Alloying and Coating Strategies for Improved Pb-Li Compatibility in DEMO-Type Fusion Reactors

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Abstract

Two strategies were explored to improve the Pb~16Li compatibility of Fe-base alloys for a fusion energy blanket system. The use of thin (~50μm) Al-rich diffusion coatings on Grade 92 (9Cr-2W) substrates significantly reduced the mass loss in static Pb-Li capsule tests for up to 5,000 h at 600° and 700°C. However, significant Al loss was observed at 700°C. Thicker coatings with Fe-Al intermetallic layers partially spalled after exposure at 700°C, suggesting that coating strategies are limited to lower temperatures. To identify compositions for further alloy development, model FeCrAlY alloys with 10-20 wt.%Cr and 3-5%Al were exposed for 1,000 h at 700°C. There was little effect on mass change of varying the Cr content, however, alloys with <5% Al showed mass losses in these experiments. For both coatings and FeCrAl alloys, the surface reaction product was LiAlO₂ after exposure and cleaning.

Key words: Pb-Li Compatibility, FeCrAl, aluminide diffusion coating, ODS

Introduction

The dual coolant lead lithium (DCLL) blanket concept (both Pb-Li and He coolants) is the leading U.S. design for a test blanket module (TBM) for ITER and for a DEMO-type fusion reactor [1]. With reduced activation ferritic-martensitic (FM) steel as the structural material, the DCLL is limited to ~475°C metal temperature because Fe and Cr readily dissolve in Pb-Li above 500°C and Eurofer 97 plugged a Pb-Li loop at 550°C [2-3]. The use of Al containing coatings or alloys has been shown to reduce mass loss of Fe-base alloys in Pb-Li [4-11], typically by the formation of an Al-rich oxide (typically LiAlO₂) that inhibits dissolution [7,8,9,11,12]. Of course, Al-containing FeCrAl alloys were developed 50 years ago at General Electric for fuel cladding [13] and an oxide dispersion strengthened (ODS) version to enable higher temperature structural applications was commercialized 35 years ago [14]. There has been renewed interest in Fe-based ODS alloys in general because of their excellent combination of creep strength and radiation resistance [15-19]. However, recent studies have focused on ODS FeCrAl [9,12,19-21]

because of potential improvements in compatibility, compared to ODS Fe-Cr compositions. This study presents current results on two strategies to improve Pb-Li compatibility of Fe-base structural alloys for the DCLL blanket: (1) Al-rich coatings which appear to be limited in temperature by Al loss during exposure in Pb-Li and (2) 3-5 wt.%Al alloy additions in cast model alloys with Fe-(10-20%)Cr **to determine appropriate Cr and Al levels for Pb-Li compatibility** as the first step in the development of an ODS FeCrAl designed specifically for the blanket application. Both coatings and cast alloys have been exposed in isothermal Pb-Li capsules as a preliminary evaluation prior to flowing Pb-Li experiments that will begin next year.

Experimental Procedure

Two groups of materials were evaluated: coated and uncoated Grade 92 (Fe-9.2wt.%Cr-1.8W-0.45Mn-0.51Mo-0.16Si-0.11C-0.06N-0.005S determined by combustion and inductively coupled plasma (ICP) analysis) specimens and uncoated cast FeCrAlY with different Cr (10-20%), Al (3-5%) and Y (0-0.06%) contents. Castings (~400g) were fabricated by arc-melting in inert (Ar) gas and drop cast into a water-cooled copper mold at ORNL. The Al diffusion coatings on Grade 92 were deposited via chemical vapor deposition (CVD) in a laboratory-scale reactor consisting of an inductively heated alumina tube with flowing H₂ carrying the AlCl_x vapor, described in detail elsewhere [22]. Coatings were deposited at 900°C for 6h, but a thicker coating was produced by adding Al/Cr powder in the reactor to increase the Al activity **in the vapor** [7,22,23]. The cast FeCrAl specimens (~1.5 mm thick and 4-5 cm²) were polished prior to exposure in Pb-Li to a 600 grit SiC finish. All specimens were cleaned ultrasonically in acetone and alcohol and their mass was recorded before and after Pb-Li exposure with a Mettler-Toledo model XP205 balance with an accuracy of ±0.04 **mg**.

Static capsule tests were performed using Mo (inert to Pb-Li) inner capsules and type 304 stainless steel (SS) outer capsules to protect the inner capsule from oxidation. One specimen was exposed in each capsule and held with 1mm diameter Mo wire. The capsules were loaded with 125 g of Pb-Li in an Ar-filled glove box. The Pb-Li was melted and cast at ORNL and had Li contents of 15.4-17 at% by ICP analysis. The Mo and SS capsules were welded shut in an Ar glove box to prevent the uptake of impurities during the isothermal exposure. After exposure, residual Pb-Li on the specimen surface was removed by soaking in a 1:1:1 mixture of acetic acid, hydrogen peroxide and ethanol for up to 72h. Post-test specimen surfaces were examined using

x-ray diffraction (XRD), a Veeco Wyko optical profilometer, and scanning electron microscopy (SEM) equipped with energy dispersive x-ray (EDX) analysis. After surface characterization, the specimens were Cu-plated, metallographically sectioned and polished and examined by light microscopy and electron probe microanalysis (EPMA) using wavelength dispersive x-ray analysis.

Results and Discussion

I. Coating

The mass change data for the coatings exposed in Pb-Li are shown in Table 1. The exposures less than 5,000h were reported previously [7,9,11]. As expected, the ~50 μ m coatings significantly reduced the mass loss. Typical cross-sections are shown in Figures 1a-1d. Since the dissolution is relatively uniform, the surface appears relatively flat on the uncoated specimens (Figures 1a and 1c). For the coated specimens, the dark precipitates are AlN (also noted in Fig. 2), formed as a result of the reaction between Al in the coating and N in the alloy. Figure 2 shows Al profiles after the 5,000h exposures. For the 50 μ m coatings (Fig. 2a), the surface Al content has dropped from 18at.% to <12% after exposure at 600°C and to ~3% at 700°C. Prior observations at 700°C are summarized in Figure 3 to show the drop in surface Al content with time and the increase in the depth of Al interdiffusion (defined as the depth to detect 0.1at%Al in EPMA line profiles). Especially after 5,000h at 700°C, it is clear that a significant amount of Al has been lost from the coating and that interdiffusion cannot account for the loss as has been observed and modeled for oxidation in wet air [24]. Even after 5,000h at 600°C, where interdiffusion is minimal, the surface Al content has dropped significantly. These results suggest that some amount of Al is being lost during exposure to the Pb-Li.

With a coating losing Al during service, one obvious solution is to create a thicker coating with a larger Al reservoir. Such a coating was created by increasing the Al activity in the vapor during the CVD process and this ~100 μ m thick coating was exposed for 5,000h at 700°C. However, this coating experienced a significant mass loss after exposure (Tab. 1). The mass loss was attributed to the partial loss of the Al-rich outermost coating layer, most likely due to spallation not dissolution. Figure 1e shows a region where the outer layer is intact and Figure 1f shows a region where the outer layer was lost. Oxide formed at the interface between the inner and outer coating layers (shown in Fig. 1e) may have led to the failure or it could have been lost during the cleaning procedure. However, there was no evidence of material lost in the solution. Figure 2b shows that this coating also lost a substantial amount of Al, the starting surface Al

composition was 36at.% and the starting Al profile is shown with the shaded dark blue area. After exposure, the surface Al content dropped to ~15% and the depth of Al interdiffusion increased to ~190 μm . The starting composition of the outer layer is within the $\text{DO}_3\text{-Fe}_3\text{Al}$ phase field and significant Al loss during exposure may have caused void formation or cracking leading to a mechanical instability. Whatever the cause of the loss of the outer layer, the strategy of using a thicker coating with a higher Al content does not appear to be an effective strategy. These results suggest that coatings may not be an effective long-term solution for the blanket. Furthermore, attempts to coat ODS Fe-Cr by the same process were not successful [23].

II. Alloying

In light of the observed durability issues with coatings, another solution is to add Al to the alloy, thereby creating a much larger Al reservoir such that minor Al losses during service may not be an issue. Commercial ODS FeCrAl alloys typically contain ~20wt.%Cr and 4.5-5.5wt.%Al [9,19]. However, such high Cr levels raise concerns about Cr-rich α' phase embrittlement [25,26], especially under irradiation. Thus, various cast FeCrAlY alloys were exposed for 1,000h at 700°C in Pb-Li and the mass changes are shown in Figure 4 as a function of the measured (ICP analysis) Cr and Al contents in each alloy. For the alloys with ~3%Al, the mass losses were between -1.8 and -2.3 mg/cm^2 , decreasing with increasing Cr content. Little (-0.4 mg/cm^2) or no mass loss was observed for the alloys with ~5%Al, **comparable to the results for the protective coatings (Tab. 1)**. Alloys with ~4%Al generally showed intermediate mass losses. In high temperature gaseous oxidation, higher Cr contents allow a protective Al-rich oxide or scale to form with less Al in the alloy [27]. However, that benefit did not appear to be significant under these conditions **with little effect of alloy Cr content on the observed mass changes (Fig. 4)**. Also at high temperature, Y is added to improve the adhesion of the alumina scale and slow its growth and this benefit also was observed for the Y-containing oxides found in ODS FeCrAl [28]. In order to evaluate the effect of Y on mass losses in Pb-Li, two pairs of specimens with nominally 13Cr-4Al and 10Cr-5Al were exposed. Only minor differences were observed in the post-exposure mass losses with and without Y, suggesting little benefit of Y under these conditions.

Examples of the surface morphology and cross-sections from the exposed FeCrAlY specimens are shown in Figures 5 and 6, respectively. In each case, XRD indicated that the surface oxide was LiAlO_2 , consistent with earlier results [9,11,12]. However, the surface oxide was not perfectly adherent, as spalled areas were detected on Fe-15Cr-5Al+Y (Fig. 5), which

showed no mass loss after exposure (Fig. 4). The oxide appeared to be slightly thinner on the 3%Al alloys (Fig. 6). Based on the undulations in the surfaces, the roughness was measured on the specimens and was found to be somewhat greater on the 3%Al alloys compared to the 5%Al alloys (roughness values are shown in Fig. 6). Figure 7 shows EPMA concentration profiles in the substrate beneath the surface oxide in two specimens with 15wt.%Cr. Two locations were measured in each specimen (solid and dashed lines) and the O profiles were used to mark the specimen surface. The nominal 5 and 3 wt.% Al alloys actually contained 4.8 and 2.9%Al as measured by ICP analysis and the EPMA analysis detected ~4.6 and 2.5 wt.% Al in the base alloy, respectively. (The absolute values do not match the chemistry. This likely reflects an EPMA measurement error. If the Al contents were actually significantly lower after exposure, then a mass loss would be measurable.) Some Al depletion was apparent to a depth of ~40 μ m from the surface as shown in the insets. Some amount of Cr depletion also was observed but not as large. The disruptions in the Cr and Al profiles were observed where the line scan intersected a Y-rich precipitate, which is depleted in Cr and Al.

Based on the results in Figure 4, several FeCrAl powder compositions were selected to fabricate ODS FeCrAl alloys. The compositions of the as-received powders are shown as stars in Figure 4. These powders will be ball milled with Y₂O₃ and other oxides and then consolidated by extrusion at ORNL [29]. The resulting ODS FeCrAl alloys will be then evaluated in mechanical and compatibility experiments. **This alloying strategy only addresses compatibility and does not appear to provide a solution to other issues such as the magneto-hydrodynamic pressure drop or address tritium control [30].**

Summary

A series of static Pb-Li capsule experiments was conducted to evaluate coating and alloying strategies to improve Pb-Li compatibility of Fe-base alloys. Thin (~50 μ m) coatings on Grade 92 steel were evaluated for up to 5000h at 600° and 700°C in order to observe the amount of Al loss from the coating and Al interdiffusion with the substrate. The coatings reduced mass loss, but the Al loss from the coating, especially at the surface, was significant. A coating with a significantly higher Al reservoir also showed a significant drop in surface Al content and the outer layer of the coating spalled in some locations resulting in a large mass loss. The interaction between Al in the coating and N in the alloy also could be a long-term problem with this strategy. A series of cast FeCrAlY specimens exposed for 1000h at 700°C suggested that Al contents near 5% minimize mass loss. ODS FeCrAl compositions with 12-15%Cr and 4.5-5%Al

will be fabricated for further evaluations. For both coatings and cast FeCrAlY, LiAlO_2 was detected on the surface after exposure. Based on the Al loss observed from both coatings and alloys, this layer appears to be an imperfect barrier resulting in Al loss during these static exposures. Future work in flowing Pb-Li is needed to evaluate the effectiveness of either strategy in a blanket.

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Figure Captions

Figure 1. Backscattered electron (BSE) images of uncoated (a,c) and coated (b,d-f) Grade 92 specimens after 5,000h Pb-Li exposures at 600°C (a,b) and 700°C (c-f). A thicker coating is shown in (e,f) and the outer layer of this coating that was lost in (f).

Figure 2. Normalized Al content by EPMA as a function of depth for coated Gr.92 specimens after Pb-Li exposure for 5,000h at 600° and 700°C for (a) ~50µm thin and (b) ~100µm thick CVD coatings. Typical coating starting compositions are shown in the shaded regions. For the thicker coating exposed at 700°C (2b - unfilled triangles), a profile from a region like Figure 1f is offset to account for the loss of the outer layer.

Figure 3. (a) Depth of Al diffusion to detect 0.1at.%Al in EPMA line profiles and (b) measured surface Al content as a function of exposure time in Pb-Li at 700°C.

Figure 4. Specimen mass change for the cast FeCrAlY alloy coupons after exposure to Pb-Li for 1,000h at 700°C as a function of Cr and Al contents. The stars mark the composition of four powder batches.

Figure 5. SEM backscattered electron image showing example of the surface after exposure to Pb-Li for 1,000h at 700°C of Fe15Cr5AlY sample.

Figure 6. BSE images of polished cross-sections of cast FeCrAlY alloys after exposure to Pb-li for 1000h at 700°C.

Figure 7. EPMA line profiles from polished cross-sections of two FeCrAl specimens after exposure in Pb-Li for 1000h at 700°C. In both cases, two line profiles were taken in different locations.

Table 1. Summary of Grade 92 Pb-Li exposures.

Sample Name	Type	T (°C)	Time (h)	Mass change (mg/cm ²)
P92	No Coating	600	5000	-1.34
P92 aluminized	Coating	600	5000	-0.02
P92	No Coating	700	5000	-6.57
P92 aluminized	Coating	700	500	0.02
P92 aluminized	Coating	700	1000	0.03
P92 aluminized	Coating	700	2000	-0.27
P92 aluminized	Coating	700	5000	0.36
P92 aluminized	Thicker Coating	700	5000	-6.06

Figure 1. Backscattered electron (BSE) images of uncoated (a,c) and coated (b,d-f) Grade 92 specimens after 5,000h Pb-Li exposures at 600°C (a,b) and 700°C (c-f). A thicker coating is shown in (e,f) and the outer layer of this coating that was lost in (f).

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