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## **LEAD-BISMUTH EUTECTIC AS A HIGH TEMPERATURE HEAT-TRANSPORT FLUID FOR THERMAL SOLAR POWER**

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### **ABSTRACT**

In order to increase the thermal efficiency and produce process heat for hydrogen production, the operating temperature of the heat-transfer fluid in thermal solar plants needs to increase, but to increase the operating temperature, new heat-transport liquids need to be evaluated. Liquid metals have been proposed as heat-transport fluids because of the large temperature ranges over which they remain liquid. One of the most studied liquid metals for non-solar applications has been lead-bismuth eutectic alloy (LBE), for the nuclear industry. The main challenge with using LBE as a coolant is that the major constituents of structural steels have high solubility in LBE. In this work, the challenges of using LBE as a high temperature heat-transport fluid are discussed, as well as initial results of high-temperature static corrosion tests of structural steels to evaluate their potential use in a thermal solar power plant.

### **INTRODUCTION**

Because global temperatures are predicted to rise, by 1.9 to 4.0 K (according to B1 scenarios) or by 3.6 to 7.5 K (according to A1F1 scenarios) [1], the need for dependable carbon-free and pollution-free energy sources increases. One of the potential options to provide this carbon and pollution-free energy is concentrated solar power (CSP), especially central receiver systems (CRSs).

CRSs are an attractive option because of their potential to reach economic competitiveness by operating at high temperatures, allowing the utilization of more efficient thermodynamic cycles and of direct hydrogen production [2]. Operating at higher temperatures would allow the use of a combined cycle (Brayton/Rankine) instead of the current Stirling or Rankine cycles, which would lead to higher thermal efficiency for the plant [3,4]. If CRSs reach an operating

temperature of 900°C or higher, it would allow the production of hydrogen from water directly, methane or the sulfur iodine process [5] without the need to go through electrical production and water electrolysis. The high operating temperature of the plant would increase thermal-storage density, and excess hydrogen produced during operation could be stored to allow a CRS plants to run 24 hours a day, even during intermittent cloud cover and peaking hours to increase the economy of the plant.

Reaching 900°C in a CRS is a challenge and new heat-transfer fluids need to be considered to achieve this goal. The reason that current CRS do not operate at these high temperatures is because current heat-transport fluids begin to disintegrate around 600°C [6,7]. A 900°C operating temperature is generally too high for any oil-based fluid, leaving only gases, liquid salts, and liquid metals as potential heat-transfer fluids. Gases have a low density and therefore less-efficient heat transport, and salts generally have high melting points [8], causing them to be undesirable. For non-solar applications, low-melting-temperature metals, like sodium, have been used as heat-transport fluids in the past. While sodium has been used successfully in these applications, its boiling point of 882°C rules out its use in this solar application, since at 900°C, sodium vapor could be released and violently react upon contact with air. This process of elimination leaves only the option of heavy liquid metals, such as Rose's metal (50% Bi, 25-28% Pb, 22-25% Sn) and lead-bismuth eutectic alloy (LBE; 45% Pb, 55 % Bi) [9,10]. Of the heavy liquid metals, LBE is the only one that has been extensively investigated as a heat-transport fluid.

The benefits of LBE are the extensive knowledge that has been accumulated and the large  $\Delta T$  (melts 125°C, boils 1670°C) [11] over which it remains a liquid. The main obstacle to deploying LBE as a heat-transport fluid is finding structural materials that can withstand the harsh corrosion environments at

high temperatures. The 900°C operating temperature is beyond the maximum service temperature of common steel alloys. Nickel-based superalloys cannot be used because of the high solubility of Ni in lead-based liquids [12, 13]. The exclusion of these alloys leaves refractory metals and Fe-Cr-Al steels as possible structure materials to be investigated. The corrosion issue can be reduced with precise control of the oxygen content of the liquid metal, allowing passive, protective oxide layers to form on the surface of the material to inhibit additional corrosion [12]. The growth of oxide layers on the surface of the steel protects it by changing the rate-controlling step from liquid-phase diffusion to diffusion of the steel atoms through the oxide layers [14]. The formation of the oxide layers is possible because lead and bismuth are less chemically active than the major components of steel, as represented by the less-negative Gibbs-free-energy changes for the formation of their oxides than for the steel-based oxides. This effect is well illustrated in Ellingham diagrams, where the free-energy lines for  $\text{Fe}_3\text{O}_4$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{SiO}_2$  etc. are below the  $\text{PbO}$  and  $\text{BiO}$  free-energy lines. This allows the formation of Fe, Cr, Si or Al oxides on the surface of the steel and changes a linear dissolution rate into a parabolic oxide-layer-growth law. This provides a range for the oxygen concentration in the LBE during operation. If the oxygen concentration is too high, then  $\text{PbO}$  and  $\text{BiO}$  precipitates start to form, which could block pipes; and if the oxygen concentration is too low, there is not enough oxygen to allow the formation of passive protective oxide layers on the surface of the steel.

In this work here, an initial, high-temperature, static-corrosion investigation into Fe-Cr-Al steels in LBE has been performed to evaluate their performance as well as the oxygen-content range.

## EXPERIMENT

An experimental setup as seen in Figure 1a has been constructed that is capable of performing static exposures of samples to LBE at elevated temperatures in a controlled environment. In the experimental setup, an Ar-2.9% $\text{H}_2$  mixture is used to reduce the oxygen content of the LBE, and air is used to increase the oxygen content of the LBE. A simple LabVIEW™ program was written that opens a valve to allow Ar-2.9% $\text{H}_2$  into the environment when the oxygen content is too high and that closes it when the oxygen content is too low in order to allow air to flow in and increase the oxygen content.

The samples are first polished on both sides to remove contamination on the surface of the metal. The samples are then placed into a crucible that contains liquid LBE. The crucible is then placed into the testing setup, the temperature is increased to the desired testing temperature, and the oxygen sensor is inserted. The composition of the tested samples can be seen in Table 1. The oxygen sensor is a DS oxygen probe from Australian Oxytrol Systems and functions on the EMF signal produced between the sensor reference and the liquid metal. In general, the sensor allows the transport of  $\text{O}^{2-}$  ions through the

electrolyte (yttria-stabilized zirconia) and measures the difference in the electrochemical potential between the reference (Pt/air) and the liquid metal of interest.

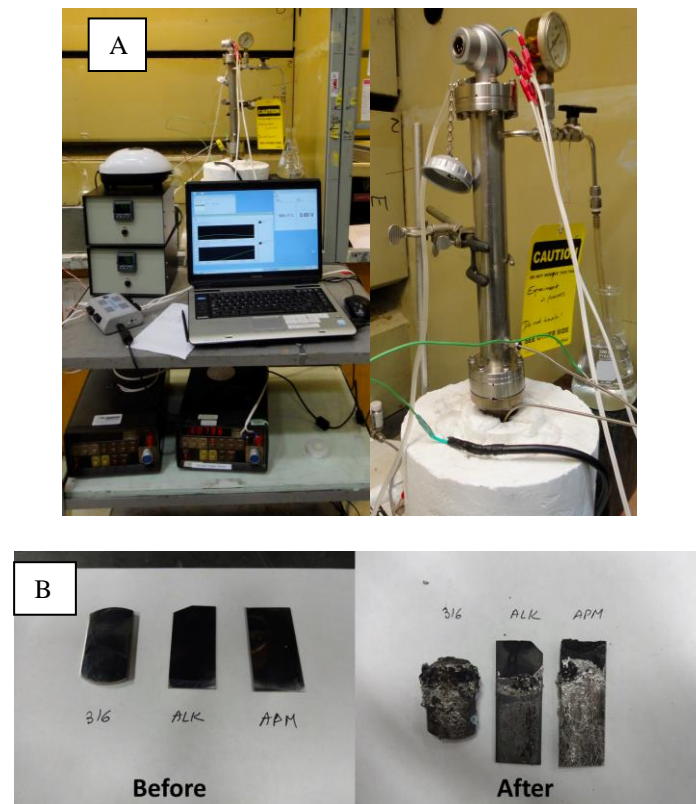


Figure 1: An overview of the experimental setup for corrosion testing of samples at UC Berkeley.

Table 1: Composition of the samples tested in LBE at UC Berkeley.

Sample	Cr	Al	Ni	Fe
<b>316L</b>	16-18%	-	10-14%	Balance
<b>ALK</b>	14-16%	3.4%	-	Balance
<b>APM</b>	20-23%	5.8%	-	Balance
<b>Inconel</b>	29%	3.4%	61%	Balance

Initial experiments have been performed that have tested a variety of samples of various lengths under a range of, temperatures and oxygen concentrations. Before and after images of the test samples for one test are shown in Figure 1b. The set of testing conditions is listed in Table 2.

Table 2: The testing conditions for the samples. All completed tests had an oxygen concentration of  $10^{-5}$  wt%.

Test no.	T [°C]	Time [h]	Samples
1	700	225	316L, ALK, APM
2	700	500	316L, ALK, APM, Inconel
3	800	400	316L, ALK, APM

After the samples were exposed to LBE, they were removed from the crucible, cut, and mounted in cross section. After the samples were polished, scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) were performed to characterize the oxide layers that had grown on the samples during the exposures. The SEM was performed with the Quanta 3D field-emission-gun (FEG) scanning electron microscope at the University of California, Berkeley; and the EDS was performed with the Oxford EDS instrument that was attached to the SEM.

## RESULTS

The EDS line scans for the three samples of 316L, APM and ALK in Test 1 can be seen in Figure 2. The testing conditions for this first experiment were 700°C for 225 hours with an oxygen concentration of  $10^{-5}$  wt%.

On the ALK and AMP samples, a rather thin and protective Al oxide layer was found, indicating that oxide layers could form with this oxygen concentration. The AMP sample had an oxide layer with a thickness of approximately 4  $\mu\text{m}$ , while the ALK sample had an oxide layer of approximately 2  $\mu\text{m}$ .

The 316L sample showed severe dissolution and thick oxides (~30 to 100  $\mu\text{m}$  of  $\text{Fe}_3\text{O}_4$  and Fe-Cr-O spinels), with aggressive LBE penetration through the oxides.

The EDS line scans for the samples of 316L, APM and ALK for the second test, which was performed at 700°C for 500 hours and with an oxygen concentration of  $10^{-5}$  wt%, can be seen in Figure 3.

This second test was paused at 300 hours to remove the samples and slice off a piece from each specimen and prepare it for cross-sectional analysis. The bulk samples were put back into the testing system for an additional 200 hours, leading to a total exposure time of 500 hours. The characterization of the 300-hour samples is not included here because they were similar to the results of the first test.

As has been stated in previous sections of the paper, Ni has a high solubility in LBE. To test whether a protective oxide layer could grow before large amounts of Ni dissolution would occur, a sample of Inconel 693 was also added to the test. During the pull-out process at 300 hours, it was noticed that an excessive amount of LBE was stuck on the samples. It was found that an excessive amount of NiBi intermetallic particles,

which are solid at temperatures below 649 °C [15], had formed. These NiBi intermetallic particles and the severe dissolution of the Inconel sample can be seen in the EDS maps in Figure 4. There is no evidence that the large amount of Ni dissolved in the bath had an influence on the formation of oxide layers on ALK and APM.

The EDS maps show a large amount of Ni dissolution as well as a potential oxide layer, consisting of Cr, Ti and Al oxides, on the surface. Figure 4 also shows that LBE penetrated hundreds of micrometers into the material in some areas.

The EDS line scans on the ALK and APM samples after exposure to LBE for 500 hours show that the APM had an oxide thickness of approximately 5  $\mu\text{m}$  and that the ALK had an oxide thickness of approximately 3  $\mu\text{m}$ . The EDS of the 316L shows dissolution of the Ni into the LBE and an oxide of approximately 40  $\mu\text{m}$  thickness.

The EDS line scans for the third test, which was at 800°C for 400 hours at an oxygen concentration of  $10^{-5}$  wt%, can be seen below in Figure 5. There were some challenges with the oxygen-sensor wire oxidizing at this temperature and having to be replaced. This replacement necessitated that the temperature of the LBE be cycled five times between 800°C and 200°C during the 400-hour test. The ALK samples formed a continuous  $\text{Al}_2\text{O}_3$  oxide layer approximately 3  $\mu\text{m}$  thick. In the case of the oxide formed on APM, partial delamination was found, and a multilayer structure with an inner Fe-Cr oxide and an outer Al oxide was present. The also appeared to be free floating pieces of oxide in the LBE, which might have resulted from the thermal cycling of the system.

The EDS line scans of the 316L shows penetration of the LBE approximately 80  $\mu\text{m}$ , with the formation of a Fe-Cr spinel layer. There also appears to have been dissolution of the Ni into the LBE.

## DISCUSSION

The ALK samples in all of the 700°C tests grew a protective, passive, single layer of  $\text{Al}_2\text{O}_3$  oxide on the surface of the steel. On the AMP samples, there was a multilayer structure, with an inner zone rich in Fe-Cr-O and an outer layer of  $\text{Al}_2\text{O}_3$  oxide. It was observed that the ALK samples grew a thinner, more protective oxide structure than the AMP did, even though the ALK had a lower Al content. These results would suggest that ALK material has better corrosion properties and would make a better choice for a structural material in a CRS CSP plant. Assuming a linear scaling law, which is known to be not appropriate and greatly over estimates the oxidation rate due to the fact that it does not account for the reduced diffusion through the oxide layer, the corrosion rate for AMP and ALK for the first test would be approximately 156  $\mu\text{m}/\text{year}$  and 78  $\mu\text{m}/\text{year}$ , respectively. These corrosion rates would lead to a loss of 4.68 mm and 2.34 mm, respectively, over a 30-year operation lifetime. The corrosion rate for the second experiment

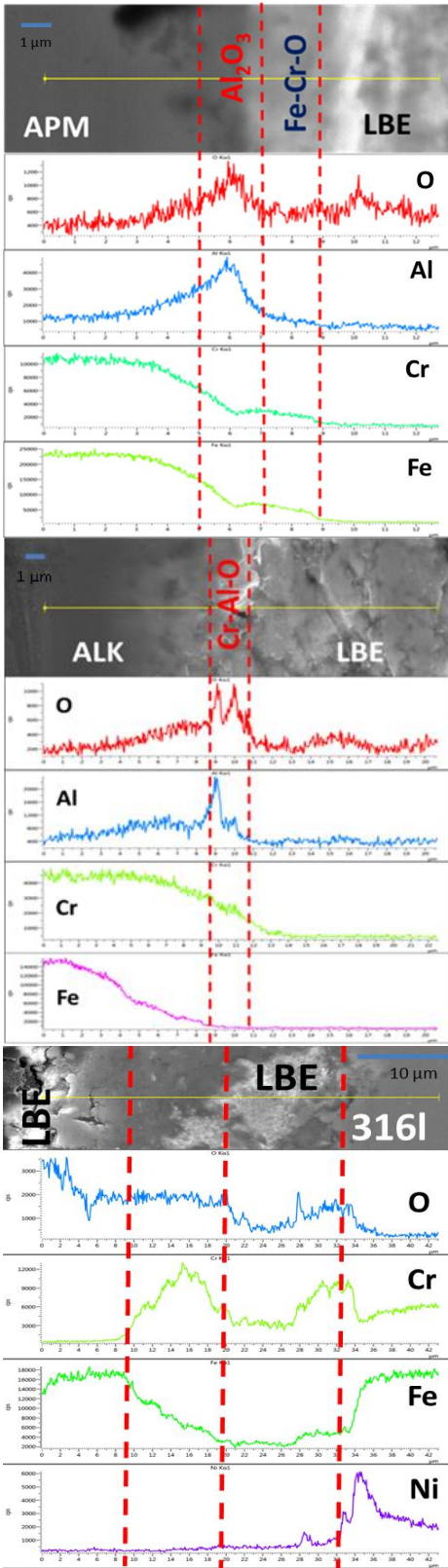


Figure 2: EDS line scans of APM, ALK and 316L after testing at 700 °C for 225 hours at an oxygen concentration of  $10^{-5}$  wt%.

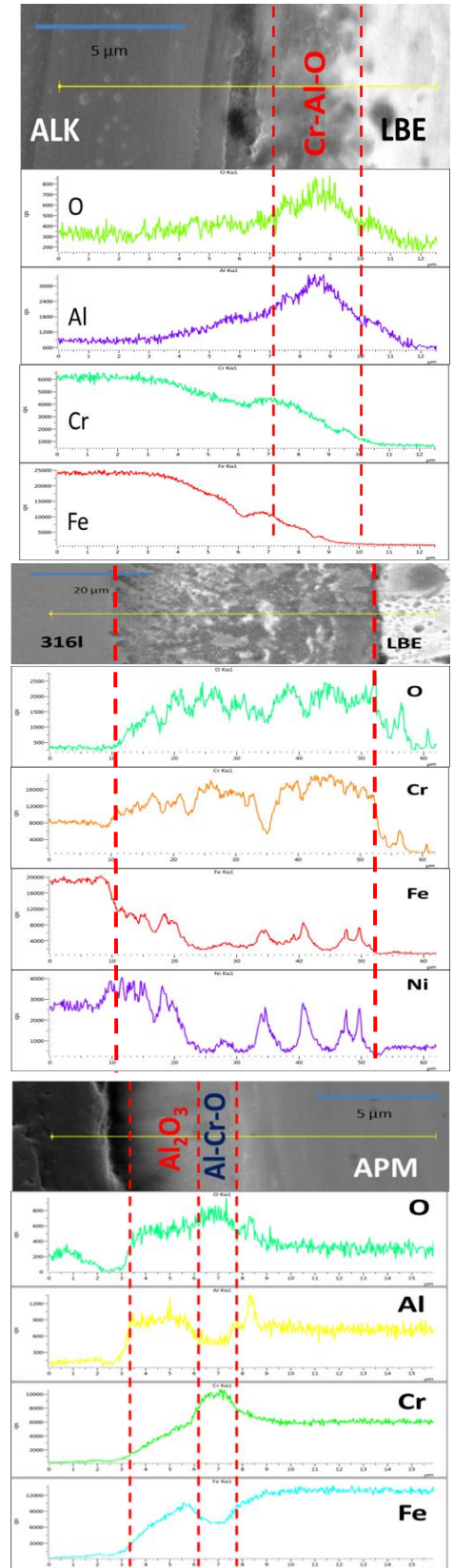


Figure 3: EDS line scans of APM, ALK and 316L after testing at 700 °C for 500 hours at an oxygen concentration of  $10^{-5}$  wt%.



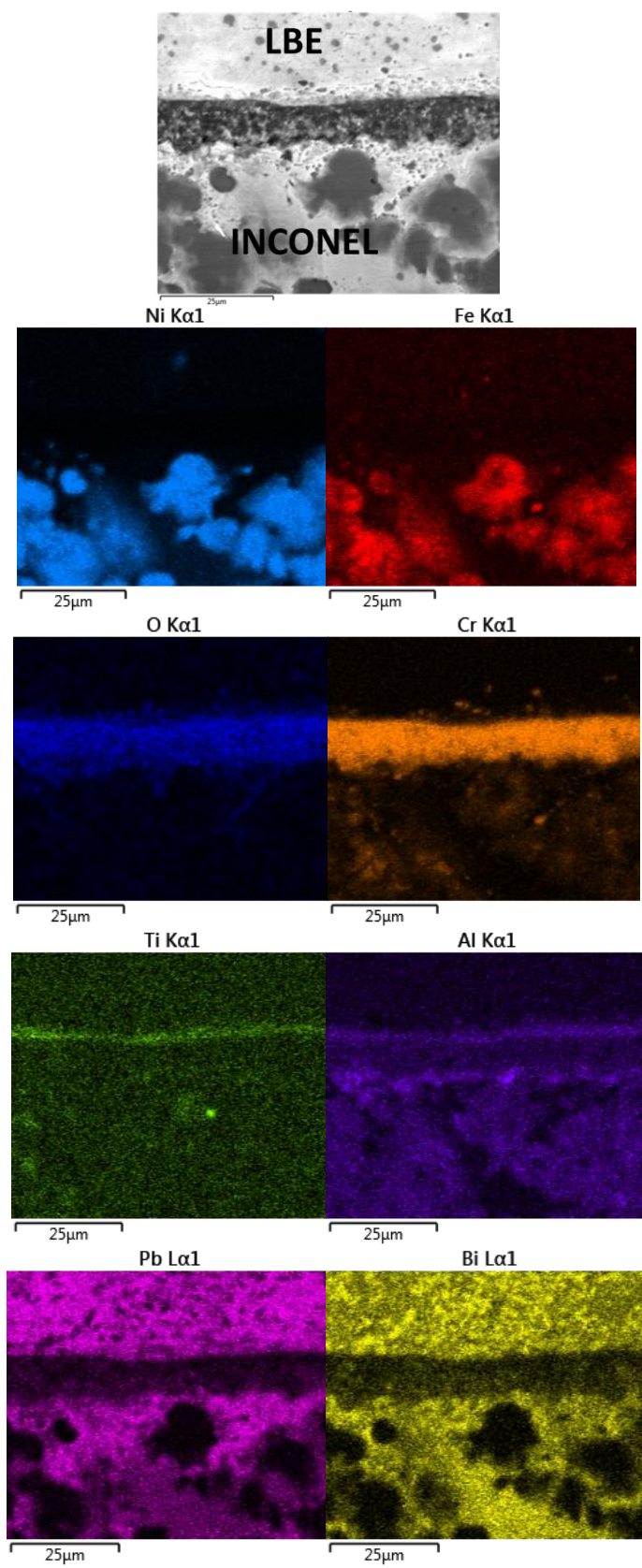


Figure 4: EDS maps of the Inconel 693 sample tested in LBE at 700°C for 500 hours at  $10^{-5}$  wt%.

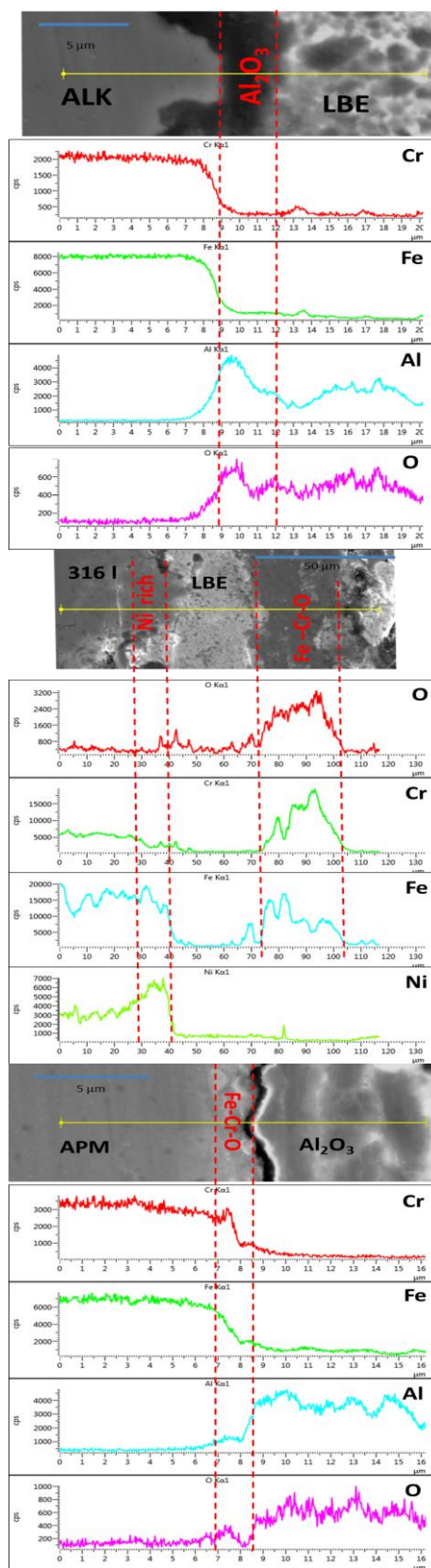


Figure 5: EDS line scans of 316L, ALK and APM from test 3 at 800°C for 400 hours at  $10^{-5}$  wt% oxygen content.

was calculated to be approximately 53  $\mu\text{m}/\text{year}$  for the ALK and 88  $\mu\text{m}/\text{year}$  for the AMP, also illustrating how the using the linear scaling law gives an overestimation of the corrosion rate. The 30-year lifetime corrosion for the second test gives values of 1.59 mm for the ALK and 2.64 mm for the AMP. If a parabolic oxide-layer-growth-law approximation would be used instead, the corrosion rate would be estimated at 23  $\mu\text{m}/\text{year}$  for APM and 12.5  $\mu\text{m}/\text{year}$  for ALK, which could be manageable corrosion rates for an LBE system at 700°C. The corrosion rates for the 30-year lifetime of the plant would be calculated to be 125  $\mu\text{m}$  for APM and 68.5  $\mu\text{m}$  for the ALK, for 700°C at  $10^{-5}$  wt% oxygen. However, these are calculated values, and long-term corrosion tests (>3000 hrs) with these conditions need to be completed to verify these values.

The results of the 700°C test of the 316L samples show that a Cr-rich oxide layer is grown on the surface of this steel. The results also show that 316L grows thick oxide layers (tens of micrometers), which makes it an unsuitable structural material for a CRS system that uses LBE as the coolant. The EDS line scans also show that LBE penetrates under the oxide layers and that Ni dissolves away, which agrees with what has been reported in the literature [12, 13, 15].

The results from the 700°C test of Inconel 693 showed deep penetrations of LBE into the material. Analysis of the LBE showed that a large amount of Ni had dissolved into the LBE. These results indicate that the Inconel 693 material is not able to grow a protective oxide structure that inhibits the dissolution of the Ni and alloying elements into the LBE. When analyzing the EDS maps of the sample in Figure 4, there appears to be a Cr oxide layer at the surface of the sample. It is possible that the Ni and Fe dissolves into the LBE and leaves behind the Cr, which then combines with the oxygen present in the LBE to form  $\text{Cr}_2\text{O}_3$ . This kind of mechanism also appears to happen with the Ti and Al in the sample, as seen by the EDS maps of these elements. These oxide layers are not protective and so cannot prevent the dissolution of the Ni and Fe.

The post-corrosion examination shows a significant difference between the oxides formed on ALK and APM steels at 800°C. From the SEM and EDS analysis on the ALK sample at 800°C, it appears that a single  $\text{Al}_2\text{O}_3$  oxide layer is grown on the surface of the steel. On the AMP sample, there appears to be a multilayer structure, with an inner region rich in Fe, Cr, Al, and O and then an outer  $\text{Al}_2\text{O}_3$  layer. From the SEM images, the  $\text{Al}_2\text{O}_3$  single layer on the ALK steel is well adhered to the sample surface while the  $\text{Al}_2\text{O}_3$  layer on the AMP steel is delaminated, which would suggest that ALK passivation is superior to APM at 800°C. However, it is difficult to evaluate whether the layer became delaminated due to the frequent thermal cycling caused by the oxidation of the oxygen sensor wire, to the temperature increase alone or to the sample preparation. Further investigations will be needed to evaluate this multilayer oxide structure. The oxide layer on the ALK material is approximately 3-4  $\mu\text{m}$ , which, if using a linear scaling law, would give a corrosion rate of approximately 66-88  $\mu\text{m}/\text{year}$ . Since only a single test was done at 800°C, it is

difficult to evaluate a parabolic scaling law for ALK, but a possible range is 14-19  $\mu\text{m}/\text{year}$  with a total of 77-103  $\mu\text{m}$  of corrosion over the 30-year lifetime of the plant at 800°C with  $10^{-5}$  wt% oxygen content.

The 316L material from the 800°C test showed severe corrosion and the formation of a Ni-rich region and a Fe-Cr-O region that is most likely Fe-Cr spinel, which is seen in the literature [12, 13, 16]. There was no formation of a Fe-oxide layer. This result shows that 316L would not be a good structural material for an LBE-cooled CSP system.

## CONCLUSION

The results of these initial experiments show that Fe-Cr-Al steels, specifically AMP and ALK, have promise as structural materials for high-temperature, LBE-cooled CRS. The AMP and ALK materials were able to form protective passive oxide layers on the surface of the steels at 700°C that prevented the dissolution of the steel alloying elements into the LBE. It was observed that ALK still showed promise at the 800°C temperature but that the AMP material started to grow thick oxide layers, leading to a high corrosion rate. Because of the thermal cycling of the experiment, though, it is not sure that the temperature alone produce this increase in the AMP's oxide thickness and delamination. From the 700°C data, it was calculated that the materials could have a manageable corrosion rate, but further investigation at longer time periods is necessary to verify these values. While these preliminary results show promise for the AMP and ALK materials additional tests at temperatures of 900°C or greater are need to evaluate their corrosion at these potential operating temperatures of future CSP plants.

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## REFERENCES

- [1] P. A. Stott J. A. Kettleborough Nature, 416, (2002), 723-726.
- [2] J. Hinkley, B. Curtin, "Concentrating Solar Power-Drivers and Opportunities for Cost-Competitive Electricity" Commonwealth Scientific and Industrial Research Organisation (CSIRO), Australia. (2011)
- [3] N. Woudstra, , T. Woudstra, A. Pirone, T. Stelt "Thermodynamic evaluation of combined cycle plants" Ener. Con. Manag. 51 1099-1110

- [4] A.M. Bassily “Modeling, numerical optimization, and irreversibility reduction of a triple-pressure reheat combined cycle” *Ener.* 32 (2007) 778-794
- [5] S. Kubo, H. Nakajima, S. Kasahara, S. Higashi, T. Masaki, H. Abe, K. Onuki. “A demonstration study on a closed-cycle hydrogen production by the thermochemical water-splitting iodine–sulfur process.” *Nucl. Eng. Des.* Volume 233 (2004). 347–354.
- [6] R. W. Bradshaw, N. P. Siegel. “Molten nitrate salt development for thermal energy storage in parabolic trough solar power systems.” No. ES2008-54174 in *Proceedings of Energy Sustainability 2008*, August 10-14, 2008, Jacksonville, Florida USA. ASME.
- [7] CRC Handbook of Chemistry and Physics. 80th ed. CRC Press, Boca Raton, Florida, USA.
- [8] R. O. Scarlat, P. F. Peterson “The current status of fluoride salt cooled high temperature reactor (FHR) technology and its overlap with HIF target chamber concepts” *Nuclear Instr. And method in phys. Research section A: Acc., Spect., Det., and Ass.Equip.*”
- [9] A.B. Abell, K.L. Willis, D.A. Lange *J. Colloid Interf. Sci.*, 211 (1999), p. 39
- [10] S. Dultz, H. Behrens, A. Simonyan, G. Kahr, T. Rath, *Soil Sci* 171 (2006) 675
- [11] Handbook on Lead-bismuth Eutectic Alloy and Lead Properties, Materials Compatibility, Thermal-hydraulics and Technologies.” OECD/NEA. 2007. ISBN 978-92-64-99002-9.
- [12] J. Zhang, N. Li. “Review of the studies on fundamental issues in LBE corrosion.” *J. Nucl. Mat.* 373 (2008). 351–377
- [13] J. Abella, A. Verdaguer, S. Colominas, K Ginestar, L. Martinelli “Fundamental data: Solubility of nickel and oxygen and diffusivity of iron and oxygen in molten LBE” *J. Nucl. Mat.* 415, (2011) 329-337
- [14] J.R. Weeks, C.J. Klamut, *Nucl. Sci. Eng.* 8 (1960) 133.
- [15] ASM phase diagrams.  
<http://www1.asminternational.org/asmenterprise/apd/>
- [16] Allen L Johnson, Denise Parsons, Julia Manzerova, Dale L Perry, Dan Koury, Brian Hosterman, John W Farley, “Spectroscopic and microscopic investigation of the corrosion of 316/316L stainless steel by lead–bismuth eutectic (LBE) at elevated temperatures: importance of surface preparation” *J. Nucl. Mat.* 2004