

Chemical compatibility of high entropy alloys with liquid PbLi

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ABSTRACT

The chemical compatibility and corrosion resistance of three different high entropy alloys of CrFeV-X, where X = CuW, CuMo, TaW, to stagnant eutectic PbLi was studied. Three nominal HEAs compositions, Cr₃₅Fe₃₅V₂₀W₅Ta₅ (H-TaW), Cu₅Cr₃₅Fe₃₅V₂₀W₅ (H-CuW) and Cu₅Cr₃₅Fe₃₅V₂₀Mo₅ (H-CuMo) were prepared by vacuum arc melting under a low pressure He atmosphere using a non-consumable W electrode and starting from pure elemental pieces with purity > 99.97. Planoparallel specimens of the HEAs were mirror polished and subjected to stagnant PbLi at the eutectic composition, (14.9 ± 1.99) % of Li, at a temperature of 550 °C, corresponding to the working temperature of the WCLL, for increasing times of 168 and 1344 h. After the tests, the microstructure of the samples was cleaned to remove adhered PbLi and analyzed by SEM/EDX and EBSD. SIMS measurements were performed to study the diffusion of into the matrix. From the concentration curves of lithium in the alloys, the diffusion differences of lithium were determined and correlated with the differences in the alloying elements. Furthermore, the corrosion behavior of the alloy showed important differences with the composition of the HEAs and their differences in microstructure. The most significant result is that W has a detrimental effect on the corrosion resistance of PbLi.

1. Introduction

The development of the liquid PbLi breeding blanket (BB) is one of the most promising technologies to provide one of the most critical components required for advanced fusion reactor designs. The use of PbLi offers multiple advantages due to its excellent heat transfer properties and ability to breed the tritium required to sustain the fusion process. As a liquid, it can withstand the extreme conditions of the fusion chamber, avoiding the extreme radiation damage that other solid BB designs must sustain, and has the potential to absorb the high energy neutrons produced during nuclear fusion, reducing the radiation damage to the structural components behind the BB [1]. Several BB concepts based on PbLi as coolant/breeder material are currently under development, such as helium-cooled lithium lead (HCLL), water-cooled lithium lead (WCLL) or dual-coolant lithium lead (DCLL) [2,3].

On the other hand, high-performance steels with more heat and radiation resistance than the RAFM steels of the ITER in-vessel components, tungsten-based materials for the armour components that must

withstand the heaviest thermal and erosion loads, such as the divertor, and Cu-based alloys for the first wall cooling system components, with CuCrZr as the reference material, are considered among the best candidates as new materials for DEMO implementation within the framework of European R&D programs for the development of fusion reactors [4–6]. However, there are many issues that need to be afforded, such as the critical joining of components of the reactor with diverse chemical composition and physical properties. The divertor designs under consideration for DEMO commonly consists of tungsten tiles facing the plasma, bonded to the CuCrZr components of the cooling system.

One of the main concerns for the implementation of the BB concept base on liquid PbLi is the chemical compatibility with the materials of the system, which includes the corrosion resistance, dissolution alloying elements, interdiffusion processes and deposition of activated corrosion products in undesirable areas [7–9]. Extensive research has been conducted on the corrosion resistance and the compatibility of reduced activation steels in eutectic PbLi under static and flowing conditions showing lower dissolution rates for the ferritic steels and an increase by

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Fig. 1. (a) Image of the system where the PbLi corrosion tests were performed. (b) View of the eight high-purity alumina crucibles inside the furnace of the system where the samples were immersed in liquid PbLi for testing.

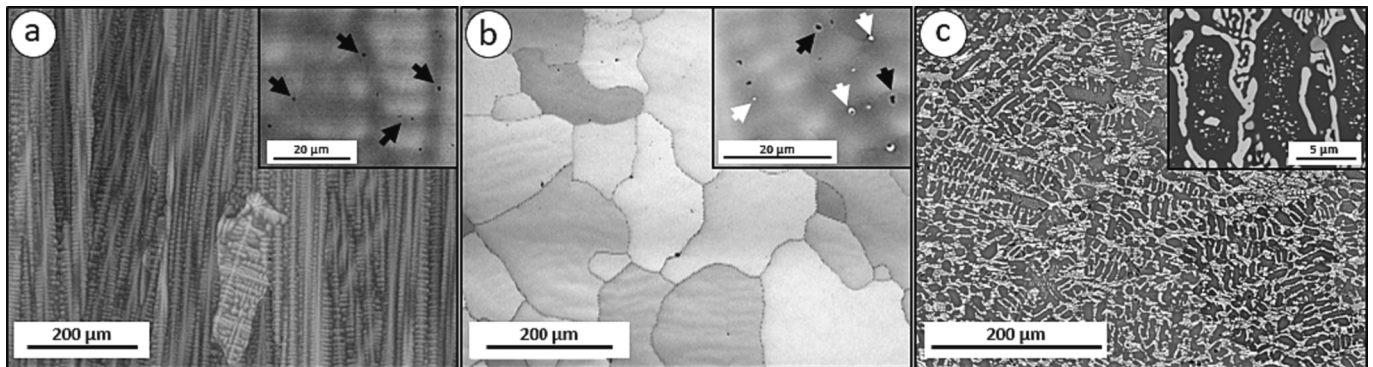


Fig. 2. Initial microstructure of the HEAs before exposure to PbLi: a) $\text{Cu}_5\text{Cr}_{35}\text{Fe}_{35}\text{V}_{20}\text{W}_5$, b) $\text{Cu}_5\text{Cr}_{35}\text{Fe}_{35}\text{V}_{20}\text{Mo}_5$ and c) $\text{Cr}_{35}\text{Fe}_{35}\text{V}_{20}\text{Ta}_5\text{W}_5$. The inset in (c) corresponds to higher magnification SEM-BSE images revealing the presence of small Ta-enriched precipitates. The black arrows in the insets point to sparse V-enriched precipitates and the white arrows to Cu precipitates.

a factor of 1.3 in the presence of a magnetic field (magnetic field 0.5 T and flowing eutectic PbLi at 500 °C) [10–13]. However, the Fe and Cr are selectively leached from the steel surface of the components, causing the alloy to dissolve in the liquid metal, with corrosion rates values in the literature ranging from 5×10^{-3} – $900 \times 10^{-3} \mu\text{m}/\text{yr}$ [10–13]. These corrosion rates limit its use for components in contact with liquid PbLi due to the degradation of their thermophysical properties and associated problems caused by mass transfer to other components of the reactor or the increase in safety risks due to retention or transfer of radioactive products [8,14]. In addition, the presence of light impurities, especially O, is very common in liquid PbLi and affects the chemical compatibility of the alloys, with adverse effects on the corrosion rates and the formation of oxide compounds [14,15]. Another major problem is the permeation of tritium from the liquid PbLi breeder to the water of the heat extraction system in the WCLL designs based on steels as structural materials, which is too high for steels and must be reduced to less in orders of magnitude to satisfy the total inventory of tritium in the

cooling water of DEMO [16].

One strategy to increase the resistance of materials exposed to PbLi and to reduce the permeation of tritium is the development of resistant anti-permeation barriers, such as Al_2O_3 or SiC coatings over the structural steel components [17]. Aluminum oxide coatings have been one of the most studied due to their excellent corrosion resistance and barrier to tritium permeation even under neutron irradiation [18,19]. However, coatings also present several back draws. The coating must remain well adhered to the substrate throughout the service life of the components under extreme irradiation conditions and must have very low erosion rates due to its thinness, which are goals very difficult to achieve under the extreme irradiation environment and operating temperatures of the BB [20,21]. The high reactivity of the liquid metal and the thermal stresses at the interface with the steels due to the differences in thermal expansion coefficients can cause the failure of the protective coating, the subsequent infiltration of lithium and the formation of tritium due to the neutron irradiation, following the formation of bubbles, causing a

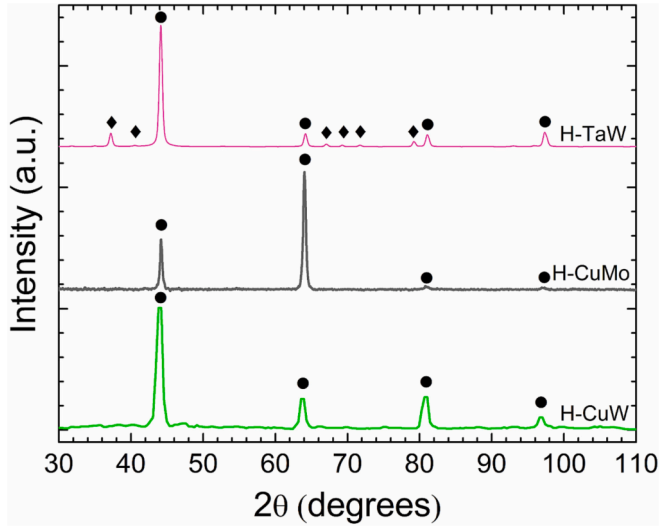


Fig. 3. X-ray diffraction patterns of the three alloys before the corrosion test. The closed circles correspond to the BCC phase (Ref. 00 012 0604, special group: Im $\bar{3}$ m (229)) and diamonds correspond to the hexagonal phase (Ref. 00 012 0604, special group: P63/mmc (194)) in the interdendritic regions.

degradation of the coating and exposing the steel.

In the development of advanced materials, high entropy alloys (HEAs) have been considered as potential candidates for use in some of the components of future fusion reactors that will be exposed to the most severe operating conditions, such as the first wall, breeding blanket or divertor components of the reactor [22–24]. HEAs have attracted considerable attention in recent decades due to their unique combination of properties such as a good balance between high strength, ductility and toughness at high temperatures, good corrosion resistance or good radiation resistance [25–29]. In addition, some HEAs have self-healing properties after exposure to radiation [30]. These alloys are composed of a minimum of 5 elements in similar proportions, between 5 and 35 at.% each, and are characterized by their high configurational entropy, which results in the formation of solid solutions instead of amorphous phases or intermetallic compounds. Although HEAs were

initially considered to present a single phase, in recent decades HEAs with reinforcing precipitates or multiple phases have been developed, some of which with improved mechanical properties [12,31,32]. However, the corrosion resistance of HEAs to liquid metals, and in particular to PbLi, has been scarcely studied and has focused on HEAs with Al as the alloying element [33,34].

In this [6] work we study the chemical compatibility of HEAs $\text{Cr}_{35}\text{Fe}_{35}\text{V}_{20}\text{-X}$, where $\text{X} = \text{Cu}_5\text{Mo}_5$, Cu_5W_5 and W_5Ta_5 in eutectic PbLi at 550 °C to verify their application as structural material in the breeder blanket. The microstructure of the as-cast and heat treated HEAs was characterized before and after exposure to PbLi, as well as the lithium diffusion into the bulk. The paper concludes with a brief comparison of the differences in corrosion behavior caused by the different elements present in the three alloys studied and aims to provide new insights into the integrity and performance reliability of new HEAs in contact with liquid PbLi.

2. Experimental procedure

2.1. Preparation of HEAs

HEAs with compositions $\text{Cu}_5\text{Cr}_{35}\text{Fe}_{35}\text{V}_{20}\text{W}_5$ and $\text{Cu}_5\text{Cr}_{35}\text{Fe}_{35}\text{V}_{20}\text{Mo}_5$ and $\text{Cr}_{35}\text{Fe}_{35}\text{V}_{20}\text{Ta}_5\text{W}_5$ were prepared by vacuum arc melting under a He atmosphere at low pressure using a non-consumable W electrode, starting from pure elemental pieces with purity > 99.97 [35]. For simplicity, the HEAs are here after referred to as H-CuW, H-CuMo and H-TaW. The buttons produced, with an average weight of 14 g, were melted 5 times and flipped between melts to ensure the homogeneity of the alloys. All the alloys were subjected to a homogenizing heat treatment for 24 h, been the temperature of the treatment 700 °C for the H-CuW and H-CuMo, and 1100 °C for the H-TaW. This annealing temperature was selected because at temperatures above 750 °C the formation and growth of a sigma phase with a brittle nature was observed for the H-CuMo and H-CuW. The microstructure of the alloys was analyzed with a high-resolution FE-SEM FEI TENEO scanning microscope equipped with an energy dispersive X-Ray spectroscopy (EDAX) detector and an electron backscatter diffraction (EBSD) system. X-ray diffraction measurements were performed by a X'PERT diffractometer using $\text{CuK}\alpha$ radiation.

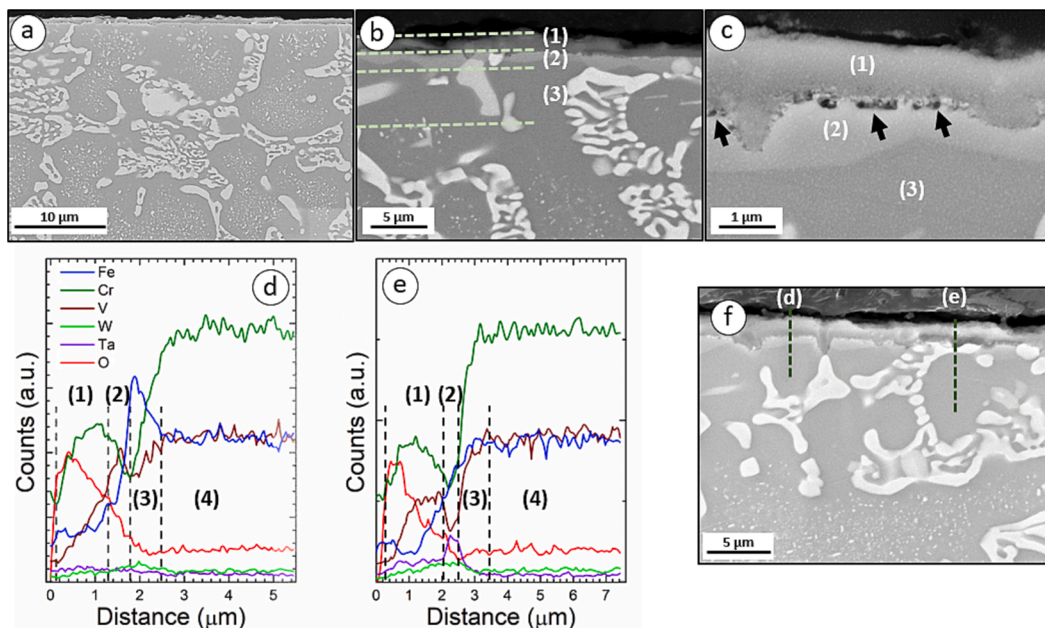


Fig. 4. (a), (b) and (c) SEM-BSE images of the cross section of H-TaW after 168 h immersion in PbLi. The black arrows indicate submicron voids. Figures (d) and (e) show the composition profiles obtained by EDS along the lines depicted in (f).

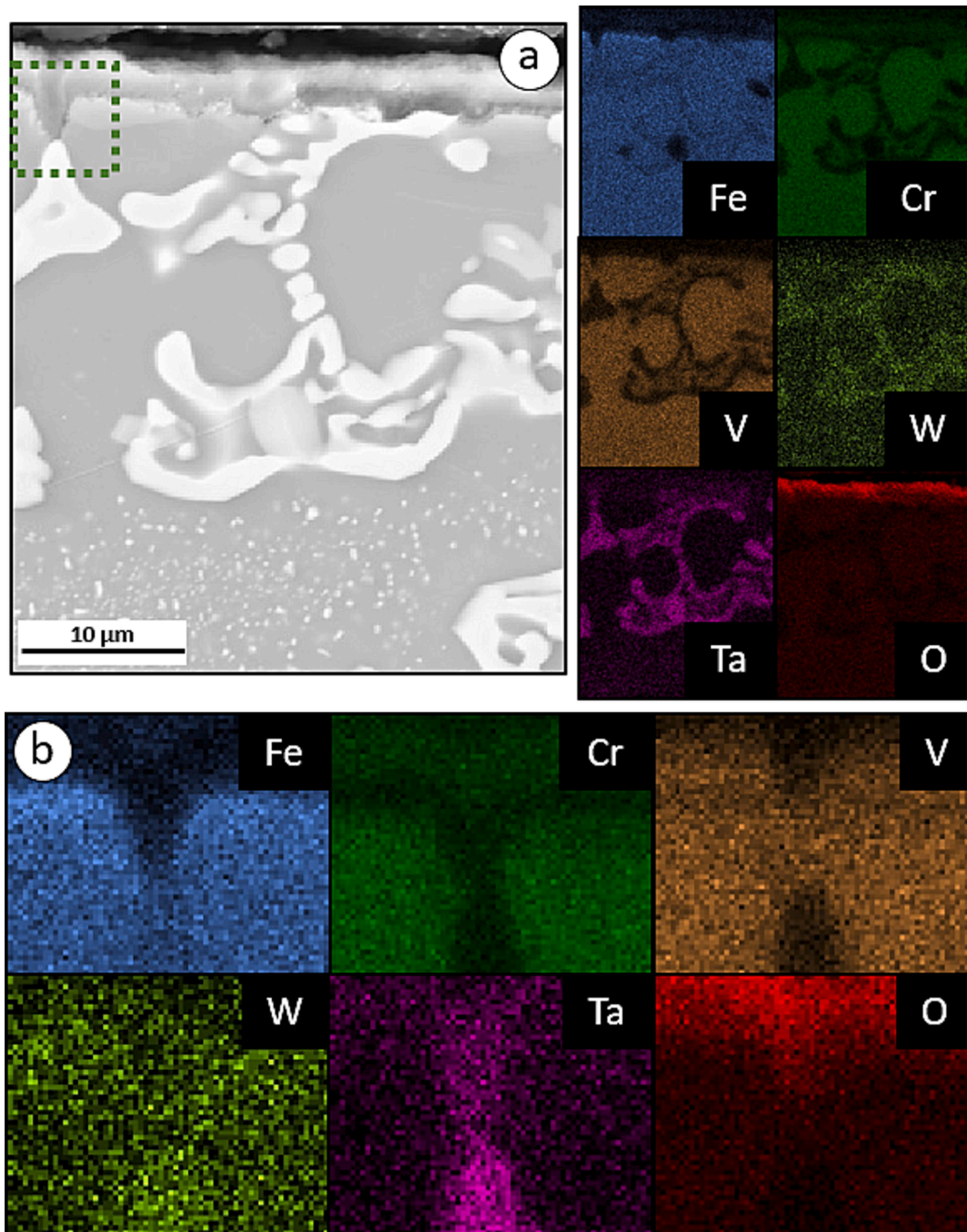


Fig. 5. (a) EDS composition maps showing the distribution of the alloying elements for H-TaW in the cross section of a sample after 168 h immersion in PbLi. Subfigure (b) shows a higher resolution EDS composition map of the square marked with a dotted line in (a).

2.2. Corrosion tests

The corrosion tests were carried out in the COES facility, which consists of a circular furnace containing a vessel internally coated with alumina to prevent corrosion by liquid PbLi and a system to facilitate the extraction of samples under controlled conditions, see Fig. 1. Flat parallel samples of the alloys were placed in the crucibles according to their composition (suspended from a wire) to prevent potential cross-contamination during the corrosion tests. The PbLi inventory of the system is 2 L and it operates under an argon atmosphere. The tests were carried out for increasing times ranging from 168 to 1344 h at a temperature of 550 °C, which is relevant for the BB system. The experimental parameters were monitored in real-time.

The incorporation of lithium into the HEA alloys and the extent of

diffusion in the bulk after the corrosion tests was studied using SIMS (Secondary Ion Mass Spectrometry) and ICP-MS (Inductively Coupled Plasma Mass Spectrometry) at different test times.

3. Results

The microstructure of the three HEAs before exposure to PbLi is presented in the SEM-EBS images of Fig. 2. The H-CuW and H-CuMo exhibits a single-phase BCC (Ref. 00-012-0604, space group: $Im\bar{3}m(229)$) microstructure, as it was determined by X-ray and EBSD measurements, with large grains containing a dispersion of submicron Cu precipitates and very sparse small V precipitates. Fig. 3 shows the corresponding indexed X-ray diffraction patterns of both alloys in the state before the corrosion test, that they are single BCC phase materials.

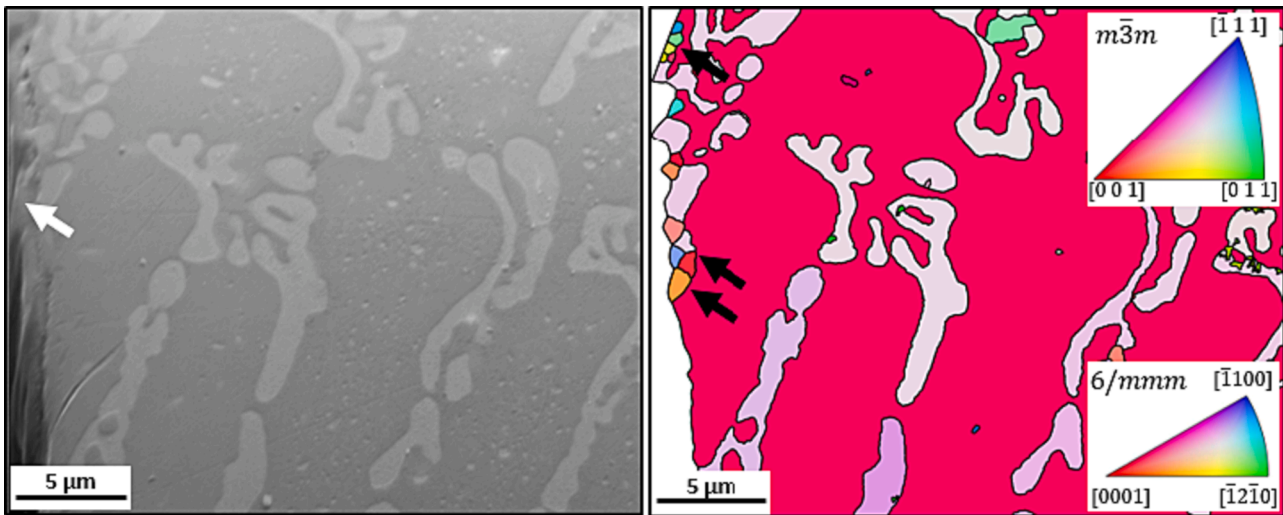


Fig. 6. EBSD results obtained on a cross section of a sample of H-TaW after 168 h of immersion in PbLi, showing the IPF maps of the reconstructed grains. The dendritic phase was indexed to a BCC phase and the interdendritic phase was indexed to a hexagonal phase. The white arrow points to the surface that was in contact with the liquid PbLi. The black arrows point to new small grains formed on the surface of the alloy in contact with the oxide scale.

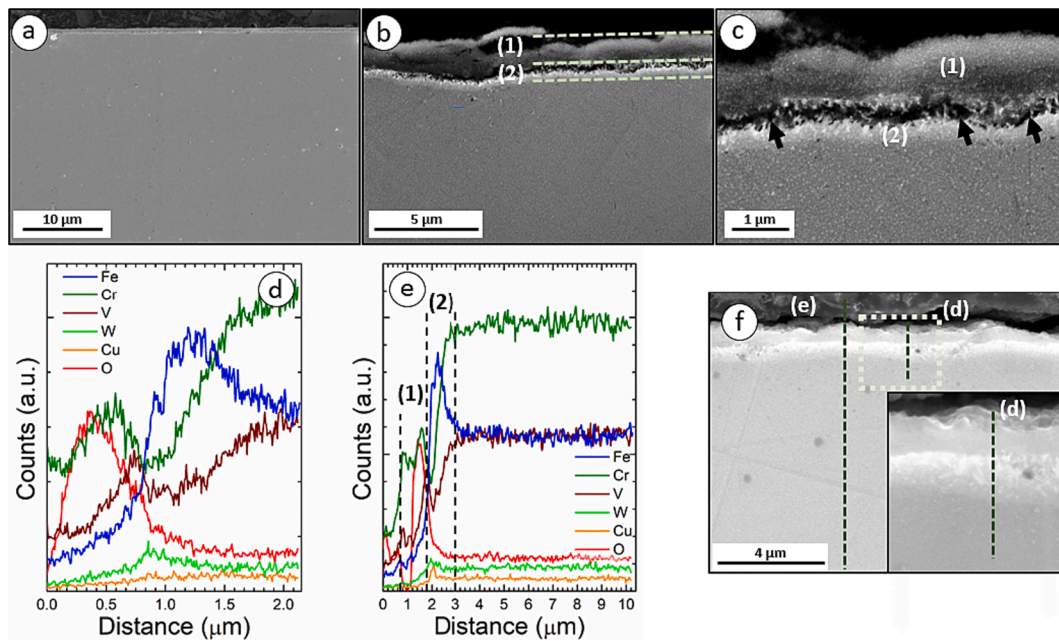


Fig. 7. (a), (b) and (c) SEM-BSE images of the cross section of H-CuW after 168 h immersion in PbLi. The black arrows points to submicron voids. Figures (d) and (e) show the composition profiles obtained by EDS along the lines depicted in (f). The inset in (f) corresponds to a higher magnification SEM image of the region marked by the dotted rectangle.

The grains have a columnar structure in H-CuW and show a contrast in brightness in the SEM-BSE image that correlates with minor variations in composition that are stable after the homogenization thermal treatment; the brighter regions are slightly enriched in W and depleted in Fe. In contrast, H-CuMo grains tend to be regular shaped. The H-TaW alloy exhibits a dendritic microstructure in which the dendrites (gray contrast) are enriched in Cr and have a BCC structure (Ref. 00-012-0604). In contrast, the interdendritic regions correspond to a hexagonal phase (Ref. 00 012 0604, space group: $P6_3/mmc$ (194)), as clearly shown in the indexed X-ray diffraction patterns presented in Fig. 3. Small precipitates enriched in Ta and W are observed in the dendrites (see Fig. 2 (c)).

The cross section of the H-TaW after 168 h of immersion in PbLi is shown in Fig. 4. The formation of distinct regions parallel to the surface

exposed to PbLi is apparent in the SEM-EBS images and in the composition map obtained from EDS measurements of the cross section depicted in Fig. 5. The outermost layer that has been in contact with the liquid PbLi, designated as 1, corresponds to oxides, mainly Cr-Fe rich oxides. This oxide scale presents a compact and homogeneous structure along the surface of the H-TaW that have been exposure to the liquid metal, and have a homogenous thickness in the range of $\sim 1.5 \mu\text{m}$. The presence of small voids is observed in the interlayer between the oxide scale and the outermost surface of the alloy, as can be seen in Fig. 4-(c). In addition, there is a variation in the composition of the inner surface of the oxide layer when it has grown over an interdendrite, presenting a higher content of V and Ta compared with the oxide grown over the dendritic phase. This difference in composition is clearly observed in the EDS profiles shown in Fig. 4-(d) and (e) (see differences in the inner part

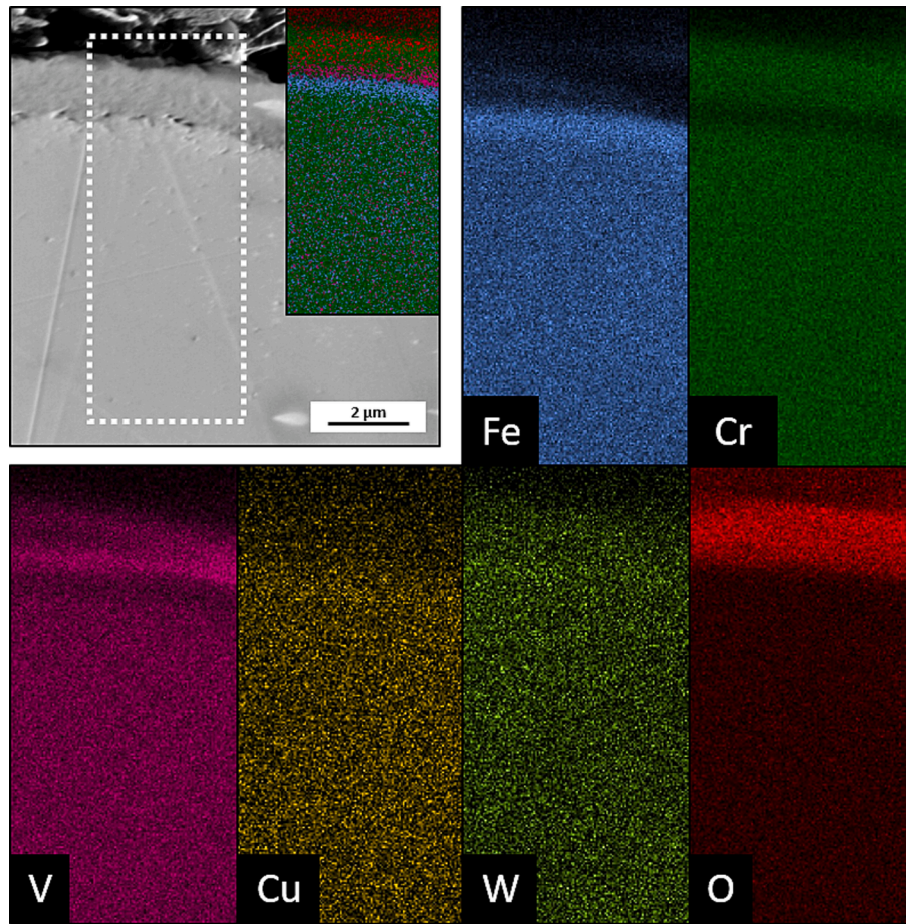


Fig. 8. EDS composition maps of the region marked by the dotted rectangle in the SEM-BSE image showing the distribution of alloying elements for a cross section of a H-CuW sample after 168 h immersion in PbLi. The inset corresponds to a superposition of the different EDS elemental maps.

of the region (1) of the EDS profiles). When the outermost surface of the alloy in contact with the oxide corresponds to a dendrite, a thin new layer enriched in V is formed, labeled as region 2 in Fig. 2. Furthermore, EBSD analysis, summarized in Fig. 6, revealed the formation of new small grains in this region, with a BCC crystalline structure equivalent to that of the dendrite.

Below the region 2, there is a layer of $\sim 10 \mu\text{m}$ depth in which the small Ta-enriched precipitates present prior to PbLi exposure are not observed, indicating that exposure to liquid PbLi has caused their dissolution. This region free of the Ta-enriched precipitates, labeled as region 3 in Fig. 4, extends throughout the material regardless of whether the surface of the alloy that has been in contact with PbLi corresponds to the dendritic or interdendritic phase. In contrast, the interdendrites found in this region do not show any appreciable changes in composition, size or morphology. Finally, there is an intermediate region depleted in Cr that starts near the inner boundary of the oxide scale and extends over the region 3, with a gradual increasing content of Cr along this last region until its initial concentration in the dendrites before the PbLi exposure.

Fig. 7 shows the cross section of the H-CuW after 168 h of immersion in PbLi. As in the case of the H-TaW, the alloy surface exposed to the liquid metal formed an oxide scale of similar thickness, $\sim 1.25 \mu\text{m}$. The oxide scale, labeled region 1 in Fig. 7, is very homogeneous, compact and consists mainly of Cr oxides. Small submicron voids are present between the interface of the oxide scale and the outermost surface of the alloy. The EDS profiles revealed that the inner part of the oxide scale in contact with the alloy is enriched in V compared to the outer oxide surface. This segregation of elements is more clearly observed in the EDS composition map shown in Fig. 8. Below the oxide scale there is a region

enriched in W and Cr depleted, labeled 2 in Fig. 7, which extends from the surface of the alloy into the interior to an average depth of $\sim 0.6 \mu\text{m}$. H-CuW shows no changes in composition or microstructure below this region. However, the boundary between region 2 and the H-CuW, which shows no changes after PbLi, does not appear to be abrupt, as can be seen in the high magnification SEM-EDS image of the inset of Fig. 7-(f). This suggests that in region 2 there are differential diffusion processes for the different elements due to the interaction of the alloy with the liquid metal, creating a composition gradient in the elemental content of region 2 that gradually changes from the composition of the alloy to the composition of region 2 in contact with the oxide scale 2. This result is consistent with the EBSD measurements carried out on the H-CuW samples tested, where there was no evidence of new grain formation in the region 2, in contrast to what was observed for the H-TaW in the equivalent region (see Fig. 6).

The microstructure of the cross section for H-CuMo is similar to that observed for H-CuW and also shows segregation of the constituents near the surface, as shown in the EDS profiles and EDS composition maps in Fig. 9 and Fig. 10, respectively. A thin and compact scale of Cr-enriched oxides developed along the surface in contact with the liquid metal, labeled 1, with an average thickness of $\sim 0.1 \mu\text{m}$. There are small submicron voids in the interface between the oxide scale and the surface of the alloy (Fig. 9-(c)). Also, the EDS profiles and composition maps of Fig. 9-(d-e) and Fig. 10 reveal that the inner part of the oxide layer in contact with the alloy is enriched in V compared to the outer oxide surface. Finally, the surface of the alloy presents a layer of $\sim 1.1 \mu\text{m}$ thickness depleted in Cr, designated as 2, with the region in contact with the oxide layer enriched in Mo and presents some regions enriched in Cu (see Fig. 9-(d-e) and Fig. 10).

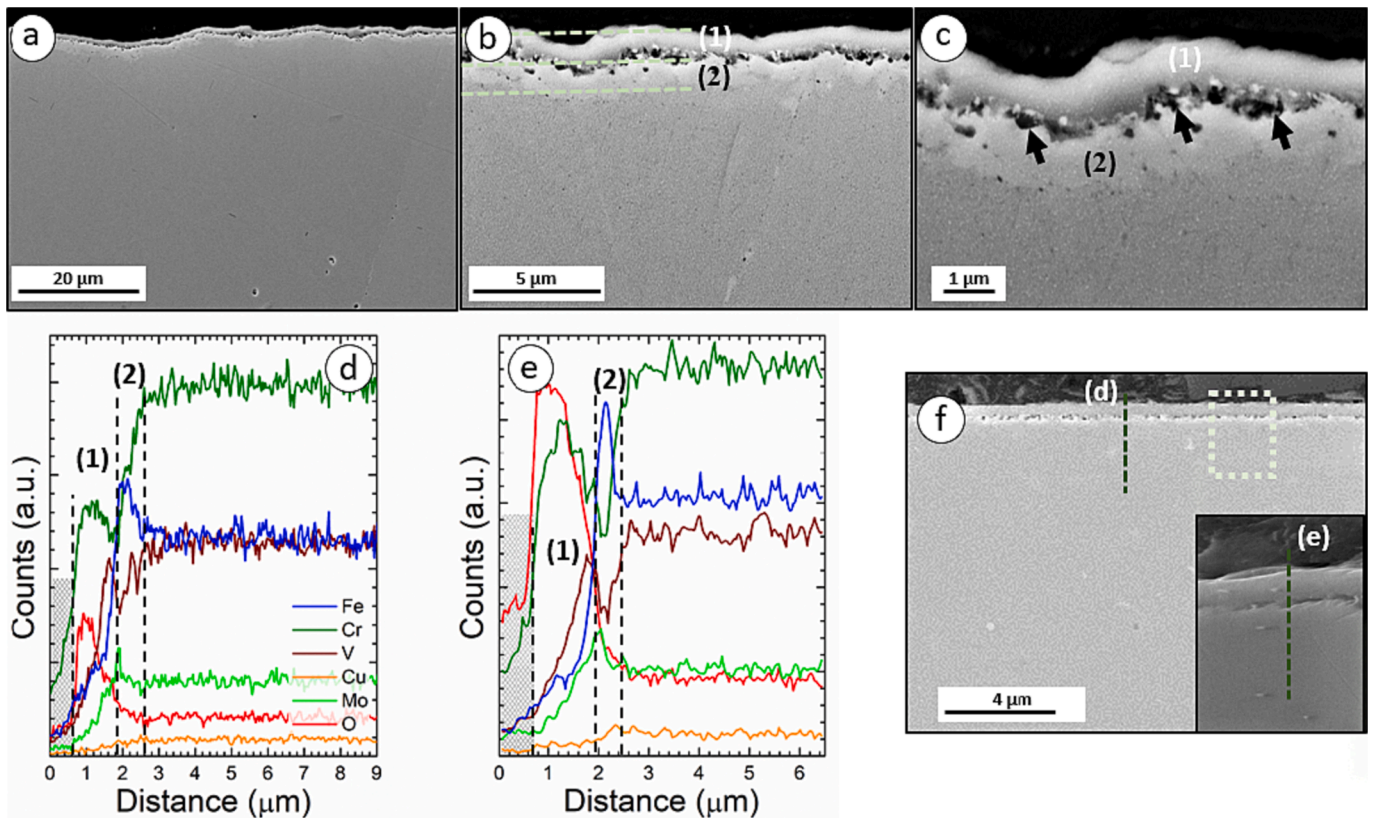


Fig. 9. (a), (b) and (c) SEM-BSE images of the cross section of H-CuMo after 168 h immersion in PbLi. Black arrows indicate submicron voids. Figures (d) and (e) show the composition profiles obtained by EDS along the lines depicted in (f). The inset in (f) corresponds to a higher magnification SEM image of the region marked by the dotted rectangle.

Fig. 11 shows the lithium diffusion profile in the three alloys after 168 h of immersion in PbLi. The study of the initial corrosion processes during the first hours of exposure to liquid PbLi is crucial to understand the initiation of corrosion and to develop strategies to mitigate it. As it can be noticed in the figure, the two alloys containing W present a similar profile in which the oxide layer is saturated with Li. From there, the Li content penetrating into the alloy decreases as it passes through the depleted chromium zone and stabilizes in the bulk, although the remaining value is almost double in the H-TaW than in the H-CuW. On the contrary, the H-CuMo alloy presents a narrow saturation zone corresponding to the interface between the chromium-depleted zone and the bulk. Beyond this area, the lithium decrease is abrupt and finally, reaching values in the matrix similar to those of H-TaW. Looking closely at Figs. 10 and 11 (b), which represents the profile of all the elements involved in H-CuMo, it is observed that the lithium signal is directly related to the upper part of region 2 enriched in Mo that of molybdenum and the region with a high density of cavities.

Fig. 11 (d)-(f) compare the results of lithium diffusion between 168 and 1344 h. The results are very interesting and show how the H-CuW alloy offers practically no resistance to lithium diffusion, reaching high levels in the bulk compared to H-CuMo and especially to H-TaW, which reaches the residual level of the vacuum chamber at $\sim 15 \mu\text{m}$ depth.

Finally, the result of the ICP-MS analysis carried out on the residual PbLi after the 168 and 1344 h corrosion tests is shown in Table.

Table 1. It should be noted that for the lower testing times, the dissolution of the HEAs is negligible in terms of the majority of elements that have passed to the molten eutectic; however, when the test time is extended to 1344 h, there is a clear loss of the base elements of the alloys, Fe, Cr and V, especially in those alloys containing W. The H-CuMo alloy seems to be the more resistant to corrosion.

4. Discussion

The three HEAs have significant initial microstructural and compositional differences that clearly influence their corrosion resistance to liquid PbLi, but they also share some common responses that help understand how composition influences their compatibility with PbLi. While the two Cu containing alloys can be defined as monophasic, the H-TaW shows a dendritic microstructure with clearly distinct parts that behave differently in contact with the liquid PbLi. The three develop a Cr-rich oxide scale on the alloy surface and present a Cr-depleted susceptibility zone. The formation of this Cr-depleted region has already been observed in RAFM steels developed for fusion applications under similar conditions as a result of the transformation of the preceding martensite laths into ferrite [11,36–38]. The RAFM steels develop a network of voids along the embossed ferrite zone in contact with the oxide scale, which promotes their erosion along the boundaries of the martensitic to ferritic transformed grains, thereby facilitating the penetration of Li or Pb into the steels. In contrast, the voids are confined to the region of the alloy in contact with the oxide scale in the HEAs and have a smaller submicron size for the H-TaW and H-CuMo, compared to the sizes of the order of $\sim 0.5 \mu\text{m}$ observed for the voids in the RAFMs, which may enhance their resistance.

The depleted Cr zone observed in the HEAs should be the result of the differential diffusion of Cr and Fe since the solubility in liquid Pb17Li is higher for elemental Fe than for elemental Cr; 47 wppm and 10 wppm at $T \approx 500^\circ\text{C}$, respectively. This is supported by the corrosion rate study of Simon *et al* [39] for pure Cr, Fe and FeCr steels with a high Cr content, where a large increase in Cr corrosion rate was observed for the steels in the presence of liquid Pb17Li. Since the Cr-depleted region in the HEAs coincides with the zone where the Li content varies with the opposite gradient, Li decreasing as Cr increases up to the initial matrix content, the Cr diffusion rate in the alloys compared to its value in elemental Cr

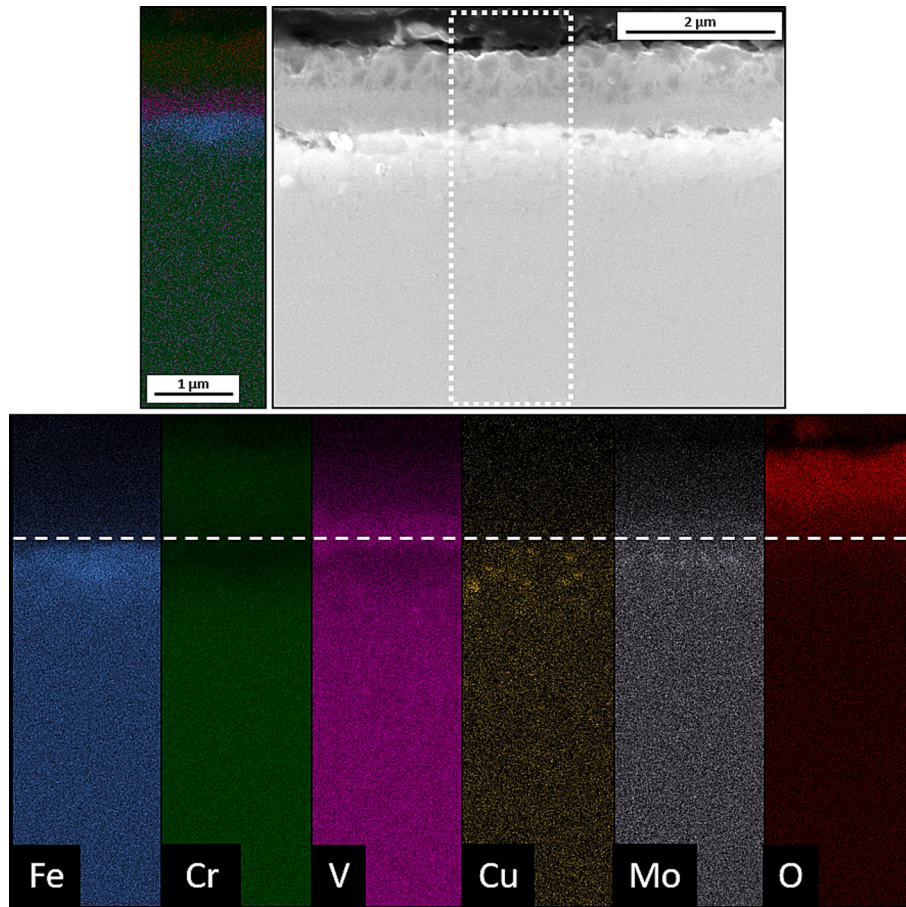


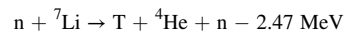
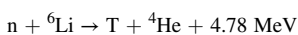
Fig. 10. EDS composition maps of the region marked by the dotted rectangle in the SEM-BSE image showing the distribution of alloying elements for a cross section of a H-CuMo sample after 168 h immersion in PbLi. The upper left figure corresponds to a superposition of the elemental maps. The white dashed line in the composition maps approximately delineates the boundary between the oxide layer and the alloy.

may be enhanced by the presence of Li, which may also be the possible explanation for its formation in the RAFMs. This effect may be similar to the enhancement of corrosion rate in non-passivating solutions of steels due to absorbed hydrogen [40].

The diffusion of elements creates a mismatch between the oxide layer and the outer part of the alloy, resulting in small voids that grow with exposure time and facilitate its detachment from the alloy and transfer to the PbLi. For this reason, the oxide layer is often not found in long-term tests. The introduction of W in the HEAs does not seem to provide in terms of performance in PbLi, neither in solid solution in the H-CuW or in the H-TaW; unlike molybdenum, which significantly reduces corrosion compared to Eurofer under the same conditions [41].

Corrosion is also caused by the dissolution of the alloys in PbLi, which can be studied by chemical analysis of the residual PbLi after the tests in conjunction with SIMS analysis. The comparison of the results obtained by SIMS for Cr and Fe with the concentrations of the same elements determined by ICP-MS in the eutectic shows that there is a clear equivalence between the increase/decrease of one of the elements in the region of the HEAs affected by corrosion observed by SIMS and the content of these elements in the PbLi, placing W as an undesirable alloying element in terms of corrosion resistance.

Furthermore, the 1344 h tests show another the long-term problematic behavior of H-WCu, where the Li content remains high and constant beyond a depth of 20 μm. The diffusion of lithium in a material operating under fusion reactor conditions has serious consequences due to the production of tritium (T) and ^4He through transmutation reactions caused by the 14 MeV neutrons generated by fusion reactions:



Hydrogen and especially helium, which has a much lower diffusivity in metals, can degrade the properties of alloys. In HEAs and RAFMs, its presence causes the formation of bubbles, vesicles and cracks and induces embrittlement [42–44]. Although lithium depletion in H-CuMo and H-TaW is also significant with depth, it does not decrease to the residual value of Li in the chamber within the susceptibility zone where changes in microstructure or initial elemental composition have been observed, indicating the limited resistance of these alloys to Li diffusion.

Finally, it is interesting to highlight the effect of precipitates on the dissolution process, which has already been pointed out by several authors [12,36,37] as being responsible for promoting corrosion of RAFM steels in molten metals. Qi Xu et al. [36] have observed C depletion and dissolution of carbides near the steel surface due to interaction with Li and/or impurities present in the molten metal as one of the factors contributing to the dissolution of RAFM steels to molten metal corrosion [45]. Consider the H-TaW alloy, which has a high content of Ta and W-rich precipitates in the bulk prior to the corrosion test. However, the precipitates completely disappear in the susceptibility zone after 168 h of immersion in PbLi. Fig. 5 (b) reveals that there is a differential diffusion of elements that promotes corrosion when the dendrites enriched in Ta and W are near the alloy surface, creating a differentiated chemical reaction zone. This mechanism should also be responsible for the dissolution of the small precipitates Ta and W-enriched. A similar situation may occur in H-CuW and H-CuMo, which contain a significant amount of submicron precipitates enriched in Cu, which are also not observed in the susceptibility zone after the test. It seems clear that these

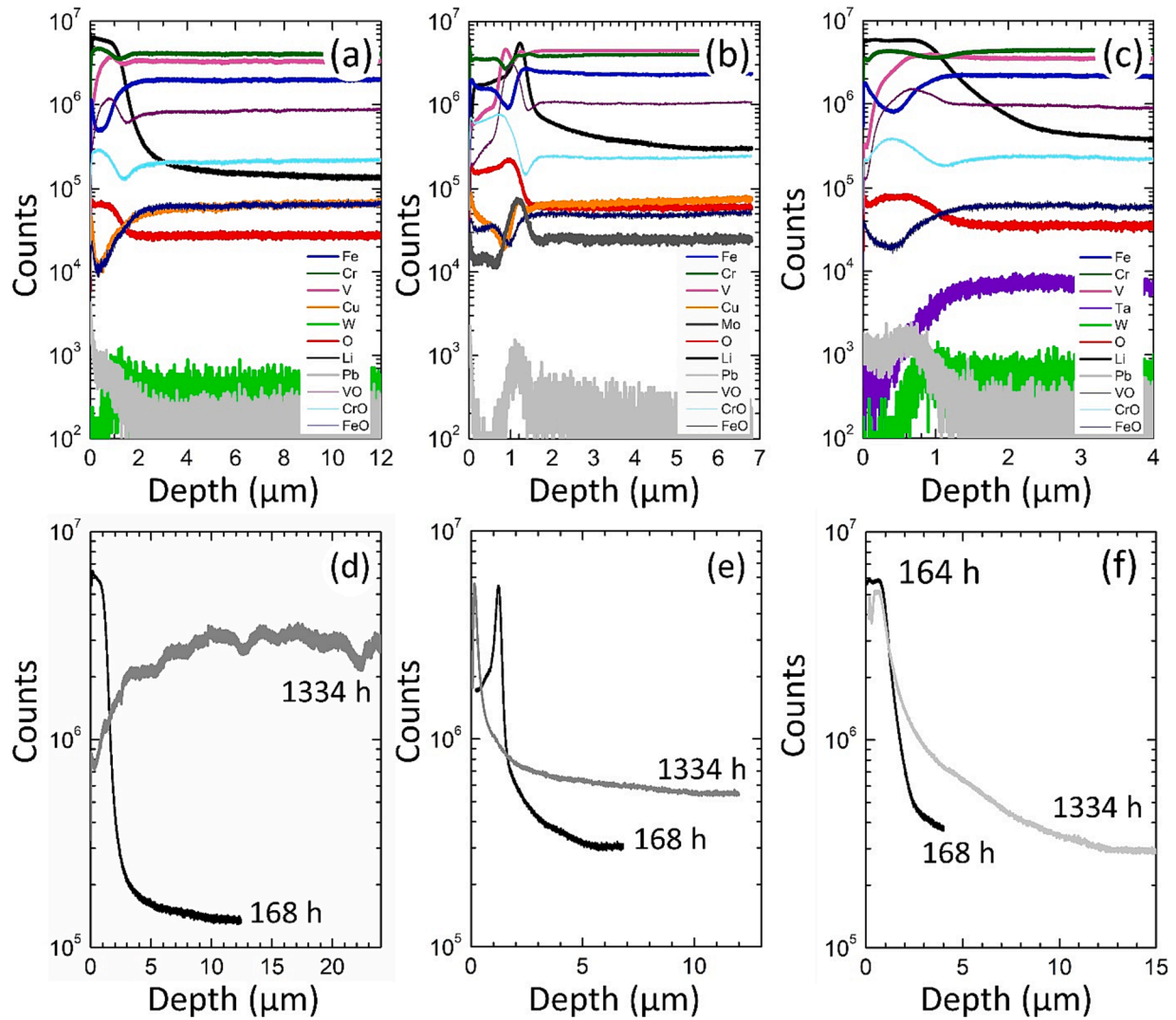


Fig. 11. SIMS profile of the elements in the HEAs after 168 h exposure to PbLi: (a) H-CuW, (b) H-CuMo and (c) H-TaW. For clarity, the oxide species detected by SIMS are depicted as thin lines. Comparison of SIMS profiles for lithium after exposure for 168 h and 1344 h: (d) H-CuW, (e) H-CuMo and (f) H-TaW.

Table 1

ICP-MS analysis of the eutectic PbLi after the 168 and 1344 h corrosion tests, showing the content of dissolved Fe, Cr and V.

HEA	Testing (hours)	Fe (μg/g)	Cr (μg/g)	V (μg/g)
H-WTa	168	<1	<0.5	<0.1
H-CuMo	168	<1	<0.5	<0.1
H-WCu	168	<1	<0.5	<0.1
H-WTa	1344	12	0.76	<0.1
H-CuMo	1344	1.2	<0.5	<0.1
H-WCu	1344	9.2	5	0.26

precipitates are dissolved and incorporated into the PbLi, but quantitatively they represent such a small amount that they cannot be detected by ICP, unlike the Fe, V and Cr. Therefore, the dissolution of the HEA matrix may be facilitated by the dissolution of precipitates into the liquid PbLi.

An interesting observation is that the interdendrites of the H-TaW in the susceptibility zone do not show significant changes after the test (see Figs. 4 and 5), although they have a similar composition to the small dissolved precipitates. This indicates that not only the chemical composition of the compounds determines their compatibility with Li, but other factors such as the crystalline structure and/or the nature of

the boundary between the different phases of the alloy should also be considered. This result illustrates the complexity of the corrosion mechanism in liquid PbLi and is beyond the scope of this work.

5. Conclusions

The main conclusions of the work are summarized below:

- The production of $\text{Cr}_{35}\text{Fe}_{35}\text{V}_{20}\text{W}_5\text{Ta}_5$ (H-TaW) was achieved. The fabrication and characterization of the single phase $\text{Cu}_5\text{Cr}_{35}\text{Fe}_{35}\text{V}_{20}\text{W}_5$ (H-CuW) and $\text{Cu}_5\text{Cr}_{35}\text{Fe}_{35}\text{V}_{20}\text{Mo}_5$ (H-CuMo) have already been reported [35]. The H-TaW has a biphasic dendritic structure compared to the single-phase structure of the H-CuMo and H-CuW, in which the dendrites have a BCC and the interdendrites a hexagonal crystalline structure.
- The incorporation of W does not provide any benefits in terms of corrosion resistance of the alloys. However, the Mo improves corrosion resistance with respect to the RAFMs
- To evaluate the chemical compatibility of HEAs with PbLi, it is important to understand the corrosion caused by the dissolution of some of the alloying components. In the three HEAs, there is a Cr-depleted zone below the outer oxide scale where the precipitates have dissolved. The incorporation of the elements of the precipitates

into the liquid PbLi could facilitate the bulk dissolution process. Therefore, the composition of the precipitates appears to play an important role in corrosion resistance. The dissolution of the carbides present in the RAMF seems to be responsible for the observed network of large voids due to several causes: the high solubility of C in the molten metal, the high diffusivity of C in the steels and the iteration of the diffused Li and/or light impurities present in the molten metal with the carbides [36]. The absence of this type of carbides in the HEAs may be one of the causes of the lower density number and size of voids observed in the HEAs in the equivalent Cr-deepened zone, which may increase their corrosion resistance compared to the RAFM steels.

- Below the susceptibility zone, the HEA is unchanged. Nucleation and recrystallization of new grains were observed only for the H-TaW, in the contact region with the oxide scale, where small grains with the same composition and crystalline structure as the original dendrites were identified by EBSD analysis.

These results indicate that HEAs require more extensive research to demonstrate the possibility of developing new alloys with optimized composition that may exhibit improved chemical compatibility and corrosion resistance to liquid PbLi.

CRedit authorship contribution statement

T. Hernández: Writing – original draft, Investigation, Validation, Conceptualization. **M.A Monge:** Conceptualization, Editing, Investigation. **F.J. Sánchez:** Methodology, Supervision, Validation. **A. Rodríguez-Lopez:** Data curation, Software, Visualization. **Y. Ortega:** Data curation, Investigation, Methodology. **L. Serrador:** Investigation, Validation. **B. Savoini:** Conceptualization, Methodology, Supervision, Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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