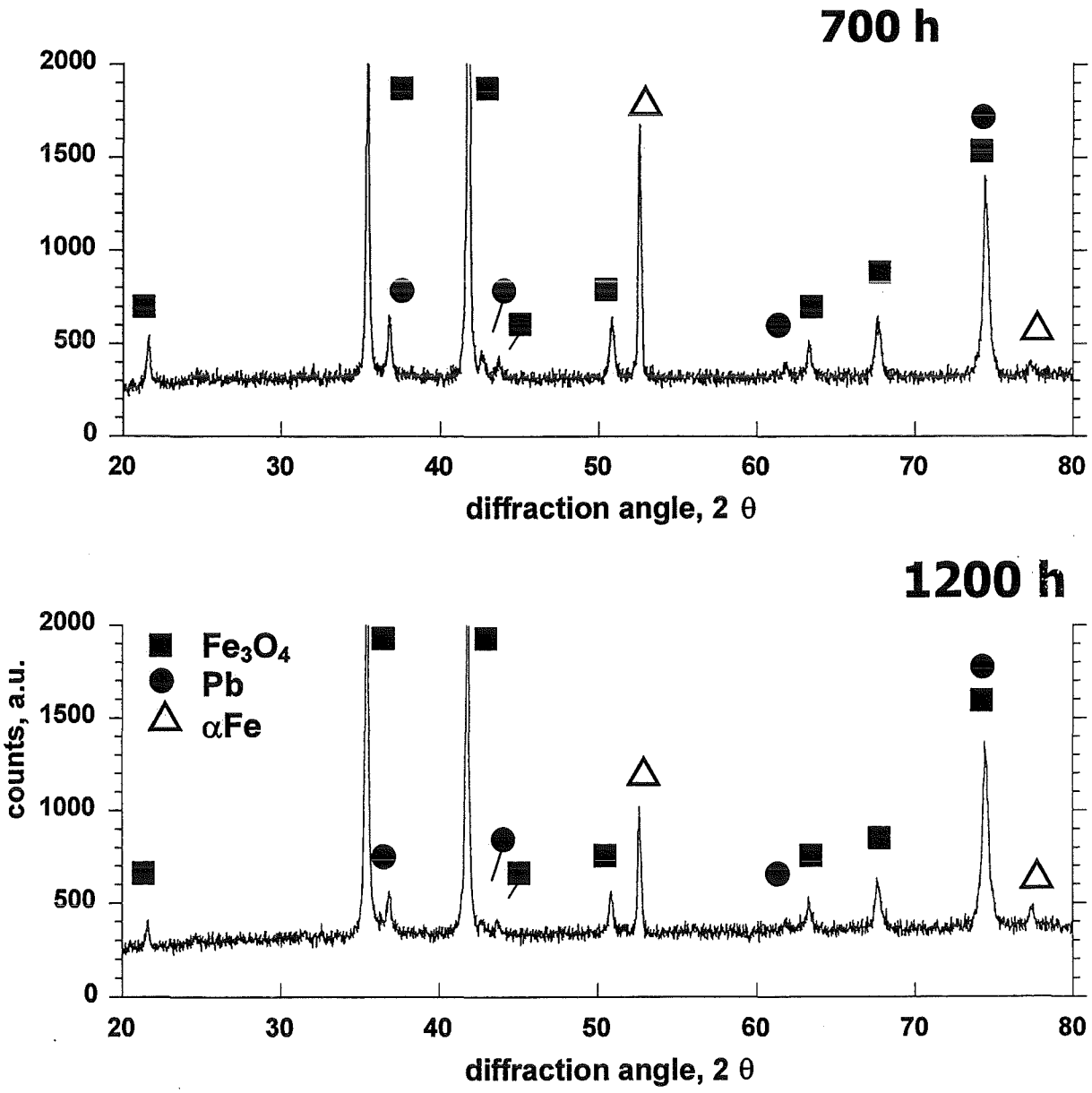
1200 h in Pb-Bi





Manet (743 K)

XRD patterns (Co Kα) SURFACE in Pb-Bi at 743 K

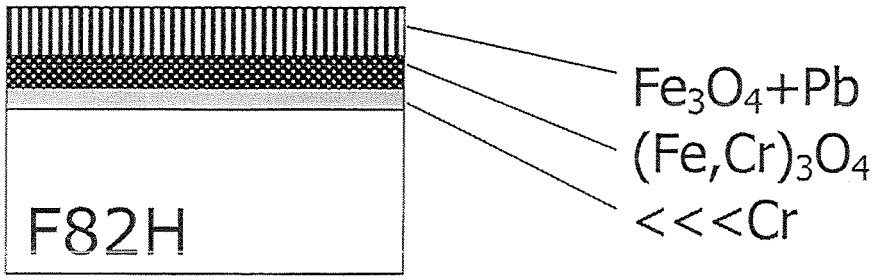


Interaction products

XRD OM

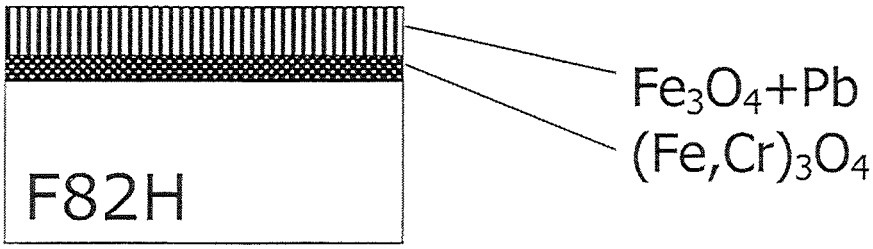
EDS SEM

✓ Pb, 793 K



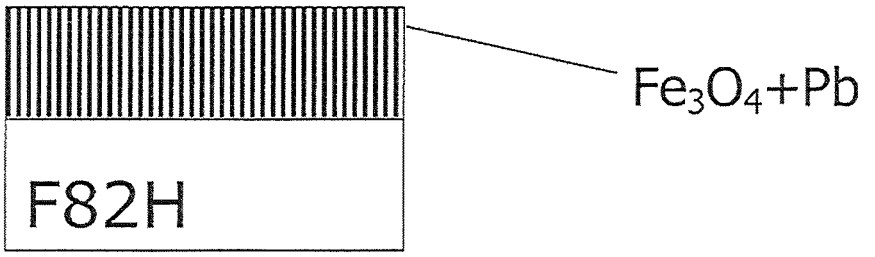
2000 h	3700 h
15	15
5	20
1-3	3-5
≈20	≈40

✓ Pb, 743 K

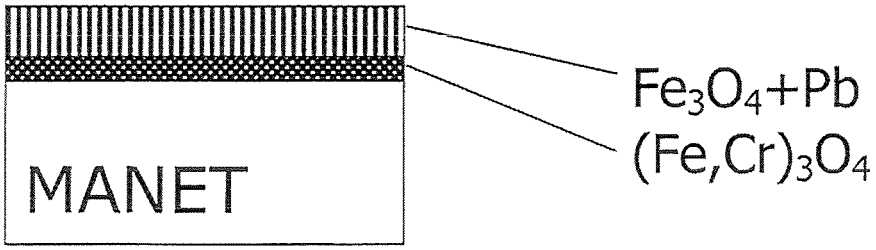


700 h	1200 h
-	10
-	12
-	≈20

✓ Pb-Bi, 743 K



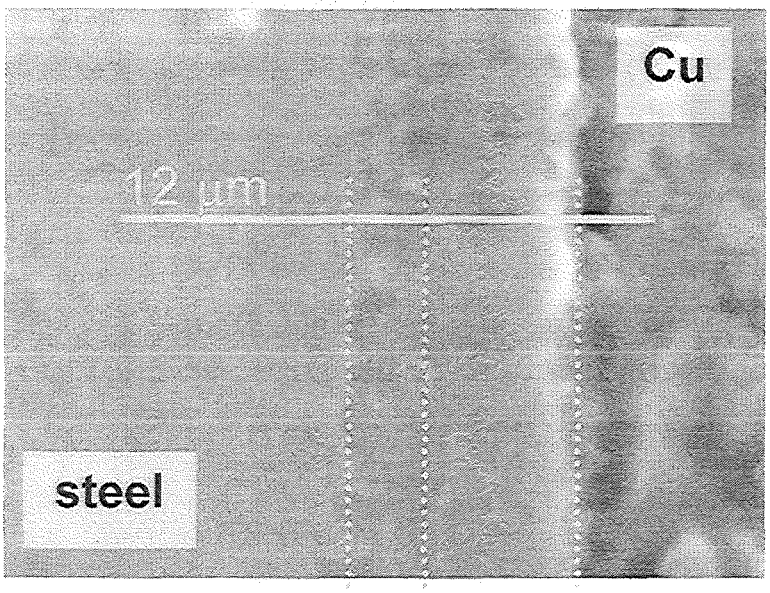
700 h	1200 h
-	80
-	≈80

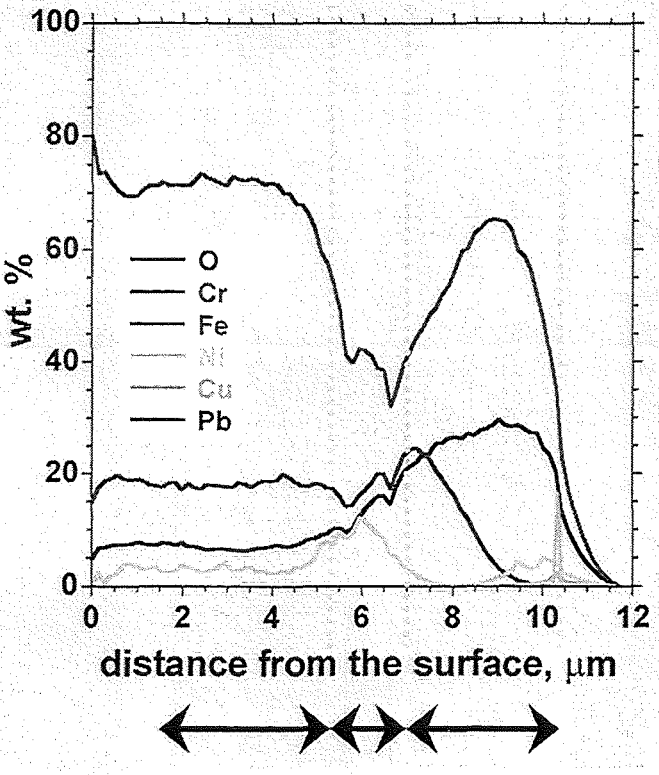


700 h	1200 h
10	10
5	7
≈15	≈17

316 LN (743 K)

1200 h in Pb

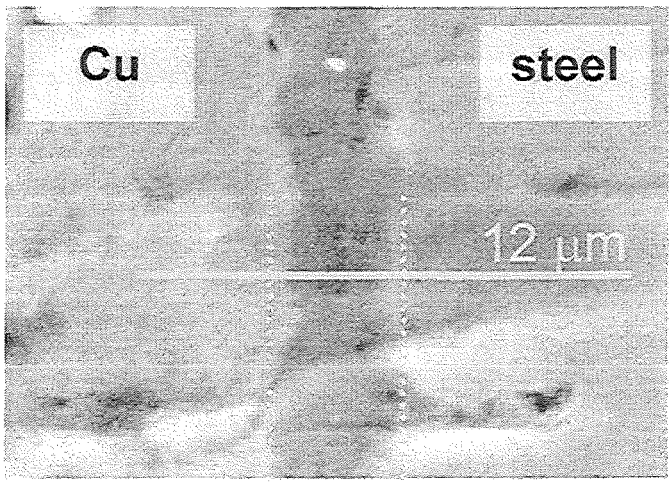


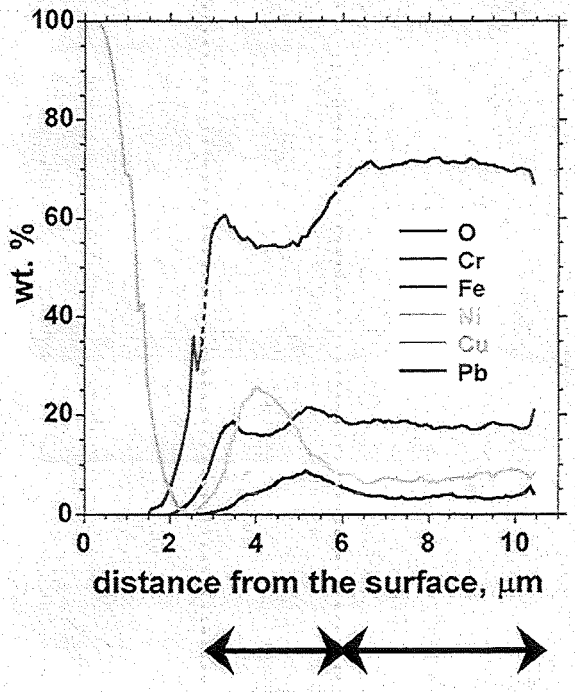


316 +Ni $(Fe, Cr)_3O_4$

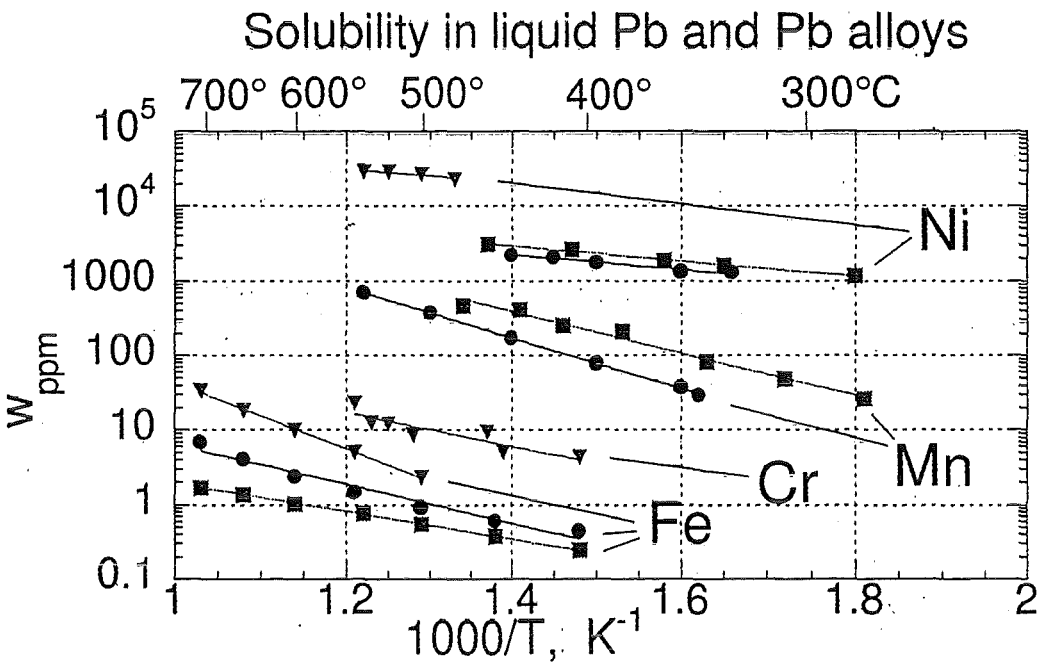
316 LN (743 K)

1200 h in Pb-Bi





$(Fe, Cr)_3O_4$+Ni 316



Mn in Pb : Barker and Sample, v. Ni in Pb.

$$\log(w_{ppm}) = 6.959 - 3380/T$$

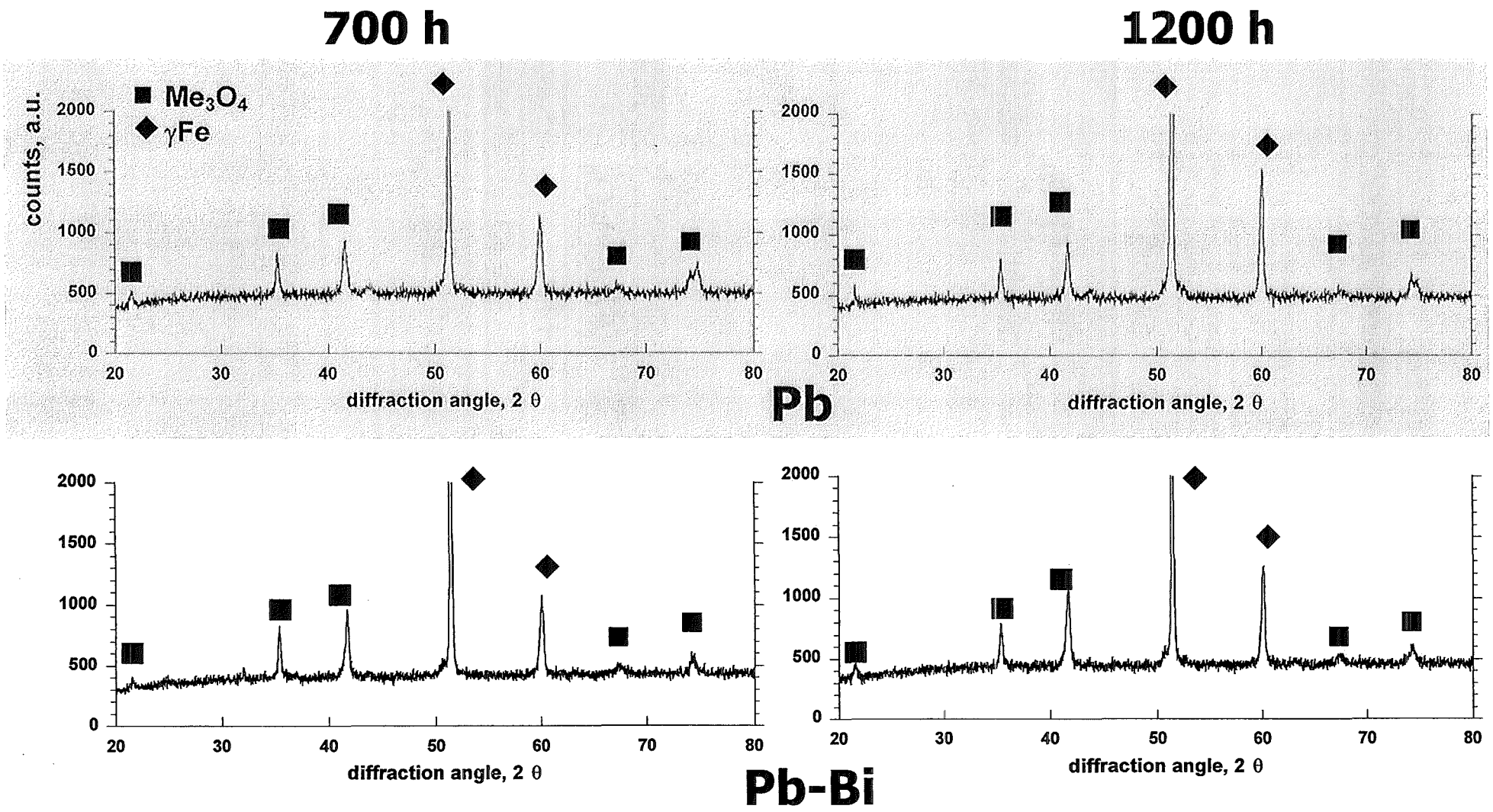
Mn in Pb-17Li : (come Mn in Pb)

$$\log(w_{ppm}) = 6.732 - 2938/T$$

Cr in Pb-17Li : Reyntjens and Van Hoe, CRAHAF

$$\log(w_{ppm}) = 2.98 - 7226/T$$

316 LN (743 K)- XRD patterns (Co Kα) SURFACE

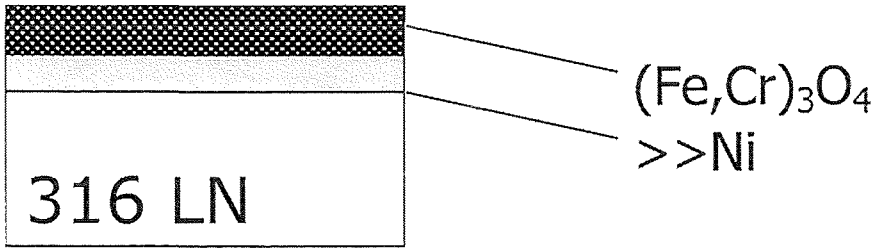


Interaction products

XRD OM EDS SEM

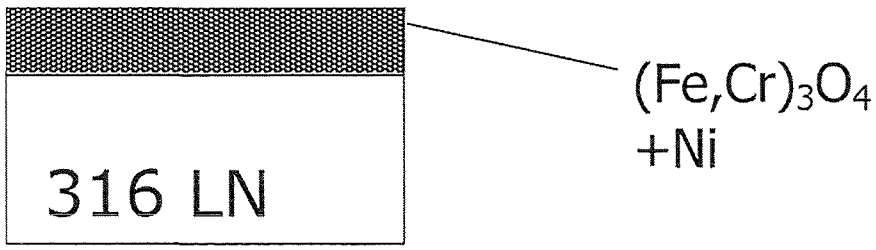
Austenitic steel

✓ Pb, 743 K



700 h	1200 h
-	3-4
-	1-2
-	≈5

✓ Pb-Bi, 743 K



700 h	1200 h
-	3
-	≈3

Notes

- **Mod. F82H: in most cases the adhesion and compactness of the oxide layer is acceptable (static conditions).**
- **Manet: the outer part of the oxide layer is brittle (after 1200 h in Pb-Bi).**
- **316 LN: the oxide layer is very thin. Will it still hinder the mass transfer in more severe conditions?**

Open points

- **Mod. F82H in Pb-Bi: higher thickness and brittleness of the oxide layer (absence of Cr)?**
- **Manet: brittle outer Fe_3O_4 layer?**
- **316 LN: Ni?**

Conclusions

- The presence of oxygen in molten lead modifies the basic mechanism of metal corrosion because of the formation of oxidation products.
- A two step mechanism is proposed for the oxidation process:
  1. oxidation of the base metal (Me_3O_4)
     * inner, Cr-containing sublayer
     * outer Fe_3O_4 sublayer
  2. The second step is the interaction between liquid lead and oxide layers. Under our conditions of exposure, no formation of ternary compounds Fe-Pb-O.

Hints

- ✓ The solubility of alloying elements in molten Pb or Pb-Bi is not the only key-parameter. The adhesion, compactness and protectiveness of the oxide layers should be also taken into account, together with their reactivity with the molten metal.

- ✓ The influence of oxygen dissolved in liquid metals on corrosion of the steels used as structural materials has been widely recognised. Therefore, control of oxygen activity in liquid metals is a topic of major concern.

- ✓ Further corrosion experiments in dynamic conditions have to be performed in order to fully evaluate the materials performance under in-service conditions.

CORROSION TESTS IN FLOWING Pb-55Bi
IPPE - ENEA

PARAMETERS:

TEMPERATURE:	1) 573 K 2) 743 K
TIME:	2000 h
VELOCITY:	1.9 m/sec
OXYGEN CONTENT:	$(1 - 2) \cdot 10^{-6}$ at. %

MATERIALS

AISI 316 L

EM 10

BATMAN 27

BATMAN 28

Behaviour of martensitic steel in lead-bismuth. Preliminary results

D. Gómez Briceno, F. J. Martín Munoz, L. Soler Crespo

Abstract

The compatibility of martensitic steels with lead-bismuth in the operating conditions of a hybrid system is dependent on the existence of a protective layer such as an oxide film. A martensitic steel has been tested under static conditions in lead-bismuth in different atmospheres, argon and argon + hydrogen, at 600°C and 400°C. Preliminary results on the corrosion behaviour of as received and preoxidised specimens have been obtained. Special attention has been paid to the analysis of oxide layer formed in the different conditions by SEM and AUGER.

BEHAVIOUR OF MARTENSITIC STEEL IN LEAD-BISMUTH. PRELIMINARY RESULTS

D. Gómez Briceño, F.J. Martín Muñoz and L. Soler Crespo

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OBJECTIVES

- TO GAIN SOME INSIGHT INTO THE CORROSION BEHAVIOUR OF MARTENSITIC STEEL IN LEAD-BISMUTH AT HIGH TEMPERATURES
- TO CHARACTERIZE THE OXIDE LAYER FORMED IN THE EXPERIMENTAL CONDITIONS

EXPERIMENTAL CONDITIONS

- **MATERIAL: F82H (7.75% Cr)**

- **SPECIMENS:**

  - As received
  - Preoxidised (600ºC, 2 hours, air)

- **GAS ATMOSPHERA:**

  - Argon (O_2 < 2ppm)
  - Argon + 10% H_2

- **STATIC TEST WITH GAS BUBBLING**

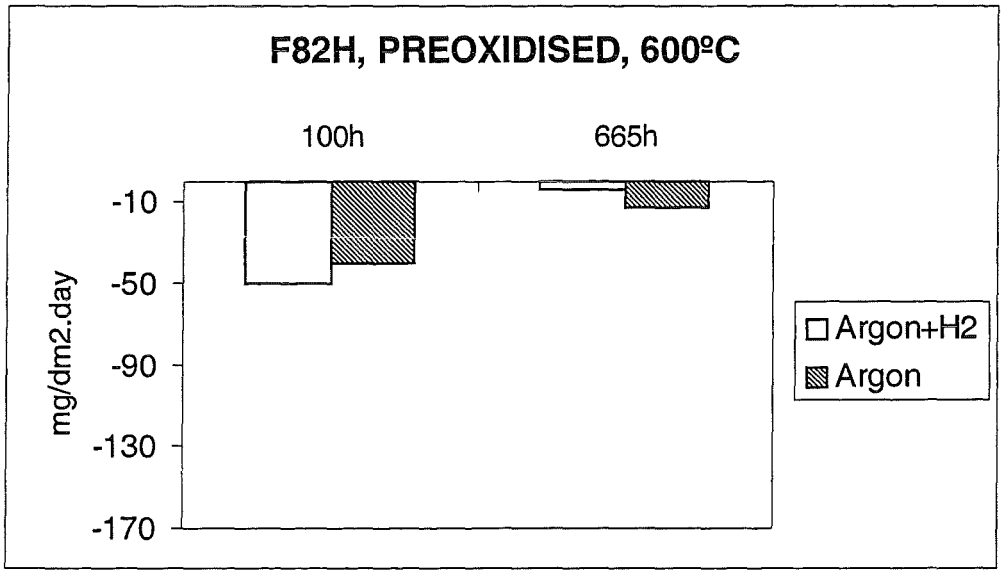
T (ºC)	100 h	665 h
400	x	(1)
600	x	x

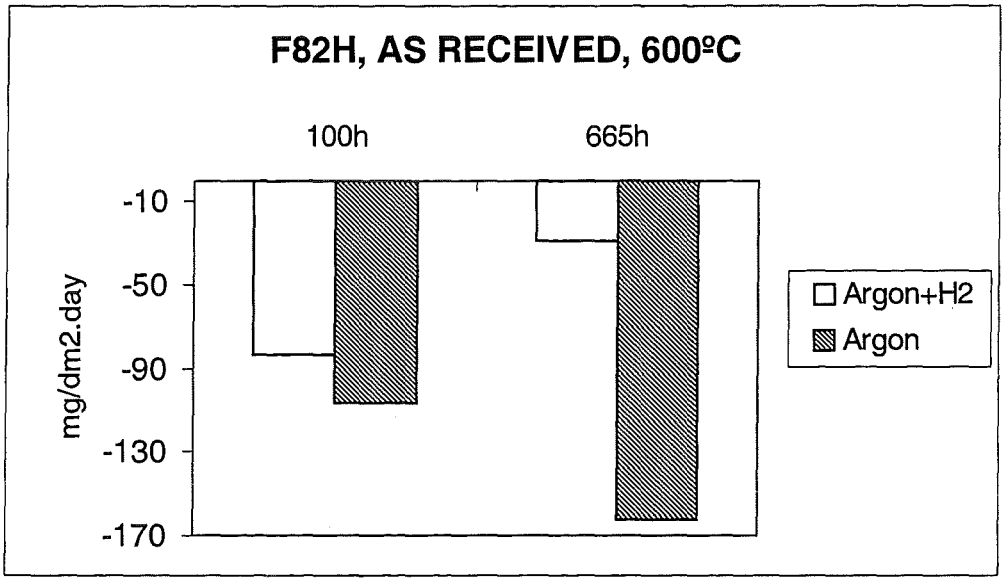
(1) Planned

EXPERIMENTAL SCOPE

- **LOSS WEIGHT DETERMINATION**
- **SEM AND METALLOGRAPHIC EXAMINATION**
- **OXIDE LAYER ANALYSIS BY EDX AND AUGER**
  - **COMPOSITION**
  - **ELEMENTAL PROFILE**
- **ESCA IS FORESEEN**

LOSS WEIGHT


F82H, PREOXIDISED, 600ºC
100h
665h
-10
-50
-90
-130
-170
mg/dm2.day
Argon+H2
Argon


F82H, AS RECEIVED, 600ºC
100h
665h
-10
-50
-90
-130
-170
mg/dm2.day
Argon+H2
Argon

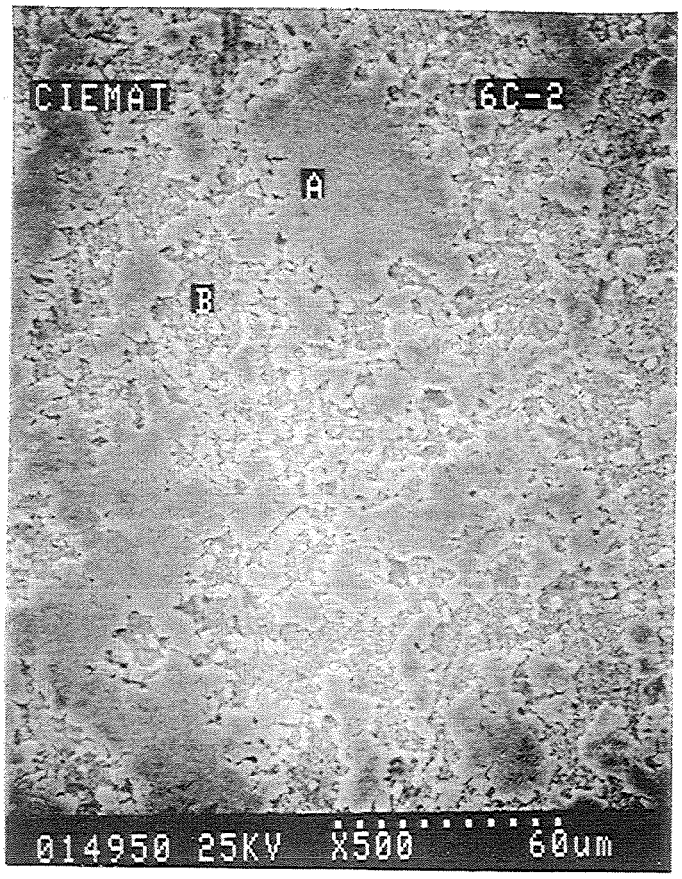
RESULTS

♦ PREOXIDISED MATERIAL

- Loss weight:
  - Small loss weight in comparison with as received specimens in both environments. It seems to decrease with the time.

- SEM an metallographic examination:
  - Apparently, no surface attack exists (100 hours)
  - In argon, areas cover by oxide layer and areas with dissolution of material at long times (665 hours)
  - In argon + H_2, no dissolved areas have been detected

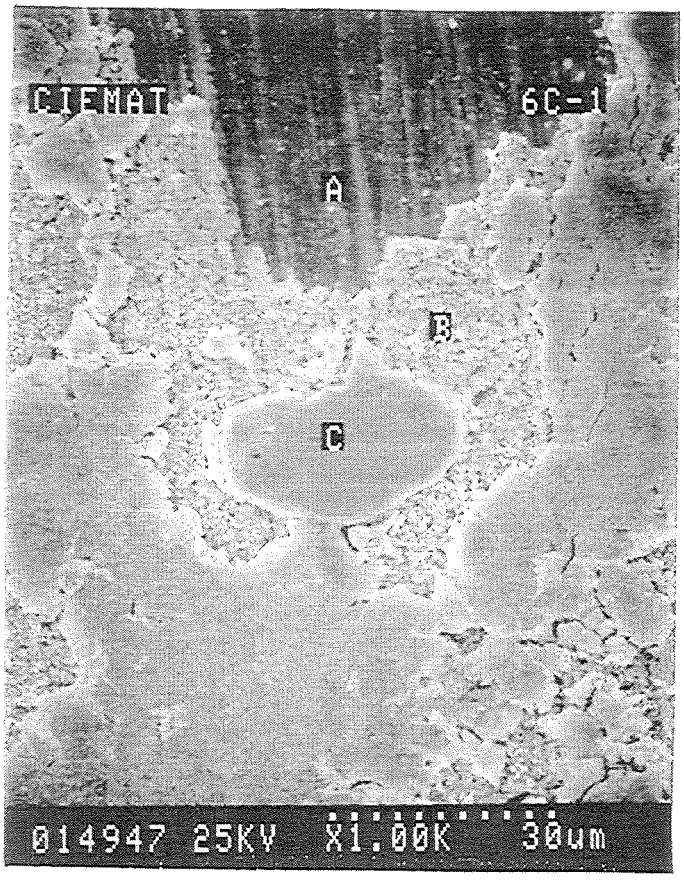
- Oxide layer analysis:
  - After 100 hours, an oxide film with two different layers, an external one rich in Fe and an internal one with Cr enrichment, is observed. Thickness up to 11μm
  - After 665 hours, an oxide layer with Cr enrichment and Fe depletion is detected. Thickness ≈ 0.4μm
  - No significant differences have been observed in the oxide layer analysis between both environments



F82H, preoxidised
Argon
600°C, 100 hours

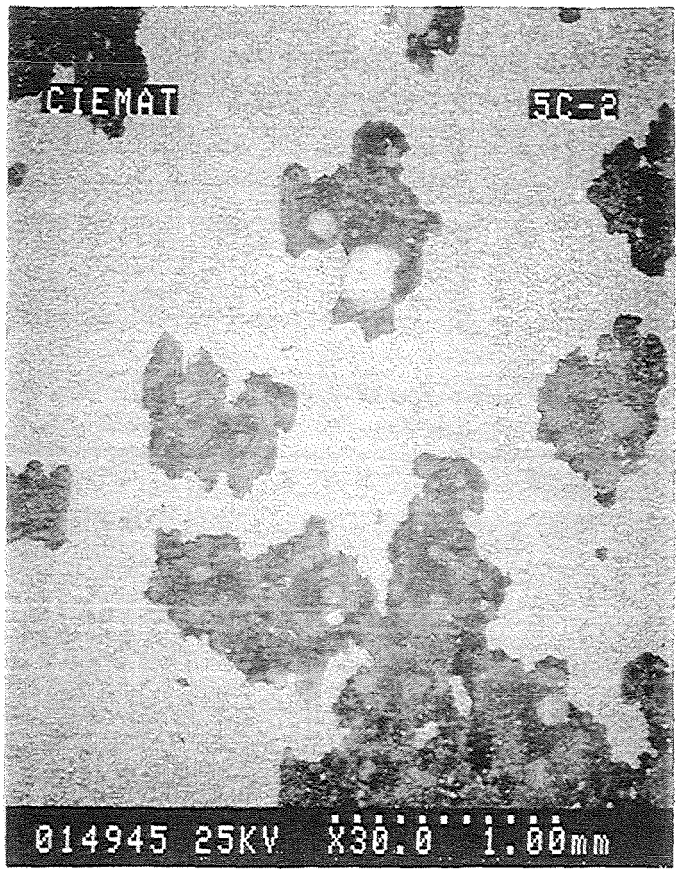
% atom.

	Fe	Cr
A	98,38	1,62
B	91,96	8,04

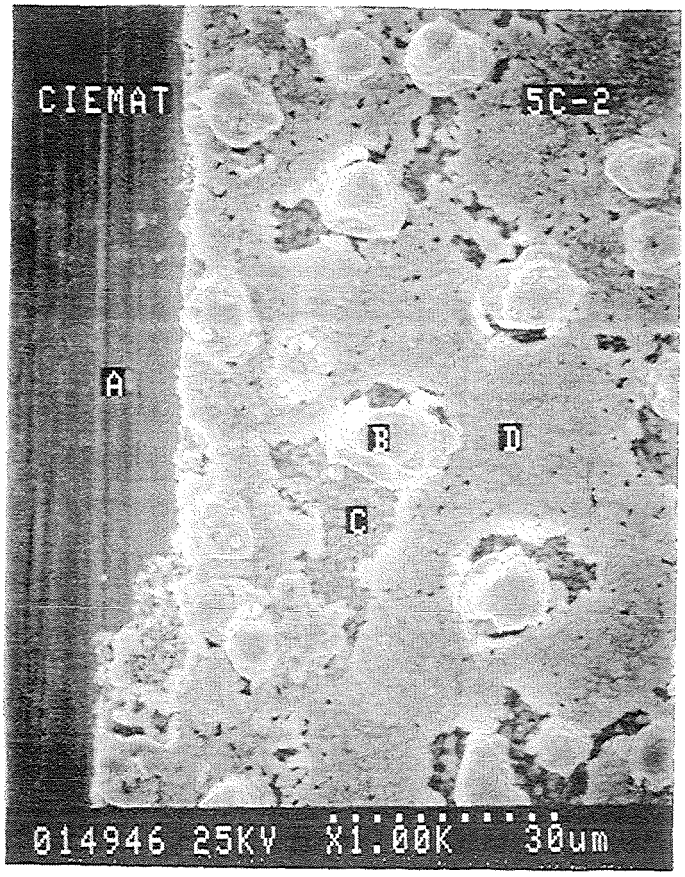


% atom.

	Fe	Cr	W	Hg
A	71,76	26,19	2,05	
B	93,16	5,06		1,78
C	98,19	1,33		0,48

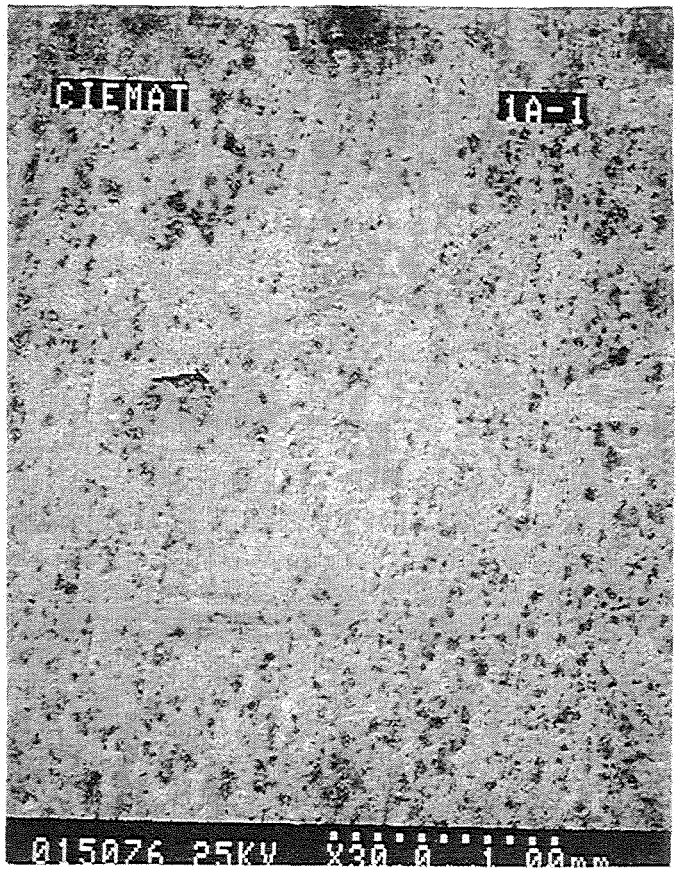


F82H, preoxidised
Argon + H_2
600°C, 100 hours

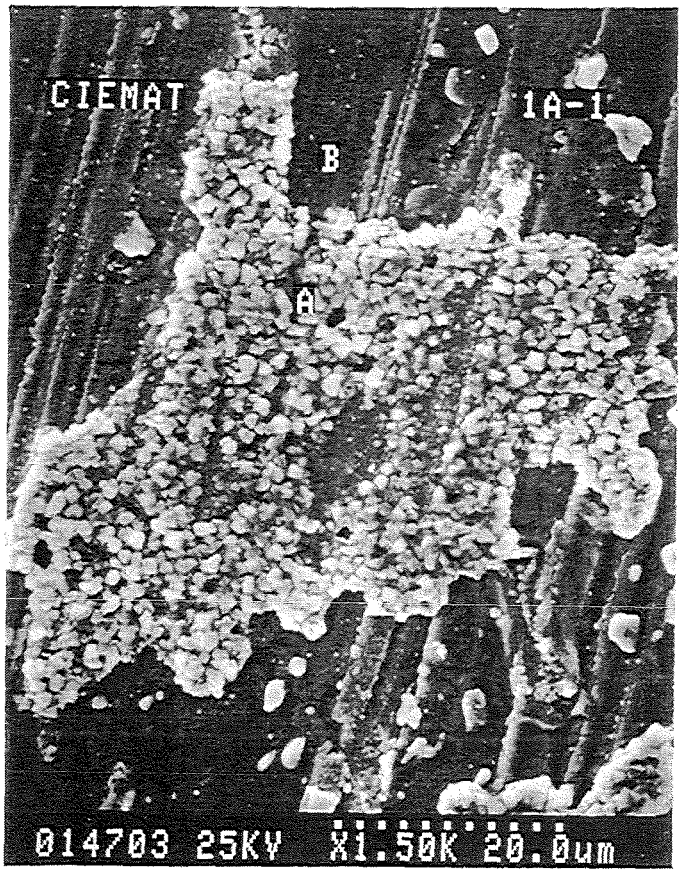


% atom.

	Fe	Cr	W	V	Pb-Bi	Hg
A	72,98	23,41	2,84	0,78		
B	98,43	0,67			0,90	
C	97,94	1,78				0,28
D	97,78	0,68				1,54

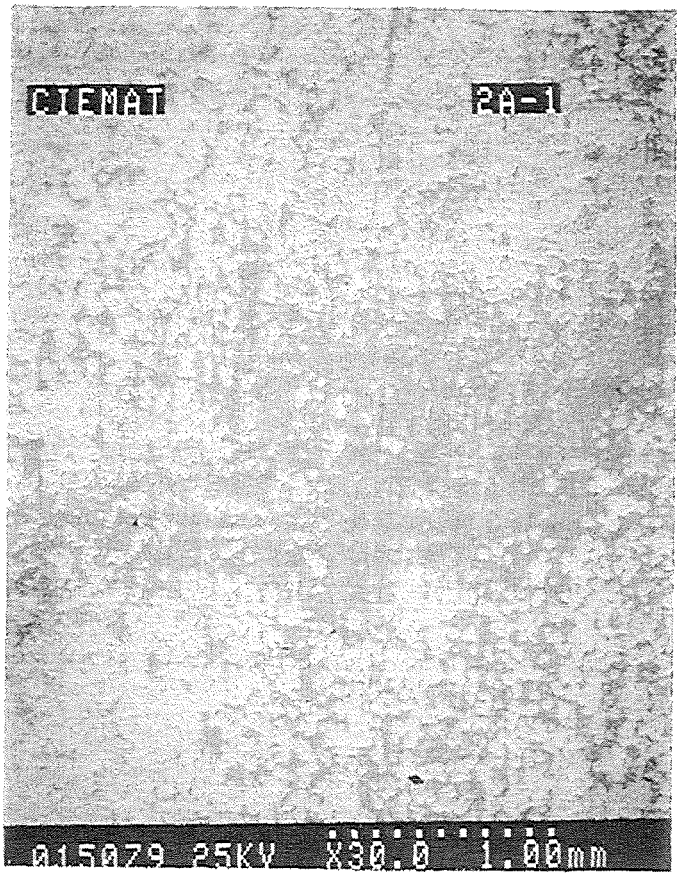


F82H, preoxidised
Argon + H_2
600°C, 665 hours



% atom.

	Fe	Cr	Mn	W	V	Pb-Bi
A	57.75	33.67	3.15	0.29	1.19	3.42
B	90.56	7.48	0.46	1.50		



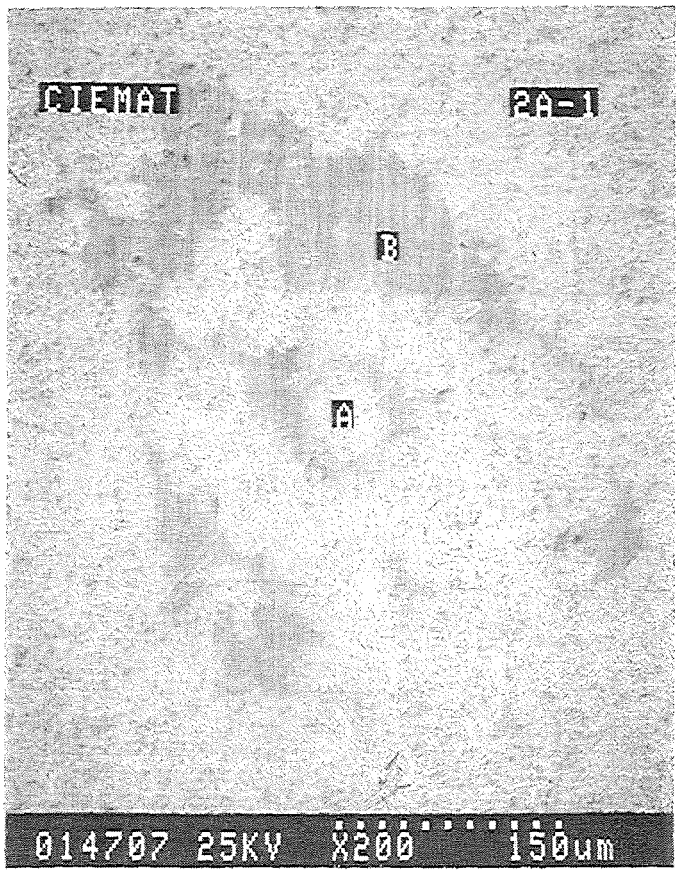
F82H, preoxidised
Argon
600°C, 665 hours

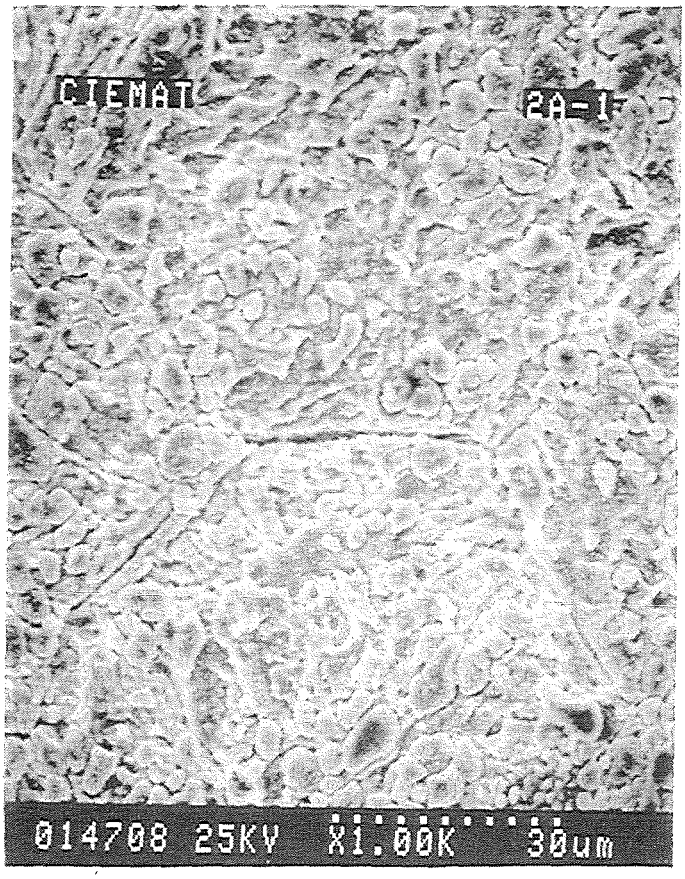
% atom.

	Fe	Cr	W	Hg
General	83.43	16.00	0.03	0.54

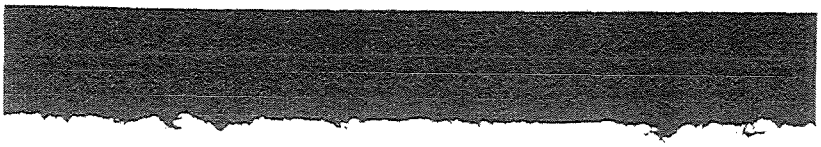
% atom.

	Fe	Cr	Pb-Bi	W
A	98.41	1.42	0.17	
B	87.87	11.23	0.26	0.64



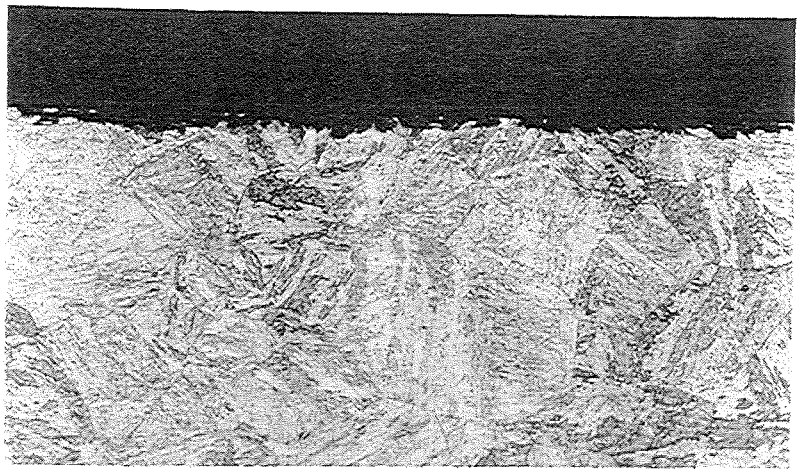


METALLOGRAPHIC ANALYSIS



F82H, preoxidised
Argon + H_2
600°C, 665 hours

x 200

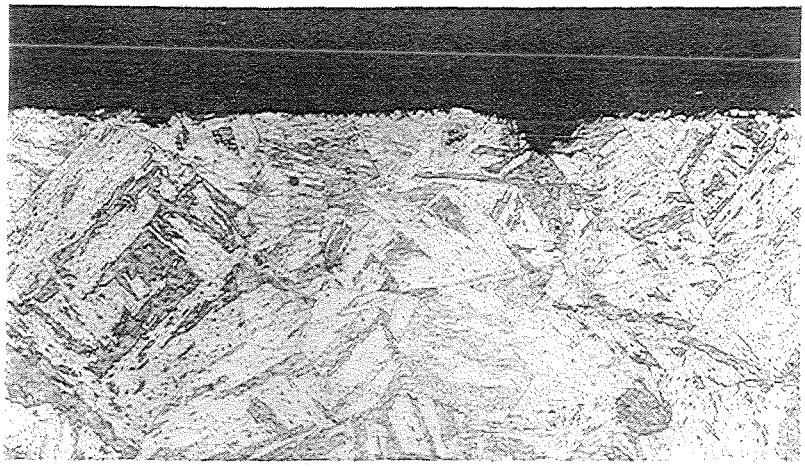


x 200

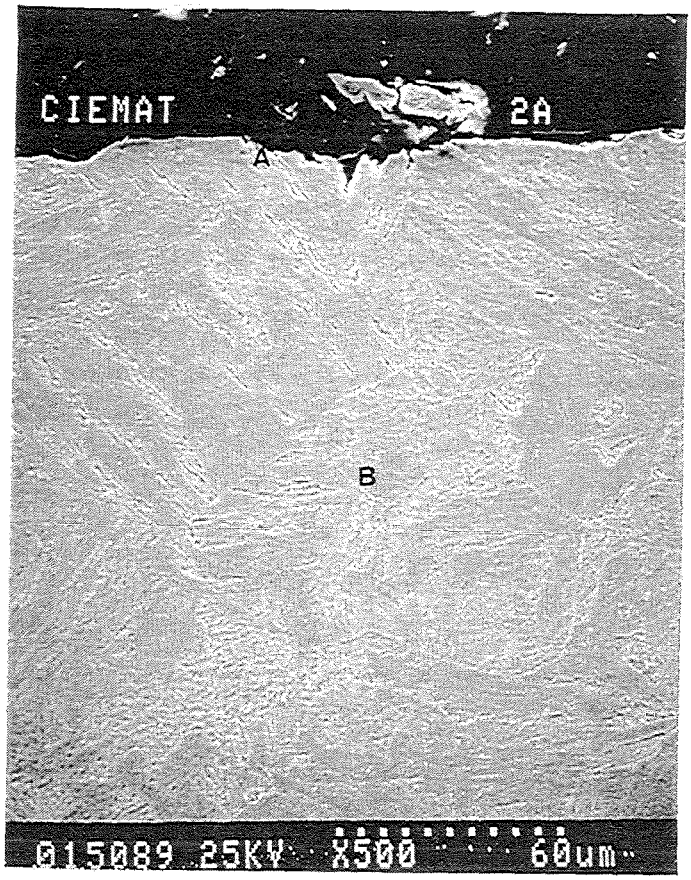
METALLOGRAPHIC ANALYSIS

F82H, preoxidised
Argon
600°C, 665 hours

x 200

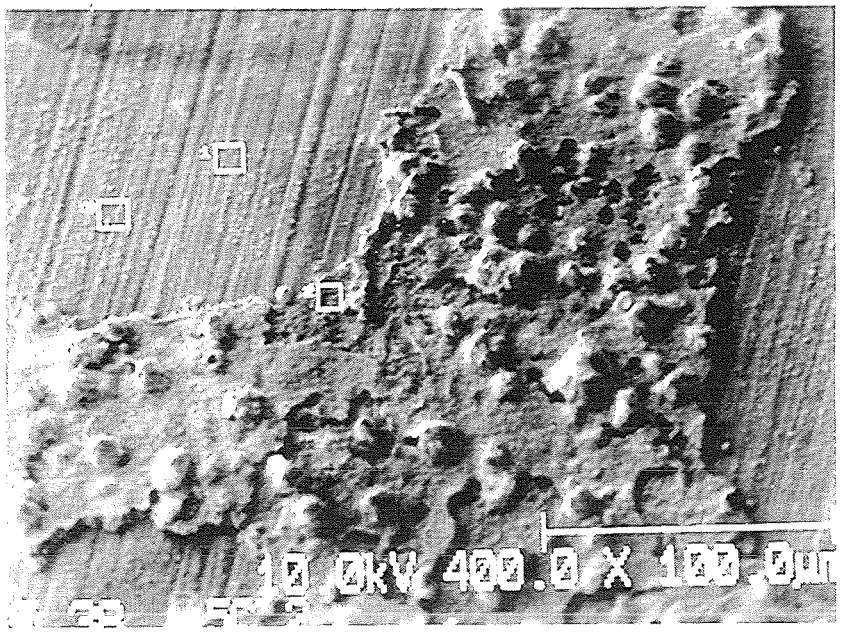


x 200

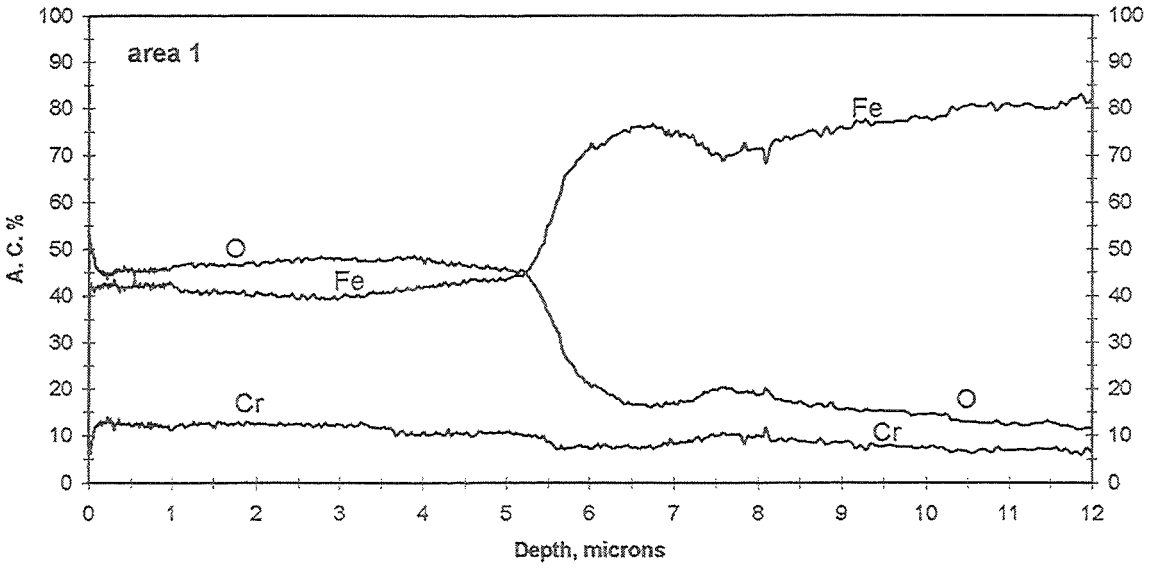


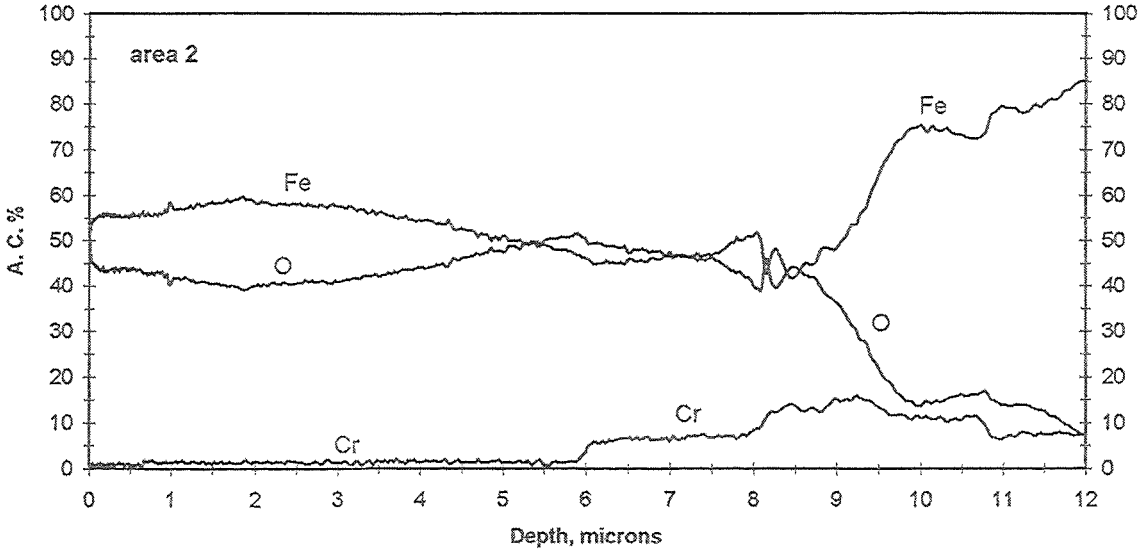
% atom.

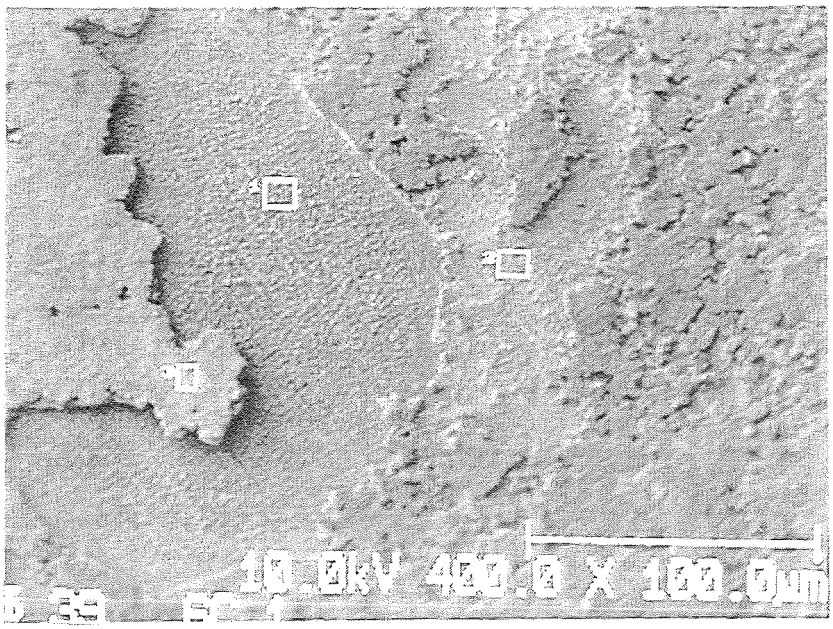
	Fe	Cr	W	V
A	92.10	7.39	0.51	
B	91.41	7.93	0.57	0.09



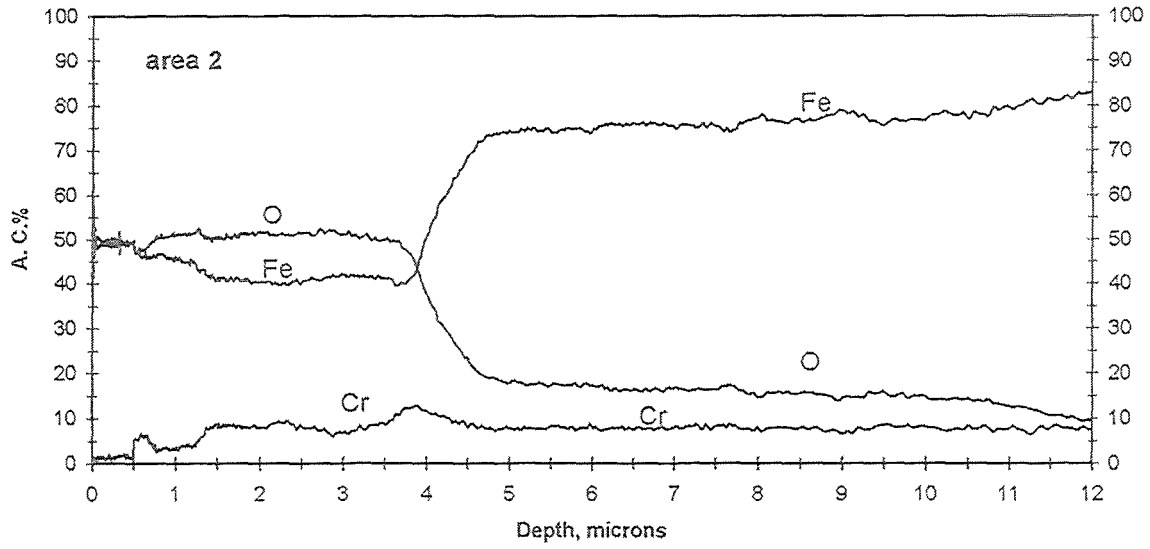
F82H, preoxidised
Argon + H_2
600°C, 100 hours

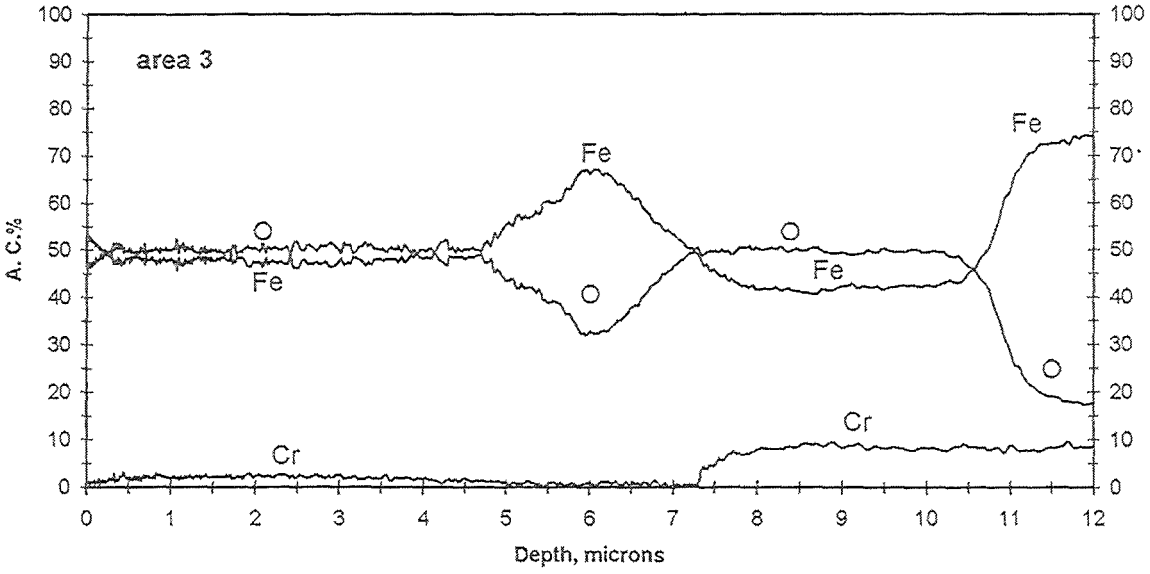


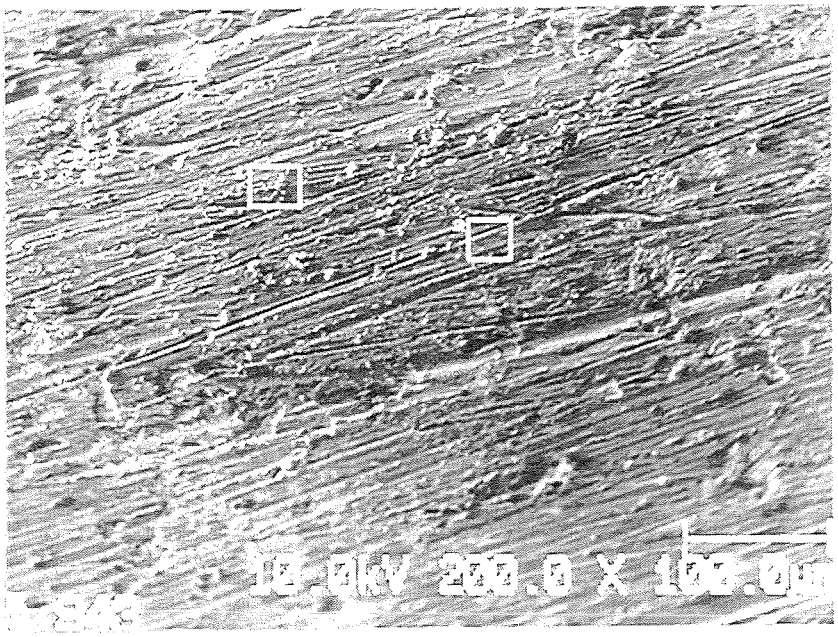




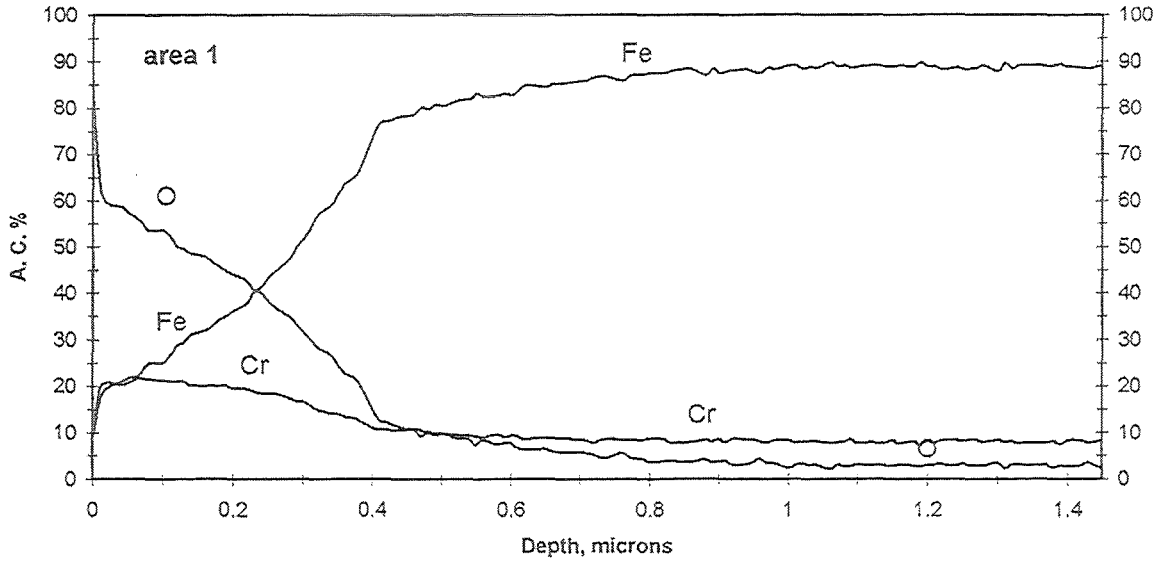
F82H, preoxidised
Argon
600°C, 100 hours

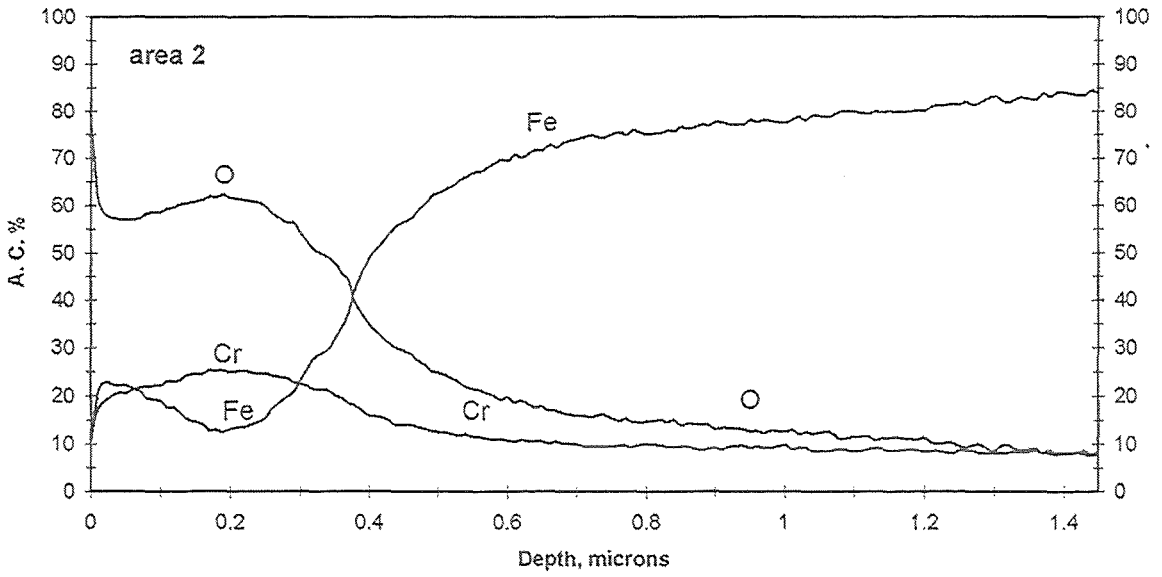


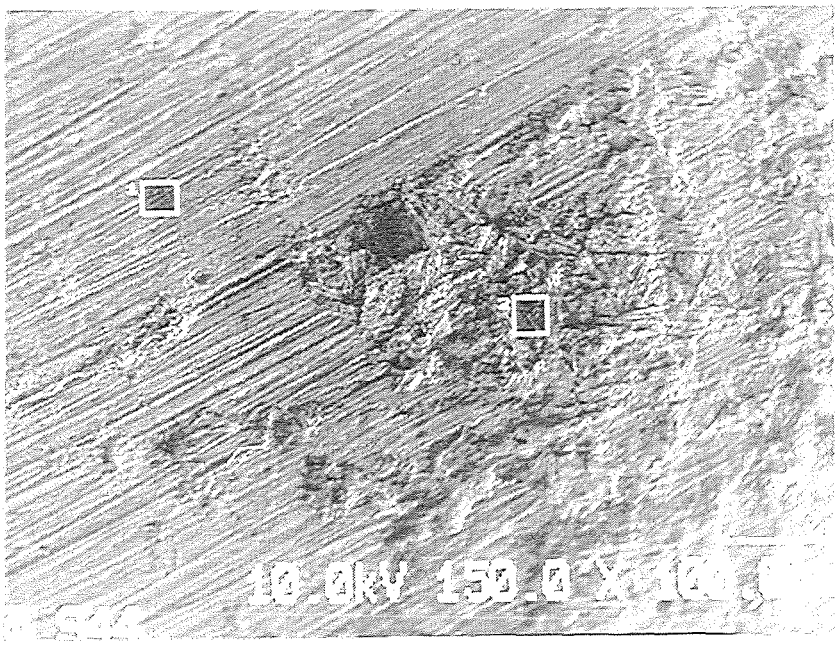




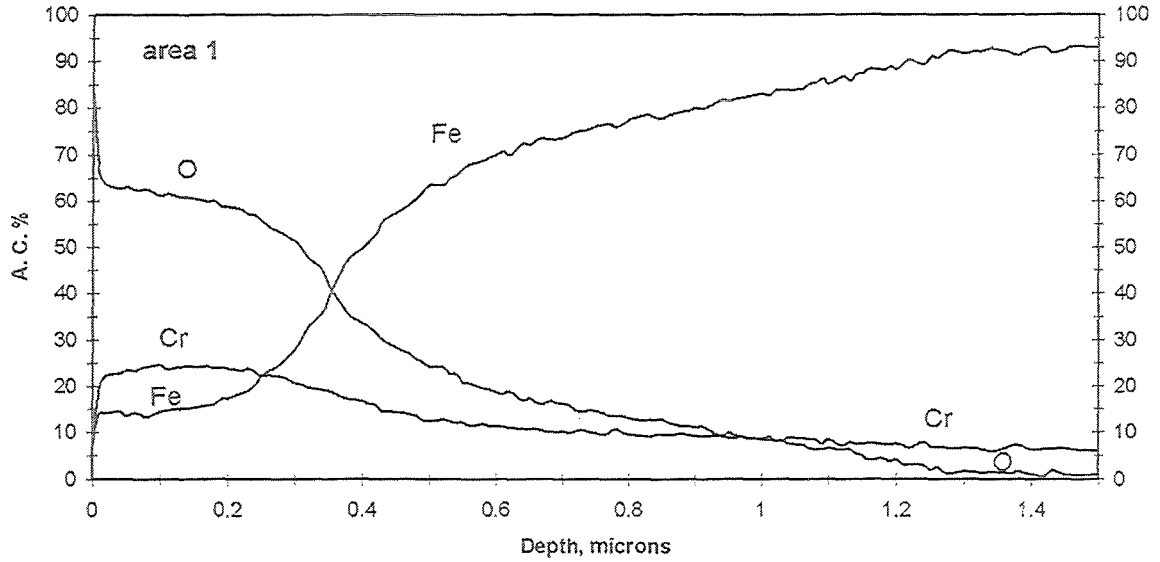
F82H, preoxidised
Argon + H_2
600°C, 665 hours

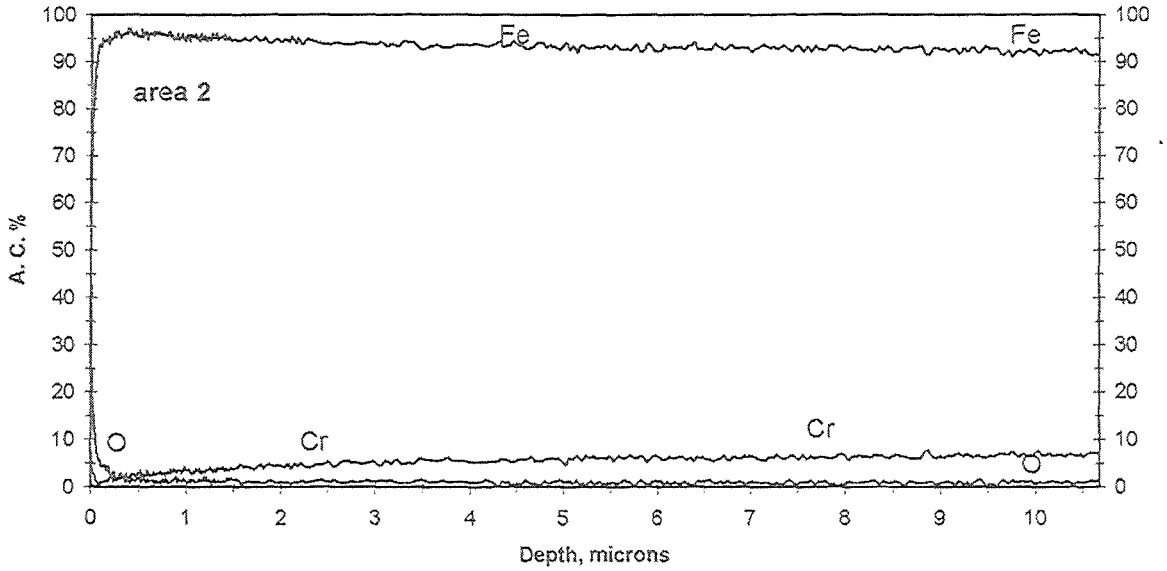






F82H, preoxidised
Argon
600°C, 665 hours





RESULTS

- **AS RECEIVED MATERIAL**

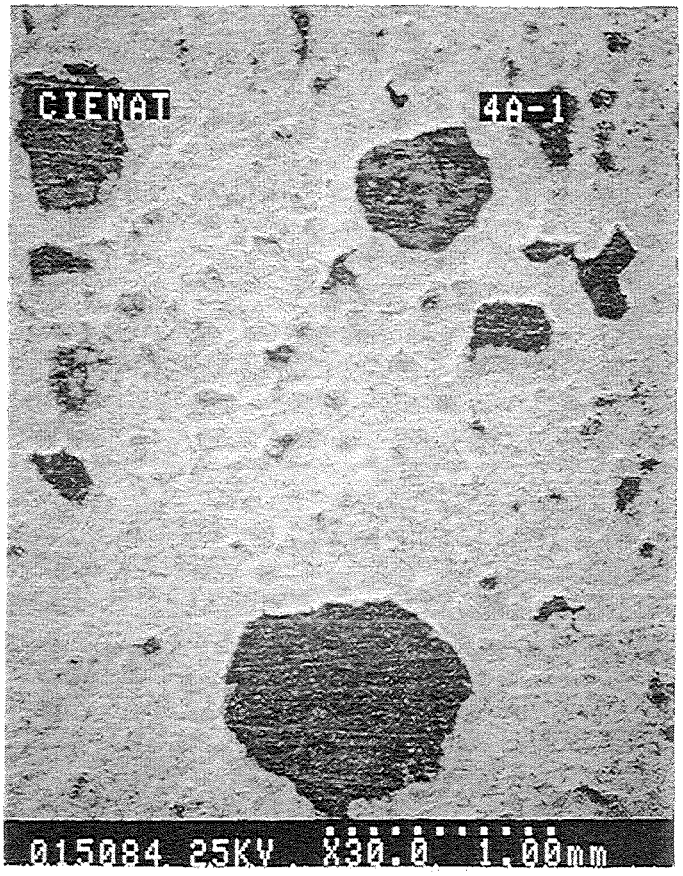
  - Loss weight:

    - Higher loss in Argon than in Argon+H_2, specially at long times
    - Much higher in as received samples than in preoxidised

  - SEM an metallographic examination:

    - Apparently, no surface attack exists (100 hours)
    - Material dissolution with Cr depletion at long times (665hours)
    - Grain boundaries are revealed at dissolution areas
    - Areas with a thin oxide layer rich in chromium

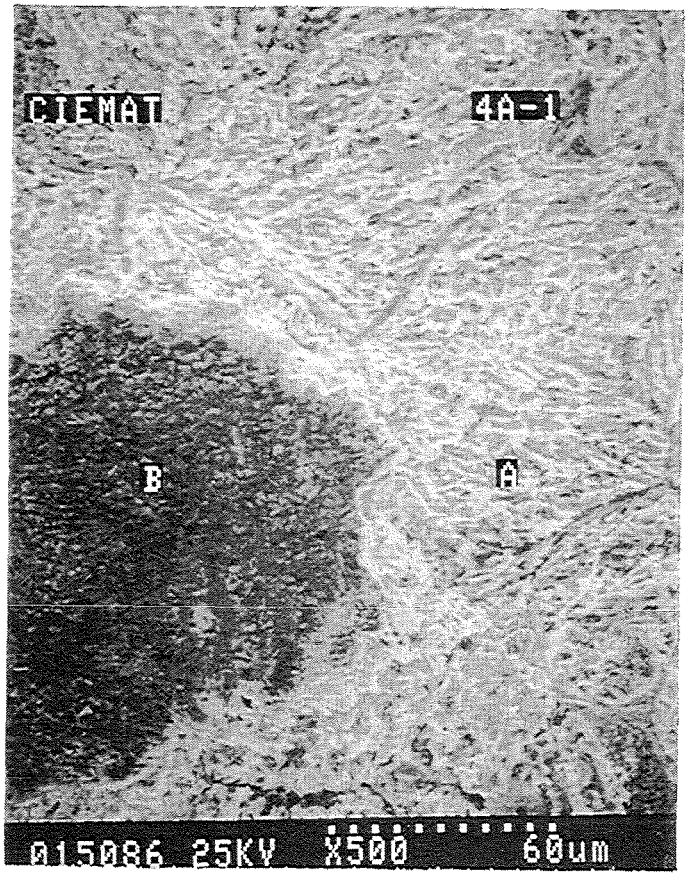
- Oxide layer analysis:
  - After 100 hours, an oxide layer O, Fe, Cr (≈ 1μm), with Cr enrichment is formed in both atmospheres
  - After 665 hours, the oxide layer shows a higher Cr/Fe ratio and lower thickness (<0.4μm) in both atmospheres



F82H, as received
Argon
600°C, 665 hours

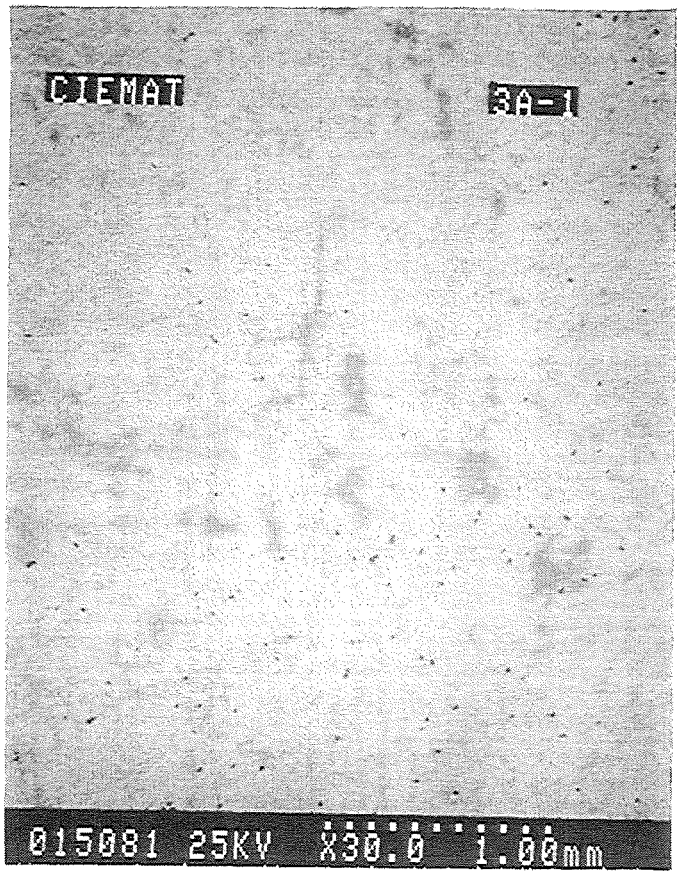
% atom.

	Fe	Cr	Si	Hg	Pb-Bi
General	77.42	7.14	0.01	8.96	6.48



% atom.

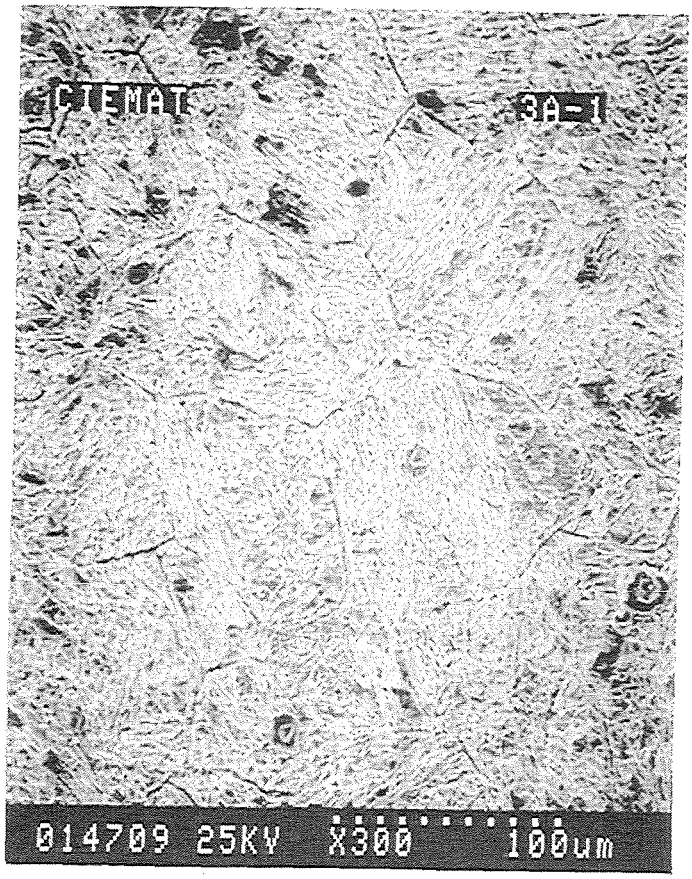
	Fe	Cr	W	Ca	Hg	Pb-Bi
A	90.79	4.18	0.25		4.68	0.10
B	92.03	2.38	1.79	0.62	1.24	1.94



F82H, as received
Argon + H_2
600°C, 665 hours

% atom.

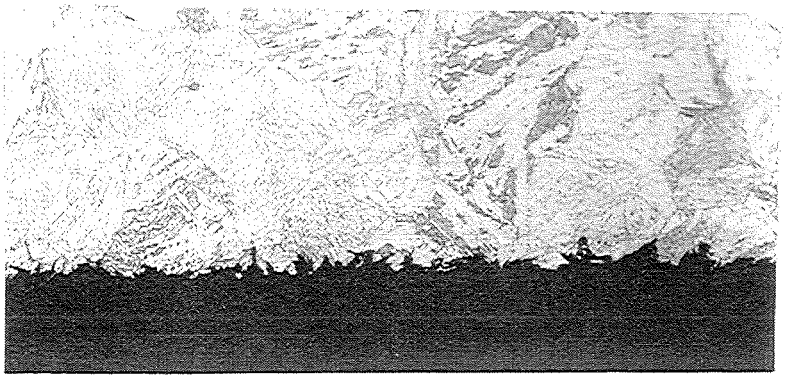
	Fe	Cr	W	Hg	Pb-Bi
General	90.81	4.91	0.62	2.58	1.07



% atom.

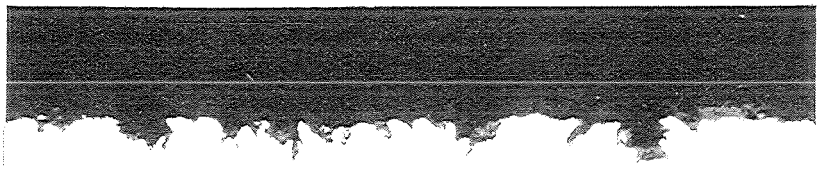
	Fe	Cr	W
General	92.58	6.15	1.27

METALLOGRAPHIC ANALYSIS

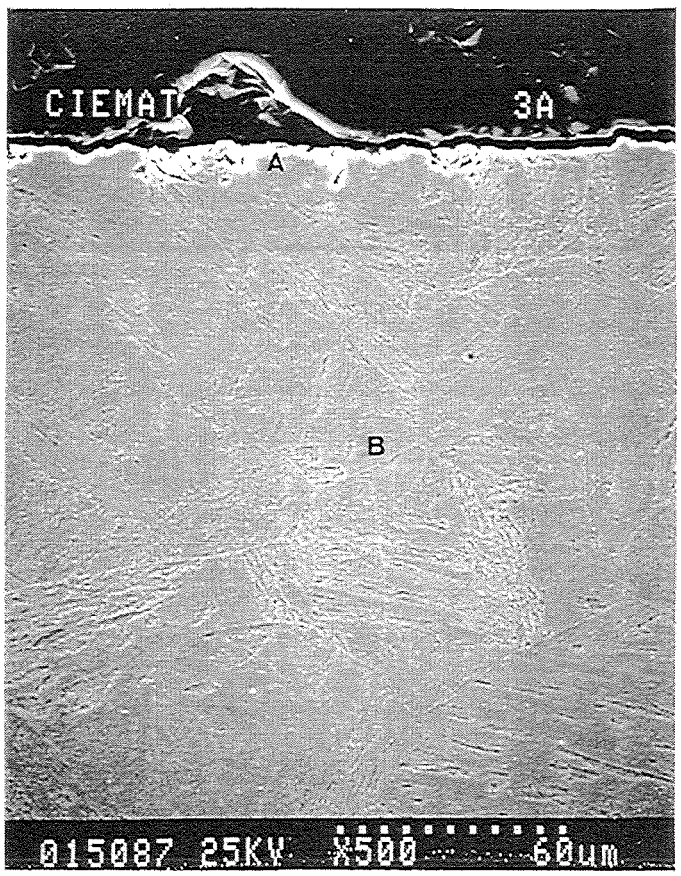


F82H, as received
Argon + H_2
600°C, 665 hours

x 200



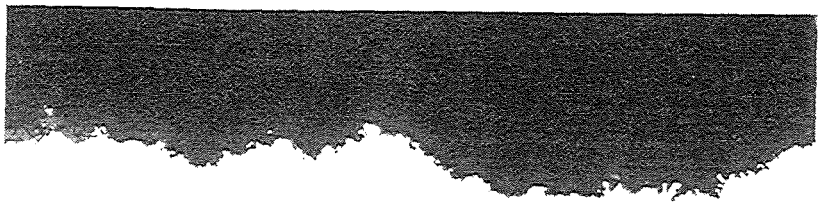
x 500



% atom.

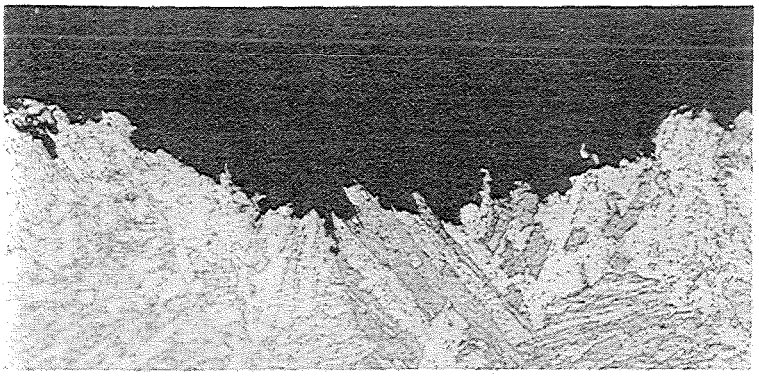
	Fe	Cr	W	V
A	95.53	4.11	0.37	
B	91.85	7.76	0.35	0.04

METALLOGRAPHIC ANALYSIS

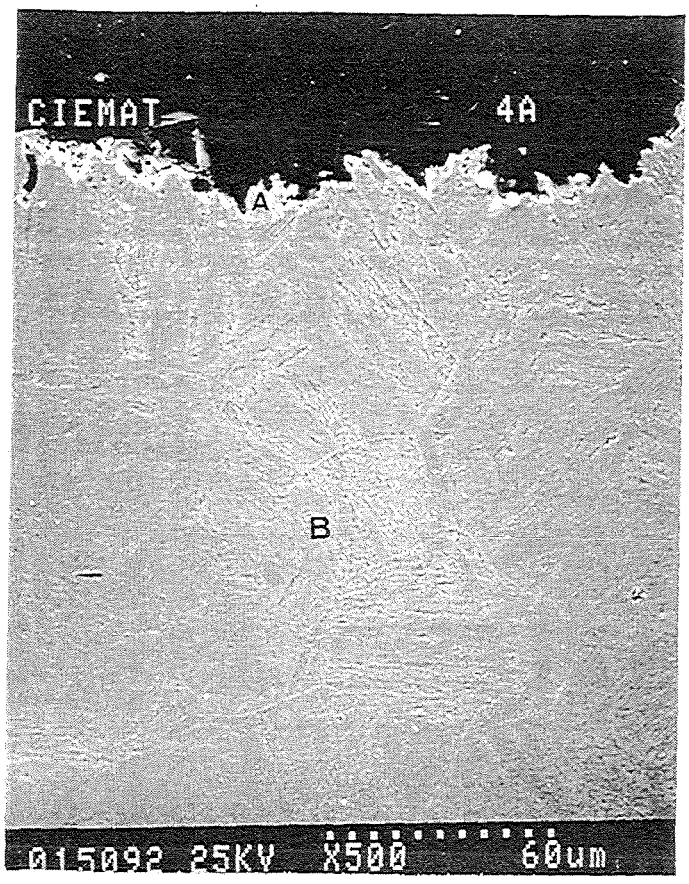


F82H
Argon
600°C, 665 hours

x 200

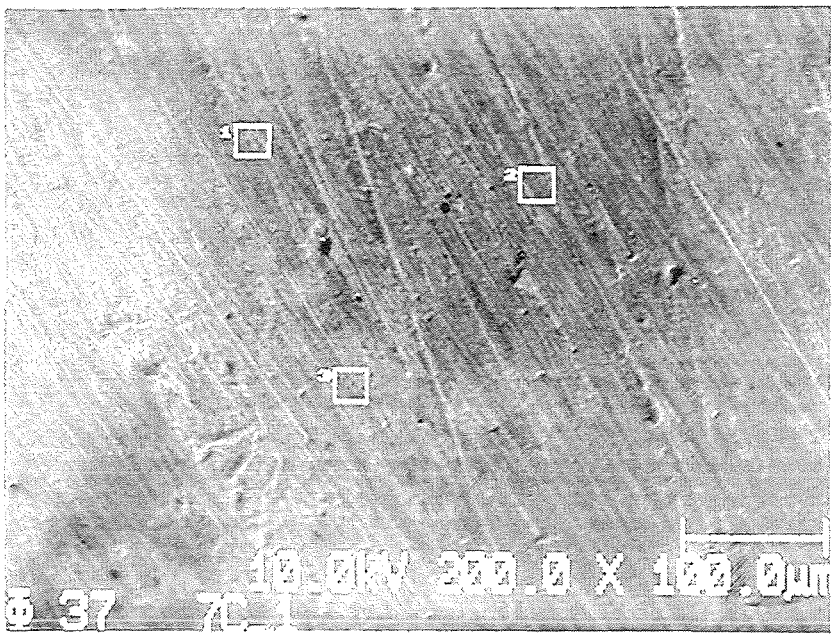


x 500

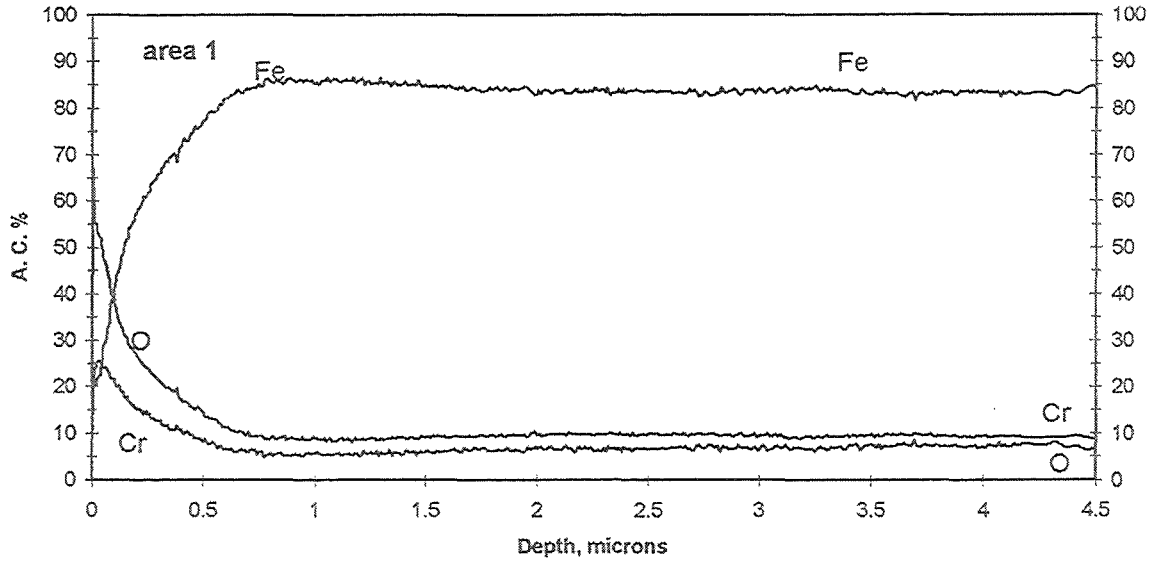


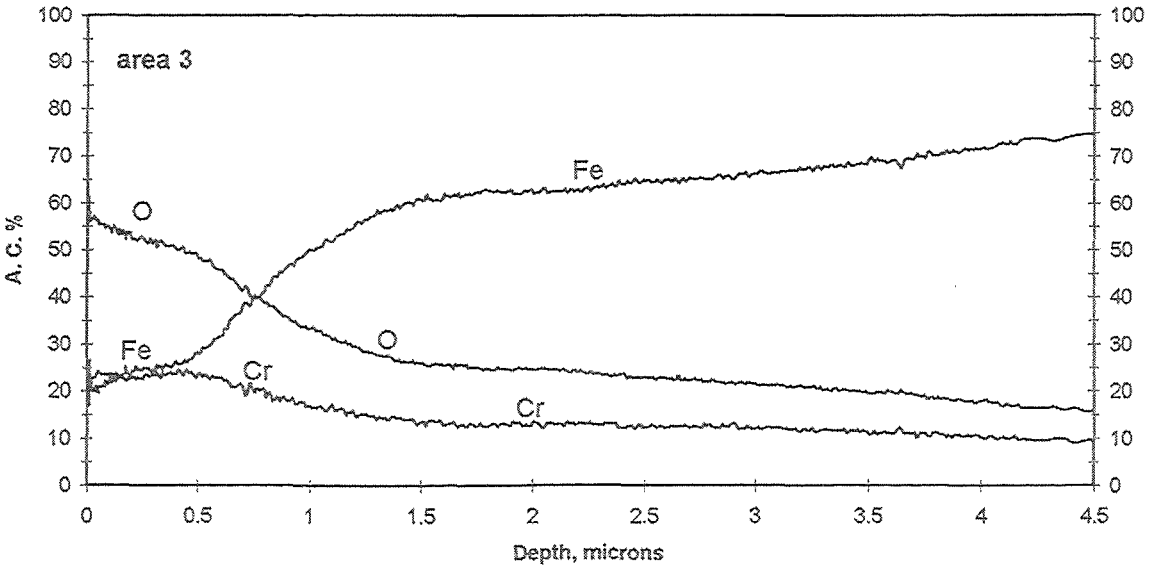
% atom.

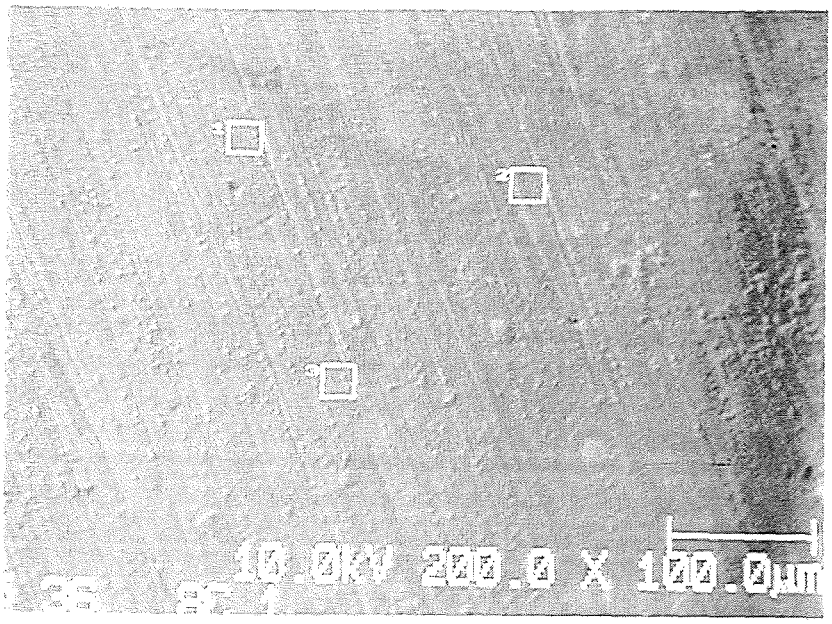
	Fe	Cr	W	V
A	94.03	4.09	0.66	0.31
B	91.03	8.33	0.58	0.05



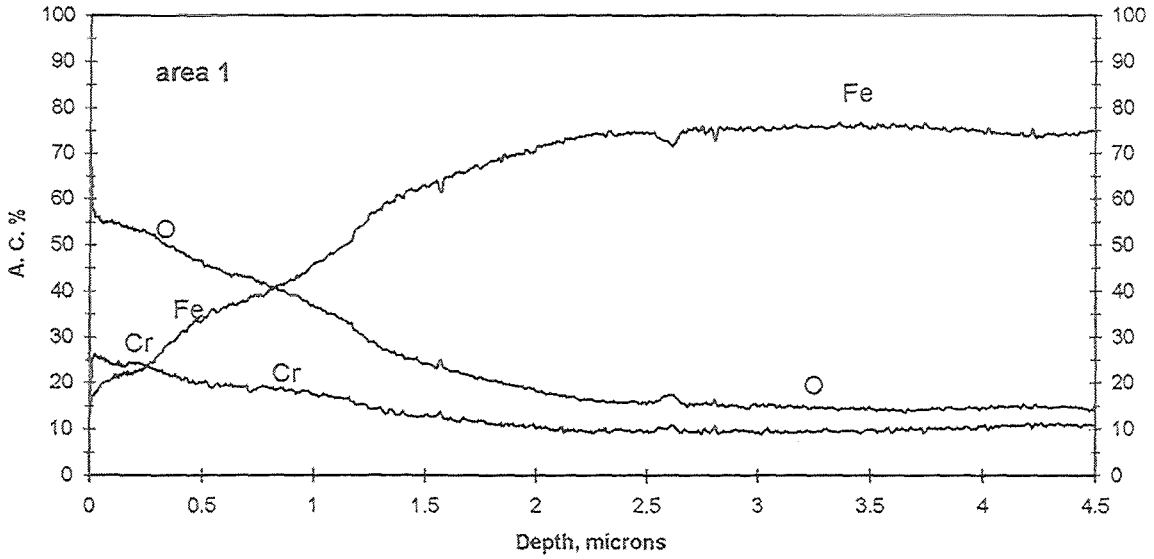
F82H, as received
Argon + H_2
600°C, 100 hours

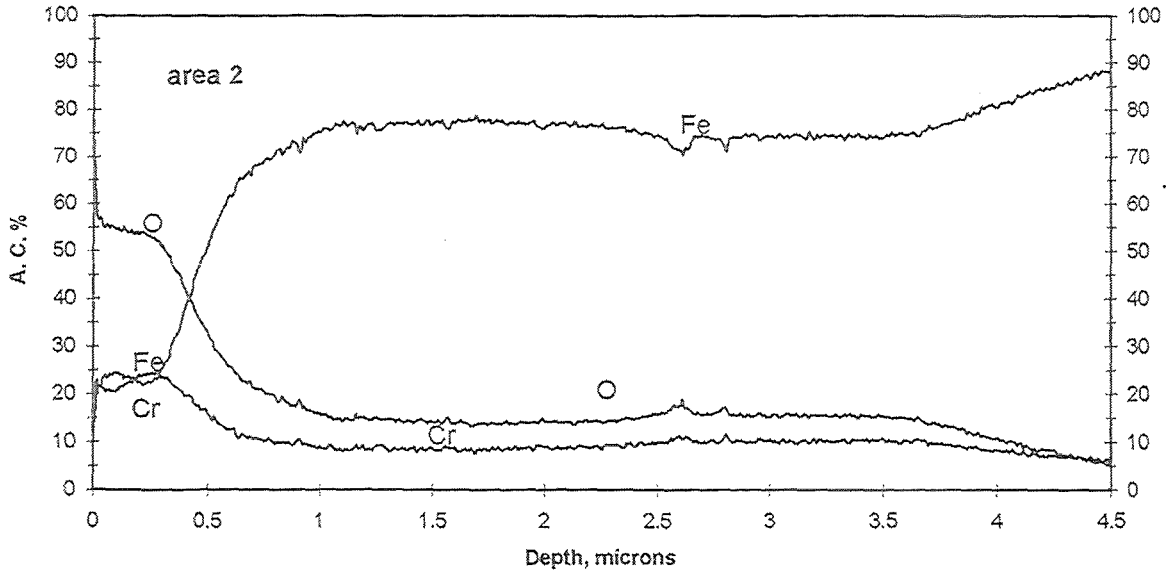


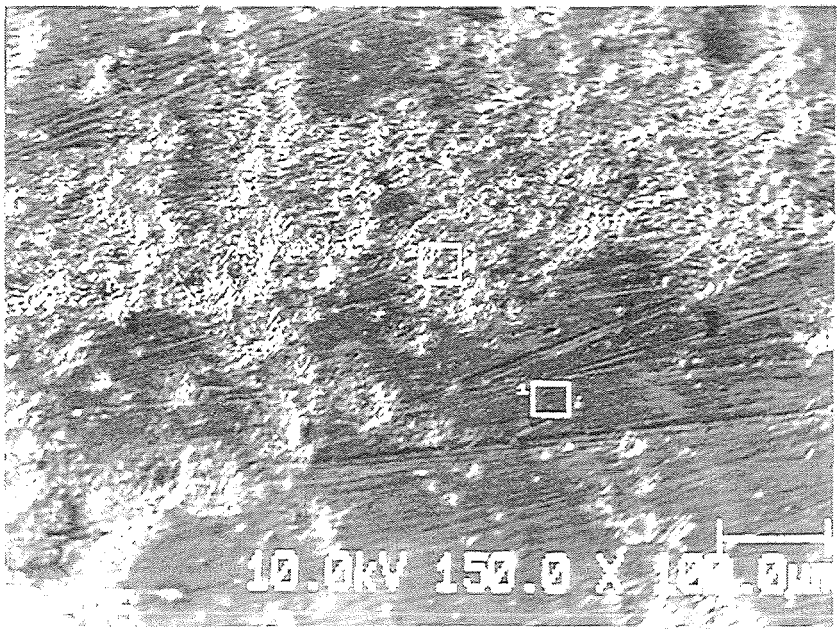




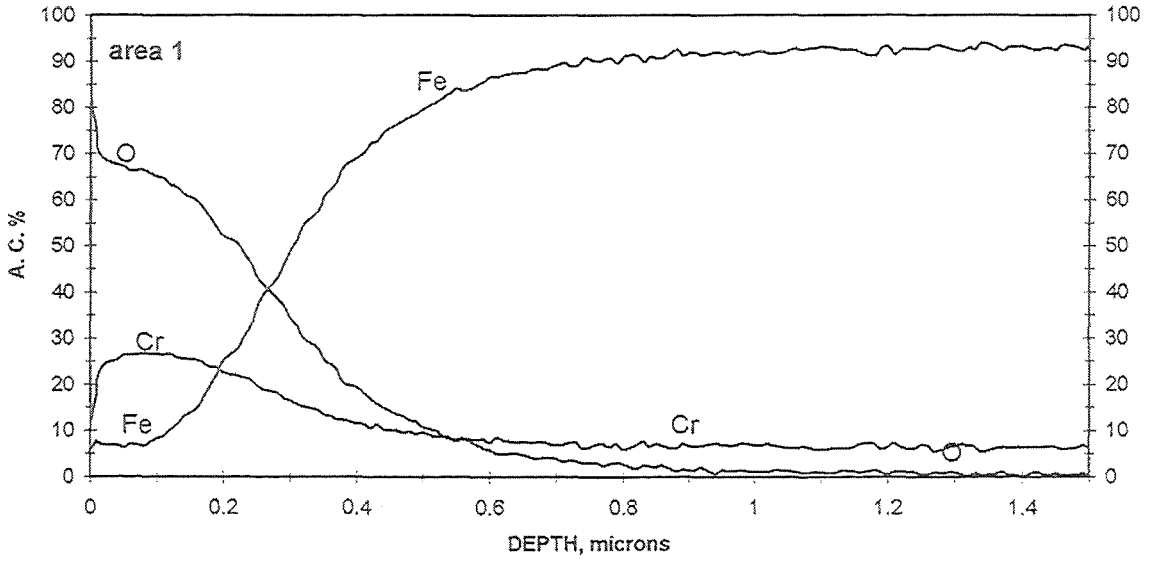
F82H, as received
Argon
600°C, 100 hours

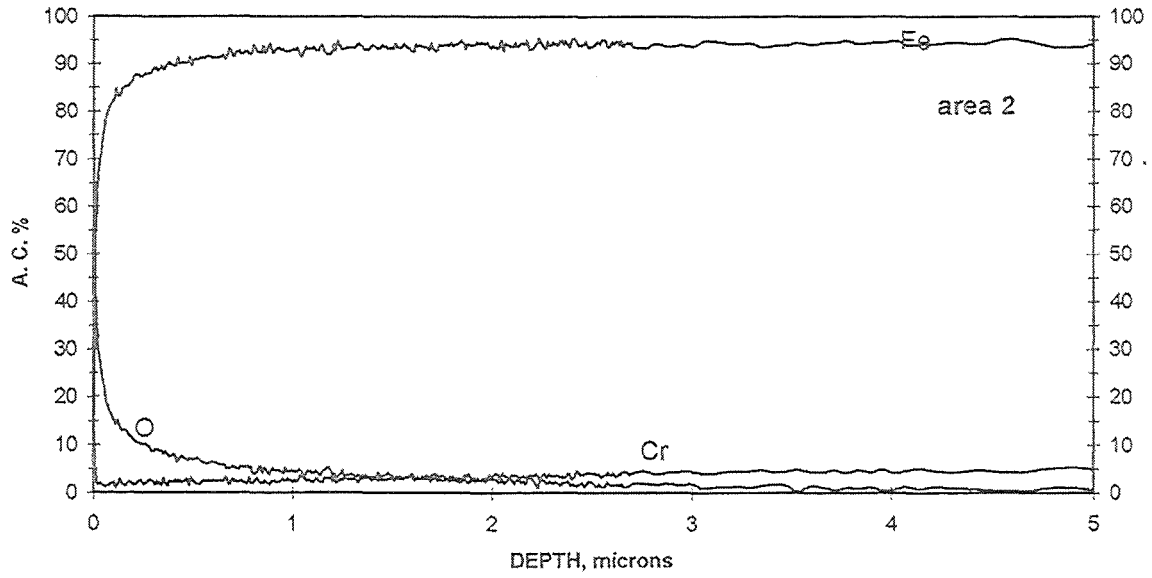


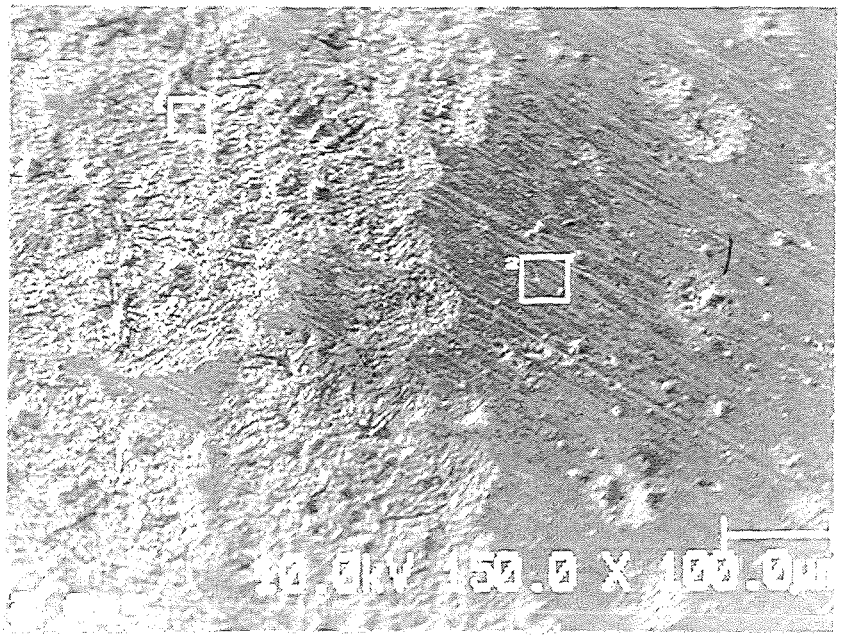




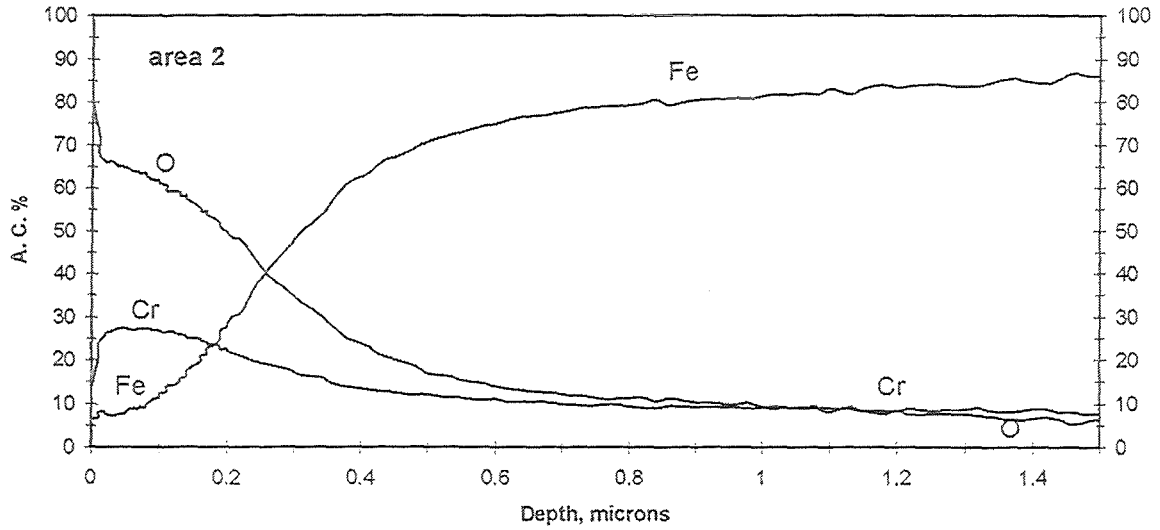
F82H, as received
Argon
600°C, 665 hours

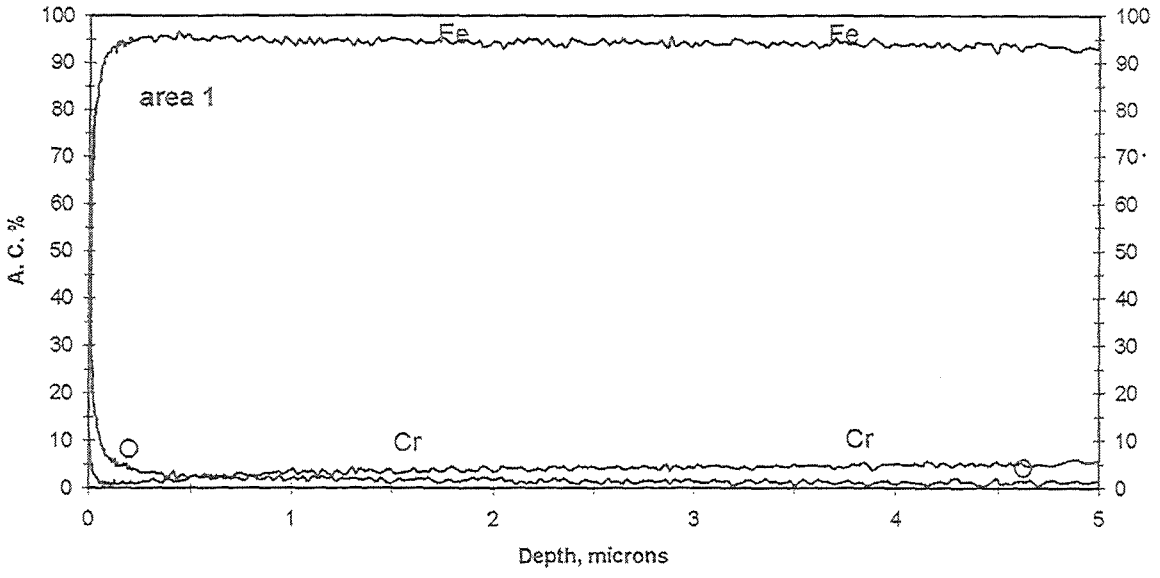






F82H, as received
Argon + H_2
600°C, 665 hours





PRELIMINARY CONCLUSIONS

- OXIDE LAYER PREVIOUSLY FORMED DELAIS THE DISSOLUTION OF THE MATERIAL IN LEAD-BISMUTH

  - THICK > 10μm
  - DOBLE LAYER: EXTERNAL Fe
    INTERNAL Cr
  - HETEROGENEUS

  ⇒ NO PROTECTIVE

- OXIDE FILMS FORMED IN LEAD-BISMUTH SHOW DIFFERENT CHARACTERISTICS:

  - THIN < 1μm
  - HIGH Cr/Fe RATIO
    (higher in as received samples than in preoxidised ones)
  - IT SEEMS AN SPINEL STRUCTURE

  ⇒ PROTECTIVE ?

OPEN QUESTIONS

- PREOXIDATION OR IN-SITU FORMATION OF THE OXIDE LAYER?
- BEST PROCEDURE TO FORM A PREVIOUS OXIDE LAYER?
- REQUIRED OXYGEN CONCENTRATION FOR OXIDE LAYER FORMATION AND AUTOHEALING?
- SOLUBILITY OF OXIDE LAYER IN LEAD-BISMUTH?

Behaviour of W and Mo in stagnant liquid Pb at 793 K

Gianluca Benamati[1] and Patrizia Buttol[2]

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Abstract

The behaviour of tungsten and molybdenum in contact with stagnant oxygen-saturated molten lead at 793 K for immersion times up to 3700 h has been investigated. Metallographic techniques (OM, SEM), X-ray diffraction and electron probe microanalyses by energy dispersion spectroscopy were performed on the tested samples. Tungsten is a candidate material for a beam window working in liquid lead in ADS systems. Molybdenum has been suggested as a coating for structural materials in contact with liquid lead. Both tungsten and molybdenum have been reported to have a very low solubility in molten lead and, consequently, to be suitable for this type of environment. Compatibility tests in stationary liquid metals are important as they give information on the corrosion mode of alloys, although further tests in circulating melts are essential to evaluate the corrosion behaviour of the material when erosion and mass transport are involved.

Both W and Mo underwent oxidation in contact with oxygen-saturated molten lead at 793 K, as a consequence of their affinity for oxygen which is greater than that of Pb. On both metals MeO_3 oxide forms (with Me=W or Mo), although the values of standard free energy of formation (calculated per mol O_2) are lower for MeO_2 than for MeO_3.

MeO_3 oxides in contact with the oxygen-saturated molten lead gives $x{\cdot}PbO{\cdot}y{\cdot}MeO_3$ type ternary compounds, as expected from the PbO-$PbO{\cdot}MeO_3$ phase diagrams. $PbO{\cdot}WO_3$ ($PbWO_4$) and $2PbO{\cdot}WO_3$ (Pb_2WO_5) formed on tungsten, $PbO{\cdot}MoO_3$ ($PbMoO_4$) and $2PbO{\cdot}MoO_3$ (Pb_2MoO_5) formed on molybdenum.

In the case of tungsten, the WO_3 layer was thin, compact and adherent to the base metal, while the ternary compounds were friable and are likely to be removed in dynamic conditions.

In the case of molybdenum, preliminary studies show that coating's performance was unsatisfactory. Cracking and lifting occurred; possibly the tendency of MoO_3 to sublimate at T = 793 K enhanced these phenomena.

Both tungsten and molybdenum are deeply affected by the presence of oxygen in liquid lead therefore their use should be limited to highly deoxidised environments. The preliminary studies on protective molybdenum coatings have not been encouraging so far.

Karlsruhe, Germany, September, 16-17th, 1999
European Workshop on Heavy Liquid Metal Technology for use in ADS

Behaviour of W and Mo in stagnant liquid Pb at 520°C

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ENEA, Bologna, Italy
Valentina Imbeni, Carla Martini and Giorgio Poli
Institute of Metallurgy, University of Bologna, Italy

CONTENTS

Introduction: aim of study

Exploratory experiments have been carried out relating to the use of molten lead as a coolant/target in ADS systems.

Compatibility of pure W and of Mo coated F82H steel with liquid Pb has been investigated on a laboratory scale in stationary conditions.

Introduction: why liquid Pb? Why W and Mo?

✓**Liquid Pb has been chosen for its unique properties such as high atomic number (Z=82), moderate melting point (327C), efficient heat removal, low vapour pressure, good neutron yeld**

Materials for ADS systems will require:

- ☐**Chemical compatibility (corrosion resistance)** ✓
- ☐**radiation resistance**
- ☐**high temperature resistance**
- ☐**fracture and failure resistance**

W and **Mo** are interesting materials for use in liquid lead as they both have been reported to have a very ***low solubility*** in molten lead.***(C.Guminski,*** Z.Metallkd. *81(1990)105)*

- Molybdenum has also been reported to be a suitable ***protective coating*** on structural steels in a liquid lead environment. (**R.C. Asher** *et al*(Corr.Sci. 17(1977) 545-557), F.Stubbins, LANL, 1996)

- Tungsten has been reported to be potentially suitable for a ***beam window*** working immersed in a liquid lead spallation target. (**C. Rubbia** et al CERN/AT/95-44 (1995)

Experimental details: tests procedure

Compatibility tests of W an Mo coating have been performed in stationary, oxigen saturated liquid Pb at 793 K.

Experimental

About 3 kg of Pb have been melted into cylindrical crucibles of alumina (d=58.5 mm, h=104 mm), in a glove-box under an Ar atmosphere (ENEA Brasimone laboratories). The samples have been placed into the crucibles and exposed to liquid lead for different times.

Exposure times

Tungsten	**1700 h**	**2000 h**
Molibdenum	**2000h**	**3700h**

Experimental details: materials

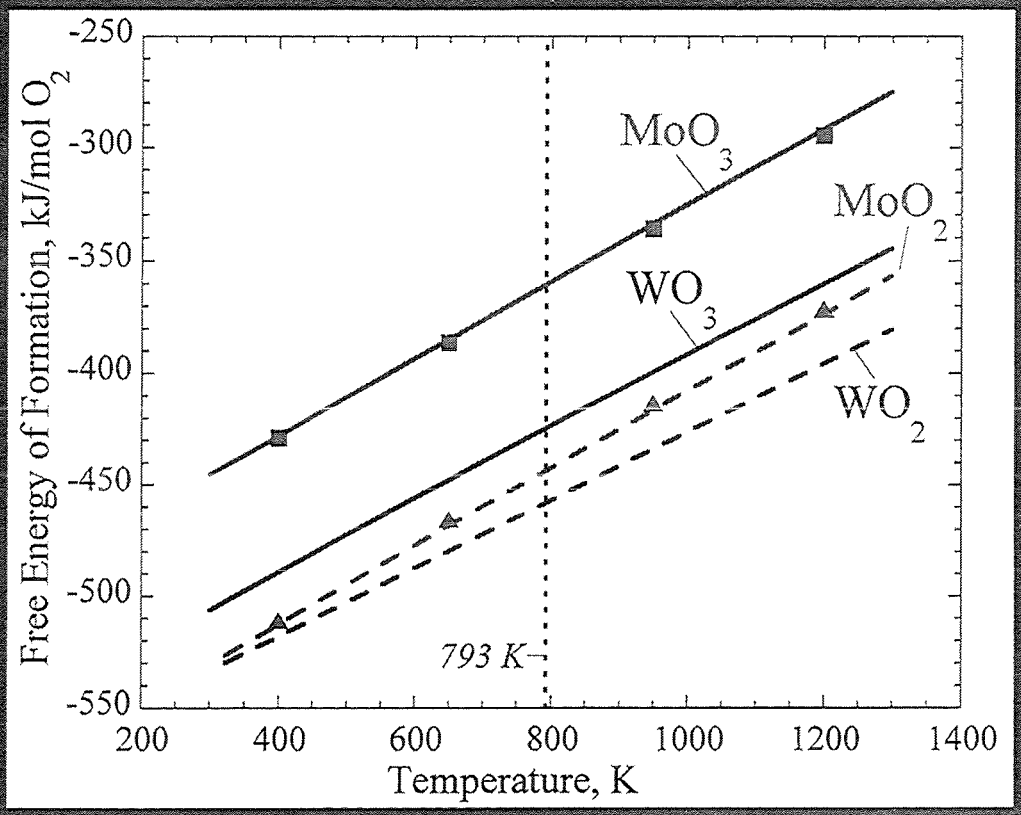
- ✓ W (high purity-99.95%) solid metal supplied by Goodfellow Co.
- ✓ Mo coating deposited by plasma spray on F82H steel
- ✓ Molten lead commercially pure

• The molten **stagnant *lead*** was in all cases ***saturated by oxygen*** at 793 K (520°C) throughout the tests, as confirmed by the presence of PbO floating on the free surface and by measurements of total oxygen content (extracted from lead as CO_2 and determined by an IR sensor) carried out ***before*** and ***after*** the tests.

C_s (oxigen saturation concentration) in Pb **is** 3.0 wppm at 743 K and 7.7wppm at 793 K (Orlov et al (1997)).

The presence of oxygen in liqui metals modifies the expecte corrosion mechanism (eg. direc solubilisation in molten Pb) leadin to the formation of oxide layers.

Thermodynamics: W and Mo oxides - free energy of formation



Lines: *O.Kubaschewski and C.B.Alcock,* Metallurgical Thermochemistry, 5th Ed., 1979
Marks: N.Floquet, O.Bertrand and J.J.HeizmannOxid.Metals 37(1992)253

In the case of Mo oxides:

$$2/3<MoO_3> = 2/3<Mo> + (O_2)$$

⇒ according to Kubaschewski and Alcock:

$$\Delta G° \text{ (kJ/mol } O_2) = - 499849 - 12.83 \cdot T \cdot \log T + 212.83 \cdot T$$

while,

⇒ according to Floquet *et al.*,

$$\Delta G° \text{ (kJ/mol } O_2) = - 499371 - 12.81 \cdot T \cdot \log T + 209.83 \cdot T$$

Thermodynamics: W oxides

WO_2, WO_3

A.Warren *et al.* (J.Refractory Metals & Hard Materials, 1996) reported that, from the 'chemical' point of view, only the two pure simple oxides exist. Yet during investigations of the structural mechanism of the solid phase transformations from **WO_2** to **WO_3** several **intermediate oxide phases** have been found. (J.P.Bonnet et al.,Oxidation of Metals, vol13, No3, 1979)

Phase	O/W ratio	Structure
- **WO_2**	2.00	**tetragonal**
- W_2O_5	2.50	
- W_3O_8	2.67	
- $W_{18}O_{49}$	2.72	
- $W_{20}O_{58}$	2.90	
- **WO_3**	3.00 ...	**monoclinic**

W oxides containing the cations W^{2+}, W^{4+}, W^{5+} and W^{6+} were detected by ***XPS measurements***.

In the temperature range of 20-600°C the oxide formed is WO_3.
A.Warren *et al.* (J.Refractory Metals & Hard Materials, 1996)

WO_2 is mostly prepared by reduction of WO_3 or tungstates, since direct oxidation of W often results in the formation of WO_3 (*see also* J.Bénard, Oxidation des Métaux, Vol.II, Gauthier-Villars, Paris, 1964, p.251, and Gmelin Handbuch der Anor-ganischen Chemie, B2, Springer, 1972).

Thermodynamics: Mo oxides

MoO_2, MoO_3 As in the case of W, also Mo only has two pure simple oxides, **MoO_2** and **MoO_3**.

Together with them several 'mixed' oxides have been reported (L.Brewer and R.H.Lamoreaux, 1980, in: ASM Handbook, Alloy Phase Diagrams, Vol.3, 1992):

Phase	O/W ratio	Structure
- **MoO_2**	2.00....	**tetragonal**
- Mo_2O_5	2.50	
- Mo_4O_{11}	2.75	
- Mo_8O_{23}	2.88	
- Mo_9O_{24}, Mo_9O_{26}	2.90	
- **MoO_3**	3.00	**orthorhombic**

MoO_2 is isomorphous with ***WO_2***.

Oxidation of Mo:

From 343 K to ~623 K (70 to ~350°C), MoO_3 nuclei of amorphous structure or nanometric size are formed on Mo surfaces.

From 623 K, Mo undergoes oxidation into **MoO_3** excluding MoO_2 and the non-stoichiometric oxides.

From 773 K (**500°C**), the **sublimation** of solid **MoO_3** begins. Under these conditions, both the formation of solid MoO_3 and its simultaneous sublimation will occur.

At 1073 K (800°C), MoO_3 melts.

N.Floquet Oxid.Met. vol37,nos3/4 (1992)

Thermodynamics: Pb-Me-O ternary oxides

W-containing compounds

According to the PbO-PbO·WO_3 phase diagram, the following compounds might be present:

⇒ **$PbO·WO_3$, i.e. $PbWO_4$**

and

⇒ **$2PbO·WO_3$, i.e. Pb_2WO_5**

Mo-containing compounds

According to the PbO-PbO·MoO_3 phase diagram, the following compounds might be present:

⇒ **$PbO·MoO_3$, i.e. $PbMoO_4$**

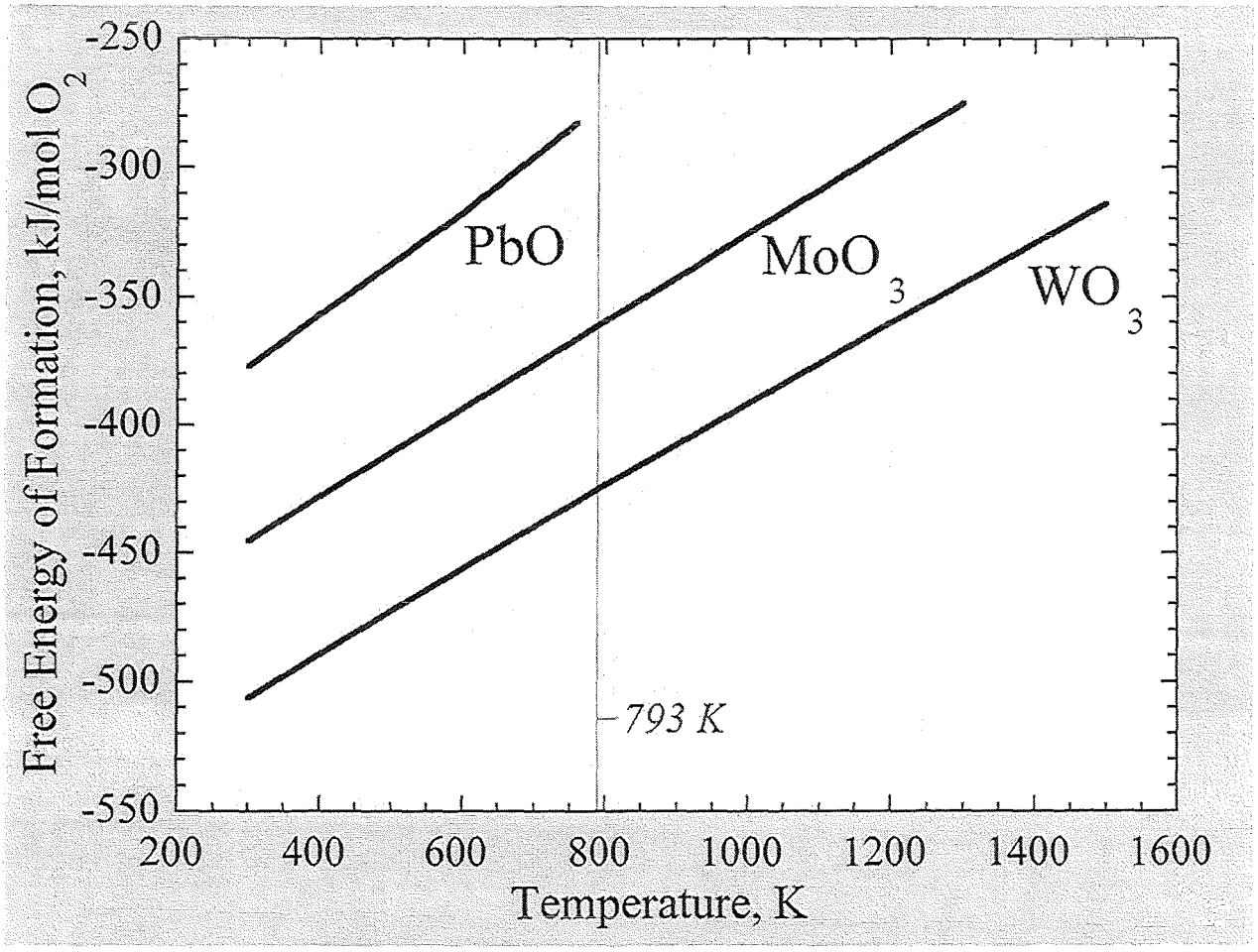
and

⇒ **$2PbO·MoO_3$, i.e. Pb_2MoO_5**

The formation of the ***Pb-richer ternary products*** is expected at the ***outer part*** of the oxidised surface layers, i.e. at the interface between the growing layers and the molten lead.

Thermodynamics: phase diagrams

Both W and Mo formed oxides as their affinity for the oxygen is greater than that of Pb.



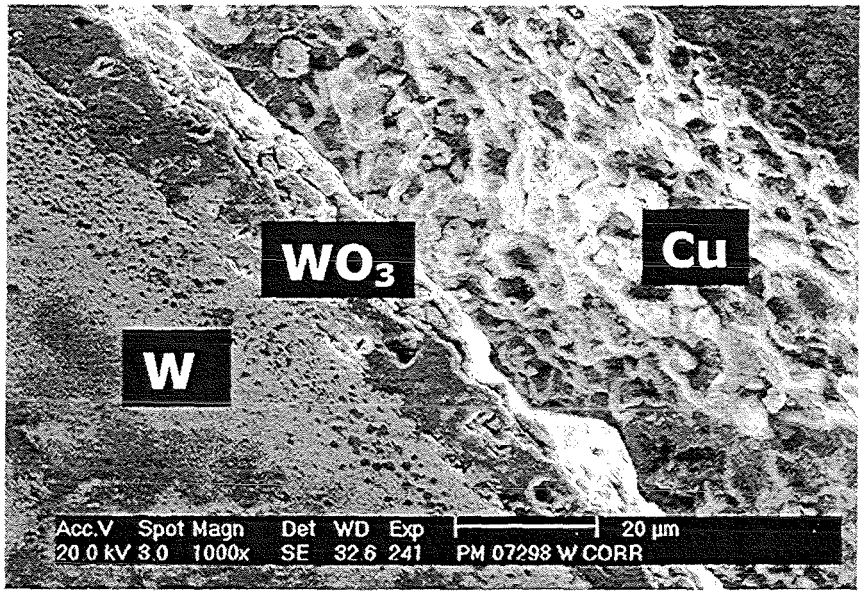
Results

- The Mo-W oxides reacted with the oxygen saturated liquid lead to give *Pb-Me-O ternary compounds*.*(Me= W, Mo)*

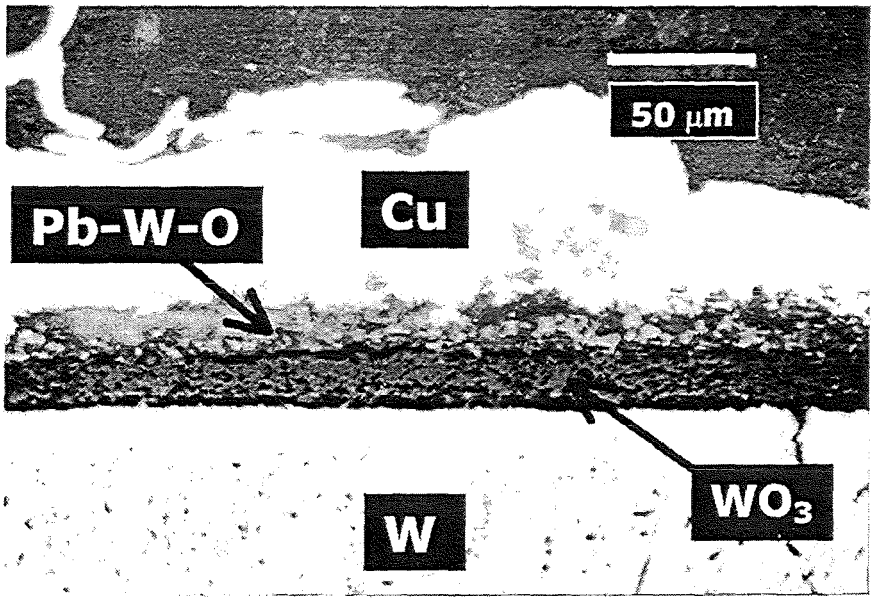
- The Mo coating was cracked and lifted after the tests, probably in consequence of the MoO_3 sublimation starting at the testing temperature and because of the bulk materials higher thermal expansion coefficient.

- WO_3 layer is thin, compact and adherent to the base metal, while the ternary compounds are friable.

Results:W-interaction products

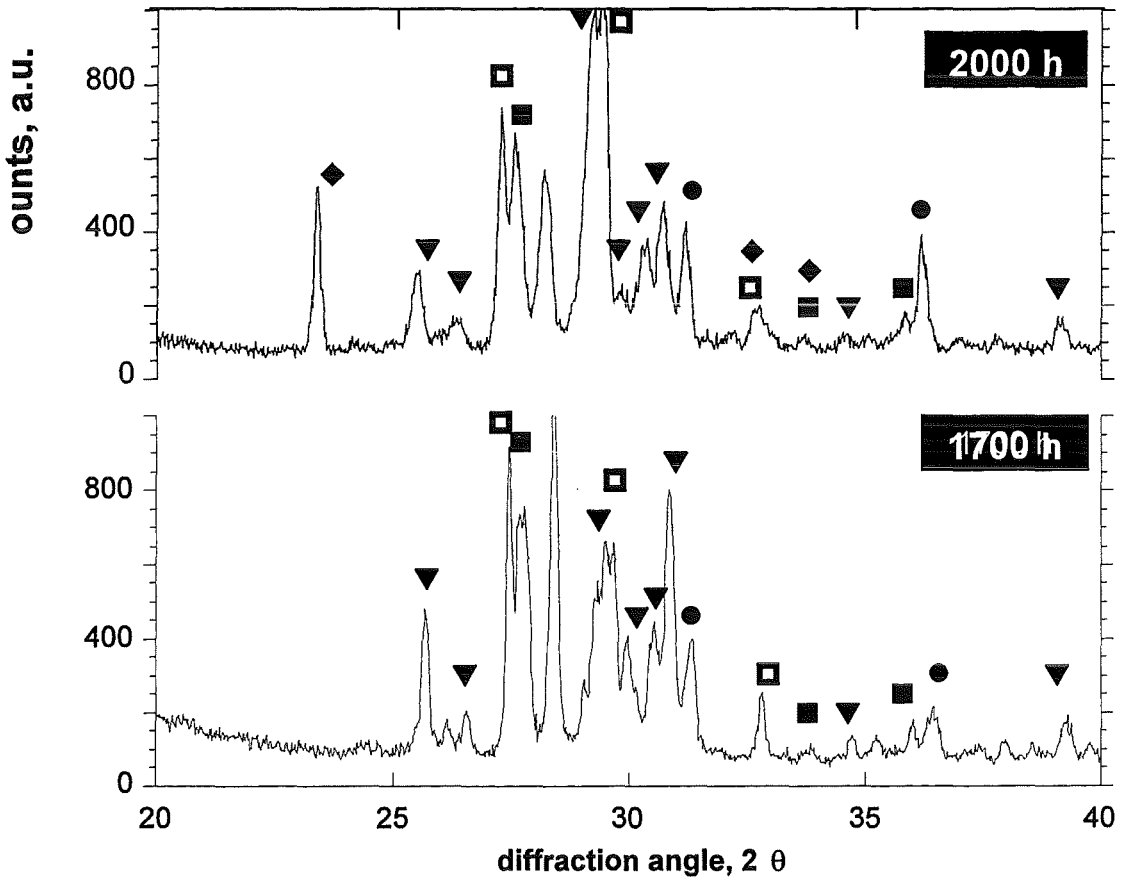


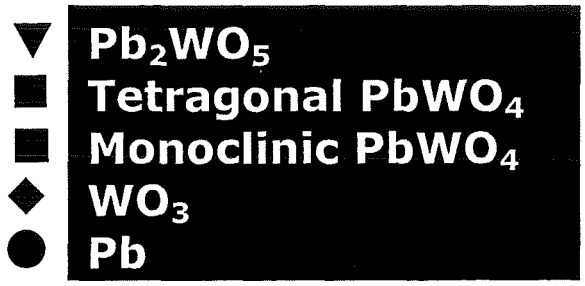
W exposed to **liquid Pb** at **793**°K for **1700h (SEM)**



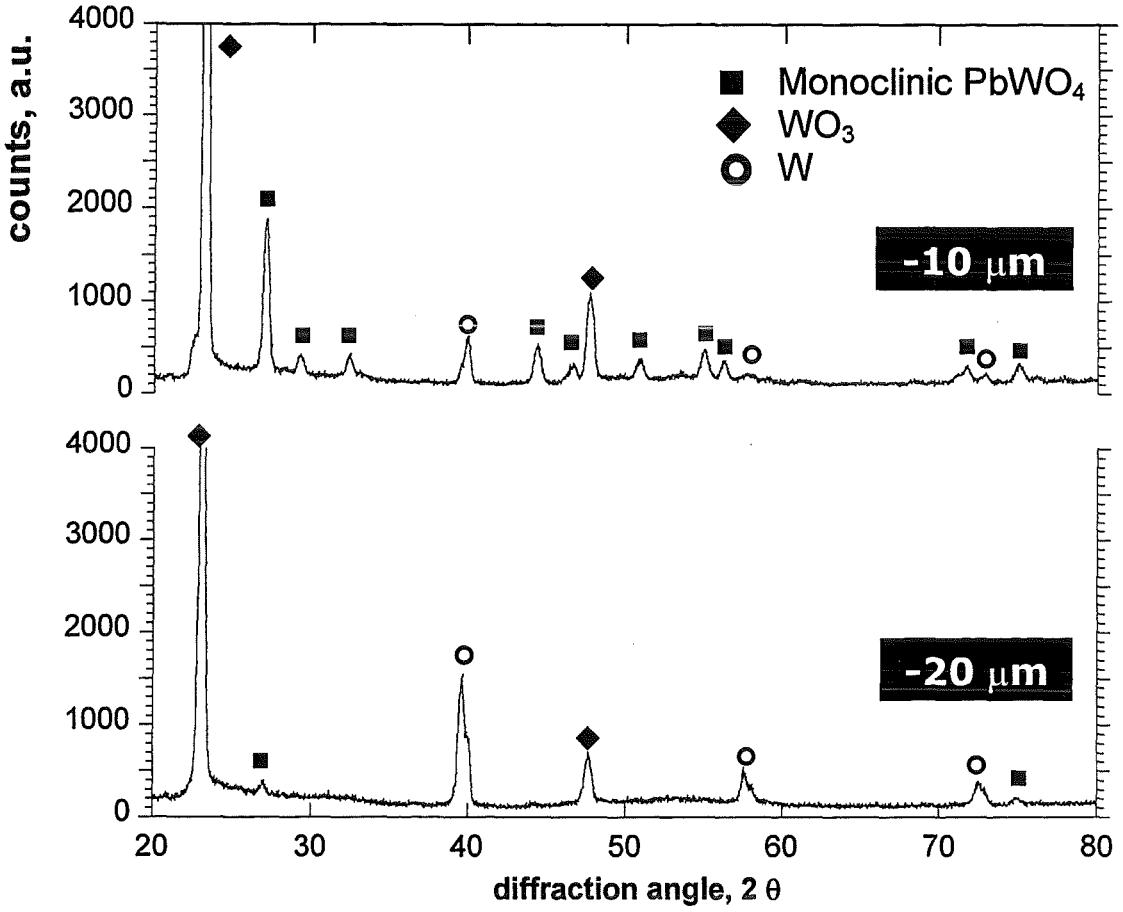
W exposed to **liquid Pb** at **793**°K for **2000h (OM)**

Results: XRD spectra (Co Kα) of W exposed to liquid Pb (1700 h-2000h) at 793 K



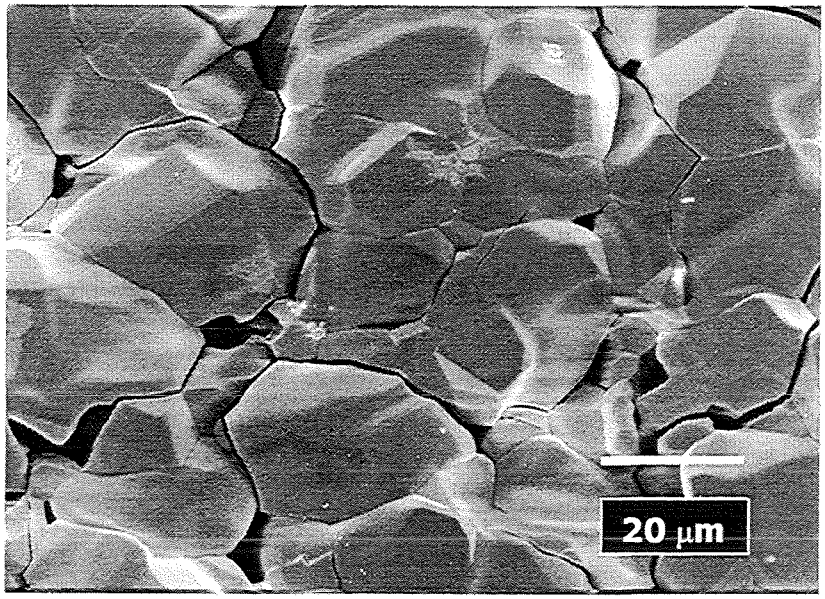


Results: XRD spectra (Co Kα) of W exposed to liquid Pb (1700 h) at decreasing distance from the surface

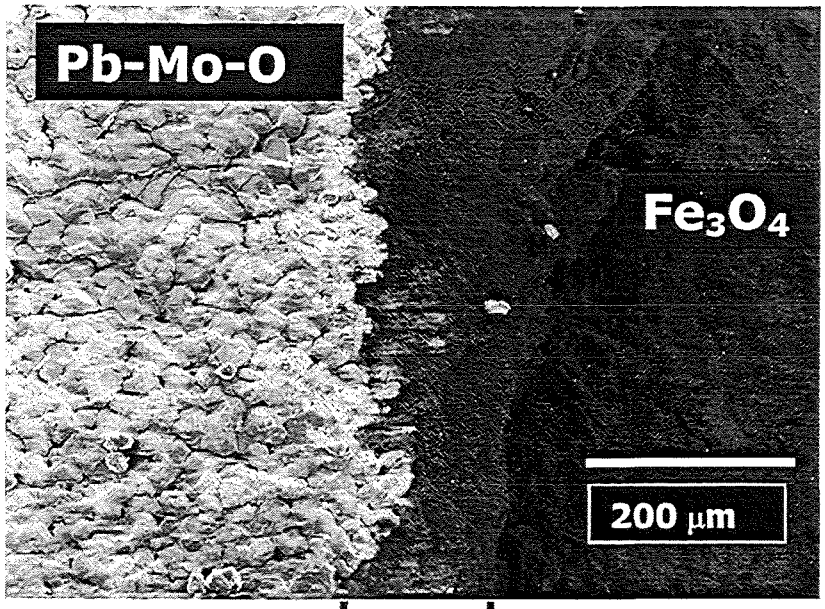


Thin layers of interaction products have been removed in order to have some information on the distribution of the different W-O and W-Pb-O oxides.

Results: Mo-interaction products



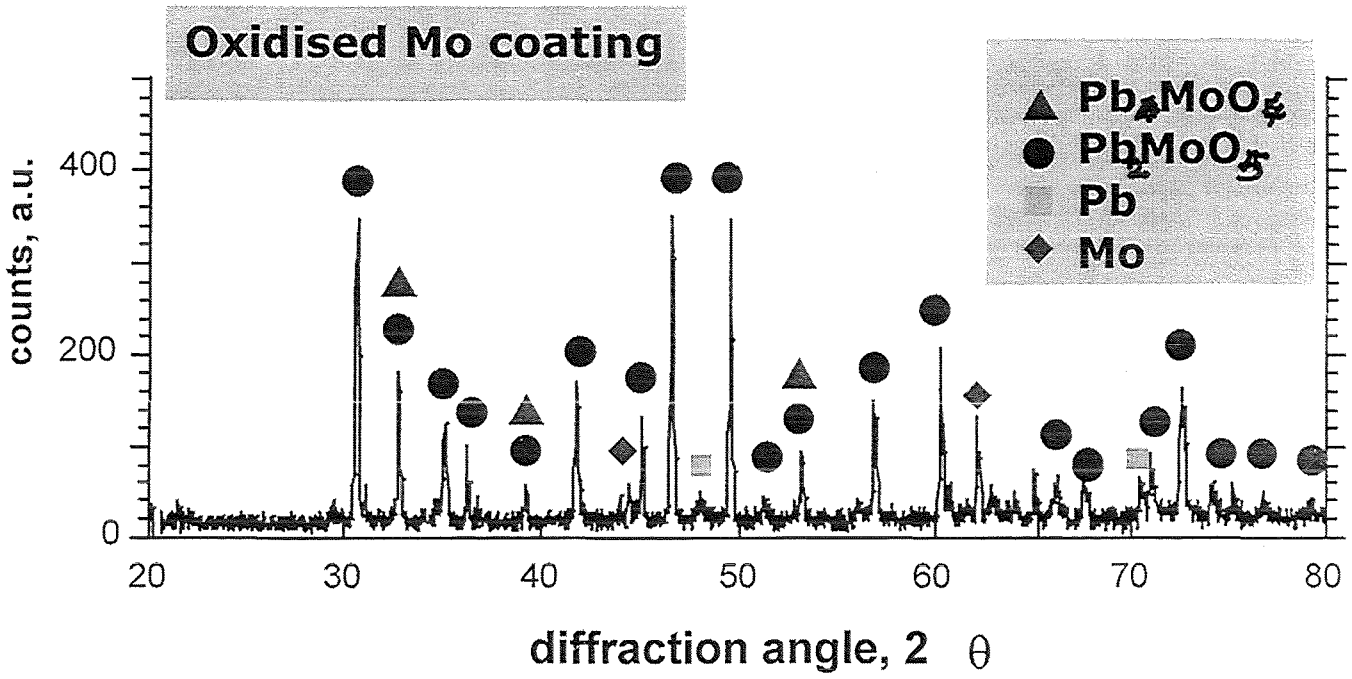
Mo exposed to **liquid Pb** at **793**°K for **3700h (SEM):** **Mo-Pb-O** ternary compounds on the outer surface

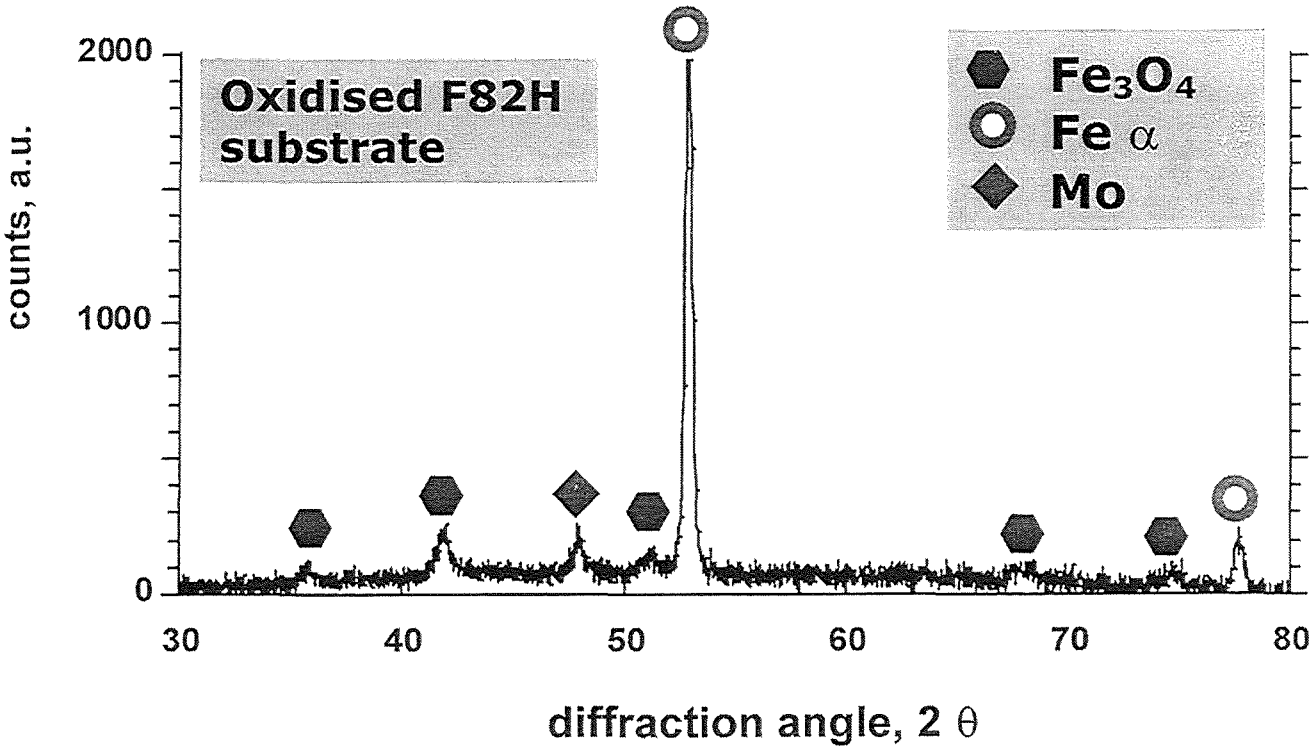


oxidised Mo coating | **oxidised F82H substrate**

Mo exposed to **liquid Pb** at **793**°K for **3700h (SEM):** **the Mo coating cracked** leaving the steel surface exposed to **liquid Pb** (formation of Fe_3O_4)

Results: XRD spectra (Co Kα) of Mo exposed to liquid Pb (3700 h)





Although there is a relationship between the solubility of materials in lead and the attack of the lead on Mo and W, the presence of oxygen strongly affects the corrosion mechanism and their low solubility in molten lead is not the only key-parameter.

WO_3 oxide has been detected although the standard free energy of formation value of W *(calculated per mol O_2)* is lower for WO_2 than for WO_3. This has been reported in the literature and has been previously discussed.

Conclusions

The W ternary compounds $PbWO_4$, Pb_2WO_5 are friable: in contact with oxigen contaminated flowing lead, their fragmentation might lead to further oxidation.

The Mo coating didn't give a satisfactory performance. Cracking and lifting led to the oxidation of the exposed coated F82Hsteel (Fe_3O_4 formation).

Use of W and Mo should therefore be limited to the case of highly deoxidised molten metal.

Investigation on oxygen controlled liquid lead corrosion of surface treated steels

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Abstract

A low alloyed martensitic steel Fe9Cr (OPTIFER IVc) and an austenitic steel 16Cr15Ni (1.4970) were exposed to liquid lead to examine their suitability as structural material for lead cooled accelerator driven subcritical actinide burners. The surface of part of the steel specimens was restructured and that of another part was alloyed with Al by treatment with high power pulsed electron beams. A corrosion test stand was constructed containing liquid lead under oxygen control at 550°C. Steel specimens were examined after 800, 1500 and 3000 h of exposure. For austenitic steel lower corrosion effects were observed especially when the surface was treated by the electron beam. No corrosion attack could be seen at all on both steels after alloying Al into a surface layer of 10 μm depth.

Forschungszentrum Karlsruhe
Technik und Umwelt

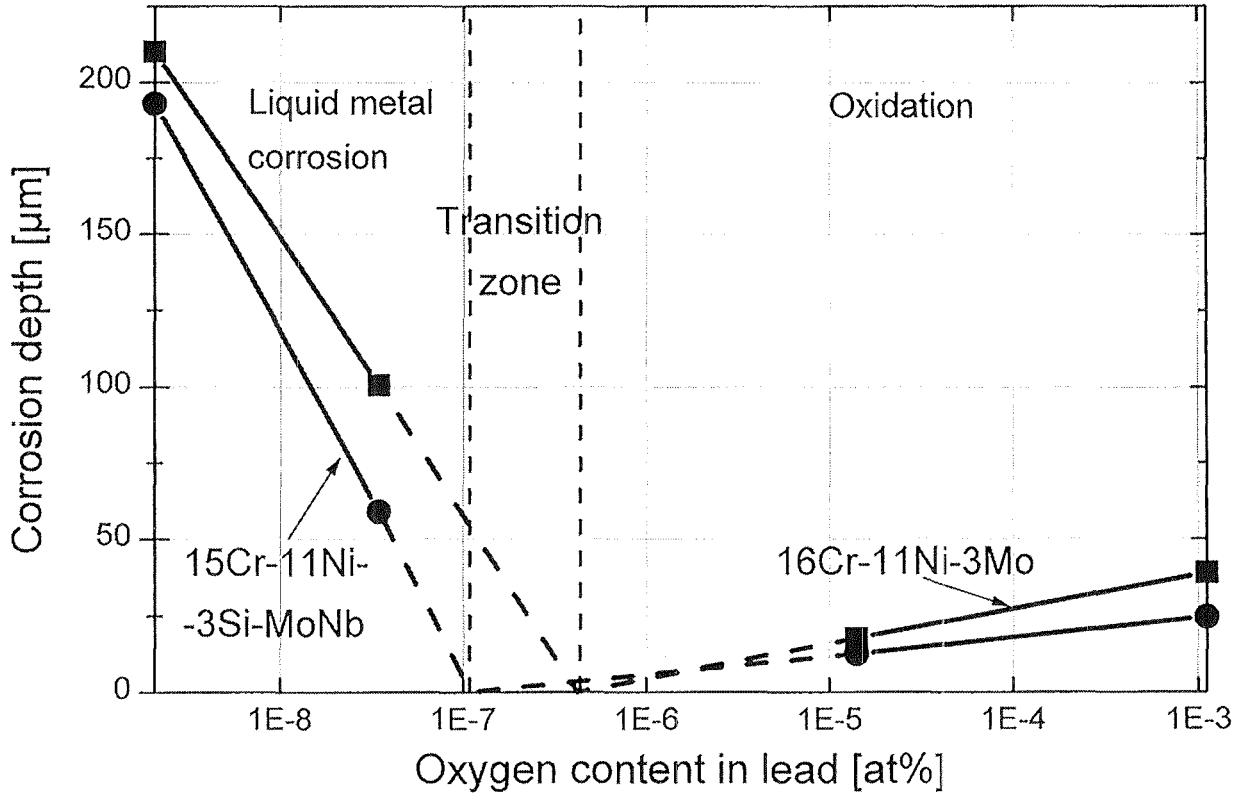
Investigation on Oxygen Controlled Liquid Lead Corrosion of Surface Treated Steels

G. Müller, G. Schumacher, F. Zimmermann, A. Heinzel

Institute for Pulsed Power and Microwave Technology (IHM)

Content

Corrosion behavior of two steels in liquid lead as a function of oxygen concentration after 3000 h at 550 °C [Markov, PROMETEY]

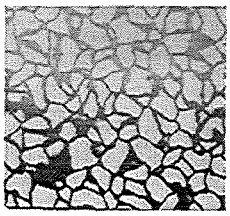


⇒ **Control of oxygen content in Pb is necessary**

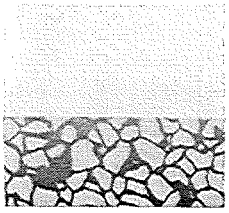
Pulsed Electron Beam Modification of Materials Surfaces

e⁻-beam

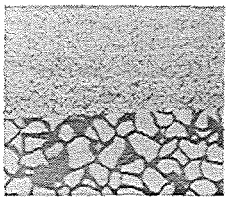
Quenching process



Volumetric Heating:
rate: $< 10^9$ K/s
time: < 40 µs

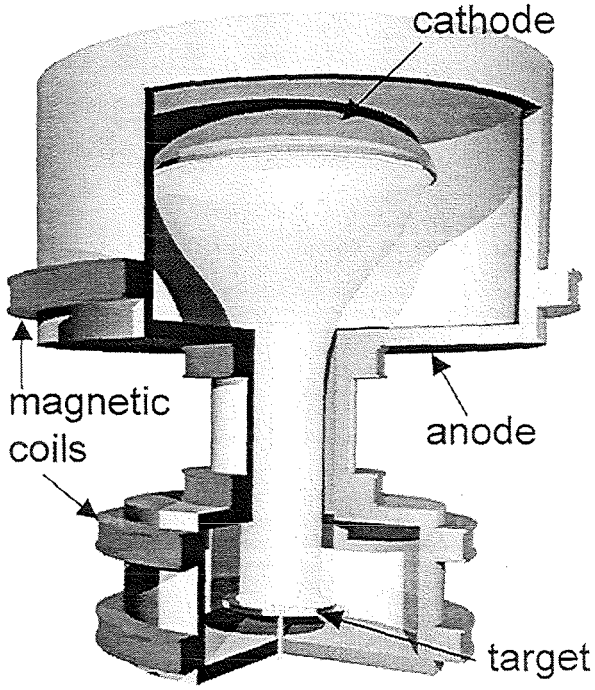


Melt layer:
depth: < 40 µm
cooling: $< 10^7$ K/s
(heat conduction)



restructured surface layer

GESA-facility



Electron beam Parameter:

Electron Energy	50 - 150 keV
Power density	≤ 2 MW / cm²
Pulse duration	1 - 40 µs
Beam Diameter:	5 - 10 cm

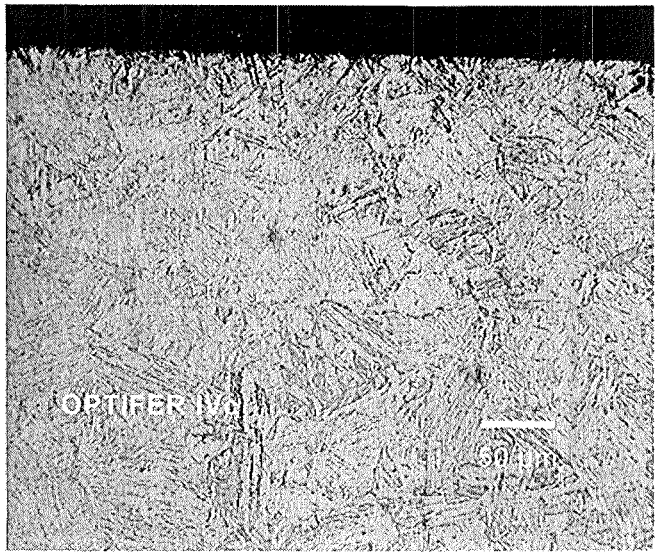
Materials for Corrosion Investigations

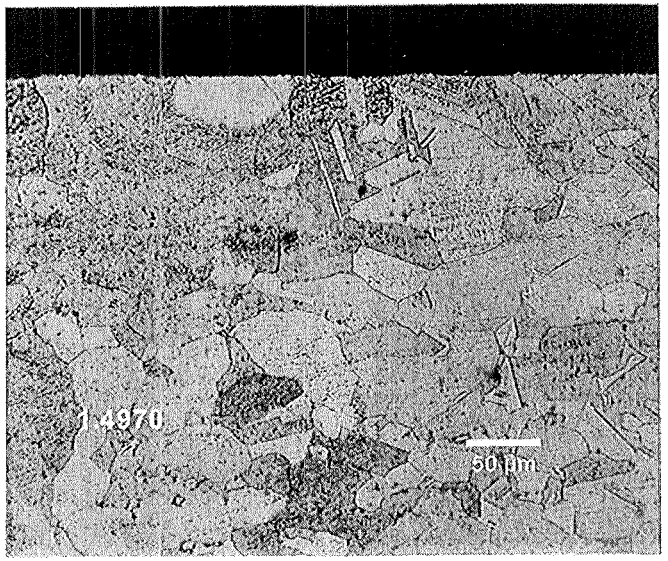
Chemical Composition of OPTIFER IVc

C	Si	Mn	P	S	Cr	V	W	Ta
0.56	0.02	0.58	0.005	0.009	9.99	0.28	0.30	0.02

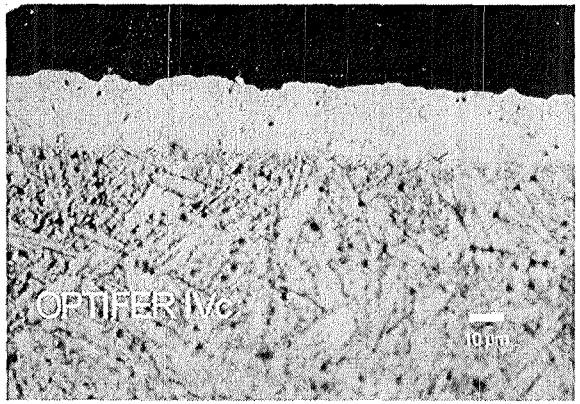
Chemical Composition of 1.4970

C	Si	Mn	P	S	Cr	Ni	Mo	Ti
0.46	0.89	1.91	0.012	0.009	16.5	13.8	0.66	0.43

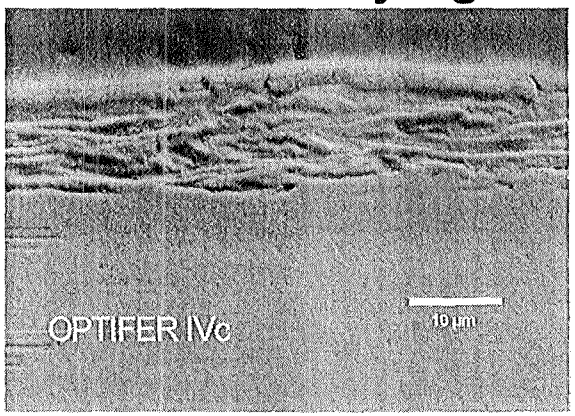




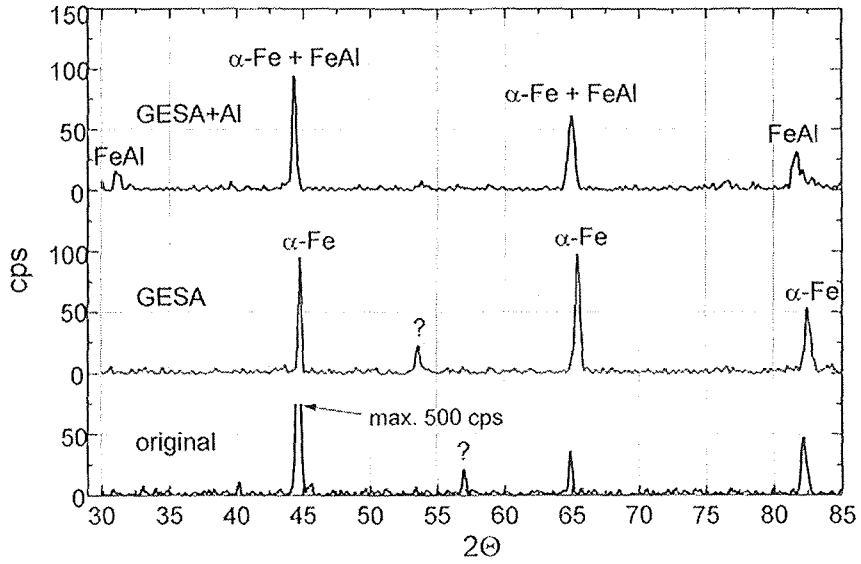
OPTIFER IVc after GESA - Treatment and Surface Alloying with Al



GESA - treated

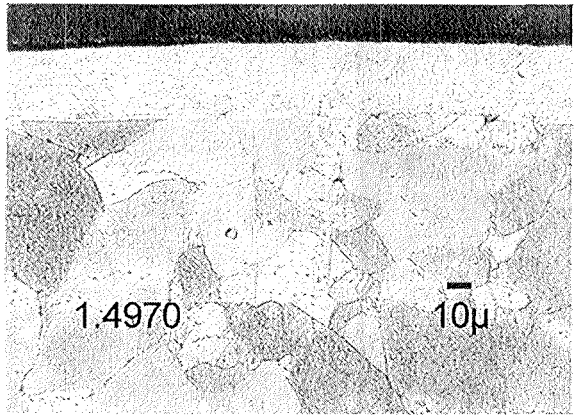


Surface alloyed with Al

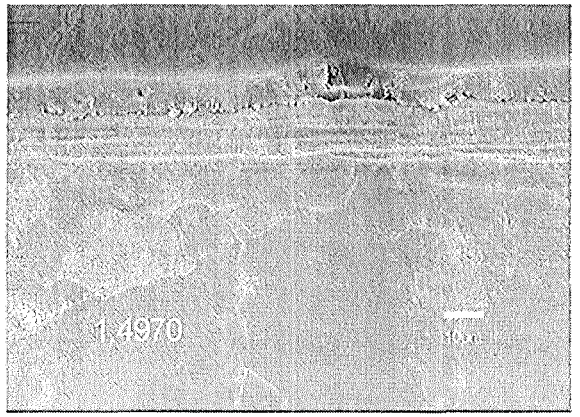


Structure Analysis

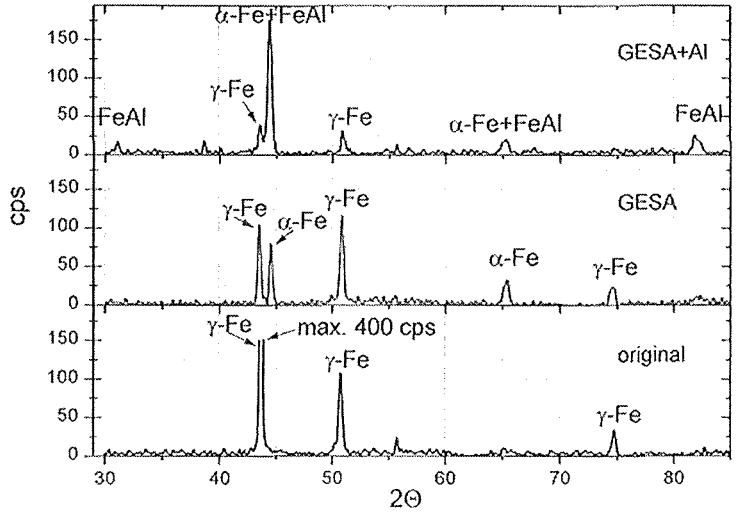
1.4970 after GESA - Treatment and Surface Alloying with Al



GESA - treated

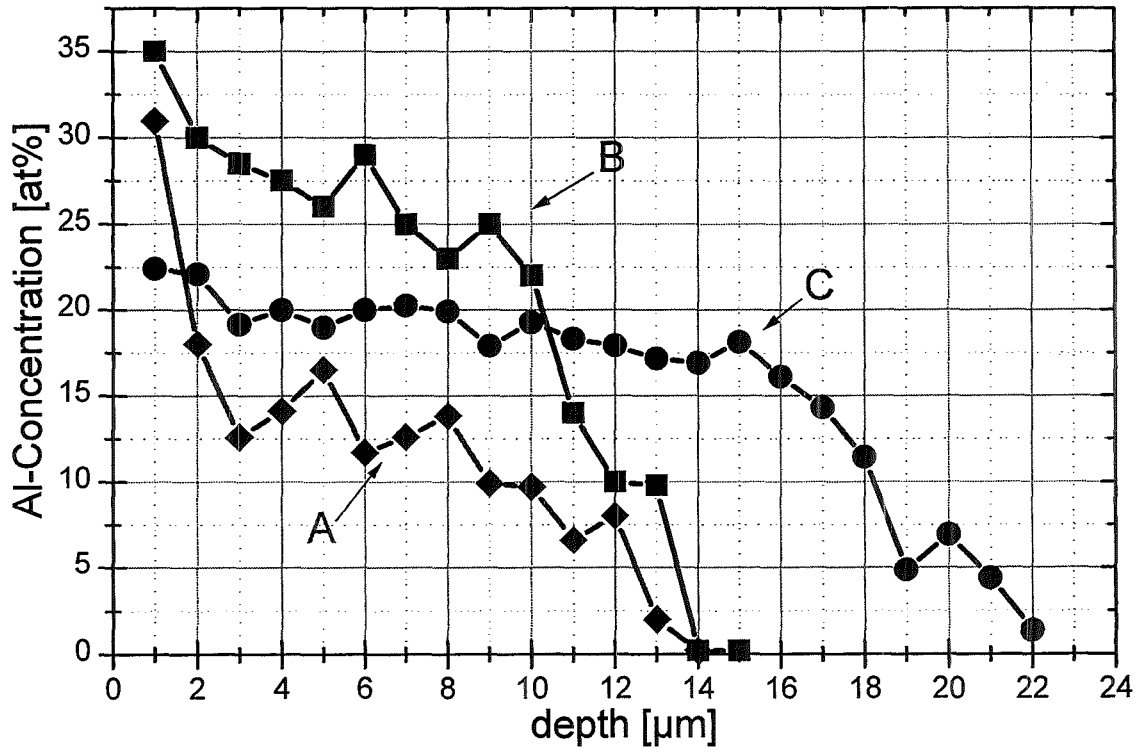


Surface alloyed with Al

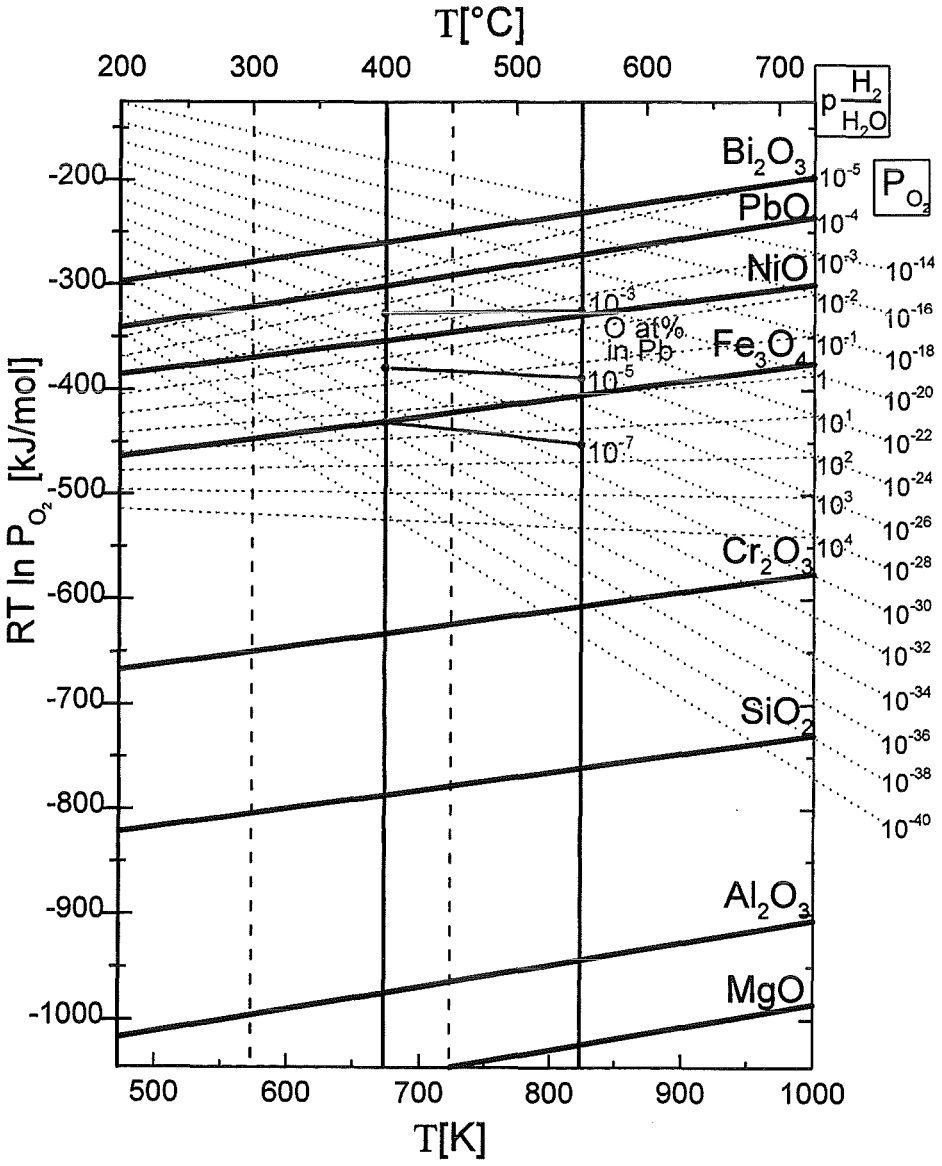


Structure analysis

Aluminum concentration for different treatment parameters



Oxygen control by H_2/H_2O ratio



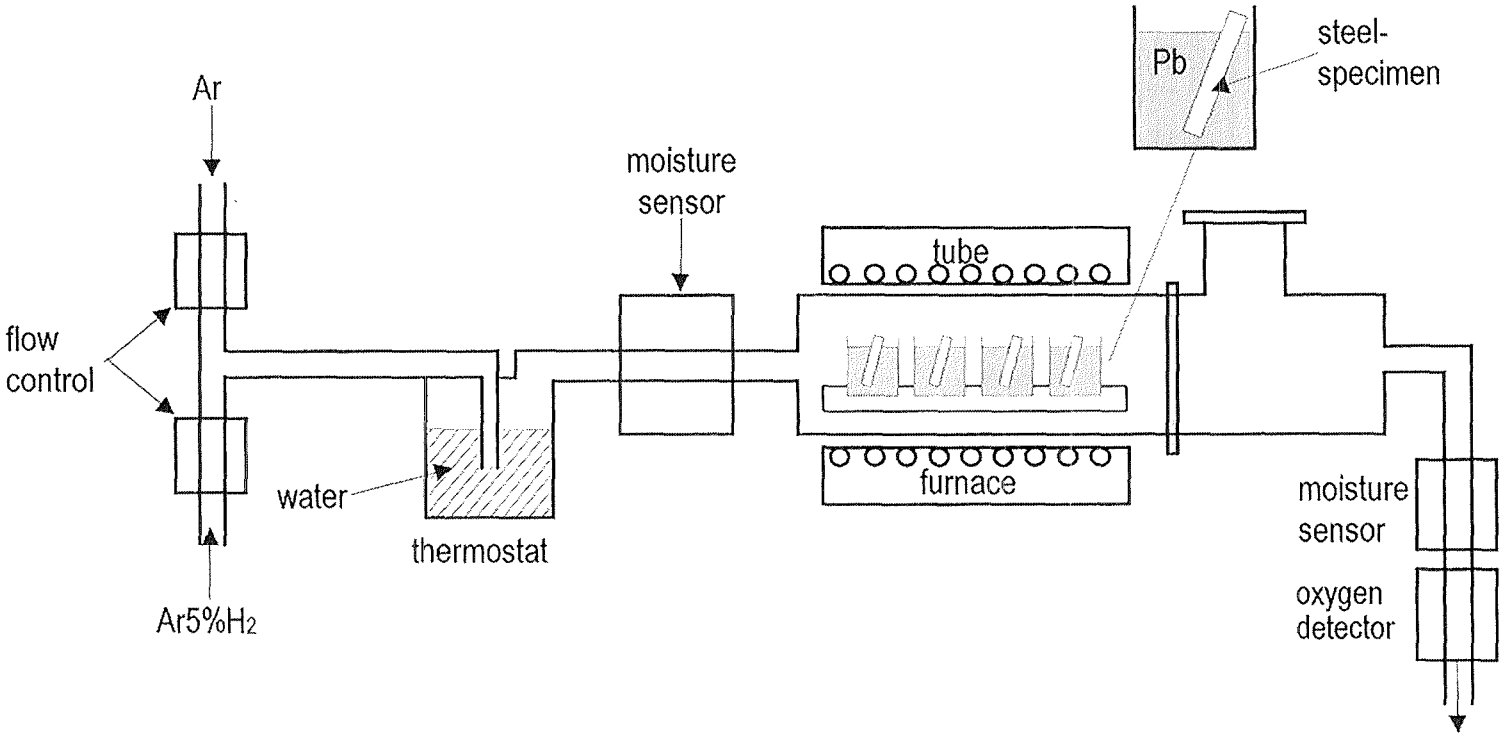
$$2\Delta G^0_{PbO} > RT \ln p_{O_2} > 0.5\Delta G^0_{Fe_3O_4} \qquad p_{O_2} = \frac{p^2_{H_2O}}{p^2_{O_2}} \exp \frac{2\Delta G^0_{H_2O}}{RT}$$

$H_2/H_2O = 0.4 \rightarrow p_{O_2} \cong 10^{-25}$ at 550 °C and 10^{-29} at 400 °C

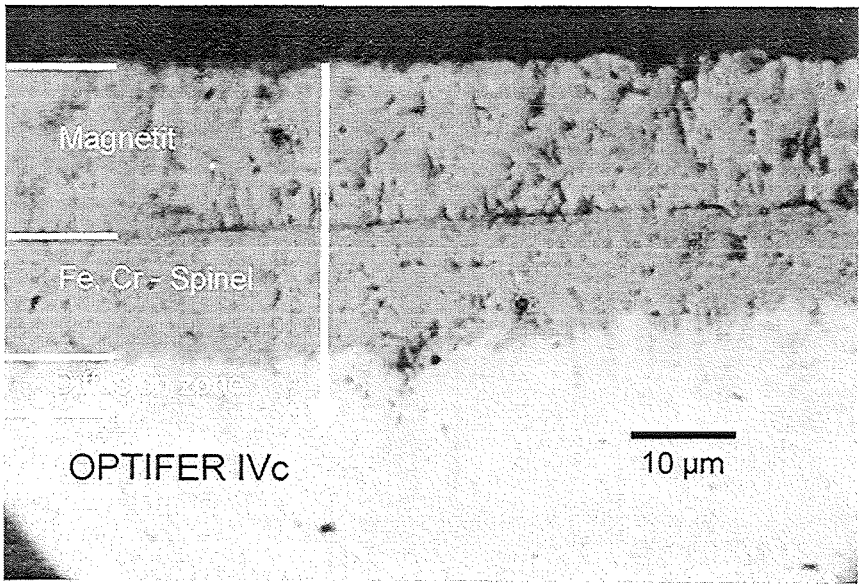
$$a_o = \gamma_o c_o = \frac{c_o}{c_{o,s}} = \left(\frac{p_{o_2}}{p_{o_2,s}} \right)^{\frac{1}{2}}$$

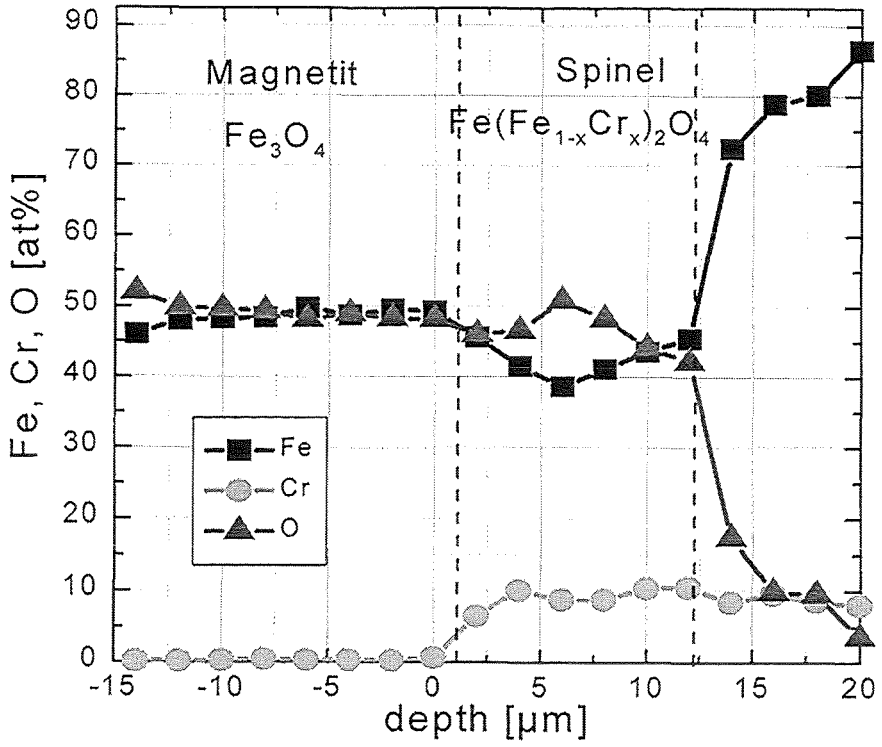
Saturation concentration $c_{o,s} = 4 \cdot 10^{-2}$ at% at 550 °C and $7{,}5 \cdot 10^{-3}$ at% at 400 °C

Corrosion test stand with stagnant liquid lead



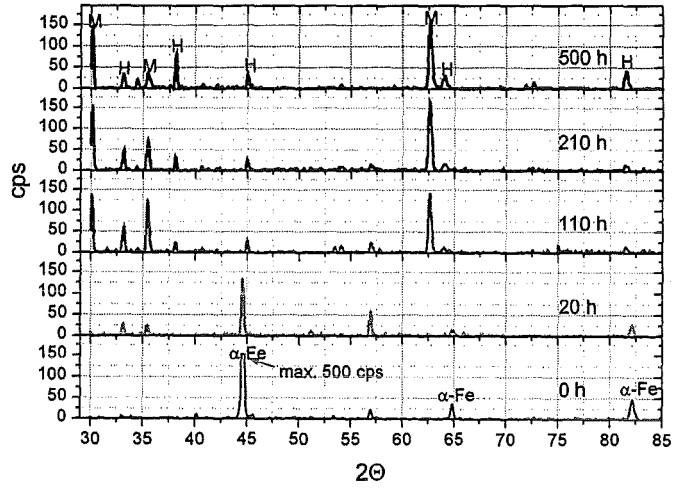
OPTIFER IVc after 470 h at 550 °C in the gas atmosphere with $H_2/H_2O = 0.4$ ($p_{O_2} = 10^{-25}$ bar)



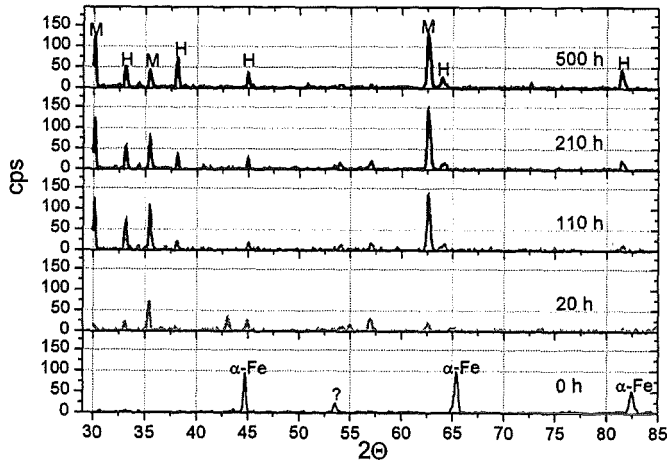


Element concentration

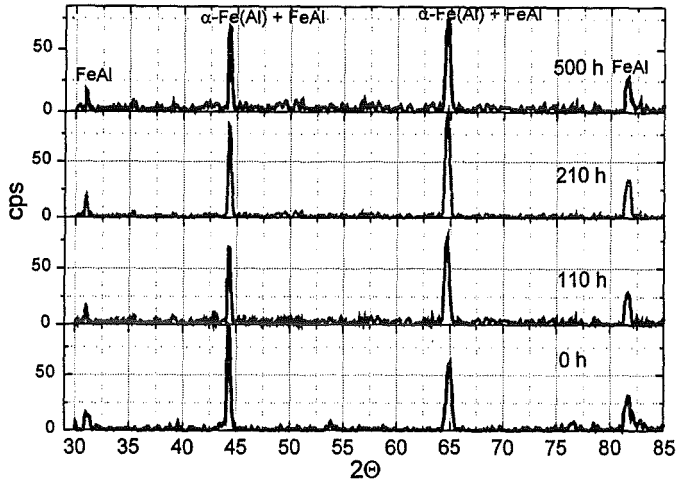
Structure analysis of OPTIFER IVc after 500 h at 550 °C in the gas atmosphere (H_2/H_2O = 0.4)



original OPTIFER IVc

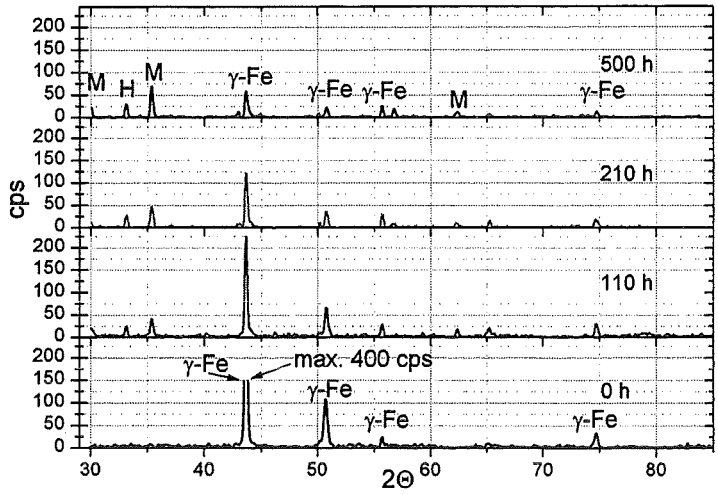


GESA-treated

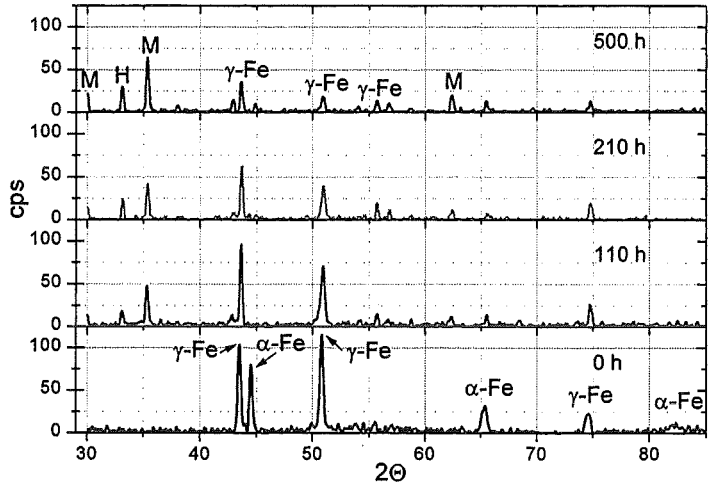


Al alloyed by GESA

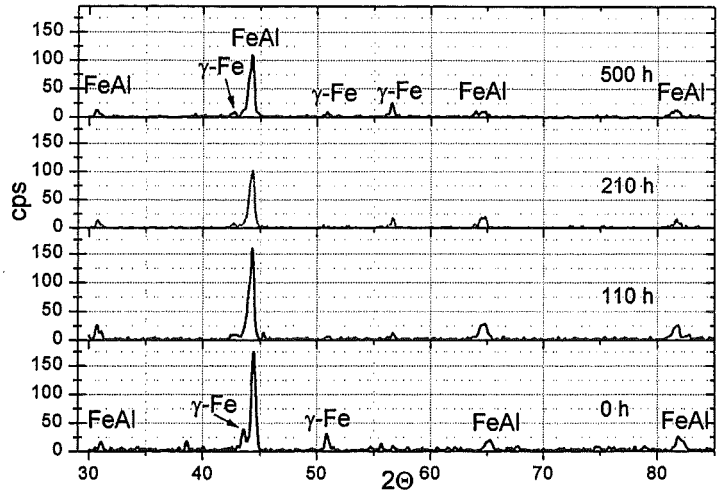
Structure analysis of 1.4970 after 500 h at 550 °C in the gas atmosphere (H_2/H_2O = 0.4)



original 1.4970

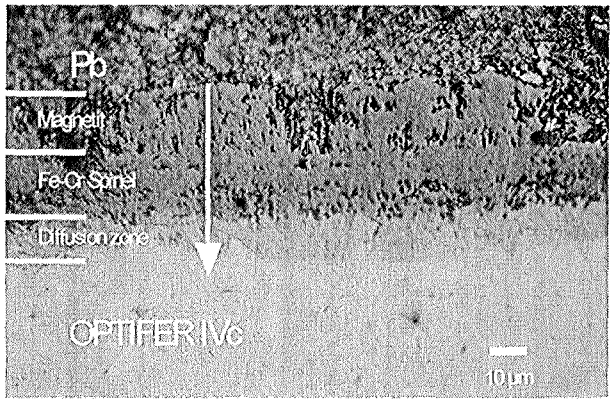


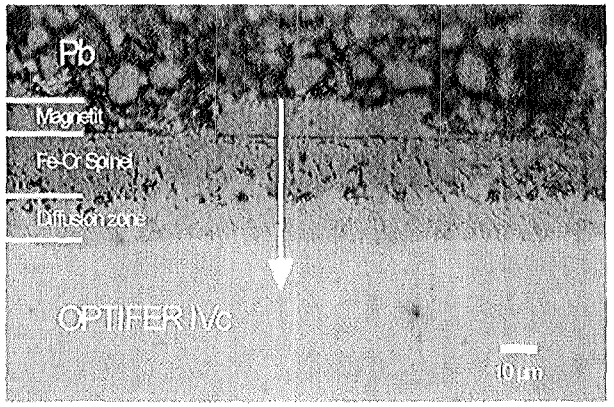
GESA-treated

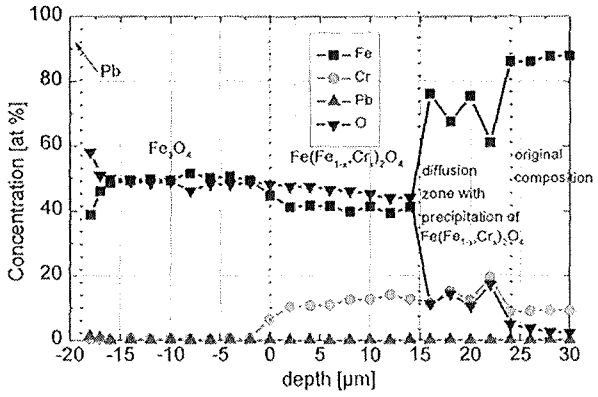


Al alloyed by GESA

OPTIFER IVc after 3000 h in stagnant lead at 550 °C with an oxygen content of $8 \cdot 10^{-6}$ at%







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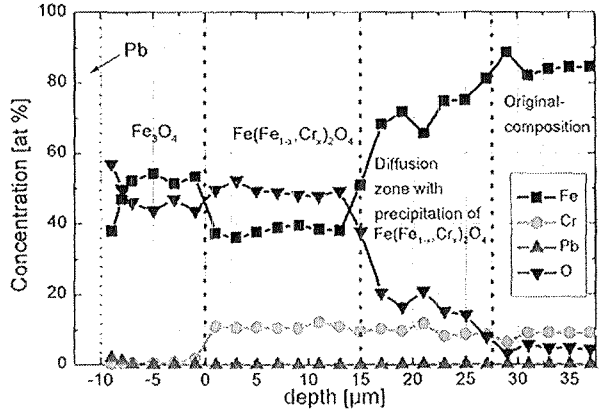
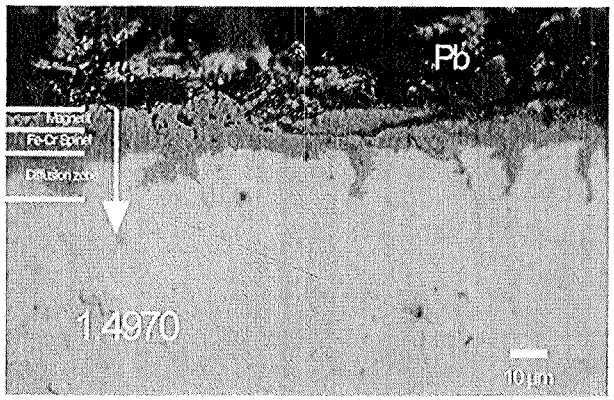
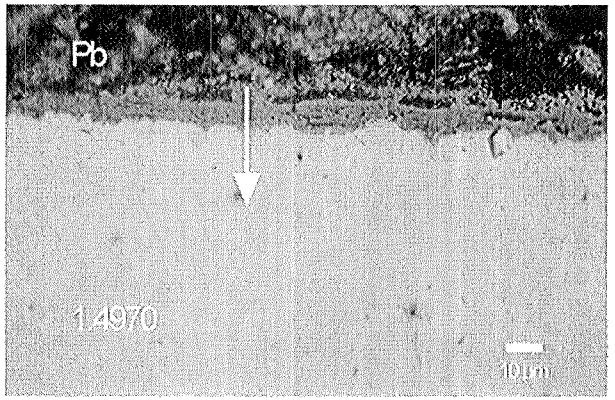
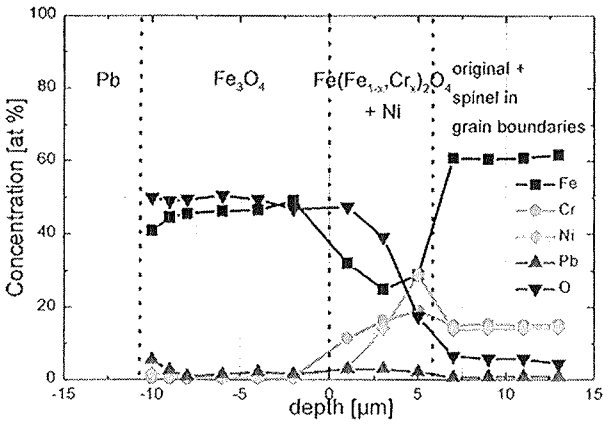


GESA - treated

1.4970 after 3000 h in stagnant lead at 550 °C with an oxygen content of $8 \cdot 10^{-6}$ at%







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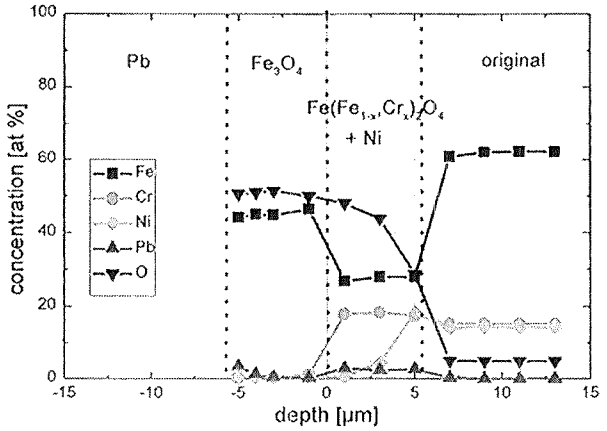
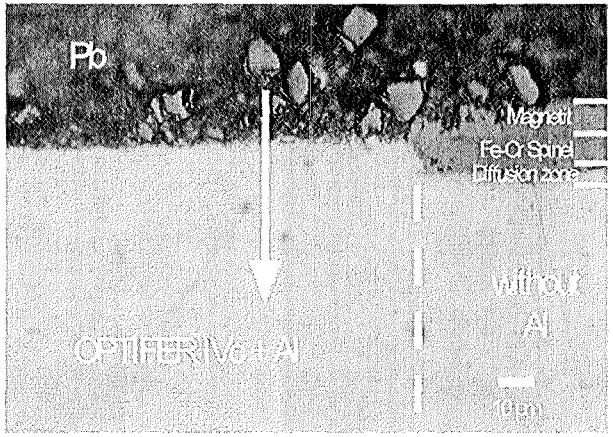
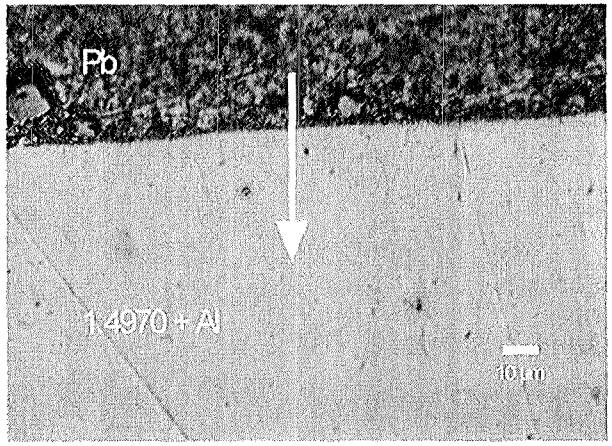
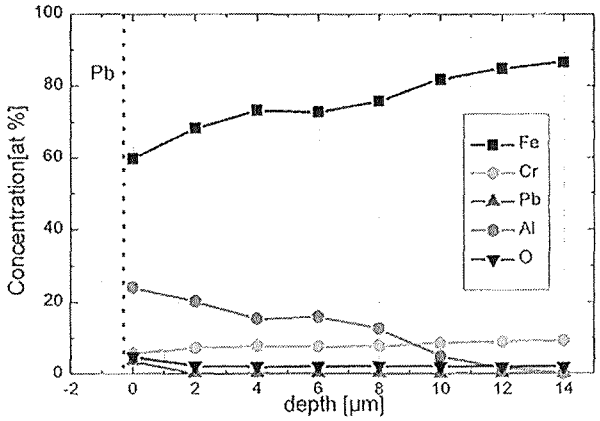


GESA - treated

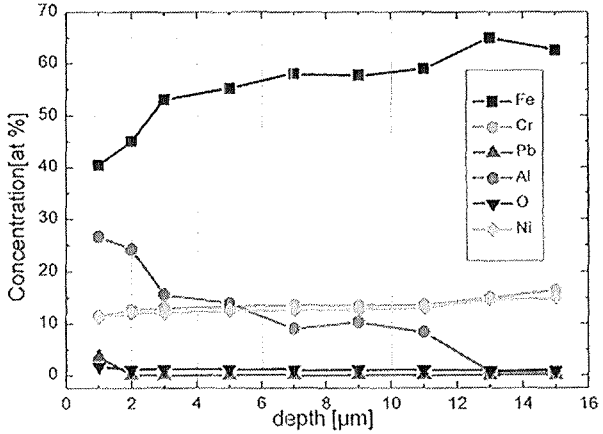
Al alloyed OPTIFER Vc and 1.4970 after 1500 h in stagnant lead at 550 °C with an oxygen content of $8 \cdot 10^{-6}$ at%





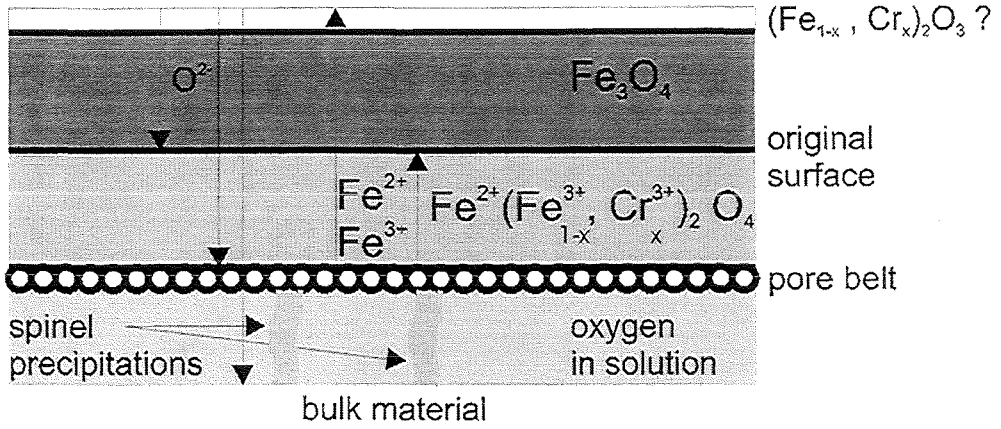


Al alloyed OPTIFER Vc

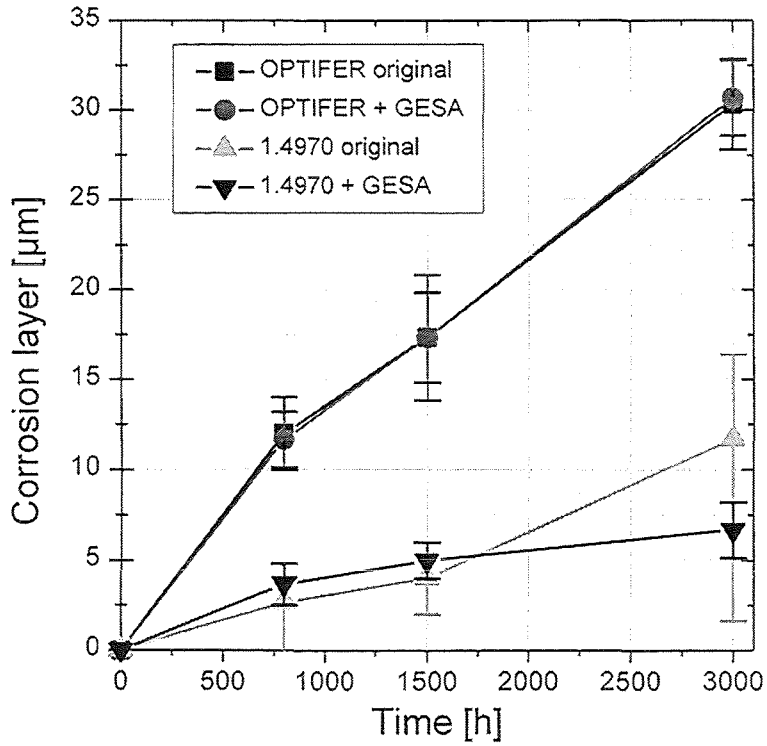


Al alloyed 1.4970

Results of Corrosion Investigations in liquid lead for OPTIFER IVc and 1.4970

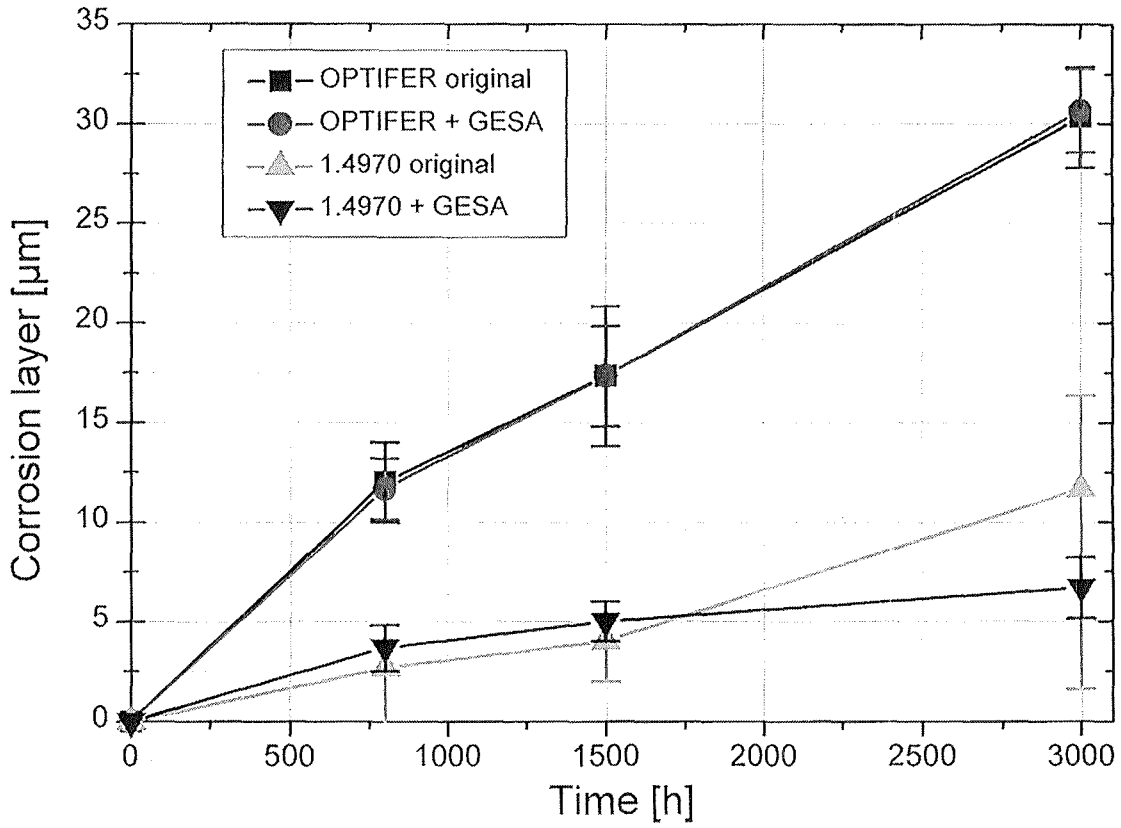


Scheme of oxidation zones and ion migrations



Oxide scale growth for OPTIFER IVc and 1.4970

Results of Corrosion Investigations in liquid lead for OPTIFER IVc and 1.4970



Conclusions from stagnant Pb experiments

- Oxide layers on steel can effectively prevent the steel from leaching of the alloy components.
- To maintain the oxide layers over long exposure time it is necessary to control the oxygen concentration in lead.
- By this procedure corrosion is changed from that of solution attack to that of oxidation.
- Thus, it is needed to find materials that form stable protective oxide scales under oxygen control in liquid lead.
- Therefore, high alloyed steels (1.4970) show better resistance in liquid lead under oxygen control than low alloyed steels (OPTIFER).
- No corrosion attack at all is observed if Al is alloyed into the surface.
- Oxide scale formation in liquid lead obeys the same principle mechanisms as in controlled gas atmosphere.
- For application of the results to Pb-, PbBi-loops, that run with controlled oxygen concentration, it can be concluded that high alloyed oxidation resistant steels should be favored. Their properties can be improved by electron pulse treatment, especially when by this process Al is alloyed into the surface.

Corrosion studies in Pb-Bi liquid alloy

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Abstract

Corrosion studies in Pb-Bi liquid alloy are necessary for materials selection. At first, we present the R&D programme which has been proposed. The aims of this programme are :
1) basic corrosion studies in static Pb-Bi,
2) corrosion studies in dynamic Pb-Bi,
3) compatibility studies in Pb-Bi containing additional impurities (spallation products),
4) structure protection studies.

To carry out the corrosion studies in static Pb-Bi liquid alloy, three experimental devices have been developed. They are :
1) COLIMET (COrrosion LIquid MEtal), to perform experiments with small quantities of eutectic Pb-Bi alloy in reductive atmosphere Ar + H_2,
2) COLIMESTA (COrrosion LIquid MEtal STAtic), for experiments with larger quantities of static eutectic Pb-Bi and in a wide range of oxygen contents measured by oxygen sensor,
3) DECO (DEposition and COrrosion), for experiments in a sealed container with a thermal gradient under inert atmosphere Ar.

The various devices and the experiments planned to be performed are described.

CORROSION STUDIES IN Pb-Bi LIQUID ALLOY

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CEA Saclay-DTA
Service de Corrosion, d'Electrochimie et de Chimie des Fluides
91191 Gif-sur-Yvette Cedex

Corrosion studies in Pb-Bi liquid alloy R&D programme

1) Basic corrosion studies in static Pb-Bi

to identify critical parameters

to pre-select materials

to define experimental procedures

2) Corrosion studies in dynamic Pb-Bi

to determine kinetics in representative conditions: effect of alloy velocity

3) Compatibility studies in Pb-Bi containing additional impurities

to study the effect of spallation products (Sn, Zn, Hg) on corrosion and embrittlement of steels

4) Stucture protection studies

to investigate protection methods against corrosion:

-in situ oxide formation

- alumininized coatings (produced by pack cementation or CVD methods)

Corrosion studies in static Pb-Bi liquid alloy

Three experimental devices have been realized:

1) COLIMET (COrrosion Liquid METal)

- Experiments with small quantities (50 cm^3) of static eutectic Pb-Bi alloy
- Reduction atmosphere Ar + 5%H_2
- No measurement of the oxygen content in Pb-Bi alloy

2) COLIMESTA (Corrosion Liquid Metal STAtic)

- Experiments with larger quantities (6 l) of static eutectic Pb-Bi
- Glove-box atmosphère (< 2 vpm O_2), oxygen saturated Pb-Bi
- Reduction atmosphere Ar + x% H_2 (5 < x< 40), oxygen undersaturated Pb-Bi
- Measurement of oxygen content in Pb-Bi by oxygen probe

3) DECO (Deposition and Corrosion)

- Experiments in a sealed container with a thermal gradient
- Cold point determines the oxygen concentration in Pb-Bi

The COLIMET device

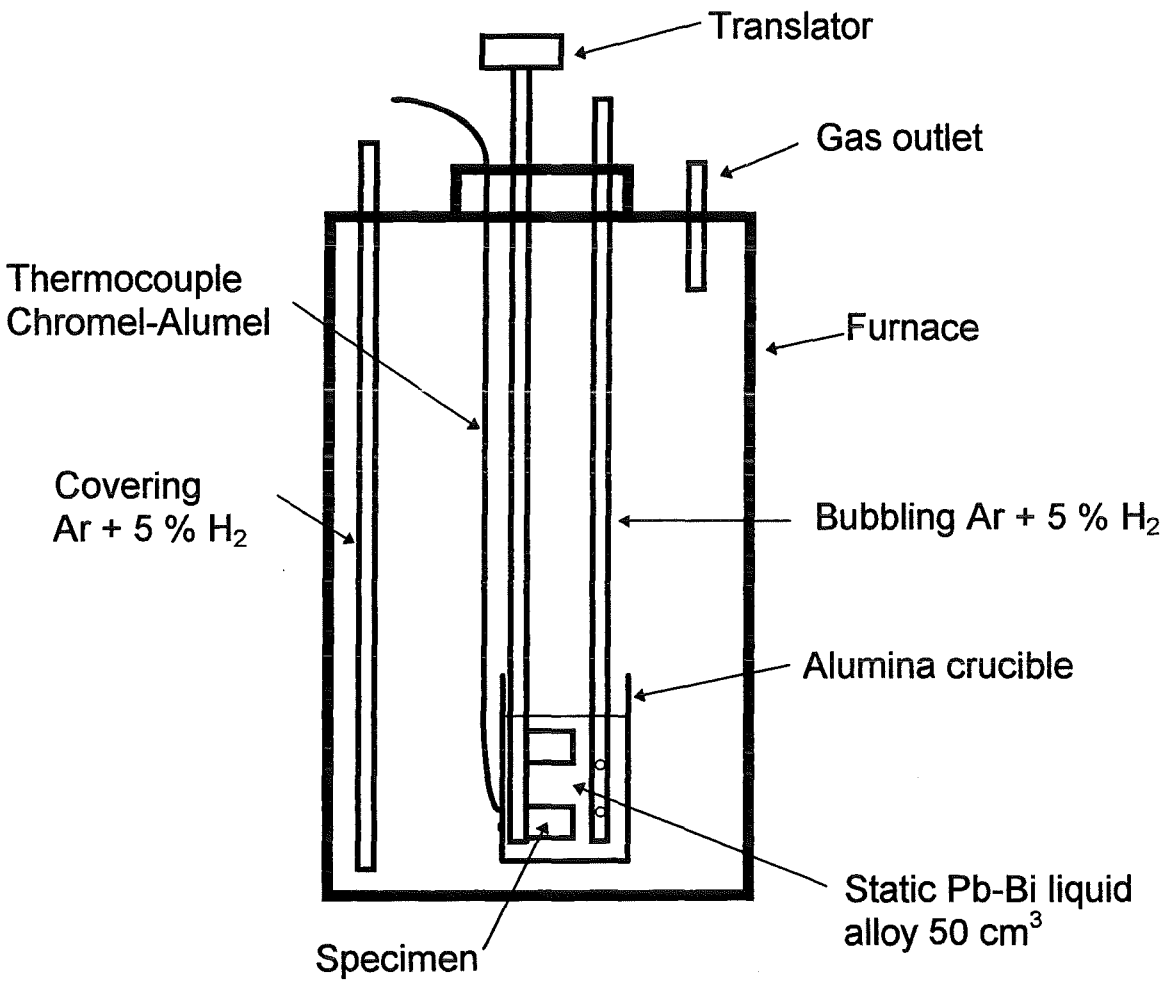
Objectives

Determination of corrosion kinetics for different steels in static Pb-Bi

Behavior of aluminized coatings produced by pack cementation (316L) or CVD methods (T91) in static Pb-Bi

Influence of spallation products (Sn, Zn, Hg) on corrosion and embrittlement of steels

The COLIMET device



Experimental conditions

Materials : 316L, T91, 56T5, F82H, EM10
aluminized 316L and T91

T = 500 °C

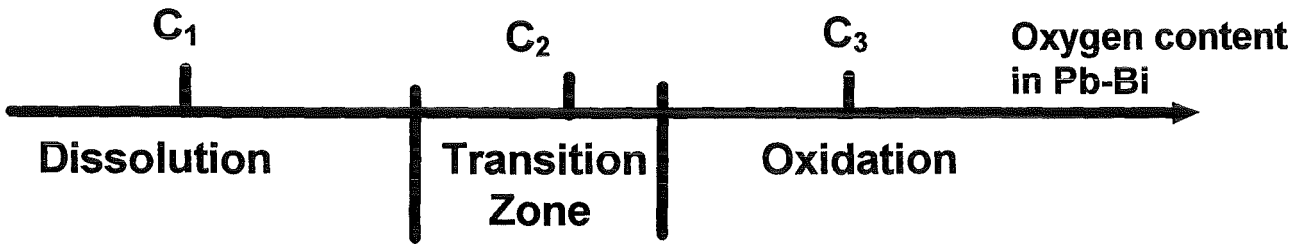
$t \geq 100$ h

Reduction atmosphere Ar + 5%H_2, oxygen undersaturated Pb-Bi

The COLIMESTA device

Objectives

Determination of corrosion kinetics for different steels in a wide range of oxygen contents in static Pb-Bi



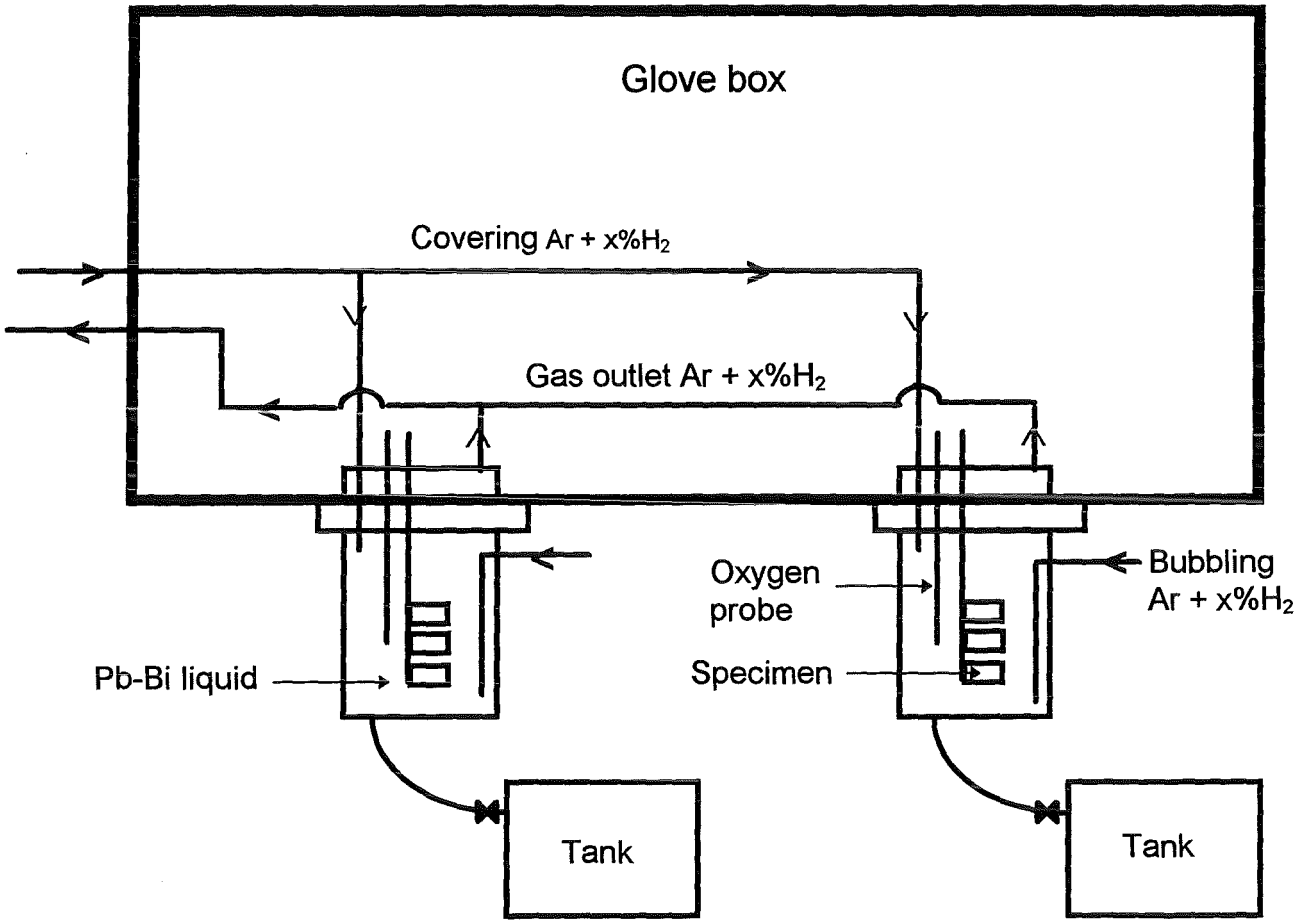
For the oxygen concentrations C_1 and C_3:

- Corrosion kinetics for different steels (dissolution or oxidation)
- Behavior of aluminized coatings produced by pack cementation (316L) or CVD methods (T91)
- Influence of spallation products (Sn, Zn, Hg) on corrosion and embrittlement of steels

For the oxygen concentration C_2 :

- Study of in-situ protective oxide layer formation

The COLIMESTA device



Experimental conditions

Materials : 316L, T91, 56T5, F82H, EM10
aluminized 316L and T91

T = 500 °C and T = 300 °C

$t \geq 100$ h

Glove-box atmosphere (< 2 vpm O_2), oxygen saturated Pb-Bi

Reduction atmosphere Ar + x% H_2 ($5 < x < 40$), oxygen undersaturated Pb-Bi

The DECO device

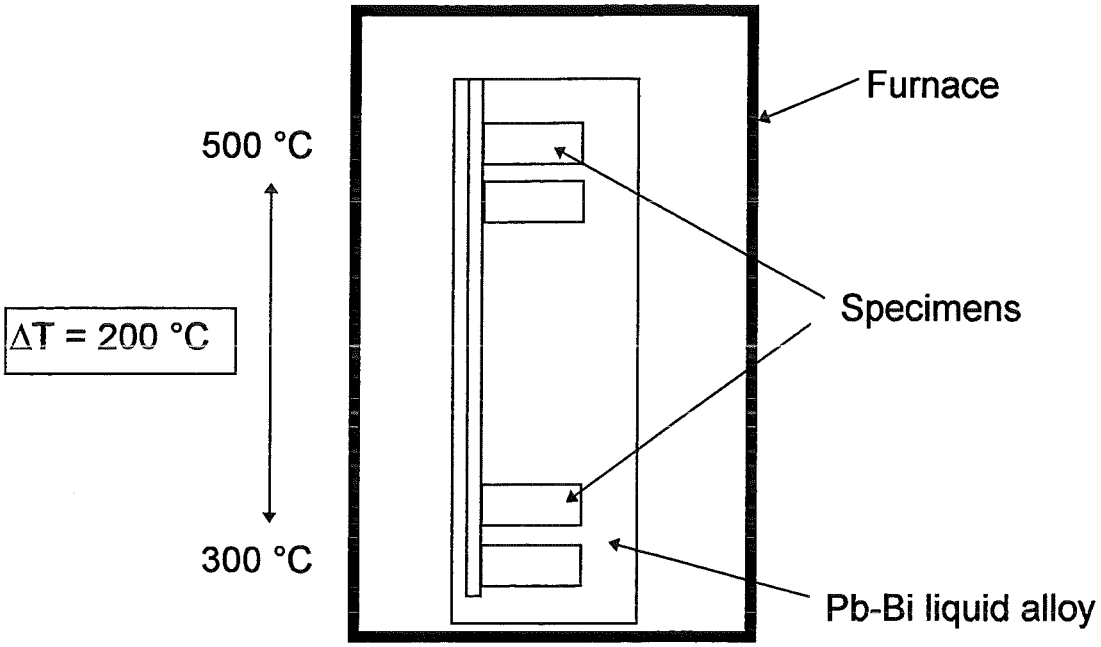
Objectives

Study of mass transport in non-isothermal conditions (between hot zone and cold zone):

- Different steels
- Aluminized steels, aluminized coatings produced by pack cementation (316L) or CVD methods (T91)

Study of the influence of spallation products (Sn, Zn, Hg) on the mass transport for different steels

The DECO device



Experimental conditions

Materials : 316L, T91, 56T5, F82H, EM10
aluminized 316L and T91

T_{hight} = 500 °C, ΔT = 200 °C

$t \geq 100$ h

Inert atmosphere Ar

Sealed container (316L austenitic steel and 56T5 martensitic steel)

Cold point determines the oxygen concentration in Pb-Bi

$C_{oxygen,\ 300\ °C} \approx 0.2$ Wppm

Corrosion studies of steels in the presence of flowing liquid Pb-Bi

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Abstract

In the spallation module, the fluid velocity is expected to exceed 1 $m.s^{-1}$. The experiments performed previously in liquid Pb-17Li have shown that an increase in the fluid velocity from 0.02 to 0.2 $m.s^{-1}$ led to an increase in the corrosion rate from 21 to 93 $\mu m.year^{-1}$ [1]. Therefore, a thorough investigation of the fluid velocity effect on the corrosion rate in liquid Pb-Bi appeared necessary.
One of the main research parameter is the oxygen content; three domains of oxygen concentrations will be studied corresponding to three corrosion mechanisms: dissolution, passivation, excessive oxidation. In a first step, the low oxygen content will be investigated (dissolution mechanism).

The rotating cylinder geometry was chosen to study the effect of the Pb-Bi alloy velocity on the corrosion of steels (austenitic, martensitic and protected with aluminized coatings). The characteristics of this device are:

- it generates a turbulent flow for low Reynolds number (> 100),
- the mass transfer equations are well-established,
- the apparatus is easy to handle and at the scale of the laboratory,
- correlation models have been developed to simulate accurately a high velocity fluid flowing in a pipe.

The CICLAD facility (Corrosion Induced by the Circulation of a LeAD alloy), which is composed of the rotating cylinder system, a purification circuit of the liquid alloy (cold trap) and a tubular test section, is at the stage of the design and preliminary plans are presented.
The results obtained in this installation will allow to predict the behavior of the spallation module.

References:

[1] J. Sannier, T. Flament, A. Terlain, Corrosion of martensitic stainless steels in flowing Pb-17Li, 16th SOFT, London, 901-905 (1990).

CORROSION STUDIES OF STEELS IN THE PRESENCE OF FLOWING LIQUID Pb-Bi

F. Balbaud[1], F. Barbier[1]

[1] : CEA - CEREM
Service de la Corrosion, d'Electrochimie et de Chimie des Fluides
Bâtiment 458 - CEA/Saclay- 91191 Gif-sur-Yvette, France

Expected results

1- Determination of the corrosion kinetics of different steels as a function of fluid velocity (from 1 to 5 $m.s^{-1}$)

2- Nature of the corrosion process : diffusion limited or dissolution limited

3- Determination of the diffusion coefficients

4- Prediction of the behavior of the spallation module (conditions : T = 500 °C, turbulent flow, v = 1-5 $m.s^{-1}$) (use of Plombières results)

Experimental techniques to study the fluid velocity effect on the corrosion kinetics

1- LOOP

- the most representative of industrial conditions
- high size and cost
- high flow rates (5 $m.s^{-1}$) difficult to reach

2- ROTATING DISK SPECIMEN

- mass transfer equations well-established
- easy construction and operation
- laminar flow over a wide range of speeds

3- ROTATING CYLINDER SPECIMEN

The rotating cylinder system

1- Turbulent flow for Re > 100

2- Determination of the nature of the corrosion process

- linear variation of the weight loss vs $\omega^{0.7}$: process limited by diffusion $\Rightarrow$ determination of the diffusion coefficient [Eisenberg]

- weight loss independent of the rotation rate : limitation by the dissolution reaction $\Rightarrow$ determination of the dissolution constant

3- Correlation with the pipe geometry : calculation of the mass transfer coefficient

- models based on the Sherwood number :

$$Sh = \frac{Kd}{D}$$

- model based on the shear stress [Silverman]

Application of a correlation model

Case of a corrosion process limited by mass transfer

Objective : simulate with the rotating cylinder a flow at a velocity of 5 $m.s^{-1}$ in a pipe of diameter 0.01m

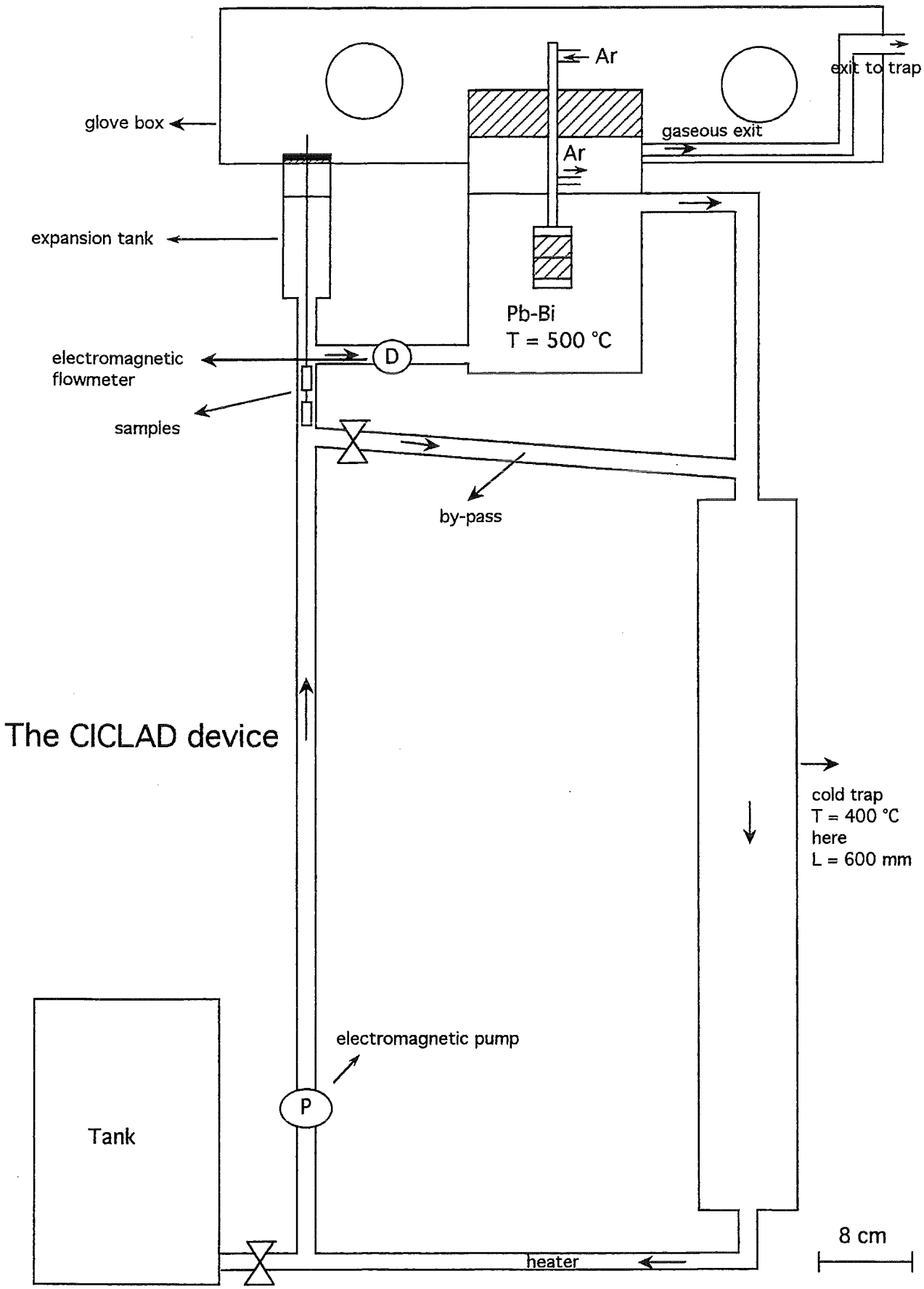
Pipe geometry :

$$K_{pipe} = \frac{0.0096\,Re^{0.913}\,Sc^{0.346}D}{d_{pipe}}$$

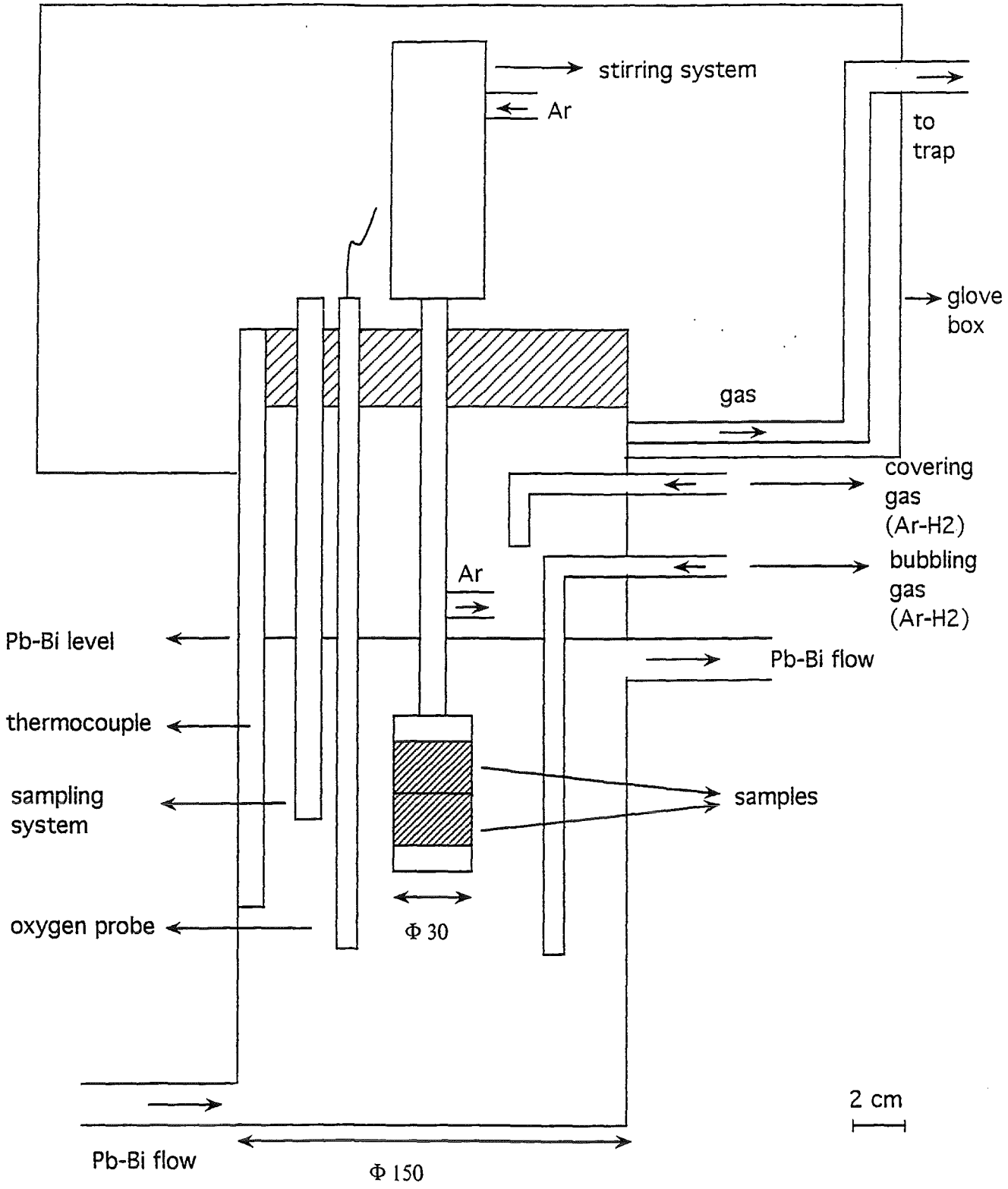
Rotating cylinder :

$$K_{cylinder} = \frac{0.0791\,Re^{0.70}\,Sc^{0.356}D}{d_{cyl.}}$$

For d_{pipe} = 0.01 m, v_{pipe} = 5 $m.s^{-1}$,
$d_{cyl.}$ = 0.03 m then $\omega \approx$ 10000 rpm


Ar
exit to trap
glove box
gaseous exit
Ar
expansion tank
Pb-Bi
T = 500 °C
electromagnetic
flowmeter
D
samples
by-pass
The CICLAD device
cold trap
T = 400 °C
here
L = 600 mm
electromagnetic pump
P
Tank
heater
8 cm

The rotating cylinder system



Planned experiments

1- Materials

T91, 316L, aluminized steels (316L, T91)

2- Conditions

T = 500 °C

1000 rpm < ω < 10000 rpm

Controlled atmosphere (flow of Ar-H_2)

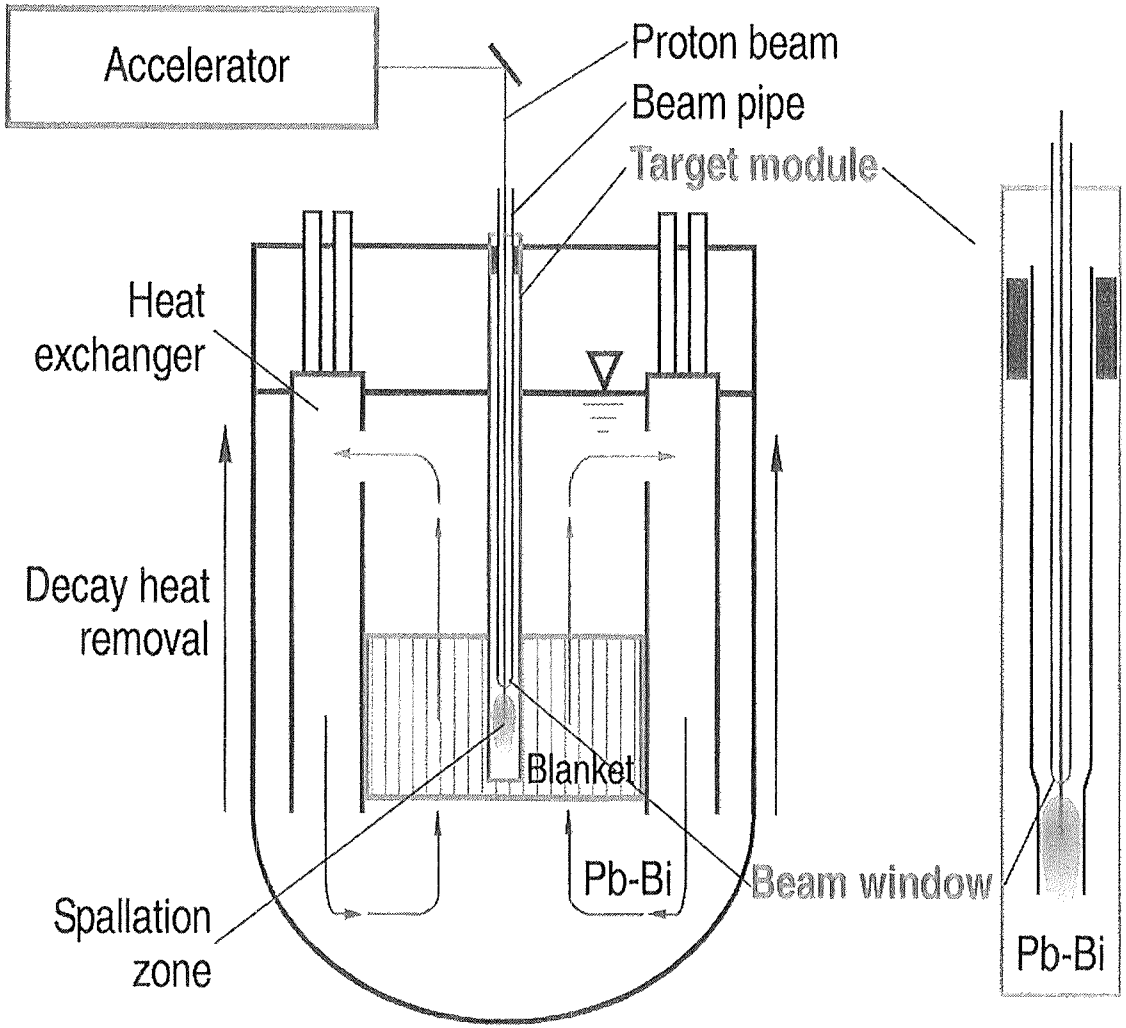
Technologies, materials, thermalhydraulics for lead alloys based ADS reactor

Authors: G. Benamati, C. Latgé, J. Knebel

Presented by: G. Benamati

Contributions: *CEA, CNR, CNRS, CIEMAT, ENEA, FZK, FZR, RIT, SCK-CEN*

Vth R&D Programme Meeting; September 13-14, 1999, Paris



ADS reactor

POWER PLANT - DEMO PLANT

Main Parameters of the Sub-critical System:

- Power MW : 1500 - 80
- Coolant: Liq. Lead - Liq.Lead-Bismuth

PCS Main Parameters:

- Inlet temp. ^{0}C: 400 - 300
- Outlet temp. ^{0}C : 612 - 400
- Coolant rate m/s: 1.3 - 0.8
- Core fuel: ^{232}Th+30%TRU - U and Pu MOX
- Core material : Martensitic Steels

Main Parameters of the Beam Target

- Beam energy GeV: 1.5 - 0.6
- Nominal beam current mA: 12- 4/6
- Max temp. in window ^{0}C: ~900 -<600
- Materials : Refractory metals- steels

Background and problems:

The use of lead alloys in ADS sub-critical systems is related to the basic advantages of these materials but some relevant problems exist.

- Good spallation media.
- Low capture cross section for thermal and fast neutrons
- No significant reaction with water and air.
- The lead technology has been proven in USSR military applications.
- The most common structural materials are severely corroded by Lead alloys;
  - ⇨ strong dissolution of transactional elements;
  - ⇨ possible LME phenomena and mechanical property degradation;
  - ⇨ combined effect of neutron and proton irradiation with liquid metal.
- Generation of spallation species inside the lead alloys.
- Po production and potential release.
- Analytical thermalhydraulic correlation in lead alloy have to be developed and validated.

Critical issues identified and deal with in the present task:

Interaction between structural materials and lead alloys.

- ⇨ Corrosion evaluation (corrosion kinetic and mech. property degradation)
- ⇨ Protection method development and validation in reactor relevant conditions (considering the existing Russian experience)
- ⇨ Purification systems and impurity control methods development and testing

Thermalhydraulic behaviour of lead bismuth alloy.

- ⇨ Fundamental thermalhydraulic experiments are an essential tool to develop and validate analytical correlations and numerical computational tools to be used in lead alloy systems.

MAIN OBJECTIVES OF THE TASK

- *To determine the corrosion behaviour of several structural materials in lead alloys;*
- *To determine the effect of species generated by spallation on lead alloys corrosion basic mechanisms.*
- *To develop and validate (also under irradiation) suitable methods in order to suppress, or at least, limit corrosion phenomena.*
- *To validate a strategy and the associated process to control lead alloys purity and guaranty safety operation.*
- *To develop and validate analytical thermalhydraulic correlation to be used in the lead alloys systems.*
- *To provide a materials data-base and guide-lines for design purposes*

The final goal is :

To demonstrate whether a sub-critical system using Pb or Pb-Bi both as spallation target and coolant is really technologically feasible.

Corrosion and protection of materials in Lead alloys (*item 1 and 2*)

Objectives:

- Determination of the basic characteristics of lead alloys corrosion;
- Creation of a reliable data-base on steels, and windows relevant materials, corrosion properties;
- Assessment of the effect of Spallation Products on the behaviour of lead alloys;
- Evaluation of the feasibility of protection methods based on "in-situ" or artificial coatings creation.

Content:

- Corrosion studies in stagnant and flowing liquid lead alloys [CEA-DTA, CIEMAT, FZK , RIT]
- Effect of spallation products on corrosion and protection methods for spallation module materials [CEA, ENEA]
- In situ protection by oxide layer formation [CEA, CIEMAT,ENEA,RIT]
- Coating development and qualification, surface treatment [CEA-DTA, CNR, FZK]
- Inhibitor studies [CIEMAT]

Mechanical behaviour of structural materials in contact with lead alloys (***item 3)***

Objectives:

- ❑ Generation of a thermodynamic data-base for multicomponent system and equilibrium phase diagram calculation;
- ❑ Evaluation of the mechanical behaviour of steels in the presence of lead alloys;
- ❑ Acqusition of understanding on the intergranular penetration basic mechanisms as function of the environmental condition and steel composition;
- ❑ Development of a numerical model able to simulate the steel/liquid metal interaction and application of this code to the LME and mechanical tests .

Content:

- Thermodynamics studies [CNRS and CNR]
- Mechanical behaviour of steels:
  - tensile and creep test in Pb alloys
  - tensile and liquid metal embrittlement in Pb-Bi [CRNS, ENEA]
- Intergranular penetration studies [CEA, CNRS, CNR]
- Realization of the Large Scale Simulation Facility (LSSF) and development of a numerical model for LME [CNRS,CEA,ENEA]

Effects of irradiation on lead alloys corrosion ***(item 4)***

Objectives:

- ❑ Verify the combined effects of mechanical loads and proton irradiation on the corrosion and embrittlement of various steels of interest for the spallation module and the sub-critical system.
- ❑ A first evaluation of the effect of neutron irradiation on basic corrosion/protection mechanisms of steels in contact with Pb-Bi alloy ;

Content:

- LISOR program (Liquid Solid Reactions under Irradiation), with the following goals :
  - Design and construction of the test loop for the irradiation experiments.[Subatech, CEA, PSI]
  - Realization of the experiments at the Injector-I of PSI. (72 MeV proton beam) [PSI, CEA, Subatech]
  - Post Irradiation Examination (PIE).[PSI,CEA]
    The materials to be investigated are ferritic/martensitic steels (9Cr1Mo, 9Cr1MoVNb), clean martensitic steels such as F82H and Optifer, and austenitic stainless steel, type 316 [CNRS,CEA,ENEA]

  The MP requested by PSI will be founded by Switzerland federal govern

- Neutron irradiation tests in capsule (with Pb-Bi) will be carried out in the BR2 reactor. The materials to be investigated are ferritic/martensitic steels (9Cr1Mo, 9Cr1MoVNb), clean martensitic steels such as F82H and Optifer, and austenitic stainless steel, type 316. The specimes will be irradiated up to 6 dpa. The results obtained will be useful not only for the target but also for a better understanding of the behaviour of materials in the sub-critical area

Impurity control and removal (***item 5)***

Objectives:

- Asses the nature and quantity of impurities present in lead-bismuth as consequence of in reactor service (impurities due to corrosion, operation contamination and so on);
- Development and validation of Oxygen control methods in large lead bismuth systems;
- Assessment the different efficiency and engineering features of the different methods to be applied in Ads sub-critical reactors
- Development and validation of "on-line" Oxygen meters and laboratory analytical techniques.

Content:

- Characterisation of the impurities present in a lead bismuth target (and sub-critical system) and develop a strategy to control the LBA purity. [CEA]
- Development and testing of different methods for Oxygen measurement and control in Pb-Bi and Pb. The following technologies will be tested:
  - Oxygen and hydrogen separate addition
  - bubbling H_2 / H_2O
  - Pb / PbO mass transfer equilibrium.

  . [CEA,CIEMAT,ENEA,FZK,RIT]
- Development and testing of oxygen sensors:
  -Industrial electrochemical oxygen sensor
  -Russian sensors
  -Specially developed sensors
  [CEA,CIEMAT,ENEA,FZK,RIT]

Thermahydraulic experiments (*item 6)*

Objectives:

- To develop and validate analytical correlations (for heat transfer, turbulence..) and computational tools to be used in lead alloys;
- To acquire a correct understanding of the heat transfer and hydraulic problems related to the use of "hot-windows" for the spallation target;
- To investigate the possible use of the "window-less" solution;
- To verify the performances of the gas-enhanced circulation system;

Content:

- Thermalhydraulic small/medium scale experiments will be performed with the following aims:
  - local heat transfer determination in Pb-Bi
  - heat transfer evaluation for a beam window design with scaled dimension .

  This activity will be carried out in KALLA Loop [FZK]
- Large-scale hydraulic experiments will be performed with the following aims:
  - to investigate and optimise the "window less" solution;
  - to verify the performances of the gas-enhanced system and develop codes able to correctly simulate the experimental results.

  The activity will be performed in CIRCE Loop [ENEA]
- Medium-scale experiments aimed at defining the efficiency of the natural circulation to transfer heat from the core region to the IHXS will be performed. The stability and the re-initiation of the transient natural circulation will be measured. A natural circulation flow model of the ADS will be developed and validated with the data obtained in the pool type facility described above. [RIT]

The Determination of Corrosion Products and Oxygen in PbBi

Christel Adelhelm, IMF I

Introduction

There are different ways to investigate the corrosion of construction material in the PbBi melt: On the one hand the material is examined by microanalytical methods like REM, EMP or AES after exposure to the melt or, on the other hand, the material compounds solved in the melt are analyzed. Former investigations showed, that the corrosion behaviour of PbBi on steel depends substantially on the oxygen content in the melt. To control the oxygen content in the melt and/or to calibrate or develop an oxygen meter for the PbBi melt the determination of oxygen in PbBi is needed.

The determination of metallic impurities in PbBi

The method of the analysis of PbBi is similar to the analysis of Pb or Pb17Li. Pb and Bi and the steel compounds solved by the melt like Fe, Cr, Ni, Mn, or Al are soluble in nitric acid. Fuoric acid is added to keep other stell compounds like V, Mo, Ti or Nb into solution. A dark residue remaining after the treatment with nitric and fluoric acid (Fe_3O_4 or other oxides) can be dissolved by using microvave heating and pressure.

The content of the steel elements are measured with ICP-OES. For reliable results the calibration solutions are fitted to the sample solutions by addition of ultra clean Pb- or Bi-salts. The emission of Pb and Bi are not interfering the emissions lines of the steel compounds that much; but the interferenz of the steel elements among each other has to be excluded.

For a dissolution of 1 g PbBi in a volume of 100 ml the steel compounds can be determined lower than 0,0005 weight-% or 5 μg/g. The detection limits are summarized in the table.

Element	Al	Fe	Cr	Ni	Mn
NWG (μg/g)	3	2	2	3	0,3
Element	Nb	Mo	Ti	V	Zn
NWG (μg/g)	2	4	0,5	0,5	5

Determination of oxygen in PbBi

Different methods for the determination of oxygen in Pb and Bi are described in the literature. Oxygen contents lower than 0,1 μg/g can be detected by neutron, charged particle or photon activation analysis.

In our laboratory carrier gas hot extraction is used for oxygen determinations in metals. A metal sample is fused in a graphite crucible above the melting point. Solved oxygen or enclosed oxides are reduced by the carbon of the crucible and the formed CO is carried by He gas to a IR detector.

The meltimg point of Pb and PbBi is much lower than the usually used extraction temperatures of 2200 to 2500 °C. Therefore the extraction parameters, temperature and time have been optimized. First results reveal, that PbO is almost quantitavely reduced by C to CO at 1550 °C. The detection limit of the oxygen determination at the optimized parameters, calculated by the standard deviation of blank values, is 1-2 μg/g.

Determination of Corrosion Products and Oxygen in PbBi

Dr. Christel Adelhelm
Institute for Material Research I, Analytical Group

- Introduction

- Dissolution of Pb17Li and PbBi
- ICP-OES and parameters for measurement
- Corrosionproducts in a Pb17Li- and PbBi-Loop

- Survey of Oxygen Determination in Pb and Bi
- Principle of Inert Gas Fusion
- Optimisation of extraction parameters and detection limits

- Conclusions

Investigation of PbBi corrosion behaviour:

1. Examination of corroded material
   - ➔ by the loss of thickness
   - ➔ by micro-area-analysis like

     optical and electron microscope (REM) or

     electron microprobe (EMP)

     Auger electron microprobe (AES)

     Ion microprobe (SNMS, SIMS)

     Photon microprobe (UPS, XPS)

2. Examination of PbBi
   - ➔ by micro-area-analysis
   - ➔ by chemical analysis

Elements of structural material (steel)

10 – 90 %	Fe	Cr	(Ni)	
1- 10 %	Mn	Mo		
0,1 – 1 %	Si	V	Ti	(Ni)
others	Al	W		

Dissolution of Pb17Li (PbBi) and corrosion products:

➔ Nitric Acid **(HNO_3)**

➔ Fluoric acid (HF) to keep Mo, Ti, V, Si into solution

Dissolution of a remaining residue:

➔ Heating of solution and residue at 250 °C, 90 bar (microwave pressure digestion)

Calibration solutions:

➔ 4 solutions with increasing content elements

➔ simulation of acid and matrix concentration (Pb, Bi)

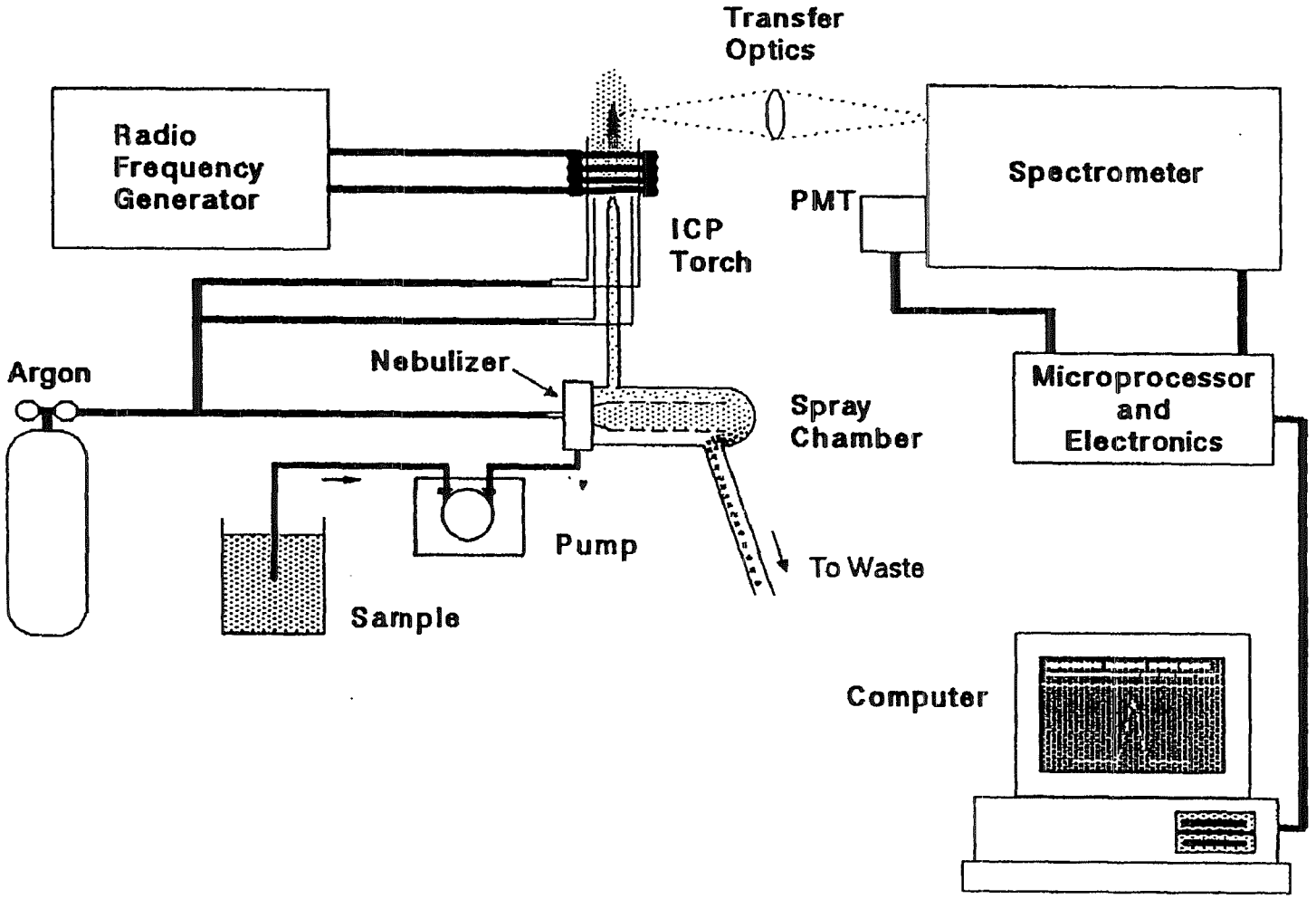
Parameters for measuring elements with ICP-OES

➔ all emission lines are checked with regard to interferences of Pb, Bi, Fe, Cr, Ni

element	wavelength (nm)	detection limit (µg/g)*
Al	396,152	3
Cr	267,716	2
Fe	259,940	2
Mo	281,615	4
Mn	257,610	0,3
Ni	231,604	2
Ti	337,280	0,5
V	310,230	0,5

* calculated for 1 g sample in 100 ml solution

Layout of Plasma 2000, Perkin-Elmer (ICP-OES)



Corrosion compounds in the magnetic trap of PICOLO and PbBi-loop (russian?)

(mass-%)

element	PICOLO I	PICOLO II	PICOLO VIII	PbBi slag
			8079 h, 480°C	
Al	0,003	0,004	0,016	
Cr	0,13	0,22	1,30	0,0003 – 1,2
Fe	3,3	4,2	19,4	0,0004 – 6,9
Mo		< 0,003	0,004	
Mn		0,005	0,0072	
Ni	0,04	0,010	0,12	0,0003 – 0,08
Ti	< 0,001	0,0003	0,0006	
V	0,002	0,004	0,0006	

Survey of oxygen determinations in Pb (off line)

Nuclear methods

- 14 MeV neutron activation analysis
  - ➔ $^{16}O(n,p)^{16}N$ – reaction
  - ➔ Interferenz by ^{19}F, ^{11}B, ^{208}Pb
  - ➔ detection limit 0,2 µg/g

- Charged partical neutron activation analysis
  - ➔ $^{16}O(^{3}He,n)^{18}F$-reaction
  - ➔ Interferenz by ^{19}F, $^{23}B(^{19}F)$
  - ➔ results: 0,99 ± 0,21 µg/g, 0,79 ± 0,36 µg/g

- Photon activation analysis
  - ➔ $^{16}O(\gamma,n)^{15}O$-reaction
  - ➔ Separation of ^{15}O by reducing fusion
  - ➔ results: 0,58 ± 0,03 oder 0,50 ± 0,13 µg/g

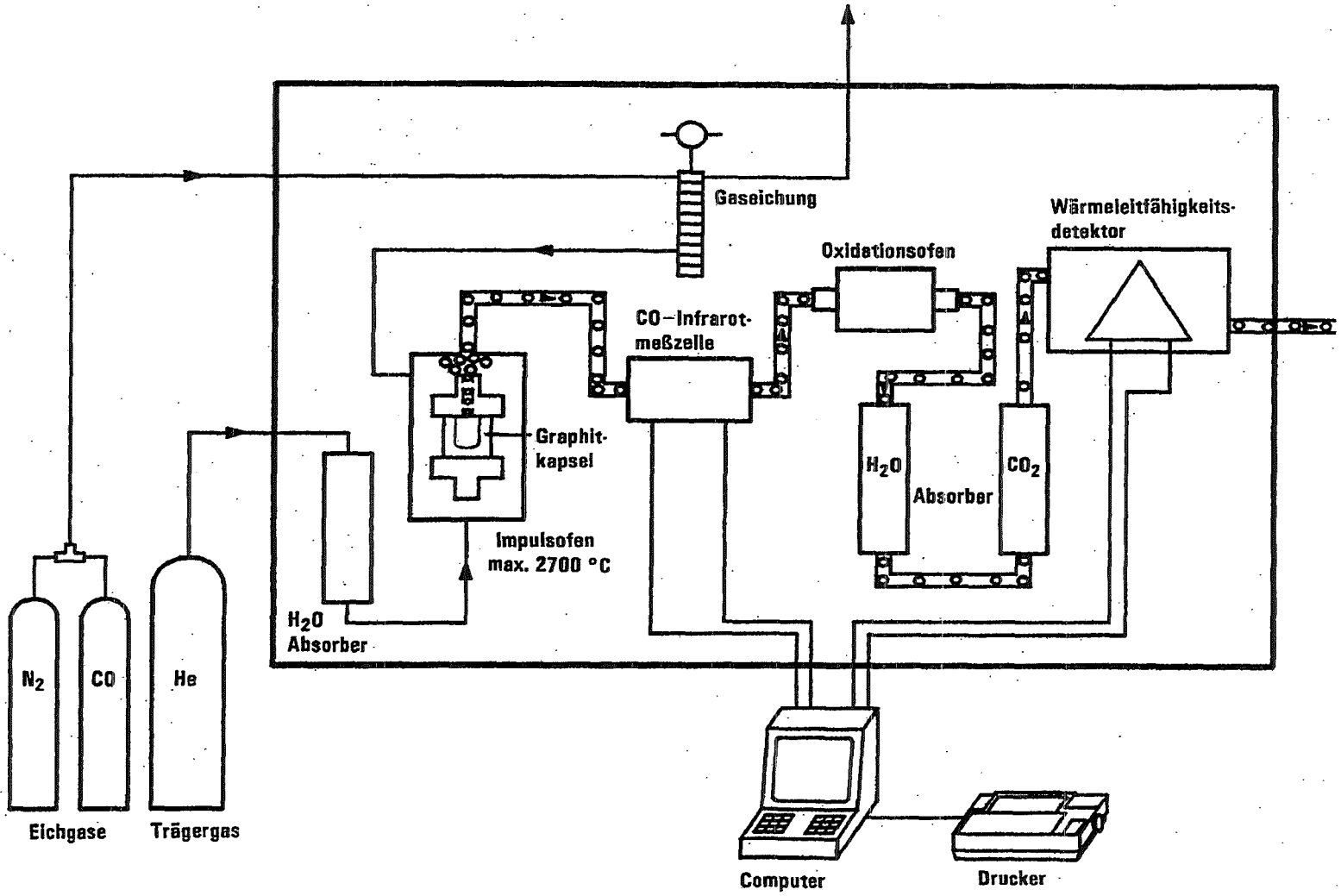
Chemical methods

- Hydrogen reduction
  - ➔ $PbO + H_2 \quad Pb + H_2O$ (700°C)
    Karl-Fischer titration
  - ➔ detection limit: ca. 0,6 µg/g
  - ➔ no commercial instrument available

- Vacuum fusion (carbon reduction)
  - ➔ $PbO + C \quad Pb + CO$ (1150 - 1750°C)
    detection: mass-spectrometer, IR-Absorption
  - ➔ detection limit: 0,5 µg/g
  - ➔ few commercial instruments available

- Inert gas fusion (carrier gas hot extraction)
  - ➔ commonly used method for the determination of oxygen in metals
  - ➔ FZK, IMF I: instrument: Ströhlein ON-MAT 850

Layout of ON-MAT 850, Ströhlein (inert gas fusion)



Principle of inert gas fusion

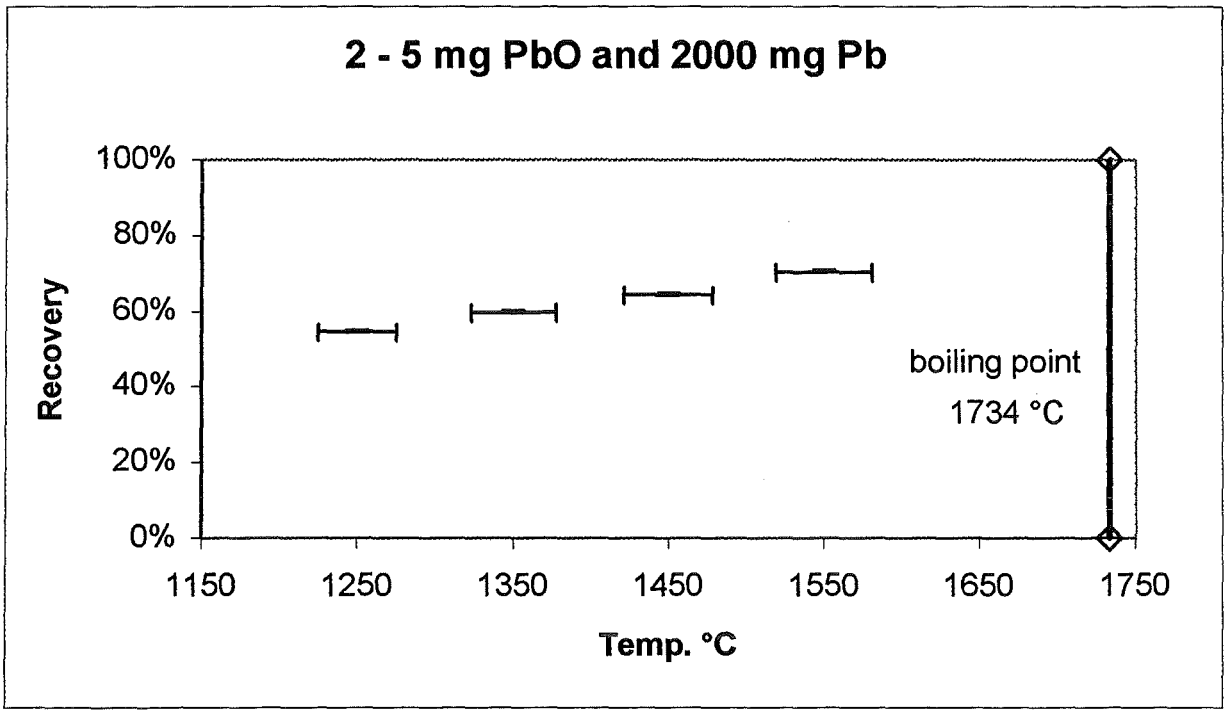
- Sample is droped in an outgased graphit crucible
- Crucible and sample is heated up to 2700 °C (heat control by sensor)
- metalloxid + C → CO + metall
- CO is detected by IR-absorption
- Calibration with 13 different gas volumes
  0,0427 6,872 ml resp. 27,9 4496,2 µg O
- Best Calibration with increasing amount of oxides:
  ➔ simulation of the extraction process

Examination of the oxygen determination in Pb, PbBi by inert gas fusion

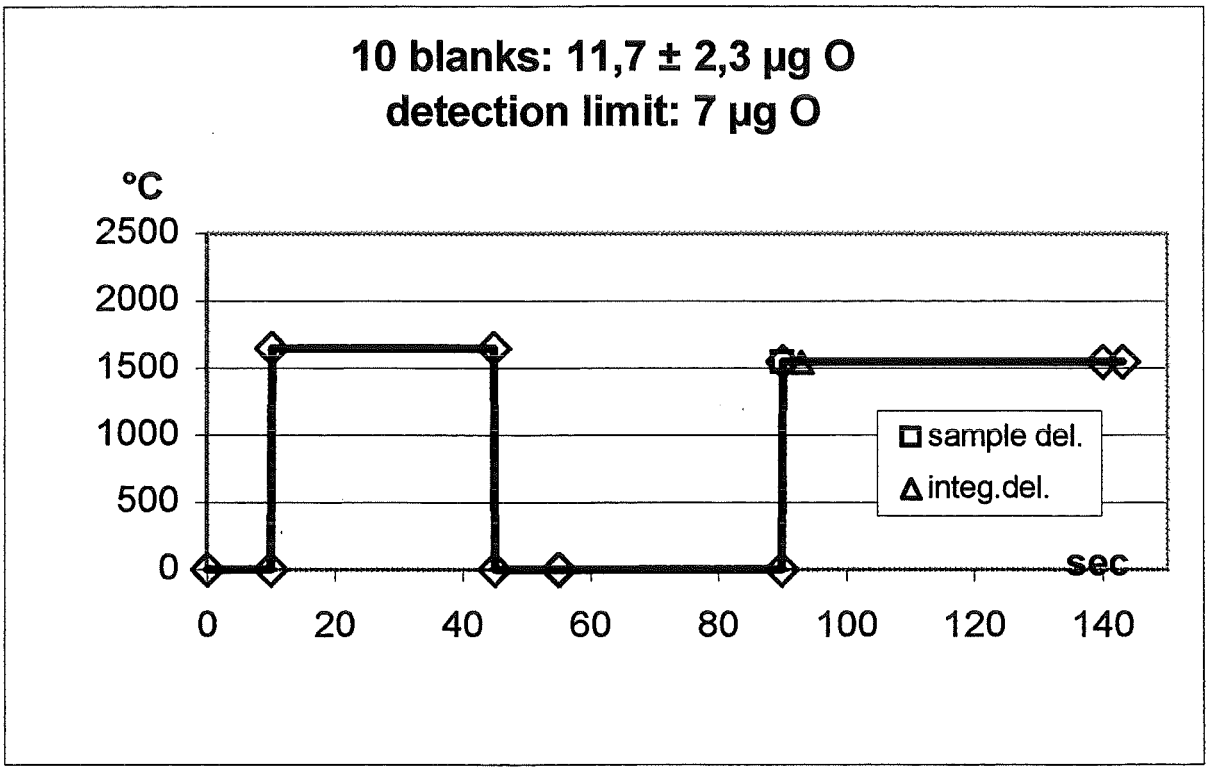
- low melting points

Element	MP °C	BP °C
Pb	327	1725
Bi	271	1560
Pb55Bi	124	1670

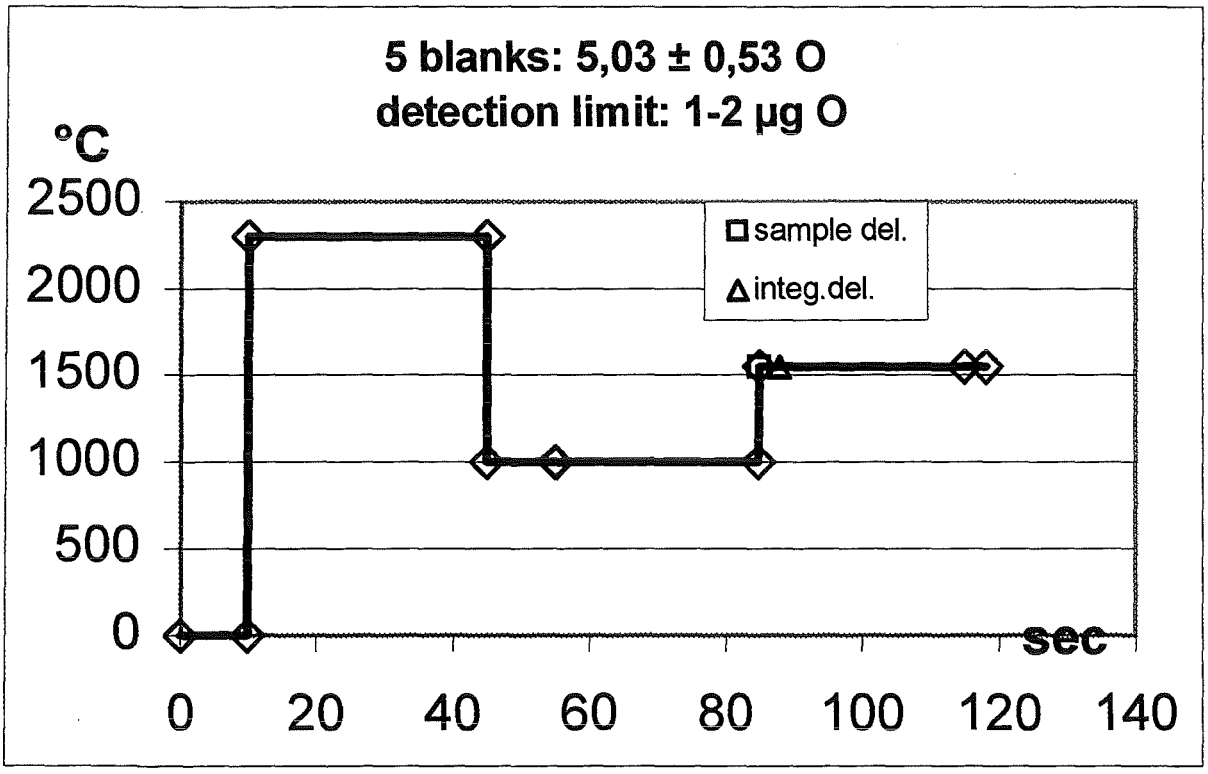
- Oxygen recovery at 1250 to 1550 °C



- **start Temp. 20 °C, analysis Temp. 1550 °C**



- **start Temp. 1000 °C, analysis Temp. 1550 °C**



Considerations to inert gas fusion

- solved oxygen and all dispersed oxides are reduced: PbO, Bi_2O_3, Fe_3O_4, Cr_2O_3 etc
- quantitative reduction of Fe_3O_4, Cr_2O_3 etc. at 1550 °C has to be tested
- oxygen at the surface of the analyzed sample has to be removed by mechanical shaping or etching

Considerations to oxygen determinations in PbBi

- carefull sampling is extremely important
  - ➔ sampling location
  - ➔ atmosphere, temperature during sampling

Conclusions

- Determination of micro amounts (< 5 µg/g) of metallic impurities by ICP-OES are possible

- Determination of oxygen < 1 µg/g by inert gas fusion seem to be possible
  Verification of the quantitative CO forming and extraction process from PbBi is necessary

- No homogenious distribution of the unsolved metall and oxide impurities → therefore

- Sampling plan for loop samples and stagnant liquid is essentiell

Literature for oxygen detemination in Pb and Pb-alloys

C. Engelmann, G.Kraft, J. Pauwels, C. Vandecasteele:
Modern Methods for the Determination of Non-Metals in Non-Ferrous-Metals
Walter de Gruyter 1985 Berlin New York on behalf of the Commission of the European Communities
ISBN 3-11-010342-7

L.Quaglia, G. Weber, J. Triffaux, J, Geerts, J. van Audenhove, J. Pauwels
Surface Treatment of non-ferrous-metals for the purpose of gas analysis
Comm. Eur. Communities, [Rep.] EUR (1979),_EUR 6602 EN

J. Pauwels
Intercomparison of analysis methods for oxygen in lead and its alloys
Comm. Eur. Communities, [Rep.] EUR (1979), EUR 6303

COMMISSION OF THE EUROPEAN COMMUNITIES

COMMUNITY BUREAU OF REFERENCE - BCR -

N°. 152 (15/2)

CERTIFIED REFERENCE MATERIAL

CERTIFICATE OF ANALYSIS

BCR No 55

OXYGEN IN REFINED PURE LEAD

Mass fraction of oxygen	Certified value (1)	Uncertainty (2)
	1.0 µg/g	0.5 µg/g

(1) *This value is an evaluated average of 98 accepted individual measurement results obtained with 4 independent methods by 9 laboratories.*

(2) *This value takes into account the precisions of the methods used and the differences between the results which may be due to systematic errors or heterogeneity of the metal (may be used as 1 × the standard deviation).*

DESCRIPTION OF SAMPLE

The samples are available as discs 30 mm in diameter and 9 mm thick.

INSTRUCTIONS FOR USE

1. Samples have to be prepared by machining on a lathe.
   Recommended conditions are set out in Eurisotop Technical Information No 90 (ITE-90).
   Surface oxygen on freshly prepared samples is evaluated at 0.3 - 0.5 µg/cm².
2. The analysis should be performed as soon as possible after mechanical preparation of the sample.
3. In the case of the present reference material, chemical etching, e.g. in CH_3COOH - H_2O_2 mixtures, has to be avoided, especially when the central part (diameter: 5 mm) of the reference samples is used.
4. The minimum quantity that can be considered as representative is 10 mg.

Brussels, November 18th, 1977.

BCR
for certified true copy

PARTICIPATING LABORATORIES

— Bari University, C.S.A.T.A., Bari (Italy);
— Bundesanstalt für Materialprüfung (B.A.M.) Berlin (Federal Republic of Germany);
— C.E.A., Centre d'Etudes Nucléaires de Fontenay-aux-Roses, DRA-SEA, Fontenay-aux-Roses (France);
— C.E.A., Centre d'Etudes Nucléaires de Saclay, Gif-sur-Yvette (France);
— CNRS, Service du Cyclotron, Orléans (France);
— Gesellschaft für Kernforschung mbH, Laboratorium für Isotopentechnik, Karlsruhe (Federal Republic of Germany);
— Joint Research Centre, Central Bureau for Nuclear Measurements, Geel (Belgium);
— Joint Research Centre, CETIS and Chemistry Division, Ispra (Italy);
— Metallgesellschaft A.G., Frankfurt/Main (Federal Republic of Germany);
— R. Bosch, GmbH, Stuttgart (Federal Republic of Germany);
— Rijksuniversiteit Gent, Instituut voor Nucleaire Wetenschappen, Gent (Belgium);
— Université Claude Bernard, Institut de Physique Nucléaire, Lyon (France);
— Université de Liège, Institut de Physique Nucléaire, Liège (Belgium);
— Vieille Montagne, Balen-Wezel (Belgium).

METHODS USED

— Charged particles activation analysis;
— Gamma activation analysis;
— 14 MeV Neutron activation analysis;
— Reducing fusion;
— Hydrogen reduction;
— Surface analysis for the determination of the correction for surface oxygen.

LEGAL NOTICE

NOTE

A detailed technical report on the analysis procedure and the treatment of the analytical data has been published (BCR-report EUR 5933) and is available at the BCR.

This reference material has been certified under a Community programme on the improvement of gas analysis techniques used on non-ferrous metals, drawn up by the Eurisotop Office, Commission of the European Communities, Brussels, Belgium.

Rue de la Loi 200, B-1049 Brussels — Telephone 735 00 40/735 80 40 ext. 5014 — Telegraphic address «COMEUR Brussels» — Telex: «21 877 COMEU B»

Commission of the European Communities

BCR information

SURFACE TREATMENT OF NON-FERROUS METALS FOR THE PURPOSE OF GAS ANALYSIS

L. QUAGLIA and G. WEBER
Institut de Physique Nucléaire de l'Université de Liège (Belgium)
D. DAVID
Université de Technologie de Compiègne (France)
J. TRIFFAUX, J. GEERTS, J. VAN AUDENHOVE, J. PAUWELS
Central Bureau for Nuclear Measurements, Geel (Belgium)

Directorate-General for Science, Research and Development
Joint Research Centre

1979

RECOMMENDED SURFACE TREATMENT FOR PURE Pb and Pb-0.2 % Sn- 0.07 % Cd, Pb-0.4 % Cu-0.04 % Te ALLOYS

- PRESHAPING OF ANALYSIS SAMPLES

3 shaping techniques were examined and found to be acceptable for samples etched subsequently in case of O and C- determinations.

1. Turning on a lathe Drehbank

Tool material : Hardmetal ISO-P35 Design : Annex 1

Tool parameters

χ	:	45°
γ	:	20 - 30°
α	:	6 - 10°
α_1	:	3 - 6°
λ	:	0°

Top radius : 0.2 to 0.3 mm

Turning parameters (Workpiece Ø : 30 mm)

Cutting speed (rpm) : 1000 - 1500

Pre-turning
Feed(mm/revol) : 0.5 - 1
Depth of cut (mm) : 0.5 - 1

Final-turning
Last 0.1 to 0.2 mm
Feed(mm/revol) : 0.01 - 0.02
Depth of cut (mm) : 0.05 - 0.1

Cutting fluid : Kerosene

2. Rolling Walzen

In order to prepare thin plates, freshly turned pieces were cold rolled with a maximum reduction in area of 10 % per rolling pass.

3. Punching Stanzen

Cutting with a punching die using kerosene as cutting fluid of round or rectangular pieces up to 10 mm thick.

- SUBSEQUENT CHEMICAL ETCHING (Annex 2)

Bath	:	3 Vol CH_3COOH (99.7 %) + 1 Vol H_2O_2 (30 %)
Temperature	:	20°C
Duration	:	45 s
Arrest	:	1 x H_2O 60 to 80°C
		1 x H_2O 20°C + ultrasonic
Drying	:	1 x CH_3OH + ultrasonic
		Stream of Argon (N 50) at 80°C

Bath Volume for 1 to 2 g samples : 100 ml

Special equipment - see Annex 2.

- TYPICAL RESIDUAL SURFACE CONTENTS

O	:	0.2 - 0.4 $\mu g/cm^2$
C	:	0.15 - 0.2 $\mu g/cm^2$

COMMISSION OF THE EUROPEAN COMMUNITIES

community reference bureau

The certification of oxygen in non-ferrous metals

Part 9 : Oxygen in lead (2nd part)

(BCR Project No 13)

Dr J. PAUWELS
Joint Research Centre
Central Bureau for Nuclear Measurements
Geel, Belgium

Directorate-General Research, Science and Education

1978

251

EUR 5933 EN

Measurement of Oxygen content in Lead alloys by means of laboratory technique.

*G. Benamati, *C. Fazio, °C. Martini

*ENEA CR Brasimone, °Università di Bologna

Abstract

In solid alloys oxygen can be present in two forms, dissolved in the alloy and bonded with the metals such as to form oxides. In this work, the technique used to evaluate the oxygen content in Pb-55Bi samples was based on the carrier gas hot-extraction method. By this method the total amount of oxygen (both the free oxygen and the bonded one (oxides)) is measured.

The carrier gas hot-extraction method consisted in melting the Pb-55Bi sample with an electrical impulse furnace in a graphite crucible containing a Cu bath. The oxygen is converted in carbon monoxide due to a reduction - oxidation reaction. The reaction can be described as:

$$[O]_{sample} + C_{(s)crucible} \Leftrightarrow CO_{(g)}$$

where [O] indicates the dissolved oxygen and the oxides.

The carbon oxide is removed with a stream of nitrogen from the furnace and converted in carbon dioxide. The amount of carbon dioxide is measured with an IR detector and is related with the content of oxygen in the sample.

The oxygen content was evaluated on Pb-55Bi samples delivered by the Stachow firm.

Moreover, a study on the preparation procedure of the samples was conducted. The preparation procedure consisted in a surface treatment in order to scrape the oxygen / oxide and moisture film that can be present on the surface of the solid Pb-55Bi. Two surface procedures were applied and after the treatment the oxygen content was evaluated. In order to check the effect of the surface treatment, oxygen measurements were conducted on untreated samples. The surface treatment consisted in mechanical pickling with a brush with brass bristles. A chemical pickling procedure was used as well. The chemical pickling procedure consisted in dipping the samples in CH_3COOH-H_2O_2 and CH_3OH solutions. For both the pickling treatments a decrease of the measured oxygen content was observed. The mean values of the oxygen content measured on the not treated samples and on the treated samples were:

Without surface treatment	=	13 (± 20 %) wppm
Mechanical pickling	=	1.6 (± 30 %) wppm
Chemical pickling	=	0.7 (± 20 %) wppm

From the obtained data it appears that additional oxygen sources, besides the oxygen dissolved or bonded in the alloy, could be due to surface contamination (layers of oxygen - humidity – oxide) in consequence of normal air contact or during the preparation of the solid.

MEASUREMENT OF OXYGEN CONTENT IN LEAD ALLOYS BY MEANS OF LABORATORY TECHNIQUE

***G. Benamati, *C. Fazio, °C. Martini**

* ENEA CR Brasimone
° Università di Bologna

THE CARRIER GAS HOT EXTRACTION METHOD

INSERTING THE SAMPLE IN A GRAPHITE CRUCIBLE CONTAINING A Cu BATH

↓

HEATING WITH ELECTRODE IMPULSE FURNACE: MELTING THE SAMPLE

↓

REDUCTION - OXIDATION REACTION:
[O] + C (s) $\Longleftrightarrow$ CO (g)

↓

CONVERSION OF CO (g) IN CO_2 (g)

↓

CO_2 (g) IR DETECTION AND CORRELATION WITH OXYGEN CONTENT IN THE SAMPLE

EXPERIMENTAL

MEASUREMENT OF OXYGEN CONTENT IN Pb-Bi SAMPLES SPECIMEN PREPARATION

✓ 1. EVALUATION OF OXYGEN CONTENT WITHOUT SURFACE TREATMENT

✓ 2. EVALUATION OF OXYGEN CONTENT AFTER MECHANICAL PICKLING

✓ 3. EVALUATION OF OXYGEN CONTENT AFTER CHEMICAL PICKLING

SURFACE TREATMENTS

1. MECHANICAL PICKLING

BRUSHING THE SURFACE OF THE SAMPLES WITH A BRASS BRISTLE BRUSH

2. CHEMICAL PICKLING

DIPPING THE SAMPLES IN

A. $CH_3COOH + H_2O_2$ - 25 °C - (HAND STIRRING)
B. H_2O - 65 °C - (MECHANICAL STIRRING)
C. H_2O - 20 °C - (ULTRASONIC)
D. CH_3OH - 20 °C - (ULTRASONIC)

RESULTS

OXYGEN CONTENT IN Pb-Bi

1. WITHOUT TREATMENT

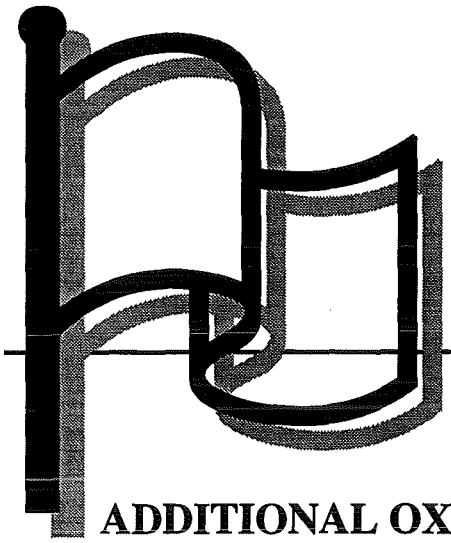
13 (± 20 %) wppm

2. MECHANICAL PICKLING

1.6 (± 30 %) wppm

3. CHEMICAL PICKLING

0.7 (± 20 %) wppm



ADDITIONAL OXYGEN SOURCES, BESIDES THE OXYGEN DISSOLVED OR BONDED IN THE ALLOY, COULD BE DUE TO SURFACE CONTAMINATION (LAYERS OF OXYGEN - HUMIDITY -OXIDE) IN CONSEQUENCE OF NORMAL AIR CONTACT OR DURING THE PREPARATION OF THE SOLID

Summary : physico-chemistry of lead-bismuth eutectic : alloy characterisation and on-line oxygen-meter validation

J. Desreumaux, G. Laplanche, J.-L. Courouau, CEA

Abstract

This presentation was intended to give comprehensive information's about the latest works achieved about the physico-chemistry of the lead-bismuth alloy through two different issues :

1- the characterisation of the alloy,
2- the validation of an on-line oxygen-meter

Various analytical techniques have been implemented for the characterisation of the lead bismuth eutectic, in order to assess the quality of different suppliers, and in order to determine the required quality for that alloy : differential calorimetry for the composition, EDX coupled to SE microscope for the observation of homogeneity, ICPMS for the metallic impurities, LECO analysis for the oxygen content, etc.

The composition measurements are consistent with each others, and correspond roughly to the composition of the eutectic. The segregation observed at the microscopic scale does not alter the overall composition of the alloy. The impurities analysis by ICPMS showed that the operation of mixing the pure metals in the proportion of the eutectic leads to a decrease of the quality due to a pollution by tin (the tank used for mixing was used for tin before). Up to now, no warranty of a defined quality for a large bulk of lead-bismuth eutectic alloys is agreed by any suppliers from the view point of metallic impurities.

The total oxygen content by the LECO method showed quite large discrepancies due to the different sampling preparation methods used : chemical etching and/or mechanical filing.

In close prospect, the work will lay the stress on lowering the detection limit for the metallic impurities by ICPMS, and improving the sampling preparation procedure with the application of standards (procedure and apparatus).

The validation of an oxygen meter for use in dynamic facilities is based on the following methodology :

1- application of the feed back from the sodium sensors, and in particular the Harwell sensors, whose efficiency have been proven on the long term. The form of the electrochemical cell is a thimble, with a sealed internal reference (tin oxide / liquid tin at the operating temperature, for instance). The thimble, which acts as the electrolyte, will be set in a circuit with the help of an housing allowing the formation of a frozen metal seal between the cells and the housing.
2- development of an industrial collaboration for the supply of prototype cells (zirconia stabilised solid electrolyte, yttria or magnesia, and internal metal/metal oxide reference electrode).
3- achievement of first validation tests in a static facility (Bipb facility), in order to validate the choice for the cell materials and their compliance with the operating conditions. This facility allows the use of various liquid metal solution : lead, lead-bismuth eutectic, with either a saturated oxygen content, or lower with the help of a Ti-Zr Getter.
4- validation on a dynamic facility (PLOMBIERES).

First results are promising, but some troublesome behaviours have been observed.

1- presence of slags in excess may affect the measurement,
2- possible chemical reaction of the electrolyte with the ceramic thimble : compatibility tests have been achieved for 1000 hours at 500°C in saturated lead-bismuth eutectic, metallurgical analysis is in progress.

In close prospect, experiments will go on with a careful control of the oxygen pollution in the Bipb facility, in order to keep slightly over the oxygen saturation line, and try to get below this saturation line using a Getter or a reducing gas, in order to complement the first qualitative results.

Physico-chemistry of Lead-Bismuth eutectic : alloy characterization and on-line oxygen-meter validation

J. DESREUMAUX ; G. LAPLANCHE ; J-L. COUROUAU

Service of Innovative Technology and Processes

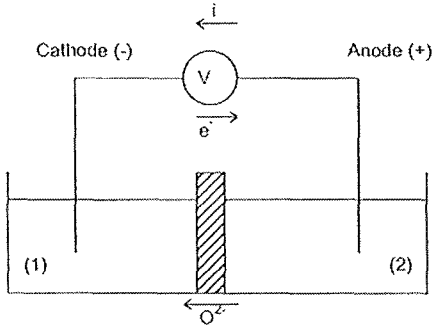
Laboratory of Physico-Chemistry and Processes

the issue

- **A good knowledge of physico-chemistry of the Lead-Bismuth eutectic is fundamental to achieve low level of corrosion, safe operations, ...**
- **First attentions were focused on :**
  - extensive literature review
    - **on the physico-chemistry of the lead bismuth eutectic (LBE)**
    - **with a peculiar attention to the oxygen**
  - characterization works on the lead-bismuth alloys
    - **various alloys produced on demand by various companies**
    - **various analytical methods were implemented for this characterization, which are mostly similar to whose used for sodium**
    - ⇨ **choose a quality specified LBE alloy**
  - qualification **works for** on-line oxygen sensors **for use on dynamic facilities**
    - **methodology pursued to obtain in a short delay an operating device (sodium support)**
    - **first experiments and conclusions**

On-line oxygen meter

- **Objectives**
  - **measure the activity of oxygen in liquid LBE in order to achieve the control of the stability against the corrosion of the facility steel**
  - **short delay for an operating device : 2001 for an experimental facility (Plombières...)**
- **Principle : electrochemical cell**
- **Methodology : as little developments as possible**
  - **from the sodium feed back**
  - **from the literatur review**
  - **starting with basic and simple experiments**
  - **develop an industrial collaboration with a specialist**



$$\frac{1}{2}O_{2(2)} \Leftrightarrow \frac{1}{2}O_{2(1)}$$

$$E = \frac{RT}{4F}\ln\frac{P_{O2(2)}}{P_{O2(1)}}$$

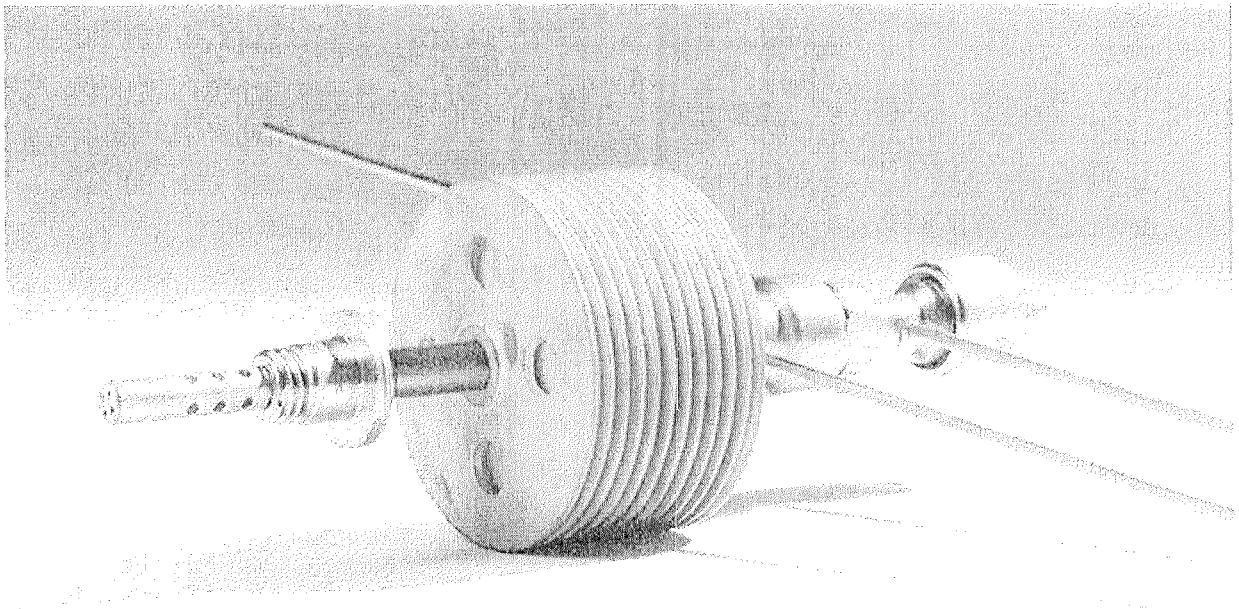
Feed-back from the sodium sensors

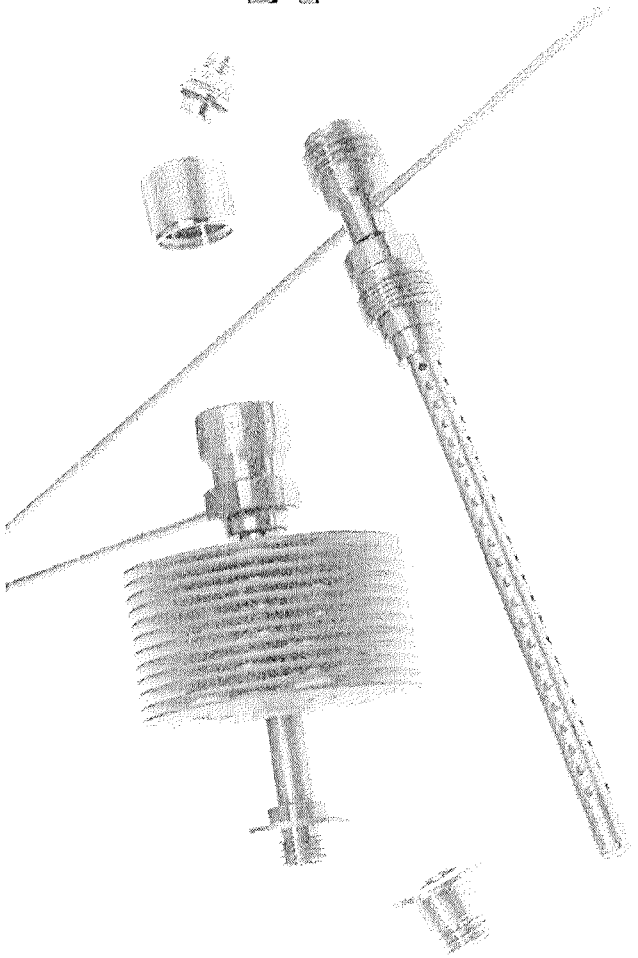
- **Wide use in physico-chemistry sodium loops for quality control and development of specific processes : over 25 years.**
- **Extensive comparison of oxygen-meter throughout the 80ies**
- **Harwell Laboratory oxygen sensor (UK AEA)**
  - **yttria stabilised thoria as solid electolyte in the form of a thimble**
  - **liquid metal/metal oxide as internal reference electrode (In or Sn)**
  - **sensor housing welded on facility pipes and providing the electrical connections ; use of a frozen sodium seal with the help of cooling fins**

  ! **no more supply by the AEA AND thoria is a nuclear material ! (cost)**

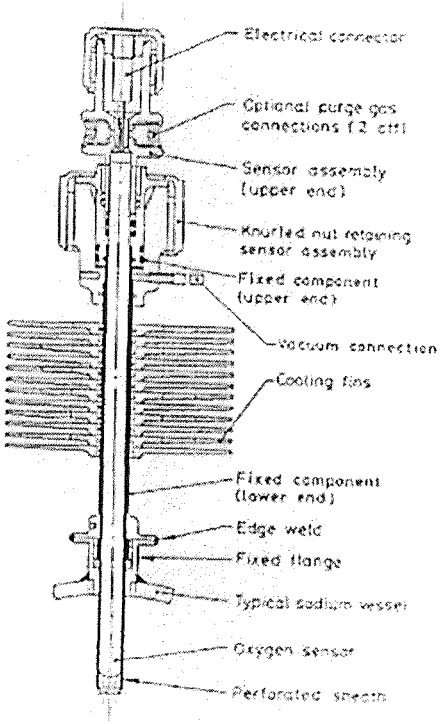
➲ **the issue of supplying identical meters for the needs of our R&D programmes on sodium technologies (loops and Phénix reactor) was first addressed in 1997.**

Harwell sensor : MK II A type





Harwell sensor : MKII A



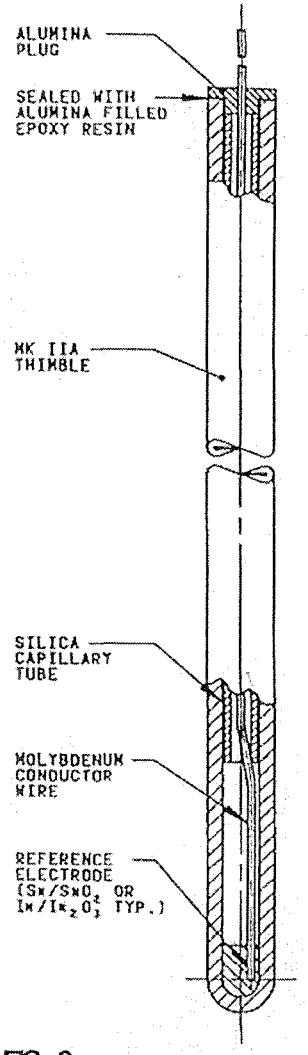


FIG. 2
MK IIA OXYGEN SENSOR

Why not zirconia ?

- **from the following acknowledgement :**
  - **Thoria was traditionaly used for sodium applications (low T)**
  - **Zirconia doped ceramics are widely used for oxygen sensors in gas or liquid phase media traditionally at high T for industrial applications**
  - **Literature review shows that electrochemical cells based on solid zirconia electrolyte were used for measuring thermodynamic properties of oxides even at low temperature**

⇨ **the following statement was then drawn : zirconia could favorably replace thoria even at low T (500°C)**

  - **operating conditions to be defined**
  - **cell materials to be choosen**

Typical behaviour

- **Cell impedance is function of**
  - **temperature : impedance is decreasing with the temperature**
  - **interfacial contact resistance between the reference electrode and the solid electrolyte**
    - **ex : use of a liquid metal reference electrode instead of the usual air/platinium foam reference, that reduce tremendously the interfacial contact impedance**
  - **metal / metal oxide couple : more the solubility and diffusivity of oxygen is great and more the interacial contact resistance is low (ex : Cu excluded) ; liquid phase.**

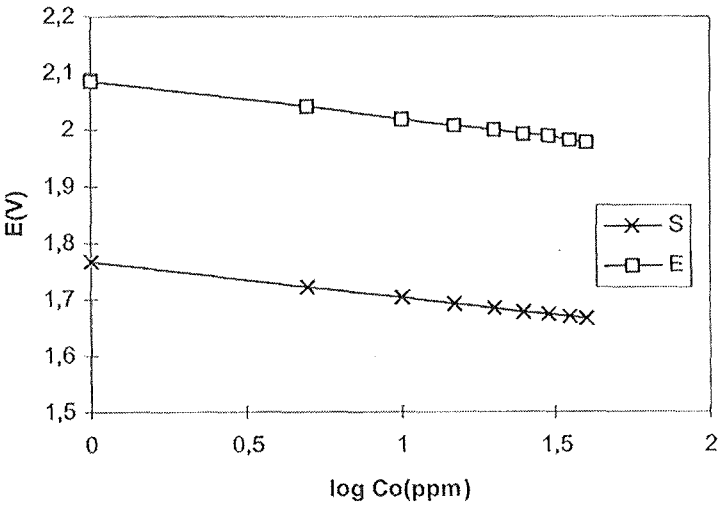
  → in effect a high cell impedance decreases the emf signal of the cell compared to the theoretical value
- **LEBD : where the conduction is purely ionic (Lower Electrolytic Boundary Domain)**
  - **when not : reduction of the emf due to the residual current and reduction of the cell life**
    - **polarisation effect due to the electronic conduction ; consumption of the internal reference**
- **Stability against corrosion of the solid electrolyte**
  - **solid electrolyte corrosion kinetics is decreasing with T and the oxygen level ; possible reaction of liquid metal with the ceramic**

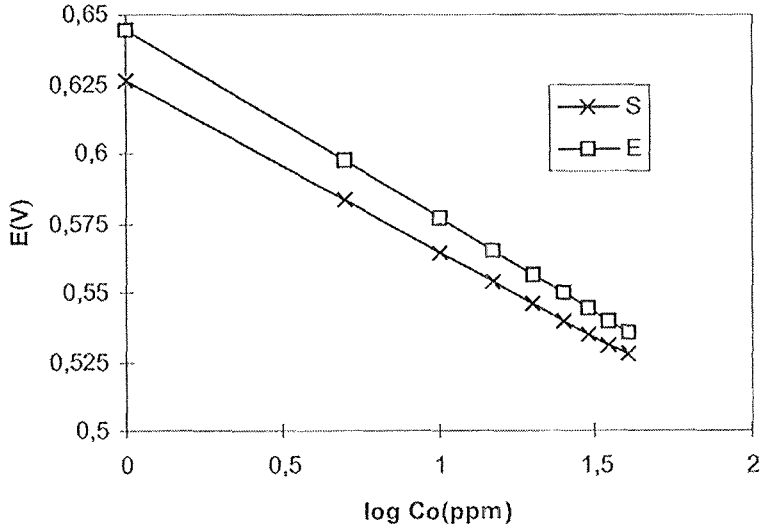
A trade-off between the operating temperature and the cell materials has to be found

Example : liquid metal internal reference

Sodium : 400°C, 0.08 m/s

Whestinghouse : Air /platinium foam (1998) / HARWELL : In /In2O3 (1996)





$$E = K_1 + K_2 \cdot T - K_3 \cdot T \cdot \ln C_o$$

(S : measure)
(E : theoretical emf)

- **better stability of the signal**
- **Very low time drift (40 000 hrs)**
- **accuracy and reproducibility**

! sensitive to thermal shocks

- **Less influence of the cell resistance on the emf which is much closer to the theoretical value : signal drift to the theoretical line is representative of the cell materials choice**
- **Calibration is still needed for better accuracy in a particular concentration range**

Objective of the first experiments

- Validate the choice of the materials **used for the cells : qualitative experiments on a small static device**
  - **doping element for zirconia : MgO(MSZ) or Y2O3 (YSZ)**
  - **reference electrode : In, Sn, Pb, etc.**
  - **conducting wire**
  - **measurement electrode**

⇒ Through the study of

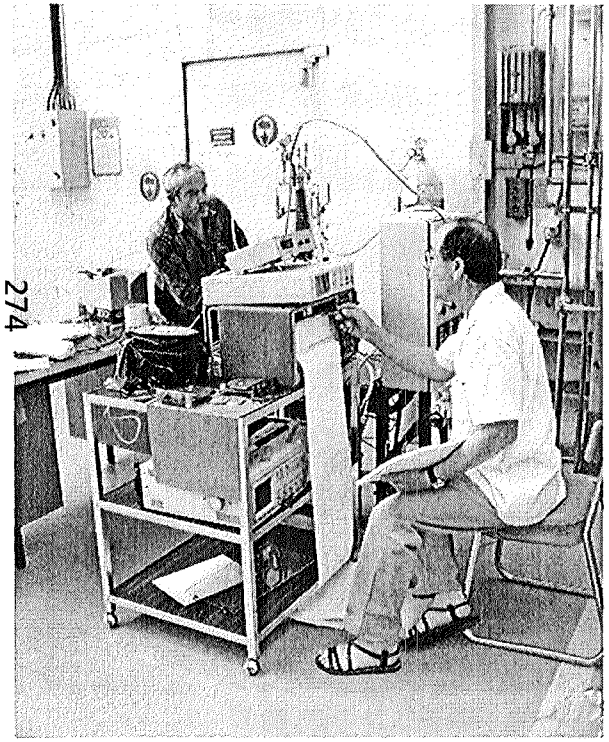
- **the stability against corrosion of the electrolyte : compatibility tests**
- **measurements of the emf and impedance of the cells at various T and for saturated or unsaturated liquid metal solution (lead and LBE)**
- **time drift and reproducibility can also be investigated**
- **ability to support thermal chock**

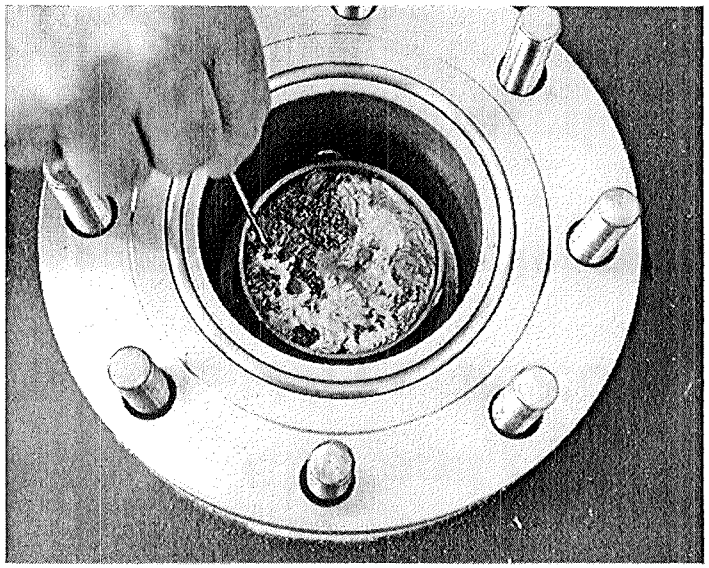
⇒ **Small static facility called Bipb and the usual compatibility device**

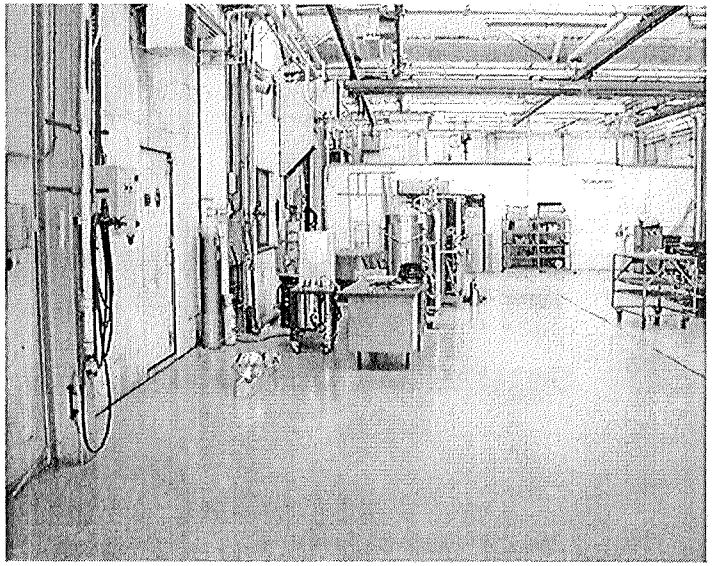
What has been done up to this point

- Industrial collaboration : CEA and HEN engaged
- Thermal shocks : from ambient to 480°C in a split second in static conditions
  - very good for MSZ, poor for YSZ but better with a lower thermal gradient or a protection
- First tests achieved on the dedicated facility, Bipb, with the first 2 HEN prototypes on :
  - lead and LBE solution at different T : emf and Z (impedance)
  - effect of the getter Ti/Zr to get unsaturated solution
- compatibility test of the zirconia with EPB
  - 1000 hours at 500°C for 2 samples : MSZ and YSZ
  - ⌛ metallurgical analysis in progress

The Bipb facility

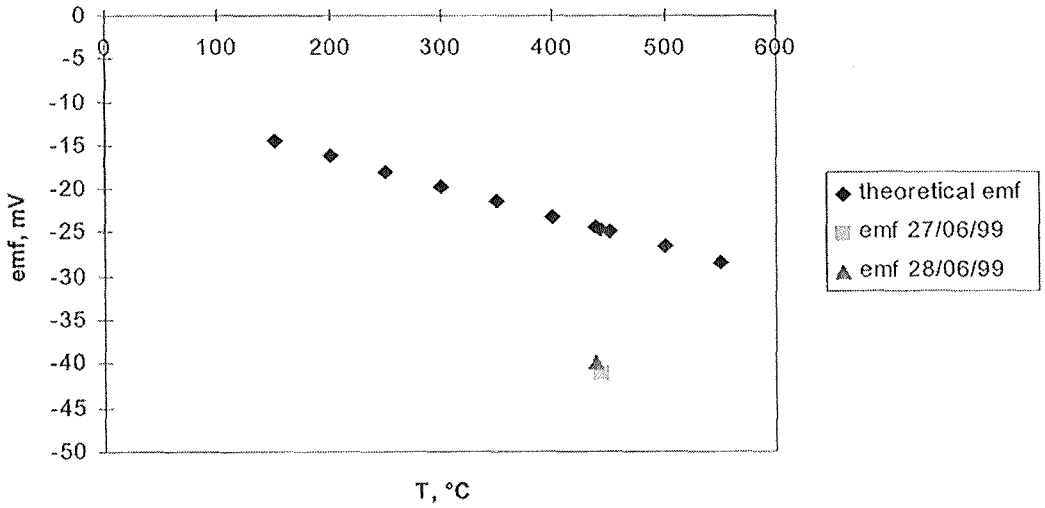


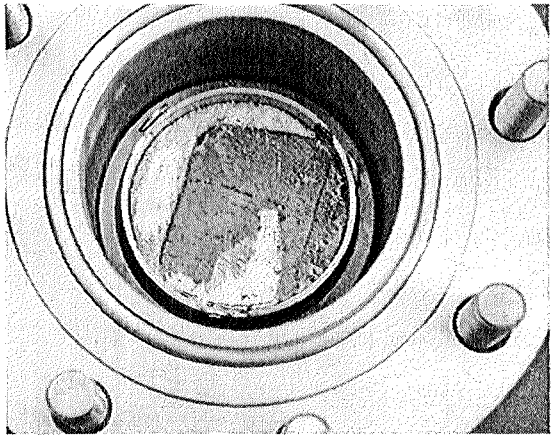


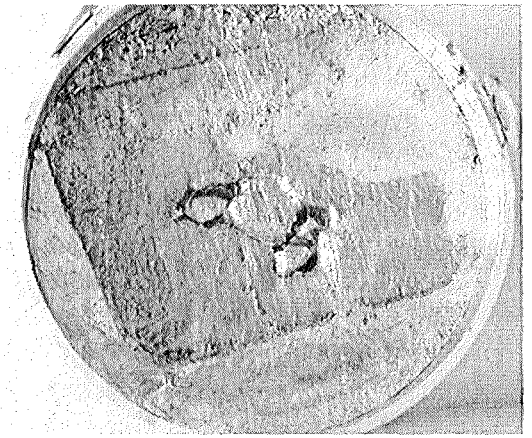


Results for Cell HEN 1

- **solution : LBE saturated in oxygen at 450°C**

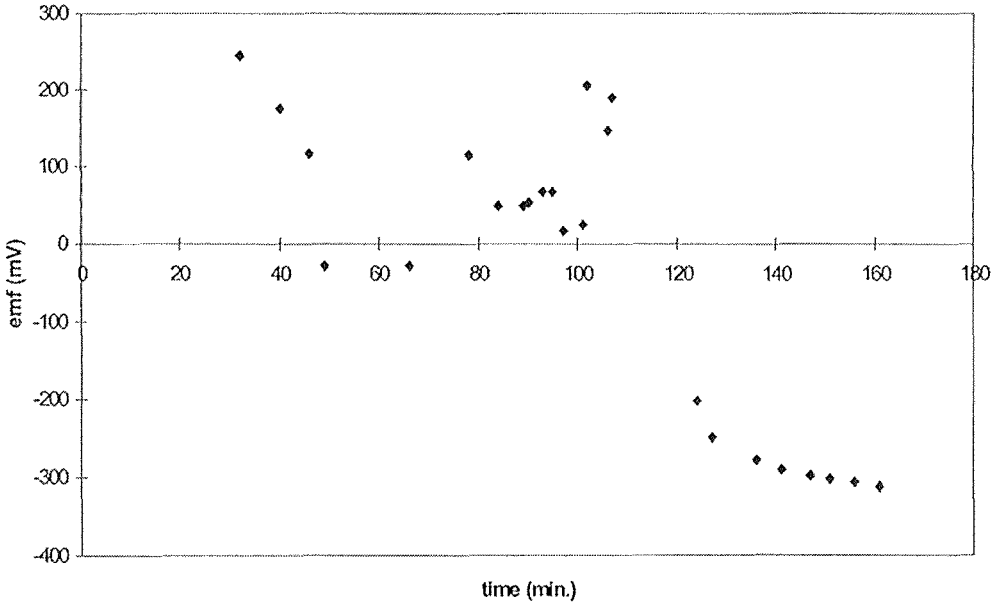


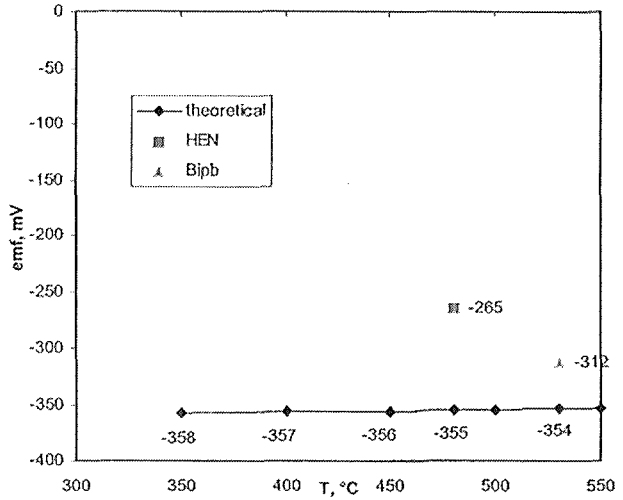


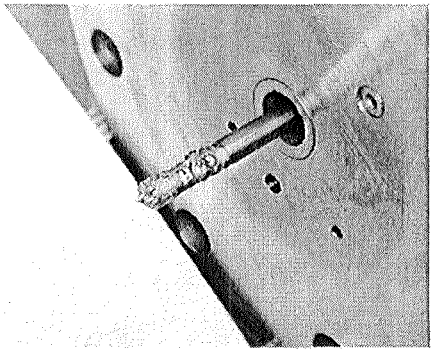


- **good reproducibility over 2 days**
- **Z = 1000 Ohms ; residual current = 2.6 mA (!!!)**
- **Is the cell reversible ?**

Results for Cell HEN 2 : lead saturated in oxygen at 530°C



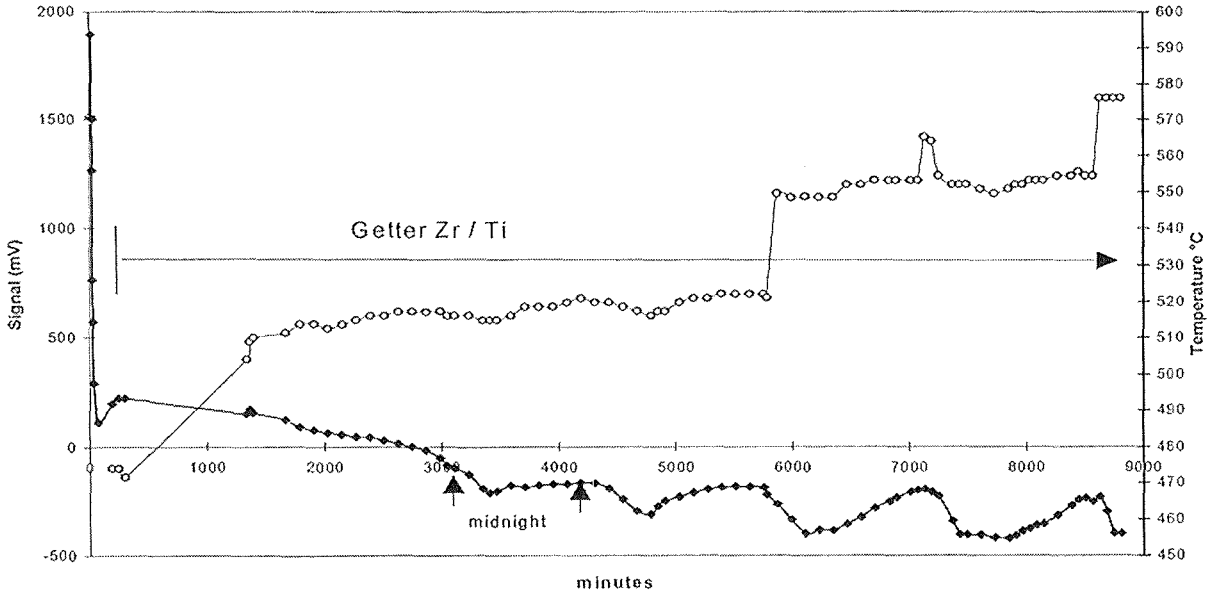


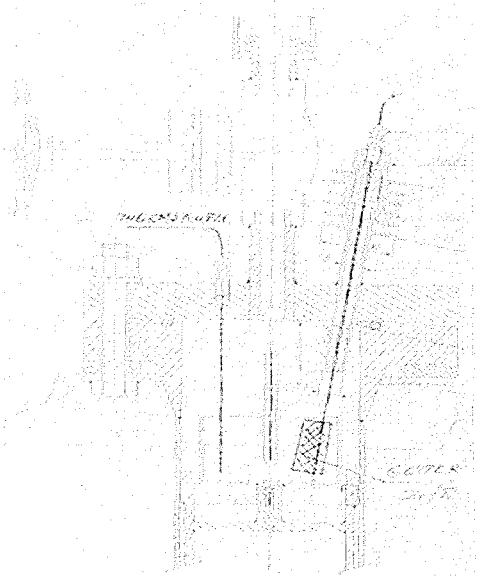


- **time to reach the equilibrium : 1 hour**
- **Z = 60 kOhms, residual current = 5 µA (!)**

Results for Cell HEN 2 :
LBE with Ti/Zr getter for several days at various T

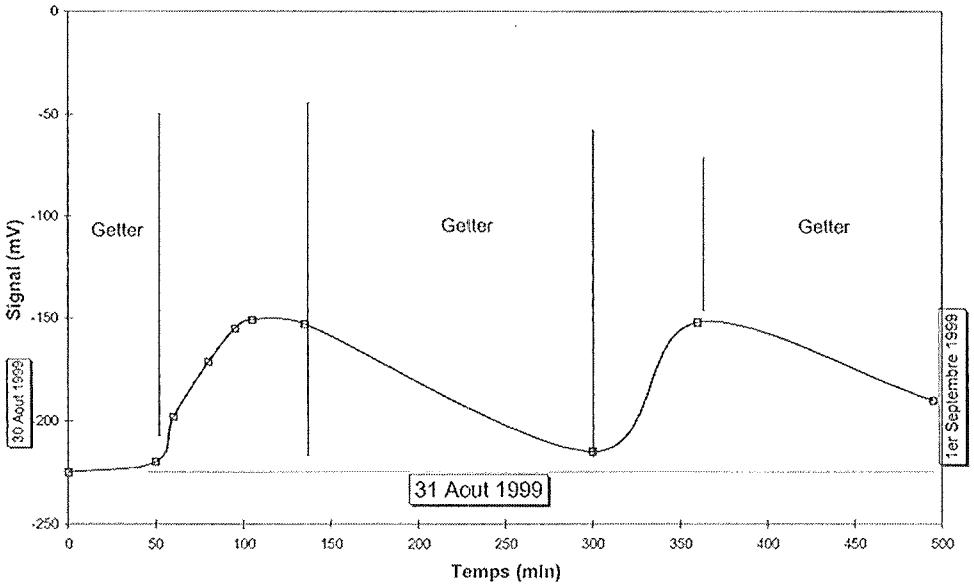
- **solution : LBE with Ti/Zr getter at 515°C for several days**

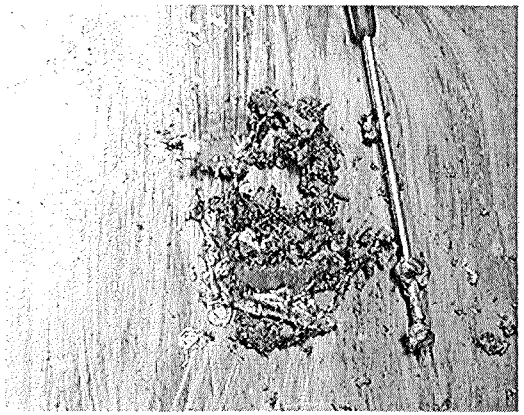




- **emf(equilibrium) at 515°C = 200 mV unsaturated solution ?**
- **time to equilibrium is longer to achieve than for lead solution**
- **scories probably disturb the experiment**
- **daily variations (!)**

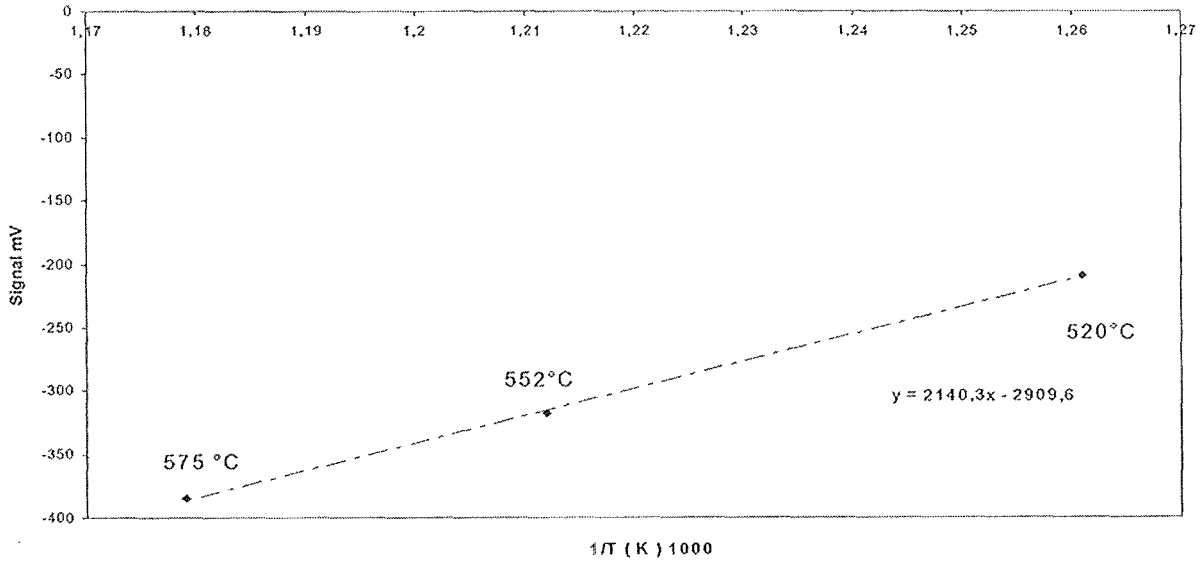
Results for Cell HEN 2 :
Lead with Ti/Zr getter at 561°C, periodic purification





- positive response of the cell to a variation of oxygen activity
- ! emf(equilibrium) saturated = 150 mV different from the previous 2 measurements
- ! Slopes should be inverted
- scories disturb the experiment : thick layer of lead oxide on the free surface discovered after the experiment
- possible interpretation : adjustment of oxygen potential with a getter has a very little effect on the reduction of the scories

Results for Cell HEN 2 : LBE with Ti/Zr getter : influence of the T



LBE saturated :

$$E^0_{EPB} = E^0_{Pb} + \frac{RT}{2F}\ln a_{Pb}$$

LBE below saturation with the hypothesis that the main oxide is PbO :

$$E = E^0_i - \frac{RT}{2F}\ln a_o$$

⇨ **Signal is increasing with the temperature, as the solubility of oxygen in LBE**

! **Variation is tremendous**

! **Layer of LBE oxide on the surface of the solution !**

In close prospect

- **First conclusions are promising but not complete (troublesome results):**
  - **either the presence of the scories was disturbing the measurement**
    - **first emf values seems more significants than the latest ones, although the first one were done in open air whereas the lastest in a controlled argon atmosphere**
  - **or a reaction may occur between YSZ or MSZ and the LBE (analysis in progress)**
- **to be continued ...**
  - **perform experiments in cleaner conditions and possibly with new prototype cells**
    - **mechanical and chemical desoxydation of the ingots after cutting and before melting**
    - **use of getter sink and argon sweep gas with a low hydrogen percentage**
  - **achieve a good desoxidation and perform a destructive test with the LECO method for a calibration point**
  - **tests in dynamic conditions on LBE loop**

Characterization of the Pb-Bi alloys : plan

- **Alloys composition according to the suppliers**
- **Specifications with regard to original metals Pb and Bi**
- **Implemented methods**

  To characterize Pb-Bi alloy

  To determine impurities
- **Results**

  Metallic impurities by ICP/MS

  Determination of oxygen

Alloys composition according to suppliers

	% Pb	% Bi
Supplier 1	44,7 +/- 1	53,3 +/- 1
Supplier 2	43 +/- 0,5	57 +/- 0,5
Supplier 3	44,7	55,5

Specifications with regard to the original metals Pb and Bi

	SUPPLIER 1		SUPPLIER 2	
	Bi	Pb (99,97%)	Bi (99,997%)	Pb (99,97)
Bi		< 250 ppm		
Pb	5,1 ppm			
Sn	< detection	< 3 ppm	< 1 ppm	< 2 ppm
Fe	0,6 ppm	< 3 ppm	< 1 ppm	
Ni	1,3 ppm	< 3 ppm	1,4 ppm	< 1 ppm
Ag	1,9 ppm	< 15 ppm	1 ppm	6 ppm
Cu	1,6 ppm	< 10 ppm	< 1 ppm	< 2 ppm
Zn	< 0,2 ppm	< 5 ppm	< 1 ppm	
Cd	< 0,2 ppm	< 10 ppm	< 1 ppm	< 2 ppm
Sb	< 3 ppm	< 3 ppm	< 3 ppm	< 2 ppm
As	< detection	< 5 ppm	< 1 ppm	< 2 ppm
Te	< detection		< 1 ppm	< 3 ppm

Implemented methods to characterize the Pb-Bi alloys

Determination of the alloy composition

- Determination of fusion temperature and fusion enthalpy by differential calorimetry
- Determination of lead and bismuth by Wavelength Dispersion X Ray Fluorescence (WDXRF) and by Energy Dispersive Spectrometry X (EDX) Coupled to Scanning Electron Microscope (SEM)
- Determination of bismuth by Atomic Absorption Spectrometry (AAS)

Observation of homogeneity

- by optic microscopy
- Energy Dispersive Spectrometry X (EDX) Coupled to Scanning Electron Microscope (SEM)

Implemented methods to determine impurities

Determination of metallic impurities Sn, Fe, Ni, Cr, Ag, Cd, Cu

- **Inductively Coupled Plasma/Mass Spectrometry (ICP/MS)**
- **Atomic Absorption Spectrometry (AAS)**

Determination of oxygen

- **LECO technique**
  - reducing melting of sample in a graphite crucible under helium
  - measure of carbon dioxide by infrared spectrometry

Results : determination of the composition

	Calorimetry		Fluorescence X	
	Pt fusion	Enthalpy	% Pb	% Bi
Supplier 1	125,3°C	20,0 J/g	58,5+/-2	40,8+/-2
Supplier 2	126,2°C	17,0 J/g	57,0+/-2	42,2+/-2
Supplier 3	125,5°C	18,8 J/g	55,7+/-2	43,1+/-2

Results : impurities by ICP/MS

	Supplier 1		Supplier 2	Supplier 3
Fe µg/g	< 30	40	< 30	< 30
Cr µg/g	< 25	2	< 25	< 25
Ni µg/g	< 2	< 10	< 20	< 20
Ag µg/g	120	130	< 20	51
Cd µg/g	< 2	< 1	< 2	10
Cu µg/g	14	15	32	14
Sn µg/g	< 5	12	< 5	87

Results : determination of oxygen in Pb-Bi

	Supplier 1 O in µg/g	Supplier 2 O in µg/g
Without etching		68 - 53 - 58 - 83
Mechanical preparation by filing	5,1 - 1,7 - 5,3	25 - 27
Chemical etching 1	4,2 - 5,8 - 4,5 2,5 - 2,4 - 2,8 - 1,9	4,8 - 5,4
Chemical etching 2	8,0 - 9,1 - 3,2	5,8 - 2,4
Chemical etching 3	4,9 - 5,3 - 5,0	4,4 - 3,2 - 3,4
Nitric etching	1,9 - 6,6 - 5,7	1,4 - 2,3 - 1,8

Results : determination of oxygen in a calibrated sample

- **Oxygen in refined pure lead BCR n°55**

  Certified value 1.0 µg/g +/- 0.5 µg/g

  Prepared by machining on a lathe

- **Determination by the LECO technique**

  after chemical etching 1

  5.4 - 6.8 µg/g

Conclusion

- **The composition is respected by all the suppliers**
- **The segregations don't seem to change the alloy composition**
- **The suppliers don't warrant the metallic impurities contents in alloy**

In close prospect

- **lower the limit of detection of metallic impurities by ICP/Ms**
- **improve the procedure of determination of oxygen in samples**

Chemical etching

- **Chemical etching 1 : acetic acid + hydrogen peroxide**

$$CH_3COOH + H_2O_2 + N_2H_4, H_2O$$

- **Chemical etching 2 : sodium hydroxide + mannitol + hydrazine**

$$NaOH + C_6H_{14}O_6 +$$

- **Chemical etching 3 : acetic acid + hydrazine + eau**

$$CH_3COOH + N_2H_4 + H_2O$$

- **Nitric etching : nitric acid at 25 %**

FIRST STEPS IN THE DEVELOPMENT OF AN OXYGEN SENSOR DEVICE FOR Pb/Bi MELTS

L. Victori, J. Barceló, J. Abellà, F. Gascó, IQS

Abstract

A potentiometric device for oxygen determination in Pb/Bi melts has been developed. The reference electrode was In_2O_3/In. The sensor was Mo and the solid electrolyte was ZrO_2/Y_2O_3.

Experiences have been made in two types of atmospheres, over the Pb/Bi melt at 773K:ultrapure N_2 and air (20% O_2). The experiment was static, not bubbling gas through the melt.

In N_2 atmosphere, the partial oxygen pressure in the melt was $1.5 \cdot 10^{-41}$ N/m^2. This value corresponds approximately to the value of PbO equilibrium pressure.
With air atmosphere, the partial oxygen pressure in the melt was $2.4 \cdot 10^{-19}$ N/m^2.

Now we are working in the correlation between partial pressure and oxygen concentration in the Pb/Bi melt.

Firsts steps in the development of an oxygen sensor for Pb/Bi melts

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Introduction

◆ Need of an oxygen control for minimising corrosion in systems containing Pb/Bi melts.

⇓

Development of an electrochemical oxygen sensor

◆ Main types of electrochemical oxygen sensors for liquid metals [1]:

- Potentiometric
  - Galvanic cell with solid electrolyte (yttria, calcia or magnesia stabilised zirconia)
  - Used in metallurgy
- Amperometric
  - Withdrawn of oxygen from a sample by passing a current through an electrochemical cell with ceramic electrolyte.
  - Sampling process very complicated

Potentiometric oxygen sensor

◆Galvanic cell formed by two electrodes connected by solid electrolyte.

- Reference electrode:
  - metal / metal oxide mixture in a closed environment
  - its potential is function of the oxygen partial pressure in this closed environment.
- Working electrode
  - inert electrode
  - it measures the potential of the redox pair PbO/Pb, that is function of the oxygen partial pressure in the melt
- Solid electrolyte
  - yttria, calcia or magnesia stabilised zirconia

Theoretical

◆ Relationship E.M.F. vs. oxygen partial pressure[2]:

$$\Delta E = \frac{RT}{F} \ln \frac{p_e^{1/4} + p_{O2(ref)}^{1/4}}{p_e^{1/4} + p_{O2(Pb/Bi)}^{1/4}}$$

p_e: partial electronic conductivity of the solid electrolyte

$p_{O2(ref)}$: oxygen partial pressure in the reference electrode

$p_{O2(Pb/Bi)}$: oxygen partial pressure in the melt

p_e [2]:

$$\log p_e = \frac{-68400K}{T} + 21.59$$

$p_{O2(ref)}$: if the environment of the reference electrode is filled with a inert gas, $p_{O2(ref)}$ can only come from the decomposition of the metal oxide

$$x\,M + y/2\,O_2 \rightarrow M_xO_y \quad \Delta G_f^\circ$$

$$p_{O2(ref)} = e^{\frac{\Delta G_f^\circ}{RT}}$$

⇓

from ΔE we can obtain $p_{O2(Pb/Bi)}$

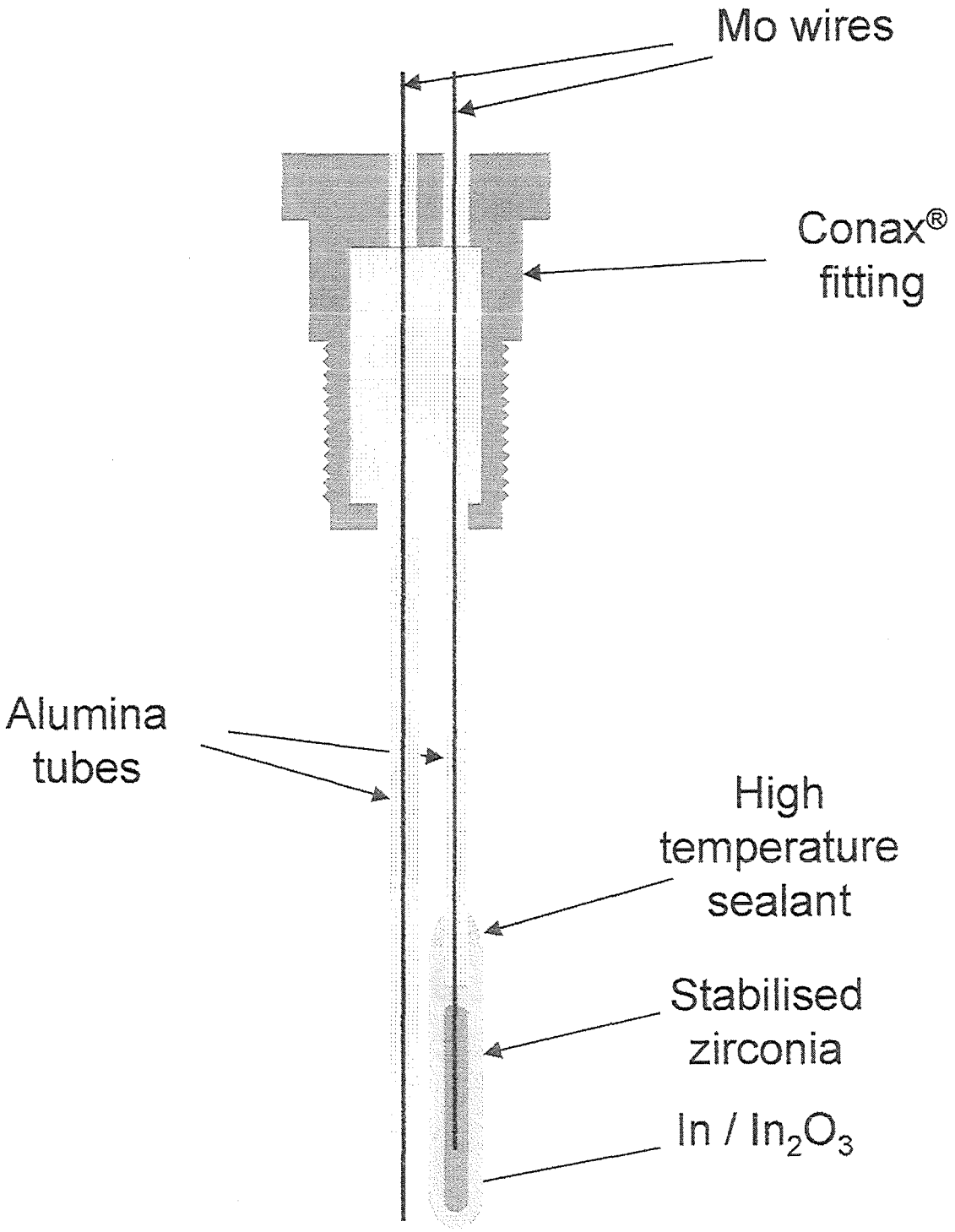
Experimental

- Sensor:
  - Reference electrode: In_2O_3/In
  - Working electrode: Mo
  - Solid electrolyte: Y_2O_3 stabilised-ZrO_2
- Lead-Bismuth alloy:

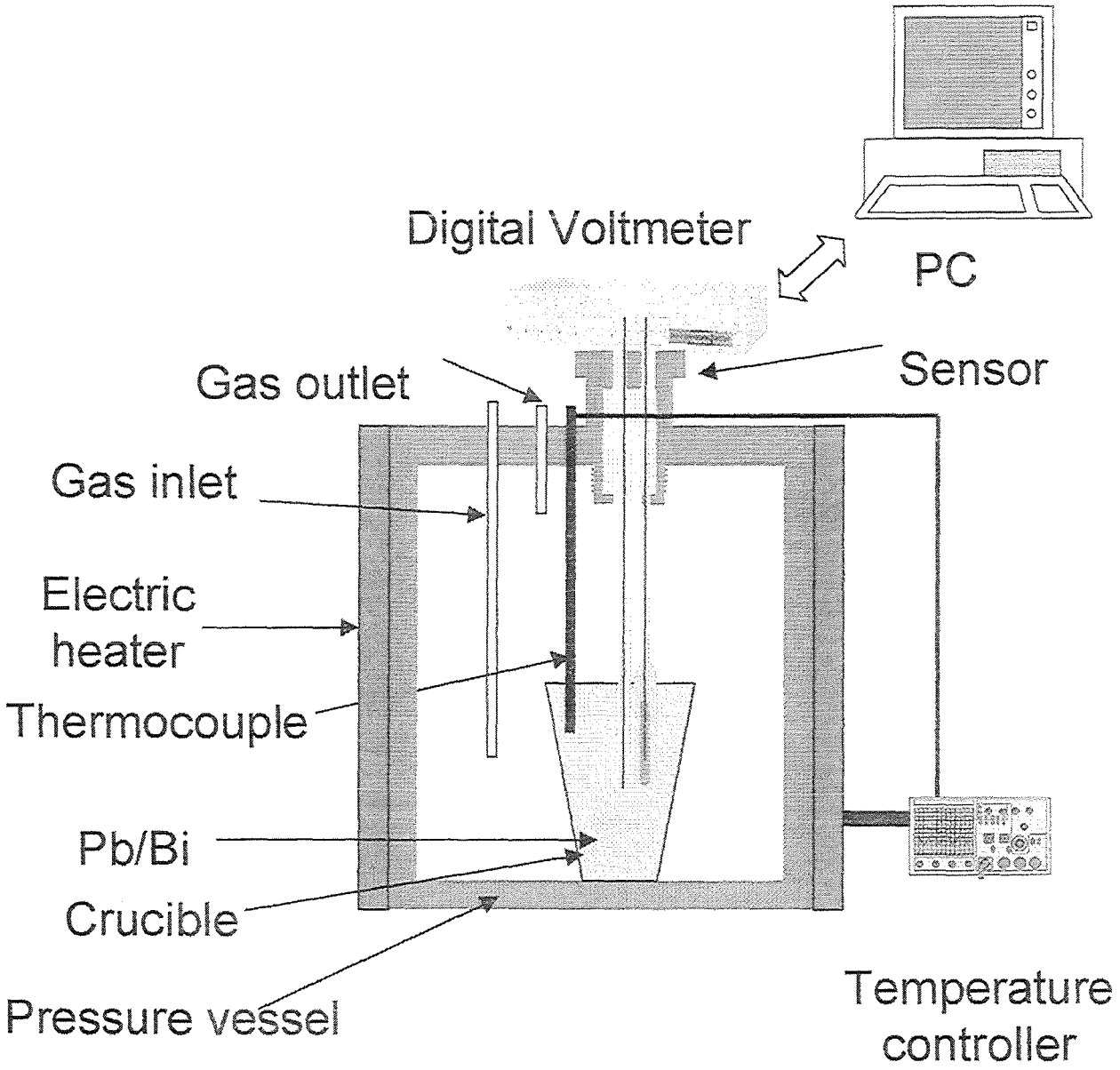
  Pb: 45%

  Bi: 55%
- Temperature: 500 °C
- Environment (the gases aren't bubbled through the melt) :
  - N_2 99.999%
  - Air (20% O_2)
- Duration of each test: 96 hours

Sensor design



Experimental setup



Results

◆ Stabilised E.M.F. Lectures for each environment tested:

- N_2 99.999%: 0.396 V
- Air (20%O_2): -0.455 V

Calculations (I)

$$\Delta E = \frac{RT}{F} \ln \frac{p_e^{1/4} + p_{O2(ref)}^{1/4}}{p_e^{1/4} + p_{O2(Pb/Bi)}^{1/4}}$$

- $p_{O2(ref)}$

Reaction of the reference electrode:

$$4/3\ In + O_2 \rightarrow 2/3\ In_2O_3$$

$$\Delta G^o_f\ (J/mol) = 3.237 \times 10^2\ T\ (K) - 9.272 \times 10^5$$

(validity range 400 - 1100 K)[3]

$$p_{O2(ref)} = e^{\frac{\Delta G_f^o}{RT}}$$

$T = 773\ K \qquad p_{O2(ref)} = 3.2 \times 10^{-31}\ Pa$

Calculations (II)

◆ N_2 99.999%:

$$\Delta E = 0.396 \text{ V}$$
$$\Downarrow$$
$$p_{O2(Pb/Bi)} = 1.5 \times 10^{-41} \text{ Pa}$$

in absence of O_2 in the environment, O_2 partial pressure comes from decomposition of PbO

$$2\,Pb + O_2 \rightarrow 2\,PbO$$

$$\Delta G^\circ_f \text{ (J/mol)} = 9.934 \times 10^1 \text{ T (K)} - 2.1872 \times 10^5$$

(validity range 400 - 1000 K)[3]

$$p_{O2(Pb/Bi)} = e^{\frac{\Delta G^\circ_f}{RT}}$$

$T = 773$ K $\qquad p_{O2(Pb/Bi)} = 4.4 \times 10^{-39}$ Pa

(theoretical value)

Calculations (III)

◆ Air (20% O_2):

$$\Delta E = -0.455 \text{ V}$$

$$\Downarrow$$

$$p_{O2(Pb/Bi)} = 2.4 \times 10^{-19} \text{ Pa}$$

the calculation of oxygen activity in lead/bismuth can be done according to the reaction:

$$\tfrac{1}{2}\, O_2 \rightarrow O_{solv}$$

the free-energy of solvatation is:

$$\Delta G_{solv} = -RT\ln \frac{a_O}{(p_{O2(Pb/Bi)})^{1/2}}$$

so oxygen activity in lead/bismuth (a_O):

$$a_O = (p_{O2(Pb/Bi)})^{1/2} e^{-\frac{\Delta G_{solv}}{RT}}$$

$$\Downarrow$$

we need reliable data (ΔG_{solv} of oxygen in lead/bismuth) in order to perform a correct conversion of $p_{O2(Pb/Bi)}$ to a_O

Calculations (IV)

- Examples of conversion of $p_{O2(Pb/Bi)}$ to a_O:

ΔG_{solv} kJ mol^{-1}	a_O mol m^{-3}	a_O mg kg^{-1}
-122	8.6×10^{-2}	1.4×10^{-1}
-132	4.07×10^{-1}	6.6×10^{-1}
-150	6.7	10.9

Provisional conclusions

◆ There is a good agreement between the value of oxygen partial pressure obtained by E.M.F. measurements in N_2 99.999% and the theoretical value calcuted using the free-energy of formation of PbO.

◆ It is necessary to obtain accurate data of ΔG_{solv} of oxygen in lead/bismuth in order to perform a correct conversion of $p_{O2(Pb/Bi)}$ to a_O.

References

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3. I. Barin, *Thermochemical Data of Pure Substances*, VCH, Weinheim (1989).

Studies on Lead-Bismuth physico-chemistry and associated technology

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Abstract

This presentation was intended to present R&D programme on the lead bismuth technology and the foreseen facility PLOMBIERES, manufactured then used to carry out the R&D programme.

The CEA R&D programme is focused on the following items :

1- control and removal of impurities,

It is necessary to investigate the consequences of the presence of impurities in lead-bismuth alloy, with regards to adequate and safe operation. The problems arising in lead-bismuth technology for target or reactor operation have to be solved on a long term basis by the choice of the policy of maintaining the liquid metal at its " maximal but feasible" purity ; this policy is summarized by five essential recommendations. It is necessary to establish the functional specifications of the purification systems, thus a characterization of the existing impurities will be based on the following items: continuous or discontinuous ingress, particulate or dissolved impurities, transfer behavior, concentration, main drawbacks related to interaction with structures, operation, contamination releases, instrumentation,... Kind of impurities investigated are : initial impurities before start-up, corrosion products, spallation products, ingress of impurities in operation such as air, coolant if different of Pb-Bi, ...One important point to underline is the necessity to obtain data on source terms, kinetics of production versus time, possible interactions between impurities,... After this step, we will propose adapted processes such as cold traps, getters, filters, Electro-Magnetic traps,...which will be investigated in term of efficiency, capacity, operability and flexibility then we will produce functional requirements for a future implementation on a lead-bismuth system : dynamic loop for target or a sub-critical reactor.

2- development and testing of oxygen control processes

We intend to evaluate various processes able to maintain the oxygen concentration at a constant value, in order to protect the structures against corrosion. The oxygen value will be defined by research teams involved in corrosion studies. The following processes : cold trapping, equilibration method, 'electrochemical pump' will be investigated and compared ; the most promising processes will be tested on a dynamic facility. We intend to focus our work on liquid solid equilibriums instead of gas systems.

3- development of sampling systems and the optimisation of the analytical methods

In order to be able to characterise the alloy composition, it is necessary to design an adapted dip sampler for analytical measurements and to optimize analytical methods for the characterization of the alloy composition and metallic impurities.

4- on-line oxygen meter validation

The development of a on-line oxygen-meter is necessary for experimental studies above mentioned and corrosion , thus it is necessary to dispose of such a sensor. For that, we have acquired industrial sensors (base of zirconia), then we evaluate the compatibility between ceramic and alloy, wetting characteristics and feasibility of the measurement in a static pot, finally we will carry out several tests on a dynamic facility, in order to identify the following parameters : accuracy, sensitivity to thermal shocks, time drift, ...Nevertheless indicious mounting also enables the risk of a thermal shock leading to a break in the ceramic to be limited

5- corrosion studies through kinetics measurements and investigation on the effects of the spallation products

Corrosion tests in stagnant or/and near isothermal conditions give an indication for preselecting materials but they do not allow to determine the maximum corrosion rate. To obtain a real determination of the kinetics, it is necessary to consider the alloy velocity, the thermal gradient (which generates mass transfer) and to purify the liquid (to supply pure liquid alloy, without corrosion products in the hot dissolution zone). Thus, it is foreseen to carry out dynamic tests. Moreover, the composition of the liquid target is expected to be modified as a function of time due to the formation of various products: light elements (H, He), fission products ($10<Z<60$) (several tens of ppm/year) and spallation products ($60<Z<84$) (several thousands of ppm/year) ; therefore, the corrosion process could be modified and has to be investigated in these realistic conditions. Finally, it is foreseen to test protected samples (in situ protection and coatings) in dynamic alloy.

A part of the programme described previously could be carried out on a lead-bismuth dynamic facility called PLOMBIERES, which is being designed. This experimental facility is foreseen to achieve physico-chemistry, corrosion and technology related R&D programmes. The current design stage shows some of the following orientations :

- structural materials : adapted to the operating temperature (austenic steels for low temperature, and ferritic steels for high temperature) and protected with a passivation process (oxide layers formation under a defined oxygen activity).
- quality control policy in order to adjust the oxygen activity to a defined value and to reduce a possible build-up of slags. The reference process for operating stage is the injection of a gaseous mix which could have either an oxidising or a reducing potential (steam, hydrogen and inert gas mix in various composition).
- one operating team and several experimental teams in order to maximise the operating time per year (load factor).

The sketch, current flowsheet and characteristics of the PLOMBIERES loops have been presented. Now the design is going on.

Conclusions :

It was on both the basis of their properties and acquired experience in the field of liquid metals, that a proposal was made to select the Pb alloys (mainly Pb and Pb-Bi) as the spallation material and eventually coolant. Nevertheless, several problems have to be solved. Even if a large experimental feedback has been obtained by the Russians for a very specific application, the possibility to use lead-bismuth for ADS has to be largely investigated and compared to other solutions, namely solid targets, gas or sodium coolant. The studies carried out at Cadarache will be a contribution to the European effort, in the frame of the 5th Framework programme, for the development of ADS systems.

Studies on Lead-Bismuth physico-chemistry and associated technology

C. LATGE*, J. L. COUROUAU*, F. BARBIER, L. CACHON***

***DRN-DER-STPI**

**** DTA-DECM-SCECF**

INTRODUCTION

- Heavy liquid metals candidates for target of ADS : Pb, Pb-Bi, Pb-Mg, Hg,...
- Pb alloys were selected for the following reasons :
  - lowest capture cross sections for both thermal and fast neutrons,
  - Pb-Bi eutectic have the lowest melting temperature (125°C), thus the energy input will therefore be limited to maintain alloy in the liquid state in the absence of the fuel bundle,
  - high boiling temperature(1670°C) considerably reduces the risk of local boiling in nominal conditions and confines the risk of vaporization,
  - the Pb-Bi eutectic has been the object of technological implementation as a coolant for Russian submarine reactors of small dimensions,
  - the Pb-Bi liquid eutectic has been selected as the spallation material of the second SINQ target at PSI.

Background

- Various manifestations of the interactions between material and structures : dissolution, temperature gradient mass transfer, impurity reactions, intergranular attack, embrittlement,...
- Moreover , due to foreseen large temperature gradient, mass transfer can be very damaging due to dissolution in the hot zone and deposition in the cold zone ; it induces transfer of particles that could initiate plugging, blocking,...and contamination.
- In hybrid systems, spallation products can modify the physico-chemical properties of the liquid, and consequently the corrosion process,
- Moreover, it is necessary to investigate the consequences of the presence of impurities with regards to adequate and safe operation ; it is necessary to demonstrate that this technology can be mastered in large systems.

Main objectives of the programes to be carried out at Cadarache

- Control and removal of impurities,
- Development and testing of oxygen control processes for liquid Pb-Bi,
- Development of sampling systems and optimization of analytical methods,
- Industrial oxygen-meters validation,
- Analysis of consequences for operation of large systems.

Control and removal of impurities

- Objective : the problems arising in LBE technology have to be solved on a long term basis by the choice of the policy of maintaining the liquid metal at the''maximal but feasible'' purity :

  - supply high purity lead-bismuth of ''nuclear grade'' ; this grade has to be specified in the near future,
  - clean the structures and gas before filling,
  - carry out a purification campaign with adapted processes in order to reach the suitable steady-state values for relevant compounds, including oxygen, (start-up purification)
  - Ensure the continuous monitoring of LBE quality as regards relevant impurities such as some spallation products i.e. compounds to be associated with oxygen and also radioactive compounds able to increase the contamination of the whole system, tritium,...
  - Limit the introduction of impurities in operation or during handling and/or maintenance operations, in the liquid metal or into the cover gas.

Characterization of impurities

- Continuous or discontinuous ingress,
- kinetics of production, ingress,...
- particulate or dissolved impurities,
- transfer behavior,
- allowable concentration,
- main drawbacks related to interaction with structures, operation, contamination releases,...

Impurities Removal

- The characterization of impurities will allow functional requirements of purification systems to be established.
- An integrated purification system, with adequate processes will be suggested then investigated.
- Processes to be investigated : filtering, cold trapping, getters, EM traps,....
  - Objectives : establish reliability, efficiency, capacity, operability and flexibility,...

Oxygen control

- For the in-situ protection of walls, and moreover, in order to avoid any precipitation of unstable species, it is necessary to control the oxygen activity. The required activity has to be defined in order to insure a safe operation i.e. the structure protection in hot and cold parts of the circuits.
- The following processes : cold trapping, equilibration method, electrochemical pump will be investigated.

Development of sampling systems and optimization of analytical methods

- **The following actions are foreseen :**
  - **design of an adapted dip sampler for analytical measurements,**
  - **optimization of analitical methods for :**
    - **characterization of the lead alloy composition (calorimetry,, X analysis, atomic absorption, X fluorescence,**
    - **optimization of analytical methods for the characterization of metallic impurities : atomic absorption, ICP-MS,...**
    - **identification and validation if necessary of methods for relevant spallation products.**

Industrial oxygen-meter validation

- Objectives :
  - to evaluate compatibility between cermet zirconia and alloy,
  - to demonstrate feasibility of measurements,
  - to establish accuracy and reliability of measurements,
  - to decrease sensitivity to thermal shocks by effective mounting,
  - to identify signal time drift, if there is one.

Corrosion Studies on a large scale dynamic facility (DTA-SCECF)

- **corrosion kinetics determination**
  - **representative to real operating conditions**
  - **influence of the spallation products on the stability of the protection**
- **measurement the mass loss versus time : samples**
- **Main constraint :**
  - **long duration of the experiment during which the stability of the operating conditions and of the liquid quality must be set to fixed values**

  ⇨ **experimental test section in parallel**

An experimental facility for the overall LBE studies : Plombières

- **Objective : make available an LBE dynamic facility in order to achieve the R&D programmes**
- **support**
  - **from the sodium knowledge**
  - **from the Pb-17Li knowledge**
  - **from the Russian submarines feedback**
- **functionnal analysis so that the loop can answer all of its objectives**
- **typical project methodology with the general design and the detailed design stages**
- **First operation first planned June 2001**

Conceptual orientation about the structural material

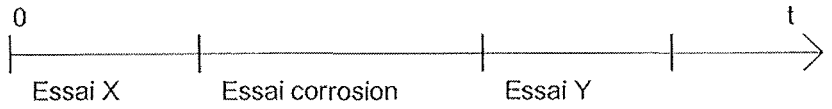
- adapted to the operating temperature
  - Austenitic steel for cold section (<300°C)
  - 9Cr 1Mo for the hot leg (Si alloying element ?)
- in-situ passivation process of the structural steels
  - with the formation of an oxides layer
  - at start-up, periodical mode, or self-healing
  - gaseous mixture to set the oxygen potential : hydrogen, steam, and inert gas

Conceptual orientation for LBE quality control

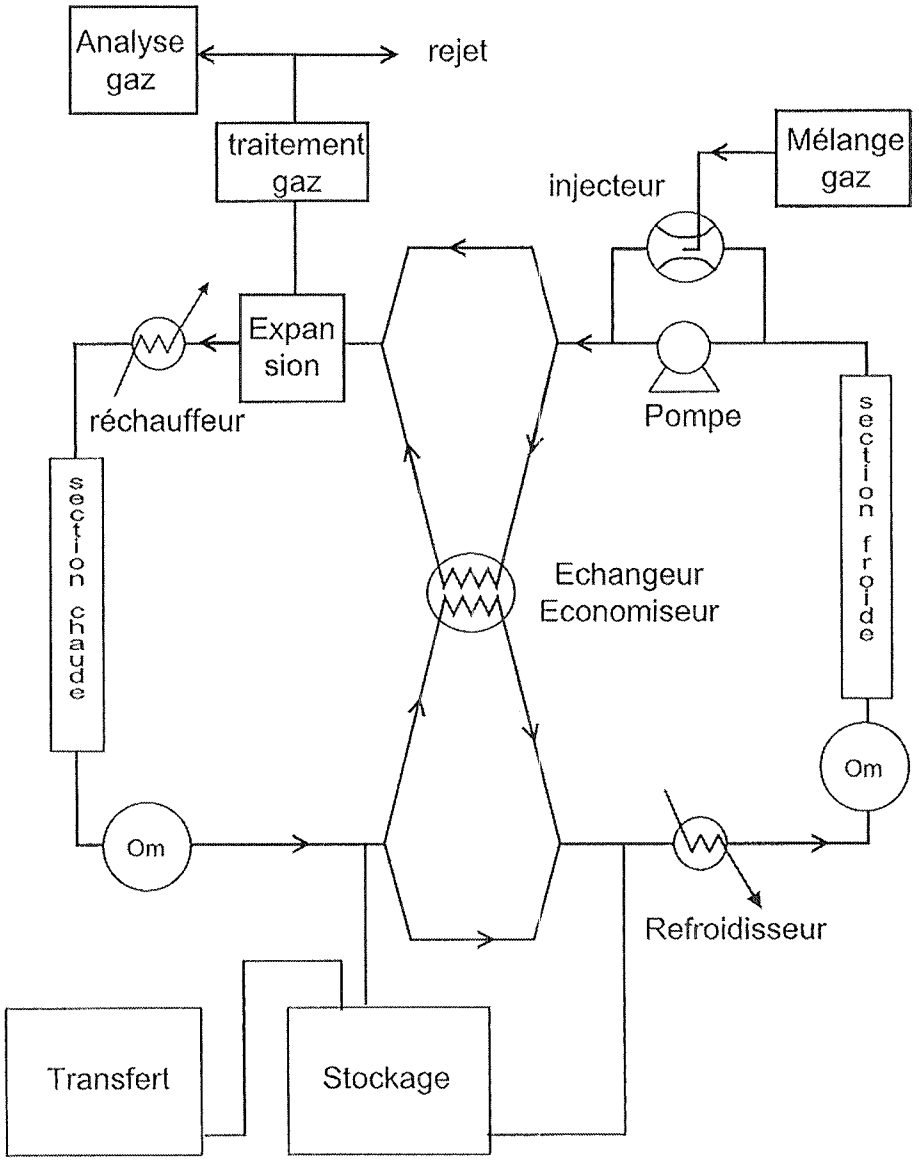
- **object :**
  - **reduce a possible scories built-up : regeneration of the LBE**
  - **adjust the O activity for the structure passivation process**
- **process : gas injection of the ternary mixture in various relative proportions for**
  - **either reductive gas mix**
  - **or oxidizing gas mix**
- **need specific measurement devices**
  - **oxygen activity in liquid metal**
  - **hydrogen level in the gas phase**
  - **liquid metal sampler**

Conceptual orientation : operating conditions

- various experimental sections in parallel
- one operating team, several experimental teams
- experiments taking place in series, except when there are no risks of interactivity, as for instance the on-line meter experiments
- **Main difficulty : physico-chemistry control of the LBE**
  - any loop, whatever its object, must focused on that particular issue



Plombieres sketch



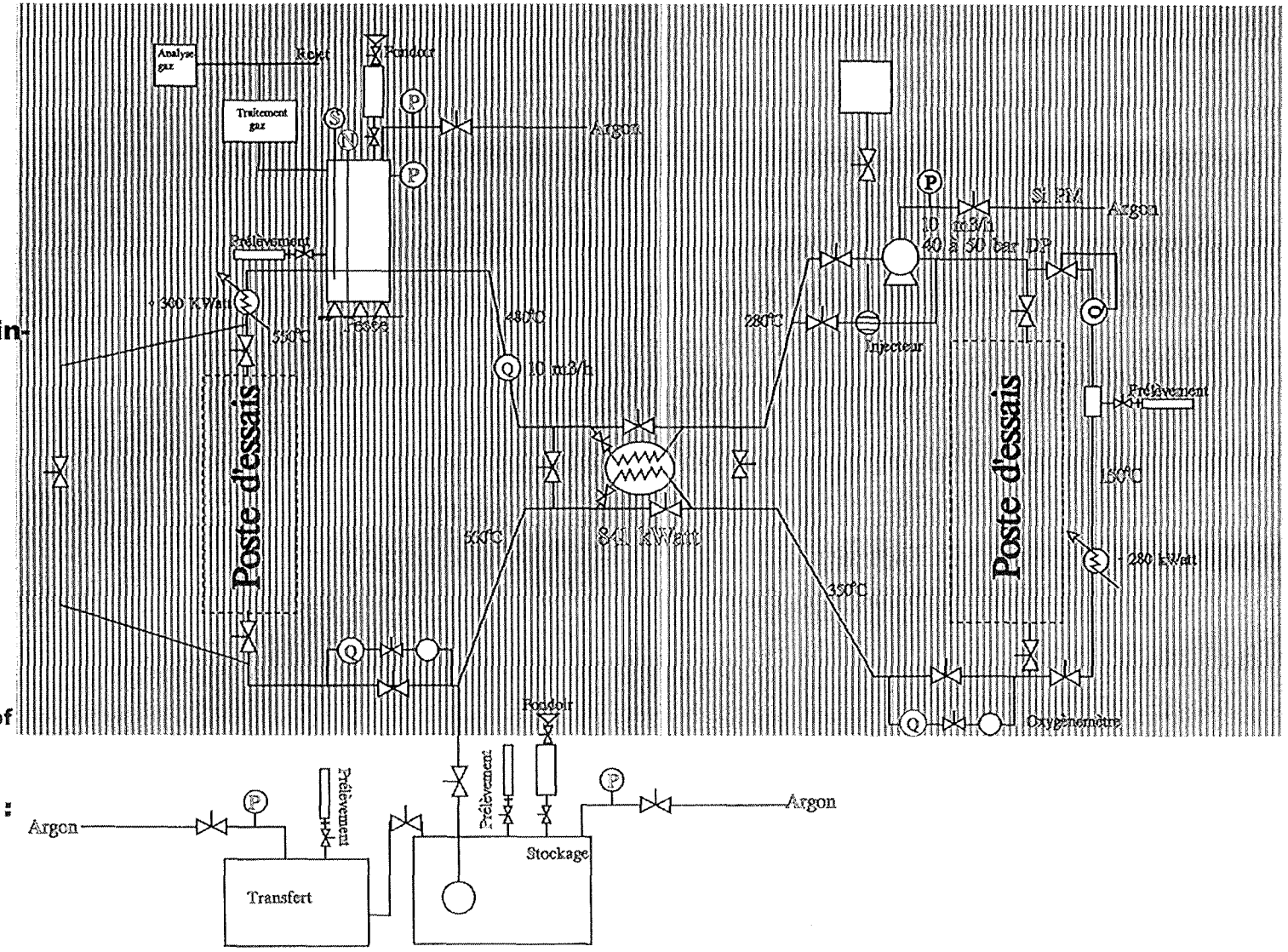
Plombieres start-up operations

- Validation of all basic elements
  - instrumentation : calibration of flowmeters, pump characteristics, pressure meter, level indicators, ...
  - sampling system
  - gas systems
- validation of the various processes set in the common operating mode of the loop
- then, experimentation

PLOMBIERES : mains characteristics and flowsheet

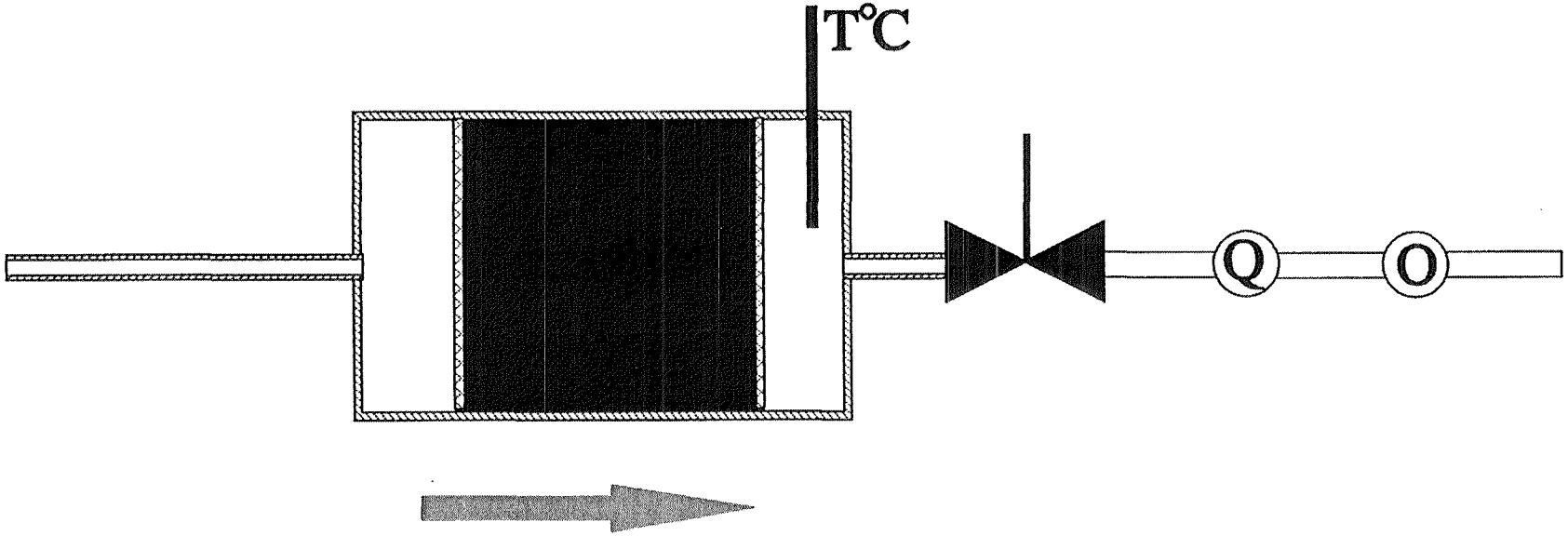
- **Objectives :**
  - **Physico - chimistry**
  - **instrumentation and technologies**
  - **corrosion**
  - **conceptual option : thermohydraulics and in-service inspection studies**

- **Characteristics :**
  - **Q_{max} = 10 m^3/h**
  - **hot leg : 550°C,**
  - **cold leg : 350°C,**
    - **150°C on a fracttion of the flowrate**
  - **storage / transfer tank :**
    - **300 litres.**



Physico-chemistry test section : example

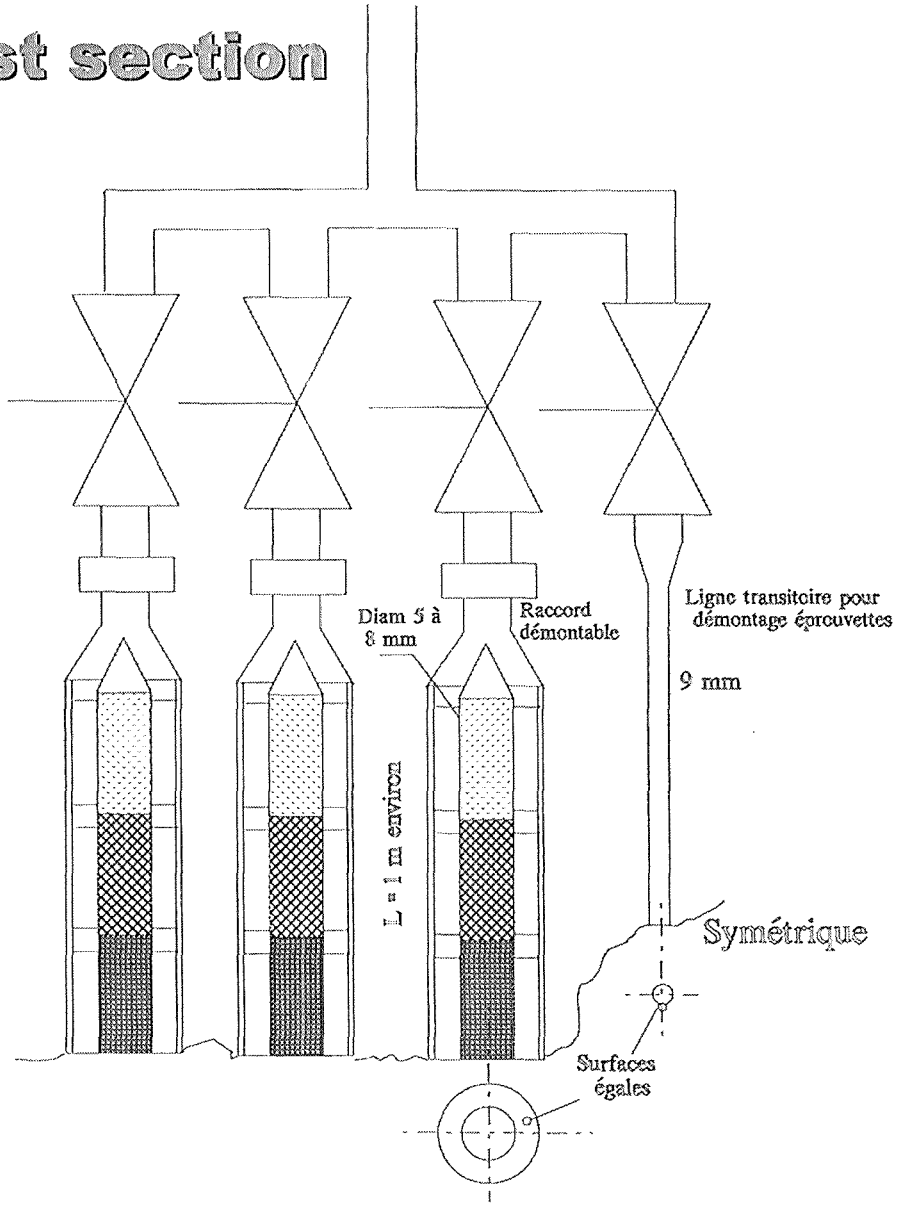
- ***equilibration method based on the oxygen solubility in LBE :***
  - **typical mass transfert unit (PbO, ...)**
  - **parameters to be studied : liquid metal speed, temperature, reactive surface , ...**
  - **auxiliary need : purification unit, specific measurement system (O, ...)**



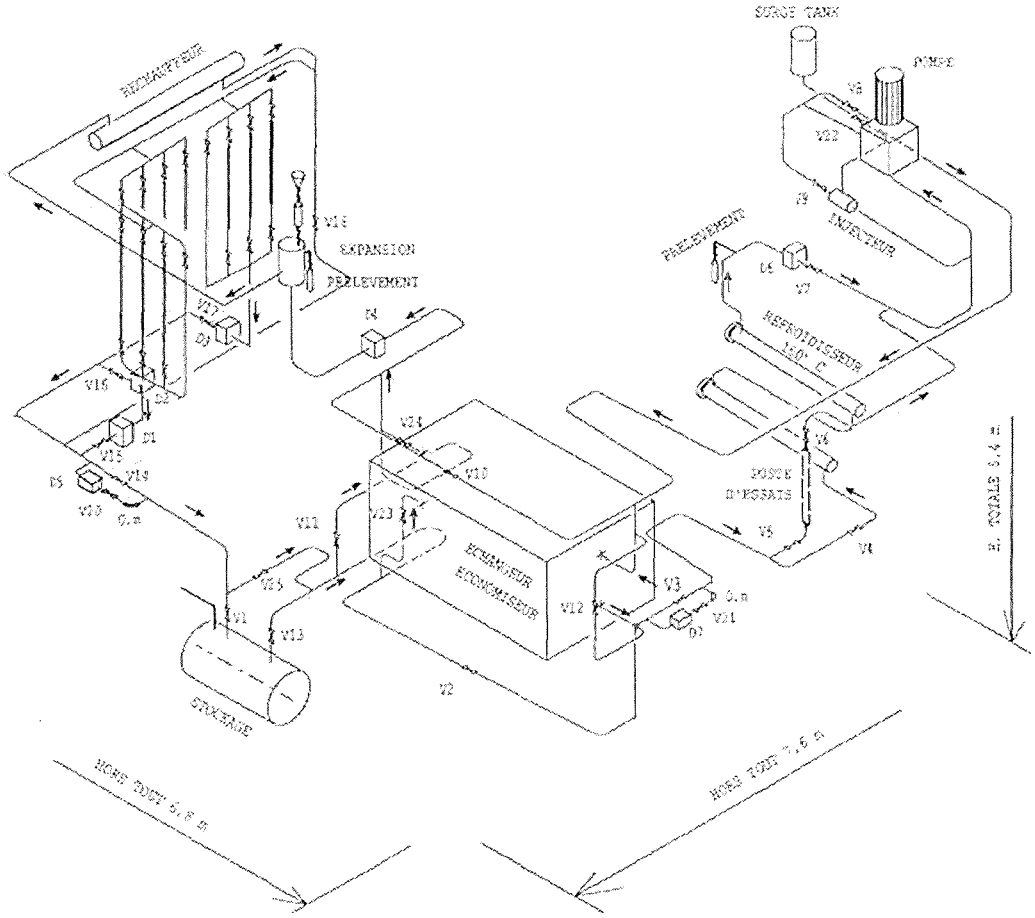
Corrosion experimental test section

- *sketch of one corrosion test section*

  - **1 module : one liquid specific flow rate (1 à 5 m/s), regulated by one flow meter and one regulation valve.**
  - **1 test pipe for 1 time.**
  - **each test pipe can be taken apart when the loop is in operation**



Isometric drawing of the PLOMBIERES project



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Conclusions

- **The possibility to use lead-bismuth for ADS has to be largely investigated and compared with other solutions.**
- **The studies carried out at Cadarache will be a contribution to the European effort, in the frame of the 5th Framework programme.**