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COMPATIBILITY OF 316L STAINLESS STEEL WITH TRITIUM BREEDERS FOR FUSION REACTORS

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I/ Introduction

Compatibility problems with structural materials are a concern for the choice of the tritium breeder for fusion reactors. In the frame of the European Programme on Fusion Technology, two types of blankets are considered : liquid (eutectic lithium-lead alloy at 0.68 wt % Li : 17Li83Pb) and solid (lithium aluminate or silicate) breeders. This paper is devoted to compatibility studies of 316L stainless steel with 17Li83Pb alloy and γ-$LiAlO_2$ ceramic.

II/ Corrosion of 316L stainless steel by 17Li83Pb liquid alloy

Two types of experiments are carried out :

- tests in small loops for an approach of the utilization temperature of 316L stainless steel,
- tests in "CLIPPER" loop in order to determine the corrosion kinetics and to study the influence of liquid alloy purification and applied stress on corrosion.

II.1 Tests in small convection loops

II.1.1 Experimental

The tests are carried out in small square thermal convection loops (fig 1) entirely made of 316L stainless steel /1/.

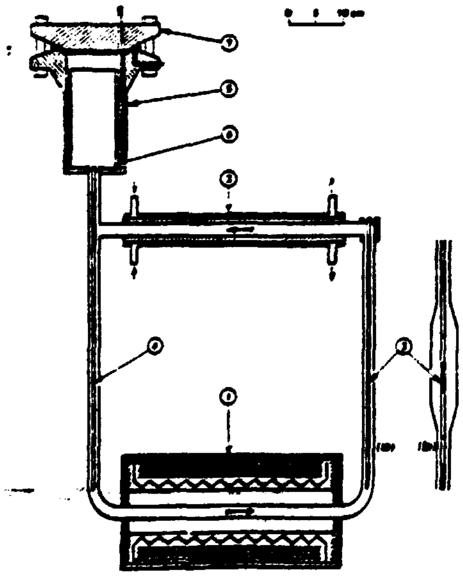


Fig. 1 : Drawing of the small thermal convection loops :

(a) test section for 450°C compatibility test
(b) test section for 400°C compatibility test

1. furnace
2. water jackets
3. hot leg specimen rod
   (▭ fully annealed 316L S.S.
   ▬ 20% cold-worked 316L S.S.)
4. cold leg specimen rod
5. surge tank
6. reversed container
7. flange with metallic seal and weldable leaps

The composition of 316L specimens and the nominal operating conditions are summarized on tables I and II. Two metallurgical states have been considered : fully annealed and 20% cold-worked. Typical aspect of eutectic lithium-lead alloy is shown on figure 2. After test, each loop is entirely dismantled, allowing to observe the specimens and also the tube of the loop.

Table I : Composition of 316L S.S. specimens (wt %)

Element	Reference 316L S.S.
Fe	65.18
Cr	17.44
Ni	12.33
Mo	2.3
Mn	1.82
Cu	0.2
Si	0.46
Co	0.17
S	0.00125
P	0.0265
Ta	0.01
C	0.024
N	0.06
B	0.0008

Table II : Nominal operating conditions of the small thermal convection loops

test	1st (450°C-test)	2nd (400°C-test)
Isothermal hot leg temperature (°C)	450	400
Isothermal cold leg temperature (°C)	390	340
Flow velocity ($m.s^{-1}$)	0.12*	0.12* 0.03**
Test duration (h)	3000	3000

* in the 20 mm diameter sections
** in the 40 mm diameter section

II.1.2 Results

At both temperatures, the specimens placed in the isothermal hot leg appear to be covered by a porous corrosion layer, constituted of ferrite and of a network of 1 to 2 µm wide channels filled with lithium-lead alloy (fig 3).The rate of ferrite formation is strongly temperature-dependent ; as shown on table III, the ferritic layer is, after 3000-hour exposure, approximately 3 times thicker at 450°C than at 400°C. In both cases, no significant downstream effect is observed along the isothermal hot leg. The influence of the other investigated parameters is less pronounced. If noticeable at 450°C (20% increase in ferrite thickness), the effect of cold-working is not obvious at 400°C, remaining in the scattering of measures. As for the lithium-lead velocity, results obtained at 400°C do not reveal a significant variation of corrosion rate between 3 and 12 $cm.s^{-1}$. Morphologically the ferritic layer appears to be very regular at 450°C and coarser at 400°C. At both temperatures the interface between ferrite and austenite is planer for fully annealed stainless steel than for 20% cold-worked steel which is preferentially attacked along the gliding lines. Differences between the loss of sound metal, calculated from weight losses measured after lithium-cleaning, and the thickness of the ferritic layer suggest that this layer is corroded on its external front while it grows at its interface with the matrix. The adherence of the ferritic layer is

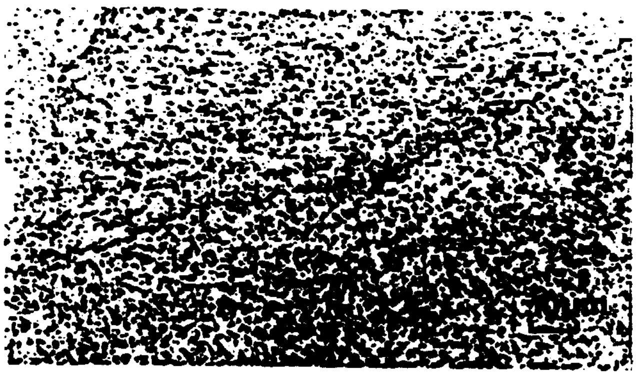
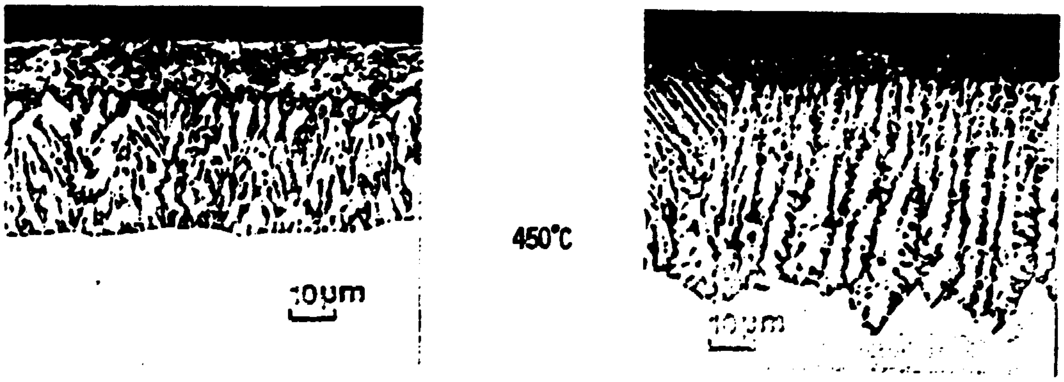
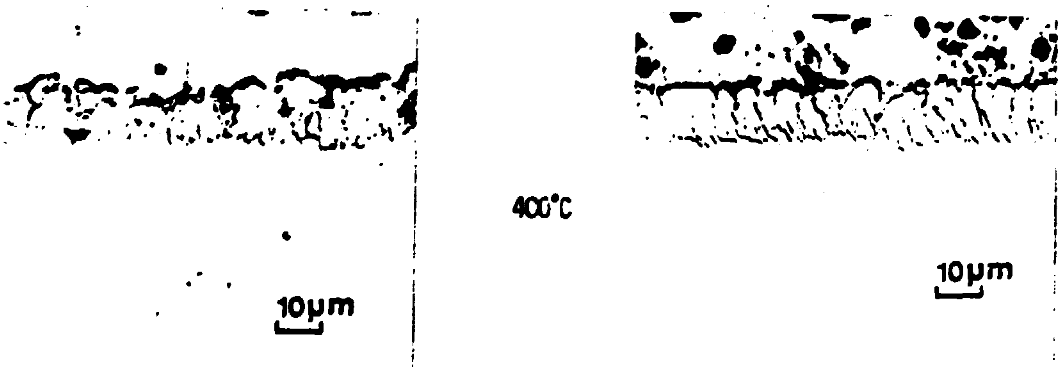


Fig. 2 : Typical aspect of eutectic Li-Pb alloy



fully annealed
$v = 0.12\ m.s^{-1}$

20 % cold-worked
$v = 0.12\ m.s^{-1}$



fully annealed
$v = 0.12\ m.s^{-1}$

fully annealed
$v = 0.03\ m.s^{-1}$

Fig. 3 : Cross section micrographs of 316L S.S. specimens exposed for 3000 hours at 450 and 400°C in the small convection loops

certainly limited, illustrated by its complete spallation when specimens are lithium-cleaned in order to determine sound metal losses.

Table III : Corrosion depth of fully annealed and 20% cold-worked 316L stainless steel at 450 and 400°C

Test	Thickness of ferritic layer (µm)		Loss of sound metal (µm)	
	f.a. 316L	20% c.w. 316L	f.a. 316L	20% c.w. 316L
450°C - 3000 h v = 0.12 $m.s^{-1}$	33 ± 5	40 ± 5	39 ± 5	54 ± 5
400°C - 3000 h v = 0.12 $m.s^{-1}$	10-15 (average :12)	10-20 (average :12)	not determined	
v = 0.03 $m.s^{-1}$	10-15 (average :12)	not determined		

Analysis of ferrite by electron microprobe technic put in evidence the following points (table IV) :

- an important nickel and chromium depletion,
- average compositions very similar at both temperatures, apart from nickel,
- at 450°C, a slight concentration gradient of nickel from the inside to the outside of ferrite.

Though the solubility of nickel in lead and also in lithium is much higher than the chromium one, the composition of ferrite shows that the mass transfer is somewhat equivalent for both metals. That means that the solubility level is probably not the prime factor in the processus of corrosion.

Table IV : Average composition of the ferrite (wt %)

Element	Fe	Cr	Ni	Mo	Mn	Si
450°C - 3000 h exposure	84.1	5.3	2.6	2.3	0.01	0.5
400°C - 3000 h exposure	87.1	5.0	0.7	2.5	0.07	0.5

II.1.3 Conclusion

These results which corroborate the ones obtained in other laboratories /2,3,4,5,6,7/, point out the relatively high corrosion rate of 316L stainless steel by flowing 17Li83Pb especially at 450°C. This being so a temperature higher than 400°C is probably not realistic for 316L stainless steel utilization and we have decided to investigate more thoroughly the behaviour of this material at 400°C by means of a larger corrosion loop "CLIPPER", described below.

II.2 Tests in CLIPPER loop

As shown on figure 4, the CLIPPER loop includes a main circuit (thermal convection loop) and a derived circuit for the purification by cold-trapping. Such a facility permits to :

- study the influence of alloy purification on 316L stainless steel behaviour,
- achieve corrosion kinetics data : for this purpose, both isothermal legs are fitted with mechanisms allowing to immerse or emerse specimen rods without loss of tightness ; during the test, one rod remains completely immersed (study of the downstream effect) ; the other one is partly emersed at given time intervals (study of the kinetics of mass transfer),
- study the influence of a stress on the 316L stainless steel corrosion : three devices allow to carry out uniaxial tensile tests in flowing and anisothermal conditions.

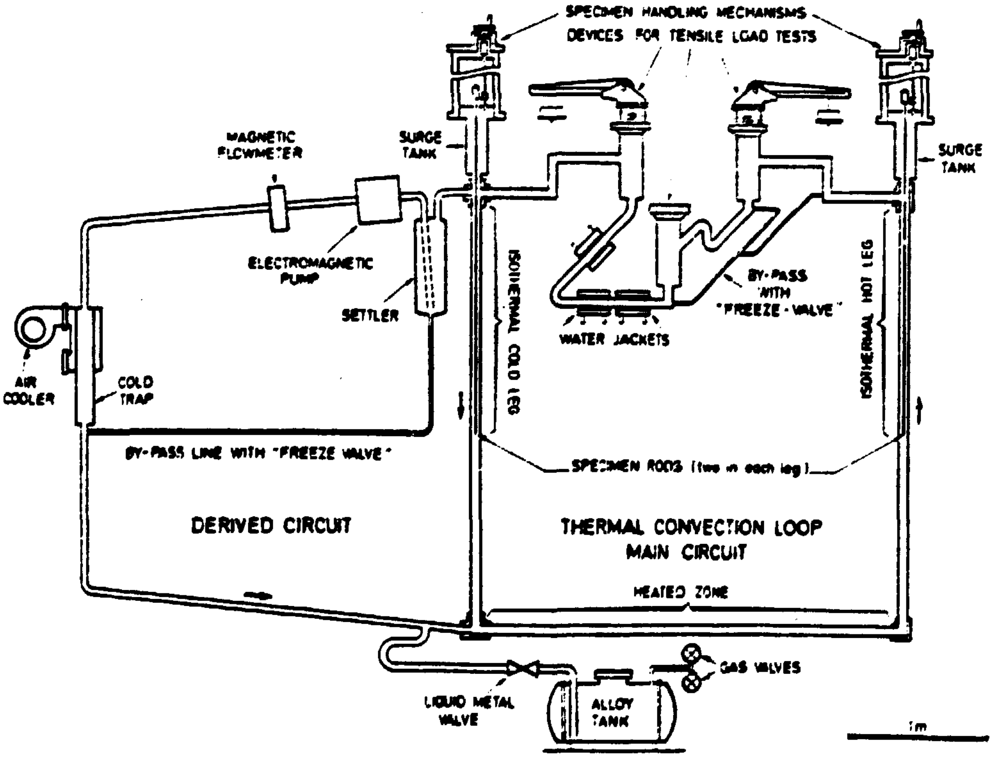


Fig. 4 : Drawing of CLIPPER loop

Up to now, this loop has worked during 4300 hours, in the following conditions :
- isothermal hot leg temperature : 400°C
- isothermal cold leg temperature : 340°C
- cold trap temperature : 250°C
- velocity in the main circuit : 10 cm.s^{-1}
- flow rate in the purification circuit : 25% of the flow rate in the main circuit.

Examinations of specimens treated in the first 3000-hour exposure corrosion test are in progress.

III/ Compatibility of 316L stainless steel with γ-$LiAlO_2$ ceramic

The compatibility of lithiated ceramics with structural steels may present two aspects :
- solid-solid reactions between the steel and the ceramic, which essentially result from the presence of impurities in the ceramic ; they are studied in containers,
- solid-gas reactions, which result from the presence of impurities (mainly H_2O) in the sweeping helium utilized for tritium extraction ; they are studied in a helium circuit.

III.1 Contact tests in containers

III.1.1 Experimental

Contact tests are carried out in containers sealed by electron beam welding under vacuum. Sandwiches of fully annealed 316L stainless steel and $LiAlO_2$ disks are maintained in contact by means of a metallic mass, ensuring a pressure of 2 g.mm^{-2} (fig 5). The composition of 316L stainless steel is given on table I. Steel specimens are simply degreased before test. $LiAlO_2$ ceramics, prepared by CEA /8/, are dehydrated before test using two procedures : under dynamic vacuum at 400°C during 12 hours or under air at 600°C during 24 hours ; after dehydration, ceramics are handled in a glove box with dry atmosphere.

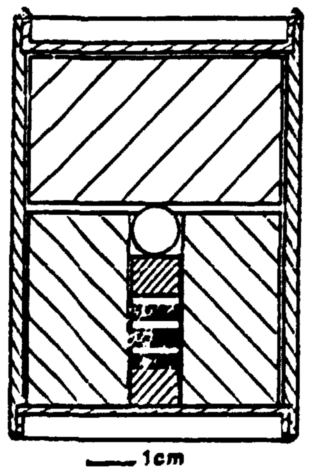


Fig.5 : Container for ceramic-steel contact test

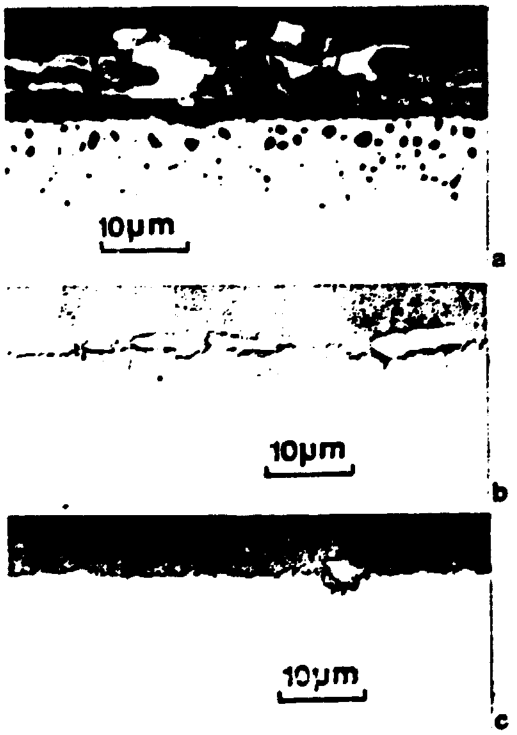
▭ S.S specimens
▬ ceramic specimens

III.1.2 Results

Up to now, a series of 500-hour contact tests has been carried out at 600°C and at 700°C.

The main phenomenon revealed by these tests is a sulphidation of the stainless steel contact surface, due to a sulphate impurity contained in alumina utilized for the preparation of the ceramics. Morphologically, the interaction between 316L stainless steel and $LiAlO_2$ containing 2000 and 500 ppm sulphate, illustrated on the figure 6-a and b, is characterized by the presence of three zones on the contact surface of the steel :

- an outer layer of irregular thickness, poorly adherent to the matrix, with large metallic and non metallic grains, more compact at 600°C than at 700°C,
- a very thin inner layer, with small grains,
- a penetration zone.



Sulphate content (ppm S)	Thickness of corrosion (µm)		
	outer layer	inner layer	penetration zone
2000	3-6	1-2	0-13
500	0-5	<1	0-4
≈0	<1	0	0

Fig. 6 : Cross section micrographs of 316L S.S. specimens in contact with $LiAlO_2$ during 500 hours at 700°C. Influence of ceramic sulphate content

As shown on table V, the nature of corrosion products depends on temperature and on sulphate content of ceramics. Corrosion extent, reported on the figure 6 for 700°C, is only slightly dependent on temperature between 600°C and 700°C and on dehydration procedures of the ceramics. If the weight variations remain always very low, sulphur penetrations may nevertheless affect resistance of the metallic material. On the other hand, no evidence of corrosion was detected with sulphate-free $LiAlO_2$ specimens (fig 6-c).

Table V : Identification by electron microprobe analysis of the elements present in 316L corrosion products

Test conditions	sulphate content (ppm S)	outer layer	inner layer	penetration zone
700°C-500 h	2000	Fe metal Cr,Mn,S,0	Si,0	Mn, S
	500	Fe metal Cr, Mn, S	Si,0	S
600°C-500 h	2000	Fe + S Cr + 0	Cr, 0	S
	500	Fe+Cr+S	Si, 0	S

III.1.3 Conclusion

These simple contact tests have completely play their role of characterization of $LiAlO_2$ fabrications, allowing to improve them on the corrosion point of view : the first aluminates prepared, which contained approximately 2000 ppm then 500 ppm sulphur were no longer used and sulphate content has been drastically decreased down to 100-200 ppm sulphur. With lower sulphur level, the tritium extraction efficiency would be affected.
These tests must be completed with :

- long term contact tests with improved γ-$LiAlO_2$
- solid-gas reaction studies, in a helium circuit described below.

III.2 Tests in a helium circuit

The device utilized for these tests (fig 7) includes mainly :

- a system for supplying wet helium
- an hygrometer
- a quartz test section

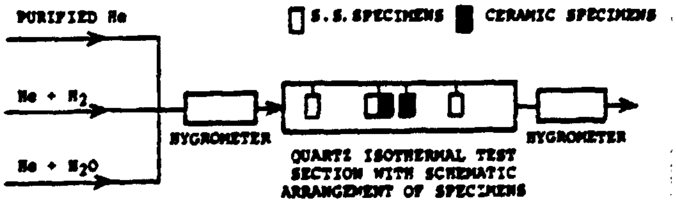


Fig. 7 : Schema of impurity-controlled He circuit for solid-gas reactions studies

Helium wetting is performed by oxidizing the whole or a part of a helium-hydrogen mixture on a bed of copper oxide-rare earth oxide pellets and by mixing with purified helium. This system allows to keep constant the oxidizing potential, fixed by the hydrogen-water vapor ratio. A special arrangement of specimens in the test section permits to study the different possible interactions between steel, ceramic and impurities of helium (fig 7) :

- steel-impurities interaction
- ceramic-impurities interaction
- steel in contact with ceramic-impurities interaction
- interaction between steel and gaseous products resulting from the reaction of ceramic with the impurities.

Experimentations are in progress.

IV/ General conclusion

Whatever the tritium blanket may be, compatibility problems with 316L stainless steel occur. The first step of our study has permitted, by means of simple experiments, to identify the main corrosion problems i.e. ferrite formation in the presence of 17Li83Pb and sulphidation when in contact with $LiAlO_2$. The second step, already undertaken in more complex facilities, should allow to carry out thorough investigations in order to achieve data required for NET blanket design.

Acknowledgements

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