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EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM

**STABILITY AND COMPATIBILITY OF HYDROGEN
BARRIERS APPLIED TO ZIRCONIUM ALLOYS**

by

**F. BROSSA, F. COEN, H.W. SCHLEICHER
and G. VOLTA**

1969



**Joint Nuclear Research Center
Ispra Establishment - Italy**

**Metallurgy and Ceramics
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Methods of deposition of different coatings and their efficiency as hydrogen diffusion barriers are described.

It was found that the most promising barrier against hydrogen diffusion is an Al-Si coating.

Results of compatibility tests between Al-Si and Zircaloy 2 are reported.

Different methods have been tried to obtain efficient coatings on laboratory scale.

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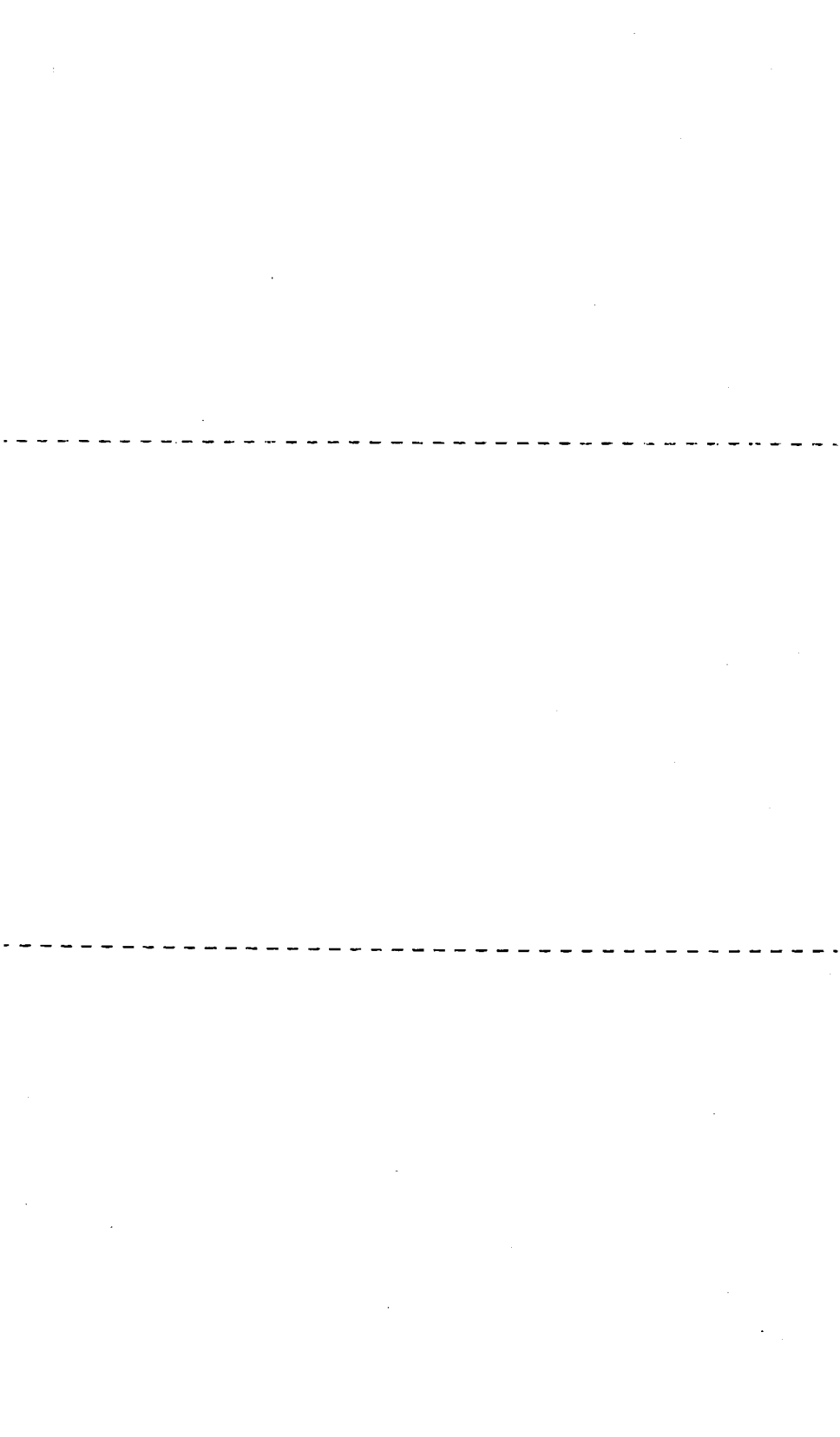
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SUMMARY

Many coatings have been tried to protect against hydrogen pick-up Zircaloy 2 in contact with terphenyl.

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Different methods have been tried to obtain efficient coatings on laboratory scale.

KEYWORDS

ZIRCALOY
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CORROSION PROTECTION
BRITTLENESS

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STABILITY AND COMPATIBILITY OF HYDROGEN BARRIERS APPLIED TO
ZIRCONIUM ALLOYS

1. INTRODUCTION. (*)

The possible use of zirconium alloys as structural and cladding material in organic cooled reactors has been studied for several years.

First results had shown that zirconium based alloys can absorb large amounts of hydrogen and thus embrittle considerably (1)(2).

More recent studies (3)(4)(5) indicate that by carefully controlling the amount of impurities present in the organic liquid the hydrogen pick-up of the zirconium alloys can be substantially reduced. If the chlorine content is kept below 0,2 ppm and the water content remains in the order of 100 ppm the behaviour of these alloys in terphenyl is considerably improved. The hydrogen pick-up of commercially available alloys such as zircaloy 2 is however still too high.

Zr-2,5% Nb alloy and ozhennite (Sn 0,2 - Fe 0,1 Ni 0,1 - Nb 0,1 - Ti 0,1) are less hydrided, but could be used only for relatively short times. New zirconium based alloys resistant to hydrogen pick-up will probably become available in the future, for the moment none of them is produced on industrial scale. A careful control of the impurity content of the terphenyl will in any case always be necessary.

The possibility of coating the surface of zirconium alloys with a material impermeable to hydrogen seems quite interesting. Research studies on this line have been carried out directly at C.C.R. Ispra and under Euratom contract at UGINE laboratories (Venthon - France).

(*) Manuscript received on September 24, 1968.

A report on the work performed under this contract will be published (6). In the present report, which is complementary to the one mentioned above some methods of coating zircaloy 2 are described. Corrosion tests in terphenyl of coated samples are also reported.

2. PROTECTIVE COATINGS AGAINST HYDROGEN PICK-UP.

The aim of this work was to find a surface coating for protecting zircaloy 2 to be used in an organic cooled reactor against hydrogen pick-up. Such a coating would be interesting for pressure tubes that have to stay, for many years in the reactor, in contact with terphenyl at 400°C. This coating should have the following characteristics:

- 1) Low permeability to hydrogen coming from the decomposition of the coolant
- 2) Good compatibility with zircaloy 2 and with the organic liquid at about 400°C
- 3) Low neutron absorption

We have mainly focused our study on aluminium and its alloys on account of the fact that this material or more precisely its surface oxide is impermeable to hydrogen (7)(8).

Other types of coating suitable either directly as hydrogen diffusion barrier or as diffusion barrier between the coating and zircaloy 2 were also studied, both in our laboratories and at UGINE.

In table I are listed the coatings which we subjected to hydriding tests in terphenyl.

2.1. Coating with metals deposited by chemical and electro-chemical processes.

Various coating methods were tried depending on the element to be deposited.

Before coating the zircaloy 2 samples were carefully pickled in one of the following dips:

1)	NH ₄ F	36 g
	HF (40%)	15 g
	H ₂ O	1 l

This dip must be used at room temperature and the zircaloy 2 must be kept immersed for three or four minutes stirring continuously (10)

2)	HCl 37%	50 %	by volume
	glycerine	10 %	by volume
	1.4 butanediol	0,5 %	by volume
	wetting agent	0,1 %	by volume
	water	to 100	

This is an electrolytic dip to be used at room temperature. Zircaloy 2 is connected to the anode (current density 20 - 30 A/dm²) and is subjected to repeated immersions for 20 to 30 seconds followed by vigorous washing in running water.

When zircaloy 2 is pickled as described above extremely active surfaces are formed and it must be coated immediately.

Copper and gold deposits have been easily obtained using commercial electrolytic dips.

The deposits of copper and gold obtained by chemical displacement from aqueous solutions resulted in porous and consequently inefficient coatings, while those obtained by cementation in molten salts were non-porous and very adherent. Copper coatings were obtained by dipping the zircaloy 2 in molten Cu Cl_2 . This bath should be used at a temperature of 400 - 500°C and must be kept free of water. The immersion time must not exceed two minutes. The deposit obtained has a thickness of 3 - 5 μ . When a thicker deposit is needed a further electrolytic deposition can be carried out.

Zinc was also deposited by cementation in molten salts, with the following bath:

ZnCl_2	10 parts by weight
LiCl	6 parts by weight
KCl	5 parts by weight

The best deposits are obtained at 500°C: at this temperature zinc partially diffuses into the zircaloy 2. The thickness of the deposits is time dependent.

Nickel has been deposited using a specially prepared solution of the following composition (9)(10):

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	190 g/l
$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$	25 g/l
NH_4Cl	10 g/l
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	8 g/l
wetting agent	0,1 g/l

This dip must be used at 40°C with pH 5 (current density 6 A/dm²). It does not contain neutron poisons, has a high wettability good electrical conductivity, and produces only a small amount of gas.

Coating of zircaloy 2 with niobium, molybdenum and tungsten by vapour phase reduction of the respective halogenides proved quite troublesome, for two main reasons:

- 1) When using hydrogen as the reducing agent the working temperature exceeds the zircaloy 2 phase transformation point.
- 2) Zircaloy 2 is corroded by the Cl produced during the reduction reaction.

The first inconvenience was overcome by using zinc to reduce the halogenides. The working temperature in this case dropped to 700°C (11). The reduction of the Cl corrosion by pre-oxidizing zircaloy 2 has been attempted. Homogeneous and uniform deposits of niobium were obtained, but their adherence was still poor. Satisfactory niobium deposits were obtained on zircaloy 2 on which copper had been deposited by cementation.

Zircaloy 2 was coated by dipping in molten metal with magnesium, antimony and aluminum. Magnesium and antimony

proved to be unsuitable as coating materials. Magnesium hardly wets zircaloy 2 and oxidizes very rapidly, while antimony reacts strongly with zircaloy 2 forming pyrophoric products. Molten aluminum reacts with zircaloy 2 forming a deposit of variable thickness ranging from 15 to 150 μ according to temperature and immersion time. Actually this deposit consists of an Al-Zr reaction layer at the interface, the rest being plain aluminum.

2.2. Al-Si coating by dipping in molten alloy.

Aluminum is a good coating for zircaloy 2 as revealed by hydriding tests in terphenyl, but the compatibility between these two materials is rather poor.

At 400°C the aluminum deposited on zircaloy 2 rapidly reacts to form brittle intermetallic compounds (9) that may crack after thermal cycling. Therefore a diffusion barrier between aluminum and zircaloy 2 had to be envisaged.

Studies carried out at UGINE (6) have shown that Al-Si-Zr ternary compounds have a greater chemical stability compared to $ZrAl_3$ and $ZrAl_2$ that are formed by direct diffusion between zirconium and aluminum.

Silicon was added to the molten aluminum bath saturated with zirconium to avoid dissolution of zirconium from zircaloy 2. An immediate advantage was that the viscosity of the bath was lowered and thus more homogeneous deposits can be obtained.

In order to increase the wettability of zirconium by

molten aluminum we have tried many fluxes. Two of them have been retained:

- 1) eutectic $K_3AlF_6 + AlF_3$
- 2) molten $Zn Cl_2$ (In a second stage zinc has been directly deposited on zircaloy in a separate bath).

The properties of the Al-Si deposits on zircaloy 2 depend strongly on the silicon content of the coating as well as on temperature and time of immersion.

In table II different coating conditions are reported, together with a short description of the characteristics of the obtained layers. Metallographic sections are shown in the micrographs n°1-8.

The study of the phases formed in the coating layer has been described in the report mentioned before (6). The thermal stability of the deposits has been investigated by carrying out heat treatments under vacuum at temperatures between 400°C and 500°C, and for times up to 1000 hrs. All the diffusion layers are still stable after 1000 hrs at 430°C. At 500°C after 100 hrs a structural transformation is noticed on all samples with the exceptions of samples dipped for 6 minutes in Al-Si-Zr alloy with 8% Si at 800°C, on which the same phenomenon appears only after 1500 hrs.

2.3. Internal cladding of zircaloy 2 tubes with Al-Si sleeves.

The hot dipping system presents some drawbacks:

- 1) Technological difficulties in coating long tubes such as the ORGEL pressure tubes that are 6 m long.
- 2) The deposits are too thin to ensure good protection over a wide period. Deposits of the order of 100μ may be destroyed by wear, and on account of the slow diffusion process between the coating and zircaloy 2.

In order to overcome these difficulties we have tried to obtain a thicker coating by bonding an Al-Si sleeve inside the zircaloy 2 tube (see 2.3.2.)

Preliminary tests were carried out to determine the optimum composition of the Al-Si alloy to be used.

2.3.1. Compatibility tests.

Tests carried out at 450°C - 500°C - 550°C with alloys containing respectively 3-5-10% Si showed that:

- 1) The diffusion process is extremely slow
- 2) The best results are obtained with the lowest silicon content (3%)

Successively, tests were performed with Al-Si alloys containing from 0,3% to 2,5% Si as reported in table III.

The lowest penetration rate was encountered with the 1% Si alloy as can be seen from fig. 1.

Further tests carried out with an aluminum alloy containing finely dispersed silicon (1%) showed that the reaction layer between the coating and zircaloy 2 is smaller

than with a coarser dispersion.

In order to be able to predict whether Al-Si and zircaloy 2 can be used in contact for the lifetime of a reactor, long time tests have been carried out.

Small Al-1,5% Si (with finely dispersed silicon) capsules containing zircaloy 2, under vacuum, were prepared. Good contact and welding was obtained by hot swaging (fig. 2). Heat treatments at 450°C up to 12.000 hr were performed under vacuum and in air.

The results showed that in both cases the diffusion process is very slow. Reaction occurs only by points and after 12.000 hr the maximum thickness of the reaction layer is 50 μ . Tests in terphenyl carried out on samples of the same type showed that after 5700 hr at 400°C no reaction had occurred at the Al-Si/zircaloy 2 interface as can be seen from micrograph n°10.

2.3.2. Bonding of the Al-Si sleeve to the zircaloy 2 tube.

Small tubes of zircaloy 2 with diameters of 20-50 mm were internally clad with Al-1/1,5% Si tubes 0,8 mm thick. The external diameter of the Al-Si tubes was between 1 and 1,5 mm smaller than the internal diameter of the zircaloy 2 tubes. The Al-Si tube was expanded inside the zircaloy 2 tubes by pushing an appropriate plug through the inner tube (fig. 3). The effect of this operation is an elongation of the inner tube. A good adherence of the tubes is thus obtained.

The air initially present in the gap between the two

tubes is expelled by the moving plug thus reducing the risk of oxidation during subsequent treatments.

The following methods have been tried to ensure the metallurgical bonding of the assembly prepared as described above:

- 1) Heat treatment under vacuum at 500°C - 570°C. No positive results have been obtained.
- 2) Heat treatment with an argon pressure inside the assembly. After 15 hrs at 550°C with a pressure of 35 Kg/cm² the tubes seemed bonded, but they separated during thermal cycling.
- 3) Spot and roll resistance welding of the two tubes. As welding is not continuous after thermal cycling the Al-Si tube is deformed in the unwelded zones.
- 4) A calibrated mandrel made of a material of a high thermal expansion coefficient, is introduced inside the inner tube of the assembly so that during the heat treatment a good contact is assured between the two tubes. We have used a SAP mandrel cooled in liquid air so as to obtain 0,1 mm clearance. The SAP mandrel had been previously anodized in order to avoid any reaction with the Al-Si tube. After heat treatment in air or under vacuum at 550°C for 15 hrs, a good bonding is obtained as confirmed by metallographic analysis and thermal cycling tests.

An interesting method to ensure a good metallurgical bonding between the two tubes in a single operation is the following: an Al-1,5% Si tube is expanded against a preheated zircaloy 2 tube at 550°C by pushing a heat resisting steel plug inside the bore under pure argon. The dimensions of the plug are such that both the sleeve and the zircaloy 2 tube are deformed. The active surfaces formed on both sides of the system

greatly enhance diffusion. At first the deformation rates for zircaloy 2 were in the order of 30 - 50% and produced a very good bonding. Further tests have shown that identical results can be obtained with deformation rate of 5 - 10%.

The tubes clad by the last mentioned method withstood 100 thermal cycles from 420°C to room temperature. Copper and zinc films, 2 - 3 μ thick deposited either on zircaloy 2 or on Al-Si, or on both surfaces enhance bonding, but create a larger reaction layer between zircaloy 2 and Al-Si.

3. HYDRIDING TESTS IN TERPHENYL.

3.1. Experimental procedure.

Hydriding tests in terphenyl were carried out in stainless steel autoclaves at 400°C with a 10 atm nitrogen pressure. The organic liquid used was OM 2 terphenyl supplied by the PROGIL Company and containing the following impurities:

Cl < 2 ppm

H₂O < 100 ppm

Every month the samples were removed, washed in acetone, weighed and put-back in the autoclave with new terphenyl. The initial H₂O content was 70 - 80 ppm, after a month it amounted only to 20 - 30 ppm, whilst the Cl content dropped from an initial 1.5 ppm to 0.5 ppm at the end of the test.

In the tests with zircaloy 2 samples coated by hot dipping in molten Al-Si alloy, the Cl content was probably higher during the first month. This assumption was formulated later on when it was found that small slabs of oxidized zircaloy 2, placed in the autoclaves as reference samples had absorbed large amounts of hydrogen. The excess Cl may have come from the flux used over the molten alloy in the coating process.

The duration of the tests ranged from a minimum of 300 hrs, up to a maximum of 12.000 hrs, for the most promising protections.

3.2. Results obtained.

The results obtained from preliminary tests of short duration of all the coatings tested (table I) confirmed that aluminum appears to be the most promising barrier against hydrogen diffusion.

Chromium coatings gave encouraging results on small plates, but this method was not investigated thoroughly in order to concentrate our research on aluminum-based coatings. All other coatings gave rise to higher hydrogen pick-up with respect to uncoated zircaloy 2. An explanation of this fact may be that the applied coatings are not as effective hydrogen barriers as the ZrO_2 which forms on the zircaloy surface by oxidation in presence of the moisture contained in the terphenyl, even if no preoxidation in steam or oxygen has been carried out. When samples are coated, the formation of ZrO_2 is prevented, and hydrogen can diffuse through permeable coatings.

In order to check the influence of silicon on hydrogen pick-up some samples have been submitted to a second dipping in pure aluminum. The results of hydriding tests have shown that Al-Si is as good a barrier against hydrogen as pure aluminum.

The results of the first corrosion tests carried out on slabs, coated by hot dipping in an Al-9% Si alloy, are given in table IV. The weight changes are not reported because they are mainly due to mechanical loss of coating fragments, rather than to corrosion phenomena. The hydriding rate of coated samples is always lower than with uncoated zircaloy 2, but a zero value was found only in very few cases.

A careful observation of the samples after the corrosion tests showed that very often the coating was broken on the edges of the slabs. To avoid this inconvenience in subsequent tests small coated tubes of diameters varying between 20 and 50 mm and 100 mm long were used. Fig. 4 shows a coated tube before the corrosion test.

In table V the coating conditions for each sample are reported, together with the results of the hydriding tests in terphenyl. Fig. 5 shows hydrogen pick-up of the samples in function of time. On the same graph we have reported the hydrogen pick-up of zircaloy 2 slabs preoxidized in oxygen that have been put in the same autoclaves as reference samples, and of oxidized zircaloy 2 corroded in "pure" terphenyl ($\text{Cl} \leq 0,2 \text{ ppm}$; $\text{H}_2\text{O} \geq 100 \text{ ppm}$). Each data given for hydrogen pick-up of plated tubes is an average of 3 or 6 analysis carried out on small samples cut from different positions of the same tube. The scatter was normally very small.

The lowest values for hydrogen pick-up correspond to the coated tubes. After the corrosion tests the Al-Si coating appeared broken in many points as can be seen from

fig. 6 and micrographs 11 and 12, that show the aspect of the coating of the two tubes that remained in terphenyl for 12.100 hrs.

Comparing the results for tubes n°153 and 163 it can be seen that in the coating of n°153 the cracks are more relevant and that the hydrogen pick-up of this tube is twice that of n°163.

The scatter in the results for the tubes coated by hot dipping is mainly due to the small thickness of the coating obtained by this method as mentioned in paragraph 2-3. For this reason tests have been carried out on small Al-1,5% Si capsules containing zircaloy 2 slabs obtained by hot swaging as previously described (fig. 2). In table VI the results of the hydriding tests of these samples in terphenyl at 400°C are reported. Prior to the hydrogen analysis, Al-Si has been removed from zircaloy 2 by abrasion on emery paper.

As can be seen there is no hydrogen pick-up with the exception of one sample. The small hydrogen adsorption of sample n°34 may be explained by the fact that black stains probably due to traces of steel coming from the swaging operation, were present on the outer surface of the sample. These stains may have prevented the formation of Al oxide at these points.

4. CONCLUSIONS.

- 1) Corrosion tests in terphenyl have shown that zircaloy 2 can be properly protected against hydrogen pick-up, by coating with aluminum.

- 2) The interdiffusion of Zr 2 and Al is strongly reduced by alloying Al with 1-12% Si. The smallest interpenetration has been found at 400°C with additions of 1-1,5% Si.
- 3) The addition of Si to Al does not reduce the hydrogen barrier properties of the coating even after 12.000 hrs at 400°C (table V and VI).
- 4) H₂ pick-up of coated Zr 2 is not influenced by impurities contained in the terphenyl, especially Cl. In a test where the organic liquid contained much Cl, the preoxidized Zr 2 reference samples picked-up large amounts of H₂, whereas the coated samples behaved better than preoxidized samples in pure terphenyl.
- 5) Even if in some points the Al-Si coating breaks off, H₂ pick-up is still low. The intermetallic compounds formed at the Zr 2/Al-Si interface which remains adherent to Zr 2 probably acts as a diffusion barrier (12).
- 6) Efficient Al-Si coatings on Zr 2 can be obtained either by dipping in a liquid Al-Si alloy or by metallurgical bonding between a Zr 2 tube and an Al-Si sleeve. In the dipping process a higher Si concentration (~ 8%) is requested in order to lower the viscosity of the molten alloy. In the solid-solid plating, the Si concentration must be kept low, in order to have a ductile Al-Si sleeve.
- 7) Both the above mentioned processes have been successfully tried on tubes on laboratory scale. For industrial application to pressure tubes, the problems to be solved are different. For dipping tubes several meters in length, appropriate containers are needed. To our knowledge they have not been

developed up to now.

In the solid-solid plating process, the main difficulty is to apply an uniform pressure on the sleeve during the metallurgical bonding operation without deforming the assembly.

- 8) From the tests carried out it can be assumed that an efficient protection against H_2 pick-up of Zr 2 pressure tubes for an ORGEL Reactor, can be obtained. Some problems remain however to be studied, mainly:

- Industrial plating of pressure tubes of actual dimensions
- Radiation resistance of the coating.

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TABLE I

TYPES OF COATINGS TESTED IN TERPHENYL .

Coating	Method of deposition
Cu	Electrolytic
Au	Electrolytic and chemical
Al	Vacuum deposition
Cr	Electrolytic and vacuum deposition
Mo	Vapour phase reduction at high temperature
W	Vapour phase reduction at high temperature
Ni-Al	Ni electrolytic, Al vacuum deposition
Ni-Mo	Ni electrolytic, Mo vapour phase reduction at high temperature
Ni-Cr	Plasma jet
Ni-Mo	Plasma jet
Ni-W	Plasma jet
Ni-Al ₂ O ₃	Plasma jet
TiC	Plasma jet
ZrO ₂	Plasma jet
SiO ₂ +Zr	Plasma jet
Al-Si	Hot dipping in Al-1/11% Si alloy
Al-Si	Metallurgical bonding

TABLE II

EXPERIMENTAL CONDITIONS FOR COATING ZIRCALOY 2 BY HOT DIPPING IN
MOLTEN Al-Si ALLOYS SATURATED WITH Zr.

Si content %	Temperature of molten alloy °C	Immersion time minutes	Remarks
1	720	6	Average coating thickness: 130 μ Average thickness of diffusion layer: 10 μ Good thermal cycling resistance: 200 cycles from 400°C to room temperature
1	720	18	Average coating thickness: 80 μ Average thickness of diffusion layer: 15 μ Two phases present in diffusion layer
1	800	6	Average coating thickness: 45 μ Average thickness of diffusion layer: 20 μ Good thermal cycling resistance 200 cycles from 400°C to room temperature Two phases present in diffusion layer
1	800	18	Average coating thickness: 110 μ Average thickness of diffusion layer: 60 μ Two phases present in diffusion layer
8	720	6	Uniform coating thickness: 80 μ Thickness of diffusion layer: 25 μ Coating cracked in some points Good thermal cycling resistance

TABLE II

(continued)

Si content %	Temperature of molten alloy °C	Immersion time minutes	Remarks
1	720	18	Uniform coating thickness of 140 μ Thickness of single phase diffusion layer: 75 μ Coating cracked in some points
8	800	6	Uniform coating thickness: 70 μ Thickness of single phase diffusion layer: 20 μ Coating cracked in some points
8	800	18	Uniform coating thickness: 160 μ Thickness of single phase diffusion layer: 50 μ Coating cracked in some points Good thermal cycling resistance
13	725	6	Uniform coating thickness: 200 μ Thickness of diffusion layer: 90 μ Coating cracked in some points
13	725	18	Thickness of diffusion layer: 165 μ Coating cracked in some points
13	810	6	Uniform coating thickness: 150 μ Thickness of diffusion layer: 8 μ
13	810	18	Uniform coating thickness: 190 μ Thickness of diffusion layer: 20 μ Three phases present in the diffusion layer

TABLE III

ZIRCALOY-2/Al-Si DIFFUSION COUPLES

Si content of alloy %	Heat treatment		Maximum thickness of diffusion layer μ
	Temperature °C	Time hr	
0,3	500	336	25
0,3	500	696	125
0,3	500	1008	128
0,3	500	1728	134
0,3	500	3360	165
0,5	500	360	35
0,5	500	672	50
0,5	500	1032	48
0,5	500	1704	80
0,5	500	3336	135
0,8	500	336	15
0,8	500	672	27
0,8	500	1032	43
0,8	500	1704	54
0,8	500	3336	90
1	500	336	25
1	500	696	30
1	500	1008	45
1	500	1728	57
1	500	3360	67

TABLE III

(continued)

Si content of alloy %	Heat treatment		Maximum thickness of diffusion layer u
	Temperature °C	Time hr	
2,5	500	336	55
2,5	500	696	50
2,5	500	1008	60
2,5	500	1728	74
2,5	500	3360	125

TABLE IV

HYDROGEN PICK-UP OF ZIRCALOY 2 SLABS, COATED BY HOT
DIPPING IN Al-9% Si, IN TERPHENYL AT 400°C.

Sample N°	Time hr	H ₂ pick-up (mg/cm ² /hr)
71	312	0
72	312	0
73	312	0,2 x 10 ⁻⁵
75	312	0,3 x 10 ⁻⁵
76	312	0,3 x 10 ⁻⁵
77	312	0
79	312	0,5 x 10 ⁻⁵
80	312	0,3 x 10 ⁻⁵
81	312	0,2 x 10 ⁻⁵
83	312	0,8 x 10 ⁻⁵
84	312	0,8 x 10 ⁻⁵
85	340	0,2 x 10 ⁻⁵
90	340	0
95	340	0
100	340	0,4 x 10 ⁻⁵
86	840	0,1 x 10 ⁻⁵
91	840	0,1 x 10 ⁻⁵
96	840	0,1 x 10 ⁻⁵
101	840	0,3 x 10 ⁻⁵
87	1480	0,2 x 10 ⁻⁵
92	1480	0,4 x 10 ⁻⁵
97	1480	0,4 x 10 ⁻⁵
102	1480	0,2 x 10 ⁻⁵
88	2000	0,3 x 10 ⁻⁵
93	2000	0,4 x 10 ⁻⁵
98	2000	0,6 x 10 ⁻⁵
103	2000	0,3 x 10 ⁻⁵

TABLE V

COATING CONDITIONS OF ZIRCALOY 2 TUBES AND HYDROGEN

PICK-UP IN TERPHENYL.

Sample	Si content of molten alloy %	Temperature and time of dipping		Hydriding test hr	H ₂ pick-up mg/cm ² /hr
		Dipping in Al-Si alloy	Second dipping in pure Al		
159	7	700°C 20 min	-	1500	0,6 x 10 ⁻⁵
161	7	700°C 20 min	-	1500	1,1. x 10 ⁻⁵
108	12	800°C 15 min	700°C 30 sec	2200	0
160	7	700°C 20 min	-	2200	0,9 x 10 ⁻⁵
162	7	700°C 20 min	-	2200	0,9 x 10 ⁻⁵
129	12	800°C 20 min	700°C 20 sec	2950	0,5 x 10 ⁻⁵
137	12	800°C 20 min	700°C 20 sec	2950	1 x 10 ⁻⁵
146	12	800°C 20 min	700°C 20 sec	2950	0,4 x 10 ⁻⁵
151	7	700°C 30 min	-	2950	0,8 x 10 ⁻⁵
109	12	800°C 15 min	700°C 30 sec	3000	0
134	12	800°C 20 min	700°C 20 sec	3600	0,6 x 10 ⁻⁵
135	12	800°C 20 min	700°C 20 sec	3600	1 x 10 ⁻⁵
138	12	800°C 20 min	700°C 20 sec	3600	0,4 x 10 ⁻⁵
152	7	700°C 30 min	-	3700	0,8 x 10 ⁻⁵
132	12	800°C 20 min	700°C 20 sec	4420	1,4 x 10 ⁻⁵
140	12	800°C 20 min	700°C 20 sec	5160	0,3 x 10 ⁻⁵

TABLE V

(continued)

Sample N°	Si content of molten alloy %	Temperature and time of dipping		Hydriding test hr	H ₂ pick-up mg/cm ² /hr
		Dipping in Al-Si alloy	Second dipping in pure Al		
141	12	800°C 20 min	700°C 20 sec	7330	0,3 x 10 ⁻⁵
143	12	800°C 20 min	700°C 20 sec	10608	0,2 x 10 ⁻⁵
153	7	700°C 30 min	-	12100	0,6 x 10 ⁻⁵
163	7	700°C 20 min	-	12100	0,3 x 10 ⁻⁵

TABLE VI

HYDROGEN PICK-UP OF ZIRCALOY 2 SLABS IN Al-1,5% Si
CAPSULES, CORRODED IN TERPHENYL AT 400°C.

Sample N°	Time hr	H ₂ pick-up mg/cm ² /hr
18	5740	0
24	1220	0
26	1220	0
27	1220	0
32	5740	0
33	5740	0
34	5740	1 x 10 ⁻⁶

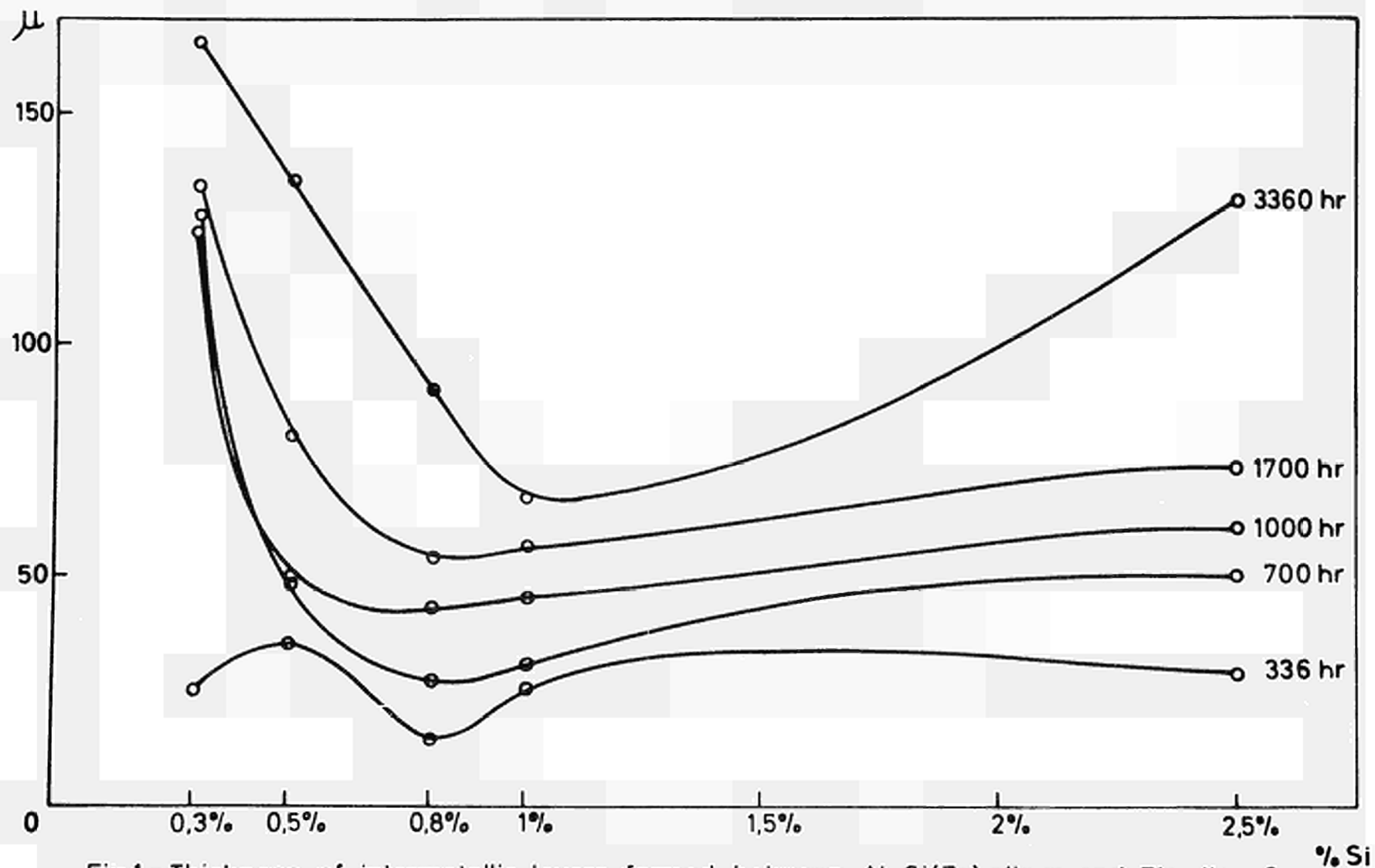


Fig.1 - Thickness of intermetallic layers formed between Al-Si(Zr) alloys and Zircalloy-2 at 500 °C Vs Si content (for different durations of heat treatment).

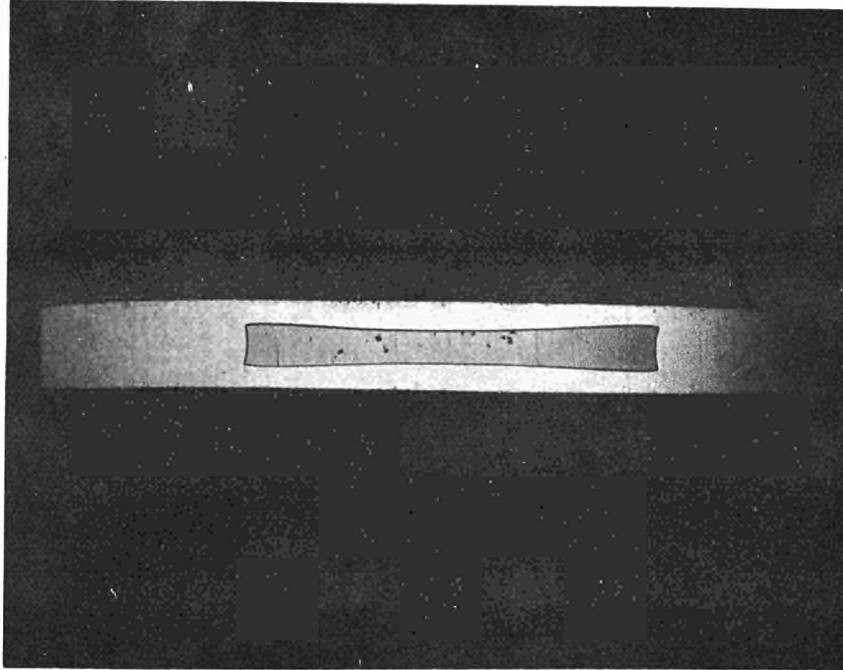


Fig. 2.- Cross-section of an Al-1,5% Si capsule containing zircaloy 2 obtained by hot swaging. (x 4)

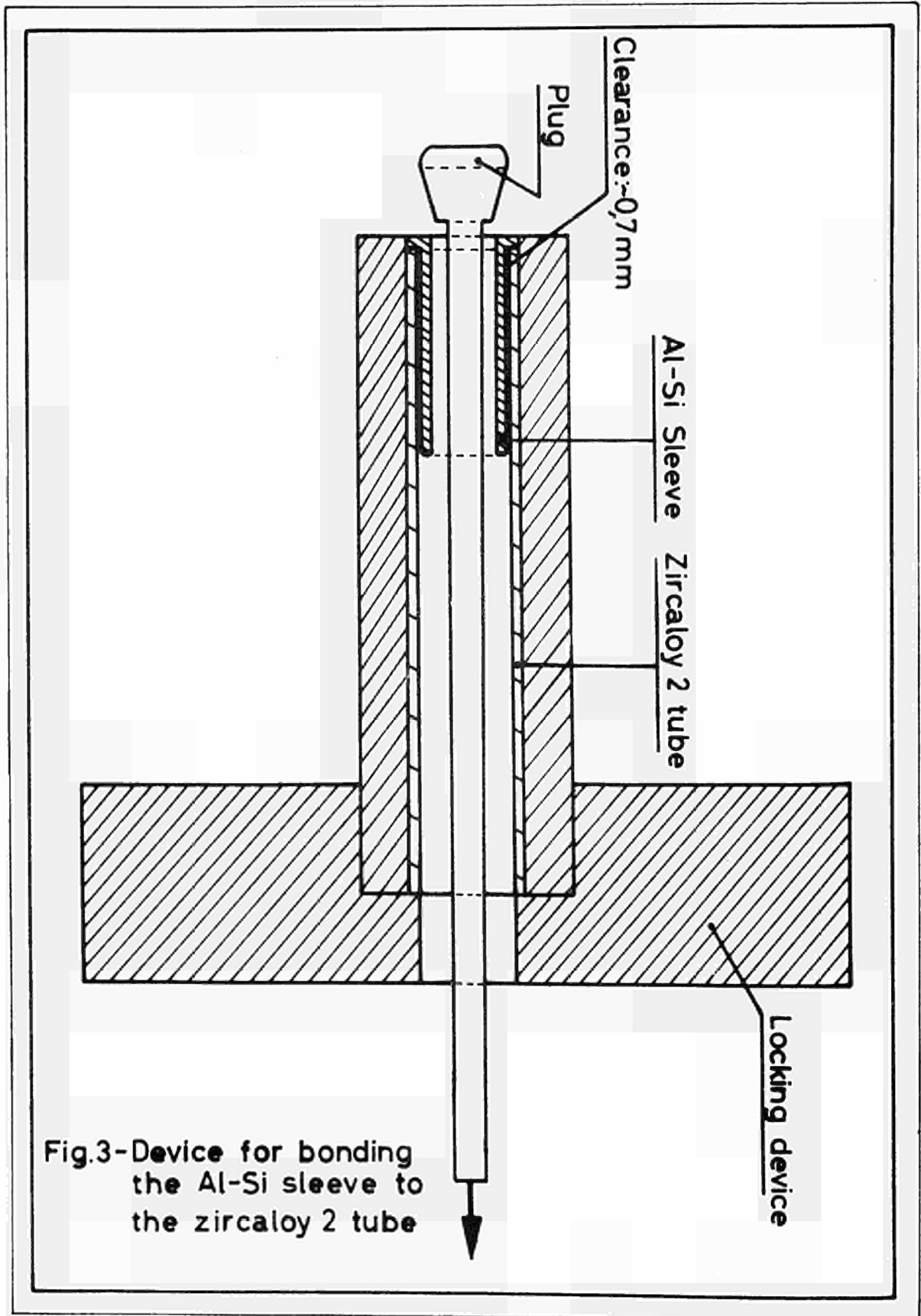


Fig.3-Device for bonding the Al-Si sleeve to the zircaloy 2 tube

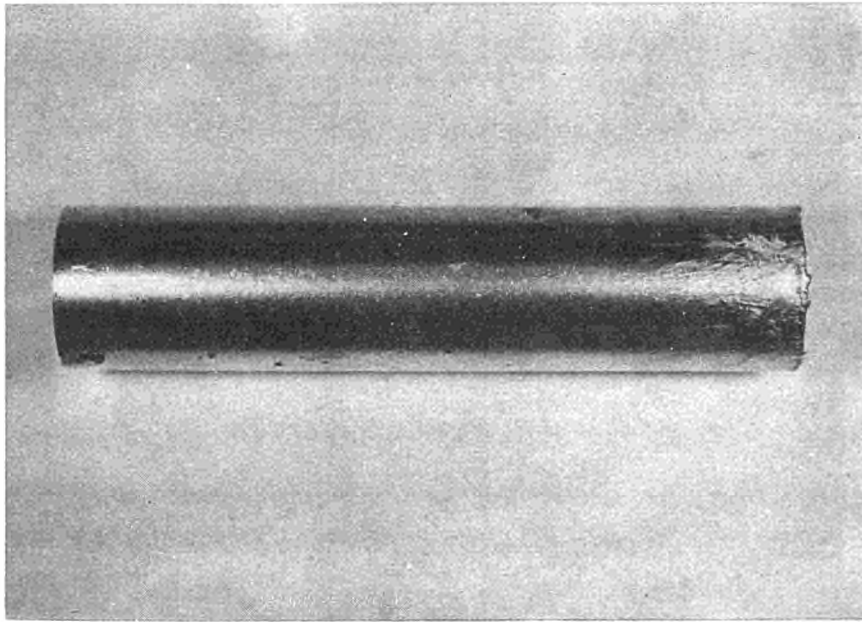


Fig. 4.- Zircaloy 2 tube coated by hot dipping
in Al-12% Si. (x 1)

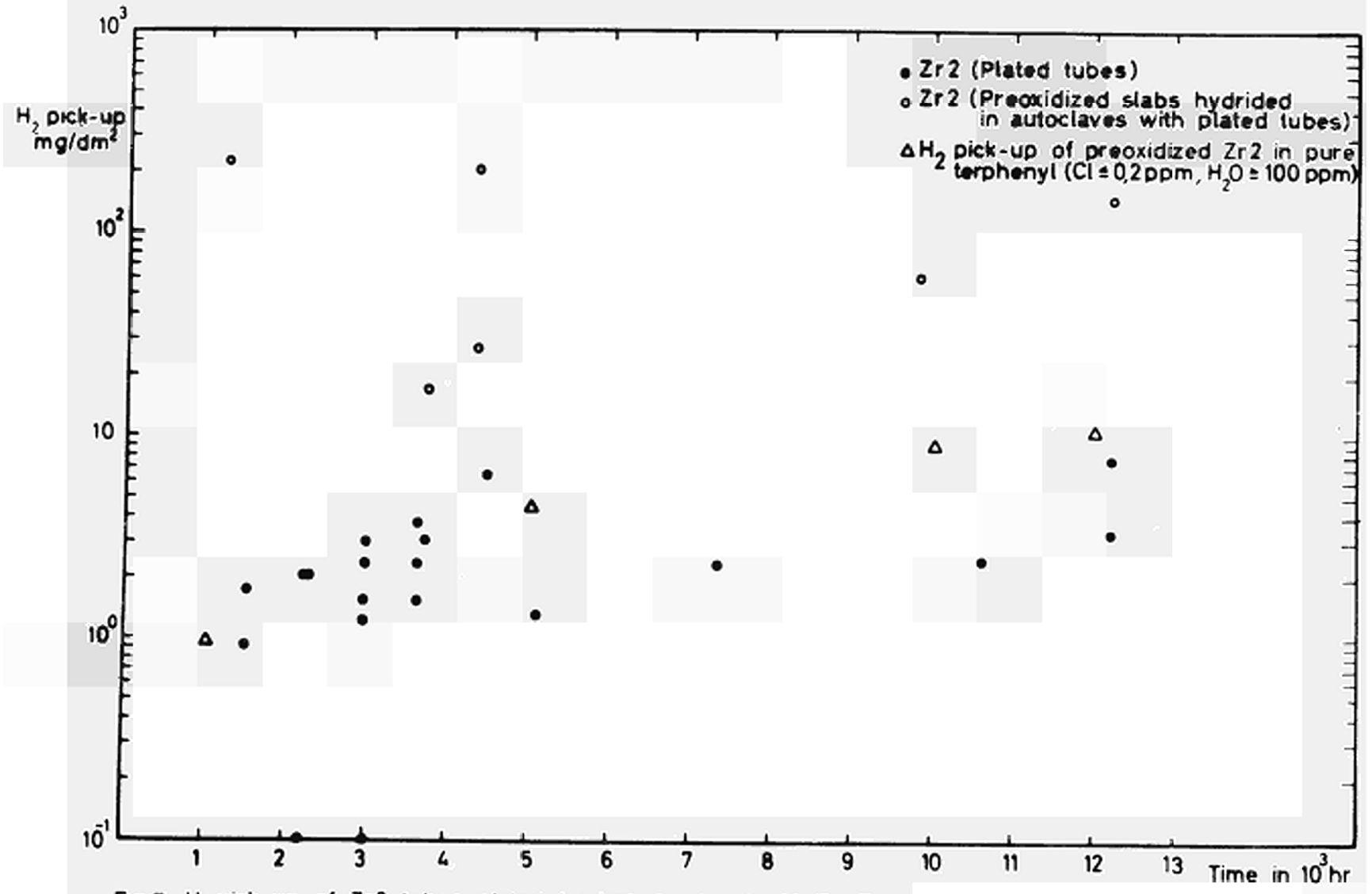


Fig 5 - H_2 pick-up of Zr2 tubes plated by hot dipping in Al-Si-Zr

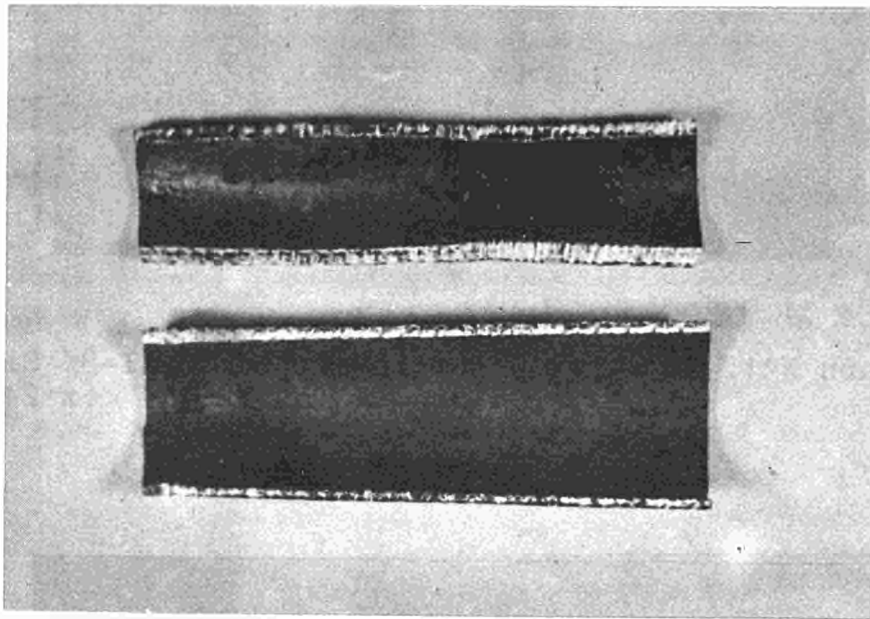
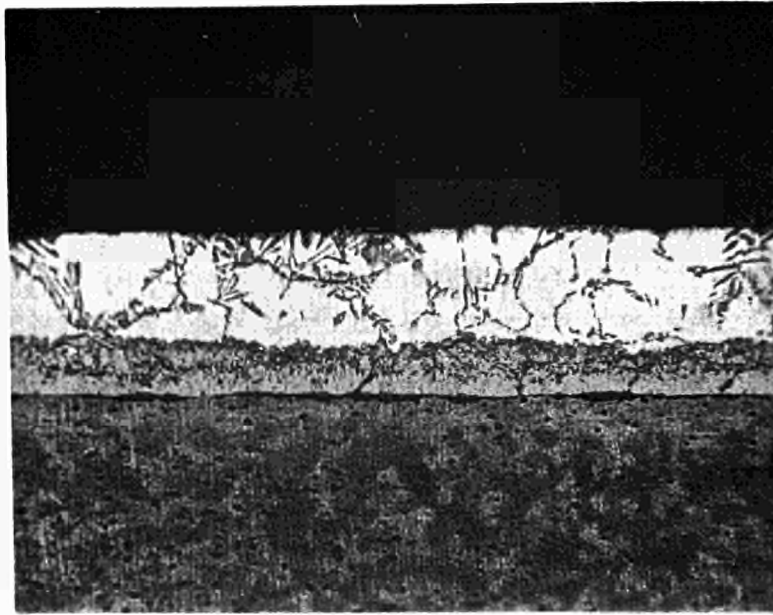
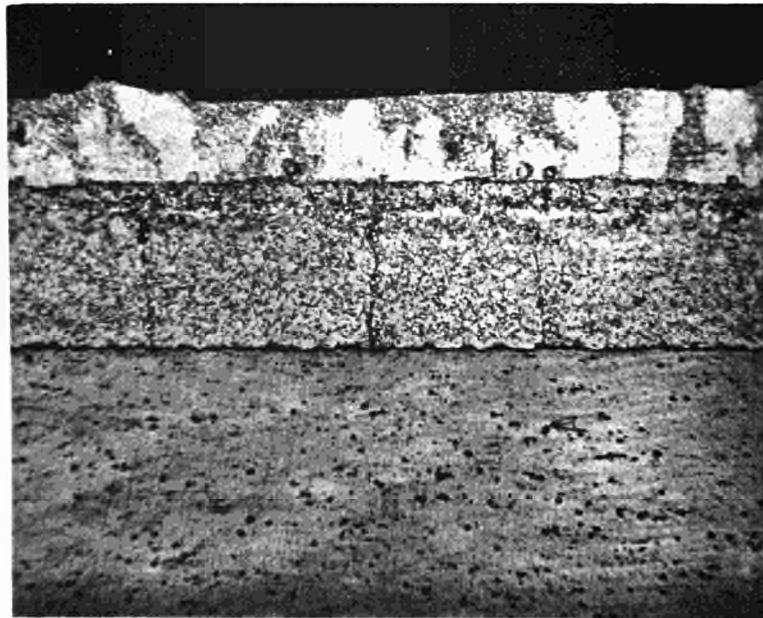


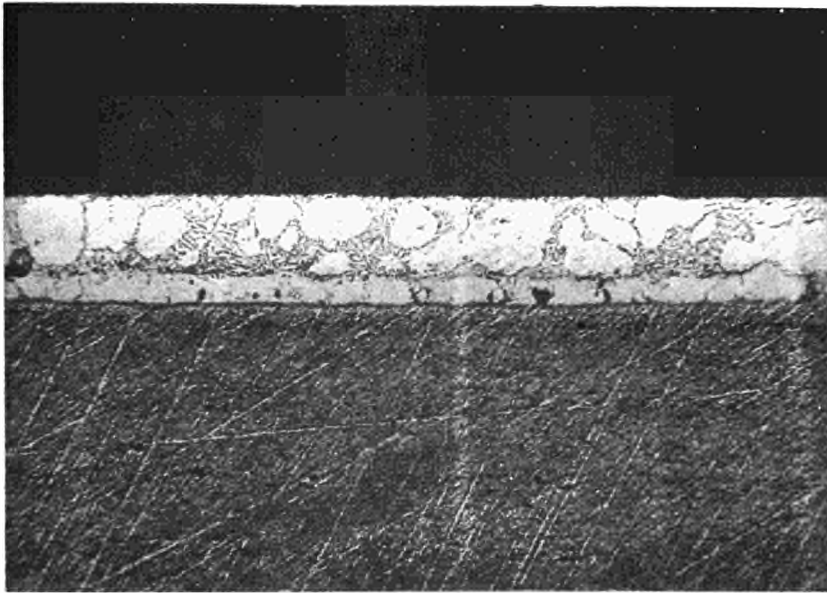
Fig. 6.- Zircaloy 2 tubes coated with Al-7% Si,
after corrosion in terphenyl for 12.100 h.
at 400°C. (x 1)



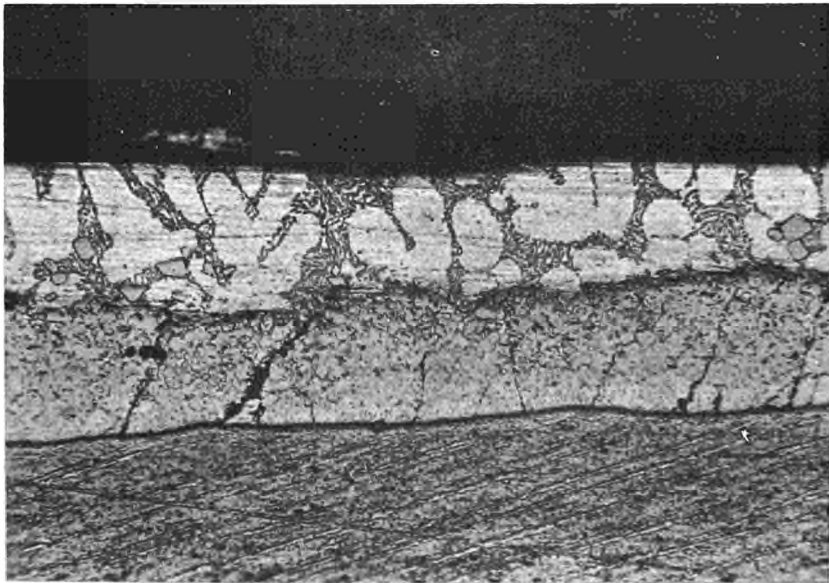
Micrograph N°1. Zircaloy 2 sample dipped in Al-8% Si alloy for 6 minutes at 720°C. (x 240)



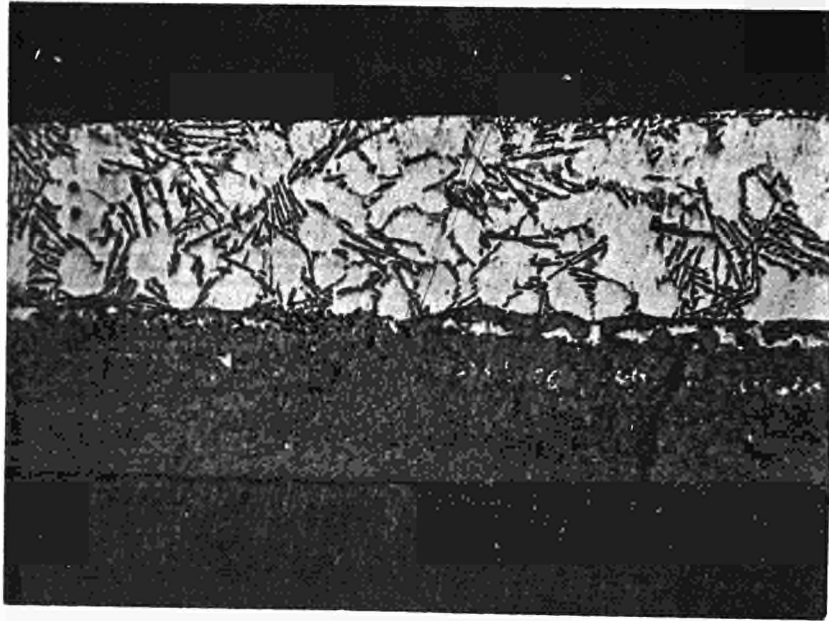
Micrograph N°2. Zircaloy 2 sample dipped in Al-8% Si alloy for 18 minutes at 720°C. (x 240)



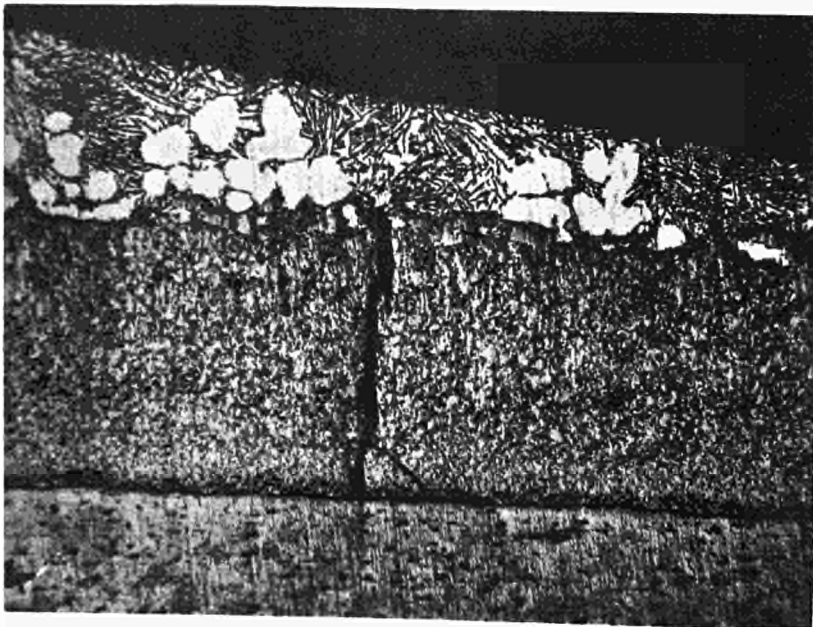
Micrograph N°3. Zircaloy 2 sample dipped in Al-8% Si alloy for 6 minutes at 800°C. (x 240)



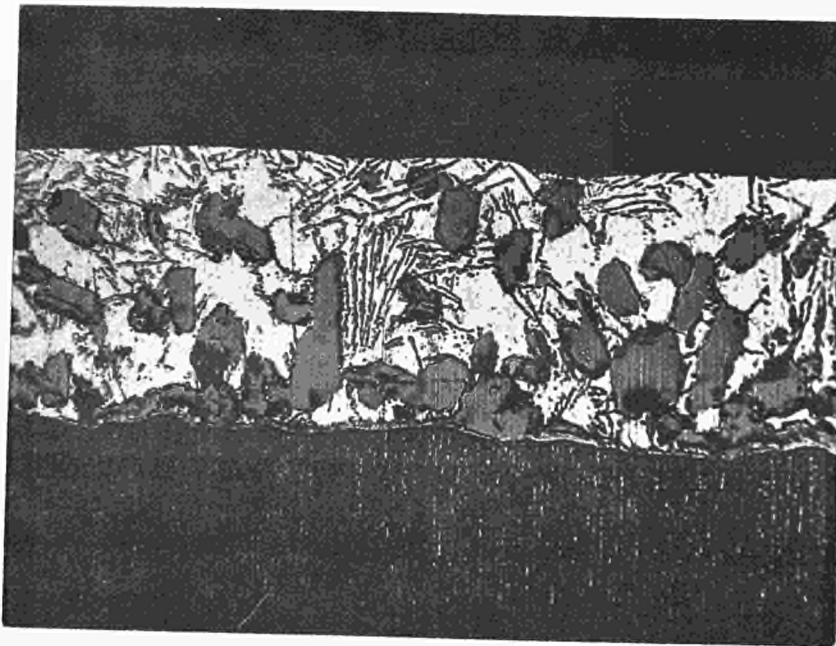
Micrograph N°4. Zircaloy 2 sample dipped in Al-8% Si alloy for 18 minutes at 800°C. (x 240)



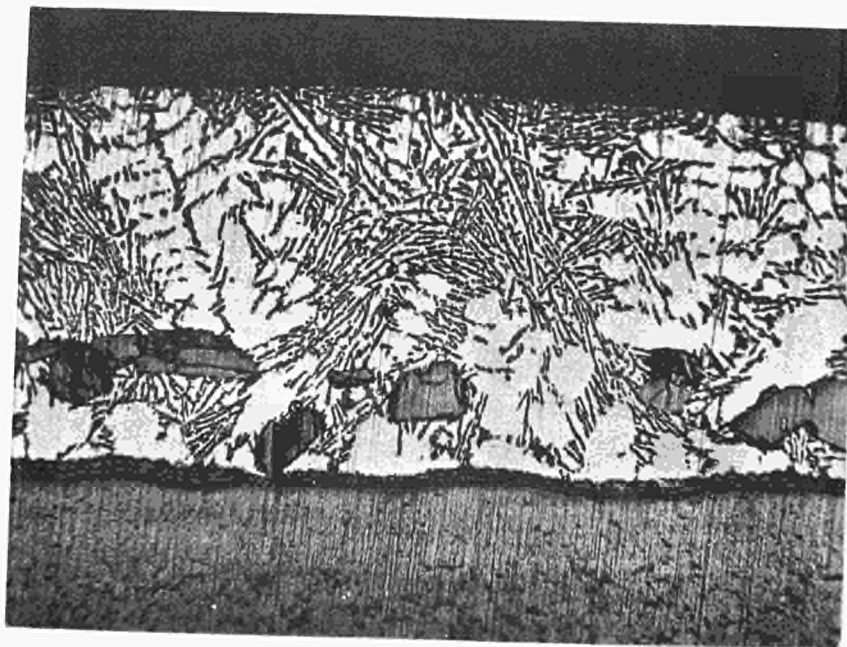
Micrograph N°5. Zircaloy 2 sample dipped in Al-13% Si alloy for 6 minutes at 725°C. (x 240)



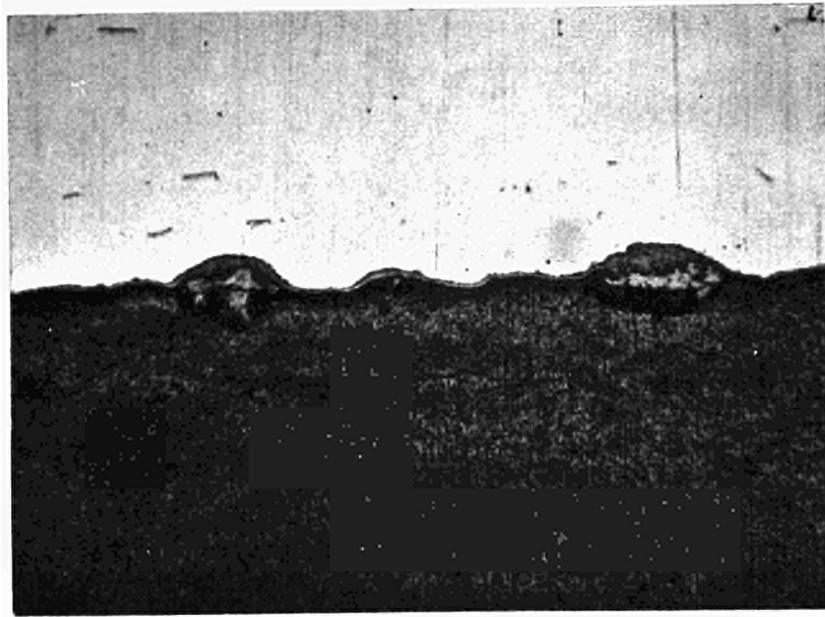
Micrograph N°6. Zircaloy 2 sample dipped in Al-13% Si alloy for 18 minutes at 725°C (240)



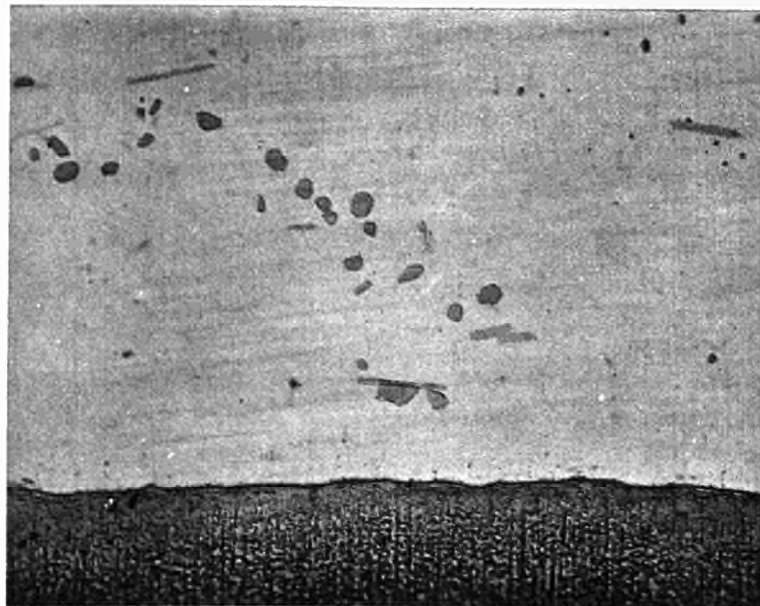
Micrograph N°7. Zircaloy 2 sample dipped in Al-13% Si alloy for 6 minutes at 810°C. (x 240)



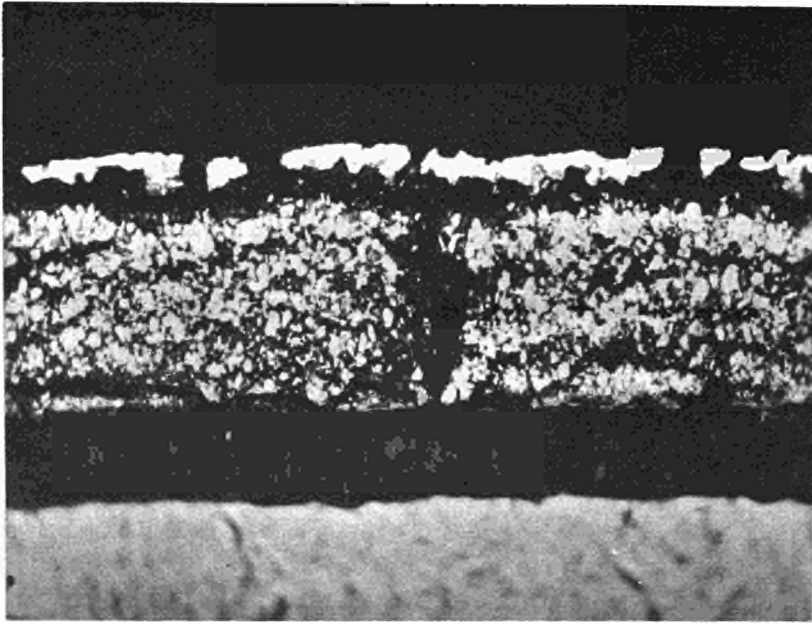
Micrograph N°8. Zircaloy 2 sample dipped in Al-13% Si alloy for 18 minutes at 810°C. (x 240)



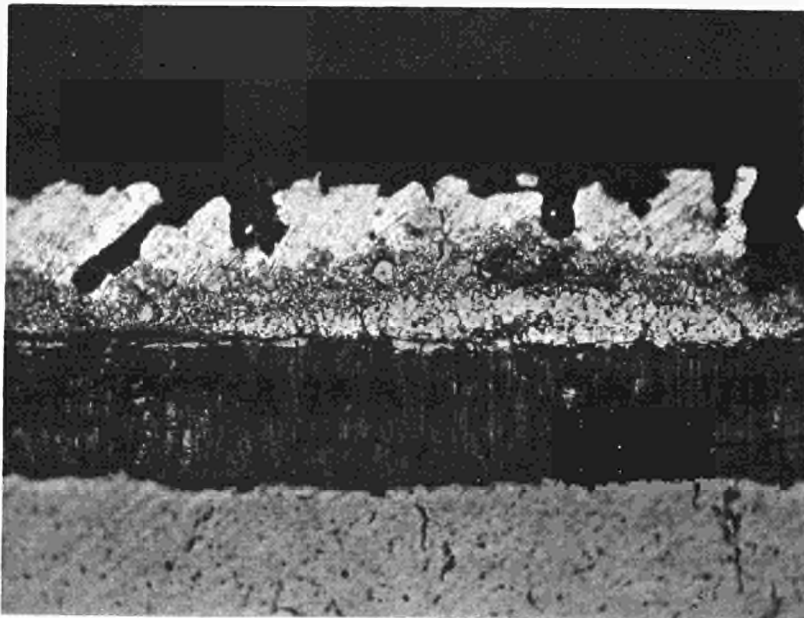
Micrograph N°9. Zircaloy 2/Al-1,5% Si sample (Hot swaged capsule) tested at 450°C for 12.000 hours. (x 240)



Micrograph N°10. Zircaloy 2/Al-1,5% Si sample (Hot swaged capsule) tested at 400°C for 5.700 hours in terphenyl. (x 400)



Micrograph N°11. Zircaloy 2 sample N°153 coated by hot dipping with Al-7% Si after corrosion test in terphenyl at 400°C for 12.100 h. (x 400)



Micrograph N°12. Zircaloy 2 sample N°163 coated by hot dipping with Al-7% Si after corrosion test in terphenyl at 400°C for 12.100 h. (x 400)

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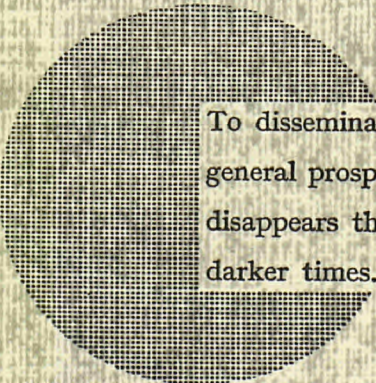
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