



The compatibility of martensitic steels with liquid Pb–17Li

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Abstract

Mass transfer experiments in liquid Pb–17Li have been conducted in an anisothermal container with pure metals, Fe and Cr, and with Fe–Cr steels (DIN 1.4914 martensitic steel and a ferritic steel; 26%Cr). These experiments have shown that the corrosion rate of pure chromium is one order of magnitude higher than that of pure iron, while the Fe–Cr steels exhibit a dissolution rate equal to that of pure iron. A mechanism of corrosion of the martensitic steel has been proposed and discussed below:

*Dissolution of the metallic elements constituting the steel: Fe, Cr, etc.

*Diffusion of the dissolved species in the boundary layer of liquid metal, with the rate determining step for the whole corrosion mechanism being the diffusion of iron.

*Diffusion of Cr element in the matrix to the solid/liquid metal interface.

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1. Introduction

Liquid Pb–17Li is one of the prime candidates for use as a tritium-breeder material in a future fusion reactor. Its compatibility with structural materials, particularly with DIN 1.4914 steel, is the subject of a significant research program in EEC [1–4]. The great number of experiments made in the last ten years shows the complexity of the phenomena. Therefore, the behaviour of the pure metals Fe and Cr in anisothermal semistagnant lithium–lead, have been compared to those exhibited by two Fe–Cr steels.

2. Experimental

2.1. Materials

The materials investigated in this study were as follows:

(a) Two pure metals:

Armco Fe (purity about 99%)

Plantzee Cr (purity about 99.6%, hot-pressed)

(b) Two Fe–Cr steels having a body-centred cubic structure (alpha):

DIN 1.4914 martensitic steel

A ferritic steel: Orion, 26% Cr

The chemical compositions and heat treatments of these steels are given in Table 1.

After machining, the specimens (20 mm × 30 mm × 2 mm) were mechanically polished with grinding paper (up to 1200 grade) and then diamond pastes (15 μm and 6 μm). Finally they were degreased before testing. The total surface areas of the specimens in the hot and cold zones were 40 and 20 cm² respectively.

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Table 1
Chemical composition (wt.%) and heat treatment of materials

Material	C	Ni	Cr	Fe	Mo	Mn	Si	Heat treatment
DIN 1.4914 Z13 CDNb V 11	0.13	0.87	10.6	86	0.8	0.8	0.4	Normalized and tempered: 2 h, 910°C/0.5 h, 1015°C/2 h, 750°C
ORION Z CD 1 1	0.002	0.1	25.4	72.1	0.01	1.05	0.21	Fully annealed at 900°C

The lithium–lead alloy was provided by Métaux Spéciaux.

2.2. Test device

All the materials were tested for 500 h with hot and cold zone temperatures fixed to 500°C and 440°C, respectively.

In order to have the metal surface to Pb–17Li volume ratio as low as possible and without limiting the dissolution rate, the tests were carried out in a molybdenum crucible which is practically inert toward lithium–lead alloy. This crucible (Fig. 1) (diameter 50 mm and height 240 mm) is enclosed within an outer AISI 304L steel container which was closed under pure helium ($O_2 < 1$ vppm; $H_2O < 2$ vppm; $N_2 < 2$ vppm). Heating of the container was performed using two heating elements, one at the top (isothermal hot zone) and one at the bottom (isothermal cold zone) of the container. Temperature control was insured by thermocouples placed in a central

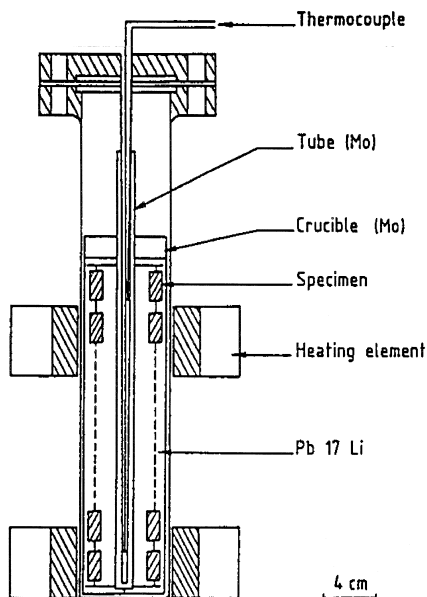


Fig. 1. Experimental apparatus.

molybdenum tube also used as a support for the specimens.

3. Results

Post test weight losses of the specimens were determined by weighing after successive immersions in an acetic acid–hydrogen peroxide–alcohol mixture (1/3:1/3:1/3) until the specimen weight remained constant. Weight losses exhibited by the hot-zone specimens are summarized in Table 2. Cross-section micrographs show the morphology of the interface between liquid metal and solid metal (given in Fig. 2). Roughness measurements of the solid metal surface before and after the test are given in Table 3.

3.1. Pure metals

As seen on the cross-section micrographs and with roughness measurements, the corrosion of pure iron and pure chromium are characterized by a uniform dissolution. However, the weight loss (given in Table 2) suffered by chromium (2 mg cm^{-2}) is more significant than that of pure iron (0.4 mg cm^{-2}).

3.2. Fe–Cr steels

The two Fe–Cr steels exhibit a uniform dissolution as shown on the cross-section micrographs (Fig. 2), and their weight losses are nearly the same (0.33 mg cm^{-2} for the DIN 1.4914 steel and 0.43 mg cm^{-2} for the Orion steel). Moreover, luminescent discharge spectroscopy analysis presented in Fig. 3 shows a chromium and nickel depletion

Table 2
Weight loss for each of the materials tested (500 h)

Material	Fe	Cr	1.4914	Orion
Weight loss mg cm^{-2}	0.43 ± 0.1	2 ± 0.2	0.33 ± 0.13	0.43 ± 0.13

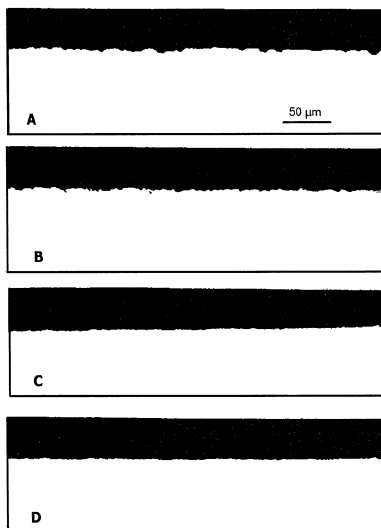


Fig. 2. Cross-section micrographs of pure metals and Fe–Cr steels. (a) Pure Fe; (b) pure Cr; (c) 1.4914 steel; (d) Orion steel.

near the surface of the DIN 1.4914 steel to a depth of about 0.7 μm .

4. Discussion

4.1. Pure metals

The homogeneous dissolution exhibited by pure iron and chromium is in good agreement with the rate-determining step which is the diffusion of the metallic species across a thin boundary layer, as observed in rotating-cylinder experiments [5].

The dissolution rate of pure chromium is one order of magnitude higher than pure iron in spite of the higher solubility of iron in the liquid metal [6]:

$$C_s(\text{Fe}/\text{Pb17Li})_{500^\circ\text{C}} = 47 \text{ wppm};$$

$$C_s(\text{Cr}/\text{Pb17Li})_{500^\circ\text{C}} \# 10 \text{ wppm},$$

where C_s is the saturation value corresponding to the solubility of the specie in liquid metal.

This is due to the fact that the dissolution rate of the two metals is controlled by the diffusion of the dissolved

species in the liquid metal and that the diffusion coefficient of iron is much smaller than that of chromium [5]:

$$D(\text{Fe}/\text{Pb17Li})_{500^\circ\text{C}} = 4 \pm 2 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$$

$$D(\text{Cr}/\text{Pb17Li})_{500^\circ\text{C}} = 8 \pm 2.5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1},$$

where D is the diffusion coefficient.

Under these conditions, the dissolution flux of pure metals can be expressed as

$$J_{\text{diss}}(\text{M}) = D_{\text{M}}(S_{\text{M}} - C_{\text{M}})/e \quad (1)$$

with M: pure iron or pure chromium; D_{M} : diffusion coefficient in the liquid metal; S_{M} : saturation solubility value of the dissolved species in the liquid metal; C_{M} : concentration in the liquid metal; e : thickness of the diffusion boundary layer.

In an approximation, the thickness of the diffusion boundary layer can be expressed by the equation for turbulent flow in a tube [2]:

$$e = 25d^{0.125}V^{-0.875}\nu^{0.55}D^{0.33} \quad (2)$$

with d : tube diameter; V : flow rate of liquid metal; ν : kinematic viscosity; e : boundary layer thickness.

Consequently, the ratio of dissolution flux of pure chromium to iron can be expressed by

$$J_{\text{diss}}(\text{Cr})/J_{\text{diss}}(\text{Fe}) = (D_{\text{Cr}}/D_{\text{Fe}})^{0.67} \times [(S_{\text{Cr}} - C_{\text{Cr}})/(S_{\text{Fe}} - C_{\text{Fe}})]. \quad (3)$$

When the bulk concentration of the dissolved species can be neglected, in comparison to the solubility, the ratio at 500°C is equal to

$$J_{\text{diss}}(\text{Cr})/J_{\text{diss}}(\text{Fe}) = 34$$

while in our tests, we obtained: $J_{\text{diss}}(\text{Cr})/J_{\text{diss}}(\text{Fe}) = 5$. The difference between the two ratios can be attributed to the fact that our assumptions are not quite correct. Firstly, the expression used to calculate the diffusion boundary layer (Eq. (2)) is not well adapted for our case where the liquid metal is semistagnant. Moreover, we assume that $C_{\text{M}} < S_{\text{M}}$, but the quantity of dissolved chromium in our test (20 wppm) and the uncertainty in the temperature dependence of S_{Cr} are such that C_{Cr} is probably not negligible. All of these features would lead to a lesser ratio.

4.2. Fe–Cr steels

The two steels: DIN 1.4914 (11%Cr) and Orion (25%Cr), exhibit approximately the same corrosion rate as pure iron. Moreover, studies made on cylindrical rotating specimens of DIN 1.4914 steel [5] have indicated that the corrosion of this material is controlled by the iron diffu-

Table 3
Roughness measurements (Ra) of the materials tested (500 h)

Materials	Ra (μm)	
	before test	after test
Fe	0.05	0.3
Cr	0.07	0.2
1.4914	0.1	0.1
Orion	0.08	0.08

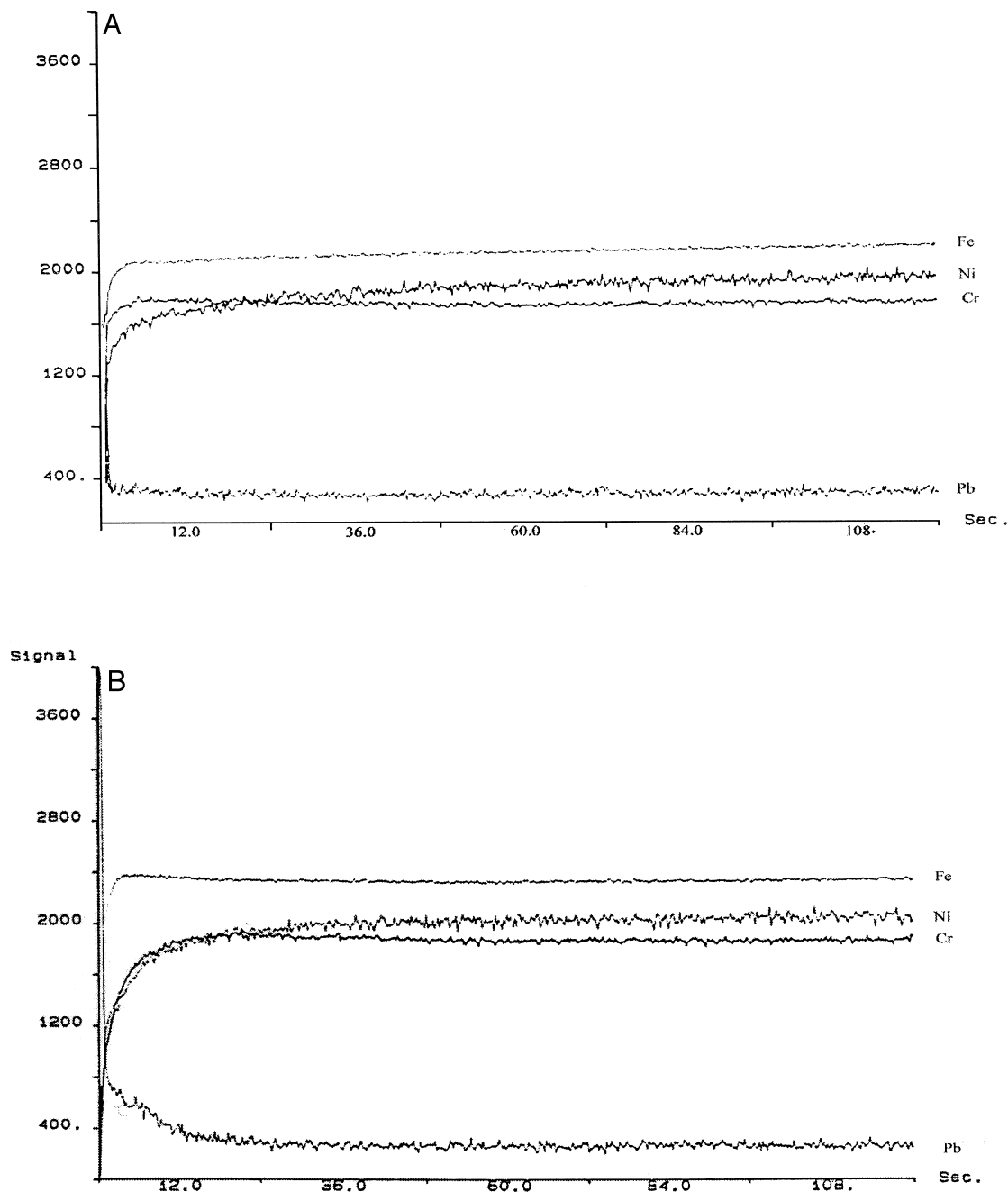


Fig. 3. Luminescent discharge spectroscopy analysis on DIN 1.4914 martensitic steel before (A) and after (B) exposure to liquid Pb-17Li (500°C for 500 h). Erosion rate = $0.03 \mu\text{m s}^{-1}$.

sion in liquid lithium-lead. Consequently, it would seem that the dissolution rate of every binary Fe-Cr alloy having the alpha structure is controlled by the diffusion of iron in the liquid Pb-17Li.

However, in spite of the same corrosion rate values for pure iron and Fe-Cr alloys, a rougher surface for pure iron

after the test is observed. This fact could be assigned to a wetting problem. Indeed, in liquid metals, the wetting of the solid metal can be strongly decreased by the presence of the superficial oxide layer covering the solid material. The oxide layer present on the surface of every metal is more significant for pure iron than for Fe-Cr alloys. Thus,

more wetting irregularities should be observed for pure iron that could explain a more irregular surface of this metal after the test.

5. Corrosion mechanism

Previous studies [1–5] made in the last ten years have shown a uniform dissolution of DIN 1.4914 martensitic steel in the presence of liquid Pb–17Li. Moreover, the parameters which have a notable influence on the corrosion rate have been determined to be the following. (1) Time: The extent of sound metal loss increases linearly with time. (2) Liquid metal flow rate: A model proposed by Sannier and Flament [2] shows that the corrosion of DIN 1.4914 steel is controlled by the diffusion of the dissolved species Fe and Cr in liquid Pb–17Li [2]. Mass transfer experiments made on cylindrical rotating specimens have shown that the chromium diffusion coefficient in liquid Pb–17Li at 500°C is three orders of magnitude higher than that of iron. (3) Temperature: An activation energy of 110 kJ mol⁻¹ has been determined by taking into account the results obtained by all of the laboratories [2]. Moreover, the present work shows the following phenomena: (4) An impoverishment of chromium content near the interface with liquid eutectic at 0.7 μm; (5) A similar dissolution rate for iron, 1.4914 steel and Orion steel.

All these features suggest that the corrosion of DIN 1.4914 steel is controlled by the diffusion of the dissolved Fe in the liquid metal, and that the mass transfer of the Cr element is controlled by the diffusion in the matrix. The following mechanism may be suggested:

- *Dissolution of the metallic element constituting the steel: Fe, Cr, etc.
- *Diffusion of the dissolved species in the boundary layer of liquid metal, with the rate determining step for the whole corrosion mechanism being the diffusion of iron.
- *Diffusion of Cr element in the matrix to the solid/liquid metal interface.

We can validate this mechanism by showing that the impoverishment of chromium may be correlated with the diffusion of this element in the DIN 1.4914 steel matrix.

Indeed, if the diffusion of Cr in DIN 1.4914 steel controls the dissolution of this element, the martensitic steel in the presence of liquid Pb–17Li could be assumed to have a superficial chromium content equal to zero. Moreover, the interface ‘solid matrix/liquid metal’ moves during the test because of the dissolution of the material.

Consequently the second Fick law becomes

$$dC/dt = Dd^2C/dx^2 + VdC/dx \tag{4}$$

with

$$C(x,0) = C_0, \quad C(0,t) = 0 \quad \text{for } t > 0,$$

V : dissolution rate of the interface; D : diffusion coefficient of chromium; $C(x,t)$: Cr content as a function of depth in the matrix x ; and time t ; C_0 : initial content of chromium in 1.4914 steel; $x = 0$: interface matrix/liquid metal. Eq. (4) can be resolved with Laplace transforms into Eq. (5):

$$C(x,t)/C_0 = 1 - 0.5 \left\{ \operatorname{erfc} \left[(x + Vt) / (2D^{0.5}t^{0.5}) \right] + \exp(-VD^{-1}x) \times \operatorname{erfc} \left[(x + Vt) / (2D^{0.5}t^{0.5}) \right] \right\} \tag{5}$$

with

$$\operatorname{erfc}(X) = 1 - \operatorname{erf}(X)$$

$$\operatorname{erf}(X) = 2\pi^{0.5} \int_0^x \exp(-y^2) dy.$$

Considering DIN 1.4914 steel exposed for 500 h at 500°C in liquid Pb–17Li, we have: $C_0 \# 11$ at.%, $V \# 2 \times 10^{-13}$ m s⁻¹, $D(\text{Cr}/1.4914) \# 10^{-20}$ m² s⁻¹ [6]. Thus Eq. (5) becomes

$$C(x,500\text{ h}) \# 1 - 0.5 \left\{ \operatorname{erfc} [3.73(x + 0.4)] + \exp(-20x) \operatorname{erfc} [3.73(x - 0.4)] \right\}, \tag{6}$$

x : μm, C : at.%

The Cr content profile deduced from Eq. (6) has been compared to the one obtained by SDL (Fig. 4). Experimentally, we observed a greater chromium depletion than predicted by the model. The small difference is probably related to the fact that we have introduced a volume diffusion coefficient value in Eq. (6), while the microstructure of DIN 1.4914 steel is such that an intergranular contribution to the diffusional process is not negligible.

An apparent chromium diffusion coefficient in DIN 1.4914 steel at 500°C was estimated using Eq. (5) and the experimental Cr profile. We obtain: $D_{\text{app}}(\text{Cr}/1.4914)_{500^\circ\text{C}} \# 1.5$ to 2×10^{-20} m² s⁻¹, which is only two times larger than the volume value.

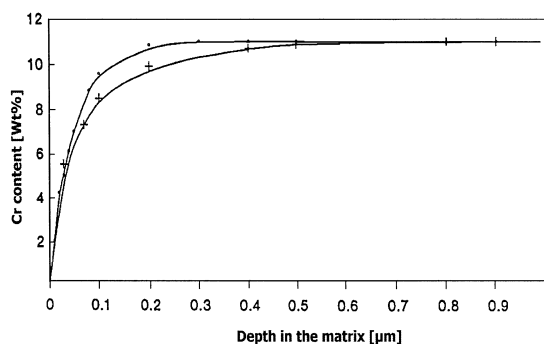


Fig. 4. Chromium content in DIN 1.4914 matrix after exposure to liquid Pd–17Li (500°C for 500 h). LDS profile: + Profile deduced from Eq. (6): ·

6. Conclusion

In this study, mass-transfer experiments carried out with pure iron, chromium and Fe–Cr steels have been conducted to elucidate the corrosion mechanism of martensitic steel exposed to liquid Pb–17Li. The study of pure metals has shown that the corrosion rate of pure chromium is one order of magnitude higher than that of iron. Corrosion rate of the Fe–Cr alloys DIN 1.4914 and Orion is equal to that of pure iron. Moreover, LDS analysis made on DIN 1.4914 steel showed that a chromium depletion occurred near the solid/liquid Pb–17Li interface which is connected with the diffusion of Cr in the martensitic matrix. Consequently, the elementary steps of the whole process of martensitic steel dissolution in the presence of liquid Pb–17Li are as follows:

*Dissolution of the metallic element constituting the steel: Fe, Cr, etc.

*Diffusion of the dissolved species in the boundary layer of liquid metal, with the rate-determining step for the whole corrosion mechanism being the diffusion of iron.

*Diffusion of Cr element in the matrix to the solid/liquid metal interface.

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