COMPATIBILITY OF CONVENTIONAL AND REDUCED ACTIVATION FERRITIC/MARTENSITIC STEELS IN LIQUID Pb-Li: A COMPARATIVE STUDY

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ABSTRACT

- The present study explores the effect of W on the corrosion resistance of Ferritic/Martentisitic (F/M) type steels.
- Corrosion experiments with Indian RAFMS and P91 steel (9Cr-1Mo) in static Pb-Li at 500-550ºC has shown that RAFM steels are more resistant to Pb-Li attack than their surrogate Cr-Mo steels.
- Analysis of surface condition and microstructure of as- received materials revealed that the better corrosion resistance of IN RAFMS is attributed to the presence of tungsten oxides in the passive layer which offers better stability against liquid metal corrosion by Pb-Li.

BACKGROUND

- Reduced Activation Ferritic/Martensitic steels (RAFMS) are promising candidate for fusion reactor applications. Substitution of Mo in surrogate Cr-Mo type Ferritic / Martensitic (F/M) steels with tungsten to form RAFM steels have improved both radiation stability and mechanical properties.
- Thus it was necessary to explore the effect of W addition over the compatibility of ferritic/martensitic steels with liquid metal/alloy coolants like Pb-Li which is one of its major qualifying criteria of structural materials for TBM like applications.
- For this purpose, a detailed investigation was carried out at Bhabha Atomic Research Center (BARC), wherein IN RAFMS and P91 steels were exposed to liquid Pb-Li under static and dynamic conditions at temperatures ranging 773 K to 823 K.
- The corrosion rate, surface chemistry and microstructure in both the materials were investigated thoroughly in order establish the role of W and Mo in the affecting the compatibility of F/M steels.

METHODS / IMPLEMENTATION

Characterisation of as-received P91 and IN RAFMS material

- The chemistry of as-received surfaces of IN RAFMS and P91 were characterized by **X Ray Photo Electron Spectroscopy** (XPS) using a PHI 5000 Versa Probe II, Focus XPS with a monochromatic Al Kα (1486.7 eV) X-ray source. The survey and high-energy resolution spectra of characteristic peaks of the elements like Fe 2p, Cr 2p, Mn 2p, Mo 2p, W 2p, C 1s, and O 1s were acquired over diamond polished surfaces of both materials in order to decipher the nature of air formed oxides
- Later, **the Electron Back Scattered Diffraction (EBSD)** examination of electro-polished surfaces IN RAFMS and P91 surfaces was also carried out for microstructure and grain size analysis using hkl software.

Corrosion behaviour of IN RAFMS and P91 in Pb-Li

- Three sets of corrosion coupons of P91 and IN RAFMs were exposed to Pb-Li under static conditions in the **fully automated corrosion test facility** within a temperature range of 500°C to 550°C.
- After exposure, all samples were washed of the adherent Pb-Li by cleaning them in a mixture of acetic acid, acetone and hydrogen peroxide in the ratio 1:1:1. Later the corrosion rate was calculated

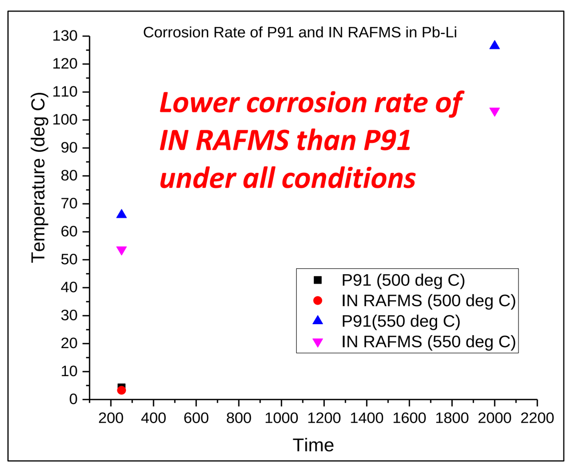
$$\text{Corrosion rate}\left(\frac{\mu g}{cm^2.h}\right) = \frac{\text{Weight Loss}\,(g)\,x\,10^{-6}}{\text{Surface Area exposed}\,(cm^2)\,x\,\text{Duration of exposure}\,(h)}$$

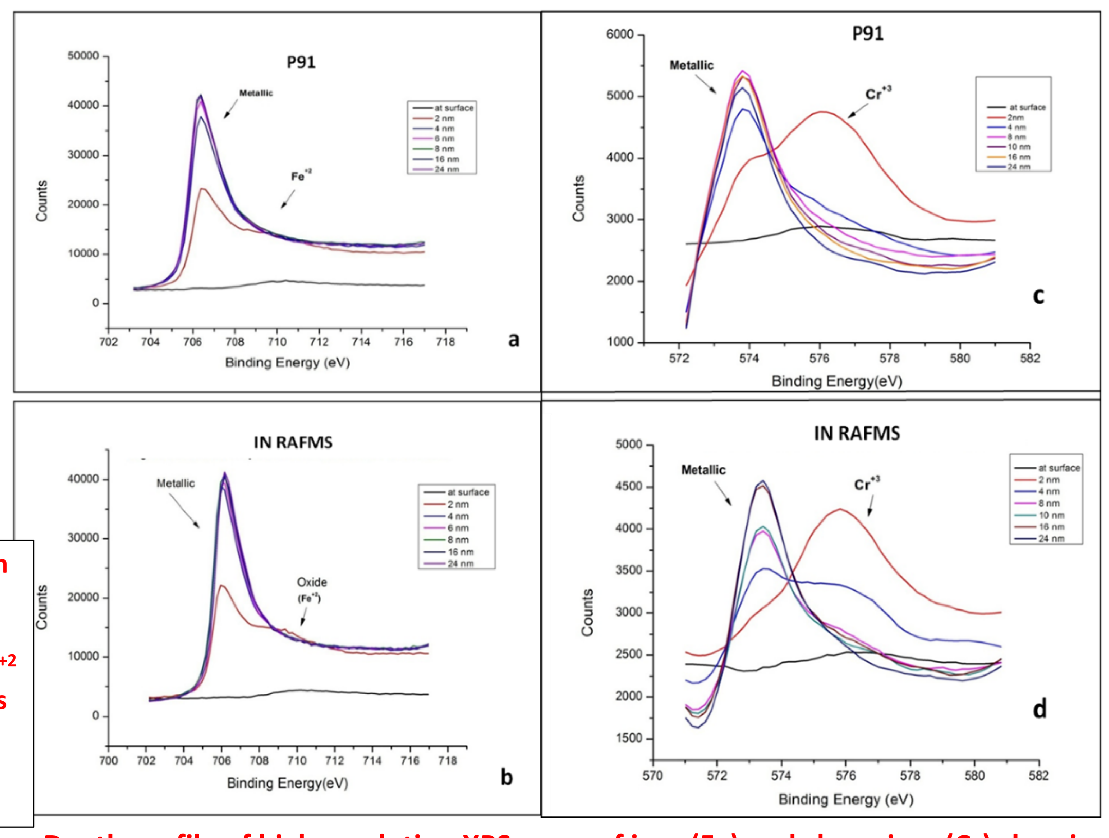
Experimental parameters for corrosion experiment in Pb-Li

Experimental Details		Temperature			
		500° C		550°C	
Time	250 h	P91	INRAFMS	P91	INRAFMS
	2000 h	-	-	P91	INRAFMS

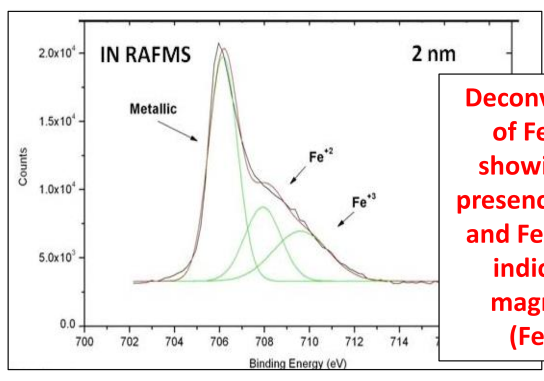
RESULTS

Results from previous studies under dynamic conditions and present study under static condition have confirmed that IN RAFMS possessed superior corrosion resistance than P91 in the temperature range of 500°C-550°C.

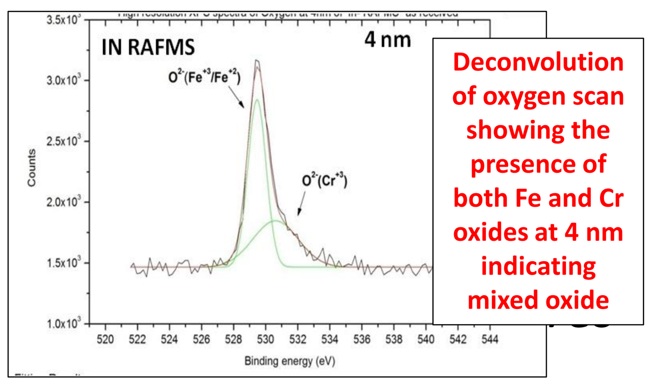




Depth profile of high resolution XPS scans of iron (Fe) and chromium (Cr) showing the presence of ~ 8nm thick oxide layer on as received P91 and IN RAFMS

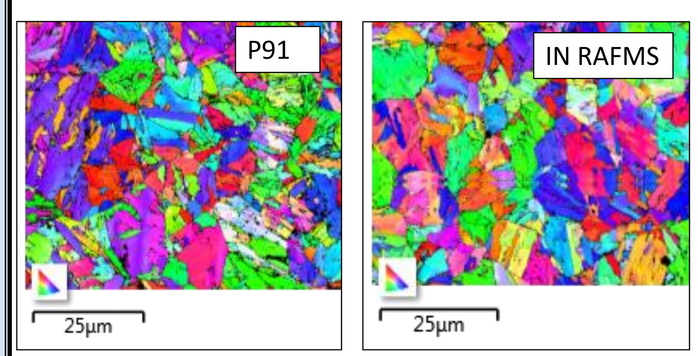


Deconvolution of Fe scan showing the presence of Fe^{+2} and Fe^{+3} peaks indicating magnetite (Fe_3O_4)

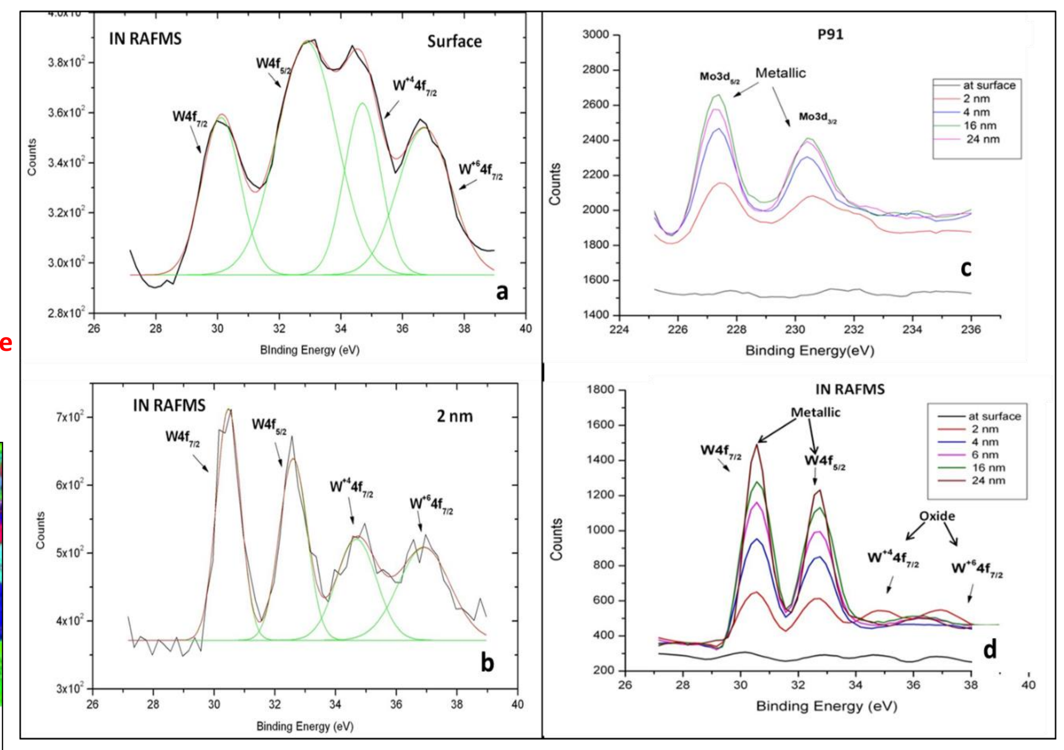


Deconvolution of oxygen scan showing the presence of both Fe and Cr oxides at 4 nm indicating mixed oxide

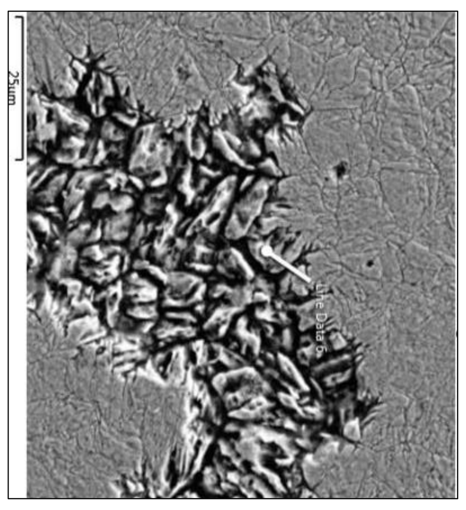
Magnetite (Fe_3O_4) is found over the surface region while Cr_2O_3 dominates the subsurface layers upto 8 nm.



EBSD Color maps on as-received materials



High resolution spectra of tungsten (W 4f) on the as-received sample of IN RAFMS on (a) surface and (b) at 2 nm .Depth profile of XPS high resolution spectra of (a) molybdenum (Mo 3d) in case of P91 and (b) tungsten (W 4f) in case of IN RAFMS showing absence of Molybdenum oxides.



Grain boundary attack by Pb-Li over IN RAFMS at 500°C after 1000 h. This is happens due to depletion of chromium at grain boundaries associated with precipitation of chromium carbides ($Cr_{23}C_6$).

	REACTIONS		ΔG, (KJ)
1	$2Fe_2O_3$ + 12 Li	→ $6Li_2O$ +4Fe	-1.83
2	$2Cr_2O_3$+12Li	→ $6Li_2O$ +4Cr	-1.23
3	WO_2+4Li	→ $2Li_2O$ +W	- 0.576
4	WO_3 +6Li	→ 3 Li_2O +W	- 0.89
5	MoO_2 + 4 Li	→ $2Li_2O$ +Mo	-0.577
6	MoO_3 + 6 Li	→ $3Li_2O$ +Mo	-0.992

Free energy change (ΔG) in reduction of surface oxides in F/M steels by lithium calculated through Factsage 7.2 software showing highest stability of W- oxides in Pb-Li leading to greater corrosion resistance of IN RAFMS

	Fe (phase %)	$Cr_{23}C_6$ (phase %)	Prior Austenite Grain diameter (μm)
P91	52.86	24.44	10
IN RAFMS	53.41	20.77	14

Analysis of phase fraction and grain size from EBSD and "hkl" software. Higher grain size and lower carbide fraction in RAFMS can reduce the intensity of grain boundary attack.

CONCLUSION

- Corrosion of IN RAFMS and P91 in Pb-Li is initiated by dissolution of the air formed oxide layer by Li and grain boundary penetration of Pb-Li. which The ~8 nm oxide layer in both materials mainly consists of oxides of iron and chromium ($(Cr, Fe)_2O_3$ /FeO).
- RAFM steels are more resistant to Pb-Li corrosion than the corresponding surrogate Cr-Mo steels like P91 mainly due to :-

a. Higher stability of passive oxide layer due to the presence of tungsten oxide layer; which can slower down the dissolution of oxide scales and thereby generates a longer incubation period.

b. The higher prior austenite grain size and lower carbide ($Cr_{23}C_6$) fraction at grain boundaries of IN RAFMS which reduces grain boundary attack.