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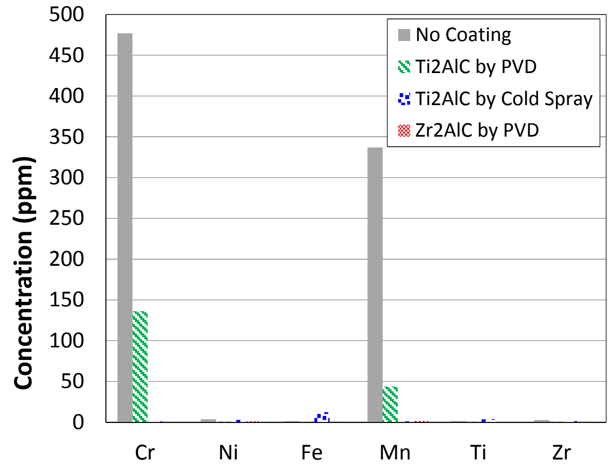
MAX Phase Materials and Coatings for High Temperature Heat Transfer Applications



Post-test salt analysis of 100 hrs immersion tests of uncoated and coated Haynes-230 coupons in commercial $MgCl_2$-KCl salt at 850°C.

Molten salts have been used as heat transfer fluids in a variety of applications within proposed Gen IV nuclear designs and in advanced power system such as Concentrating Solar Power (CSP). One of the main problems with using molten salts as heat transfer fluids is that they can cause corrosion in many materials at elevated temperatures. MAX phase materials have metallic electrical conductivity, thermal conductivity, and mechanical strength while having the chemical resistance of ceramics. These properties make it ideal for heat transfer applications. Coatings of MAX phase materials on high temperature alloys would be a low cost method to create heat transfer systems for high temperature power cycles. This work developed coating technologies for MAX phase materials on Haynes-230 and characterized the corrosion of the coatings in the presence of commercial $MgCl_2$-KCl molten salt. Cold spraying of Ti_2AlC and physical vapor deposition (PVD) in combination with annealing of Ti_2AlC or Zr_2AlC were tested to determine the most effective form of coating MAX phases on structural substrates. Corrosion testing at 850°C demonstrated that Ti_2AlC by PVD was slightly protective while the Ti_2AlC by cold spray and Zr_2AlC by PVD were completely protective. Post-test salt analysis showed 71% and 87% reduction in the Cr and Mn concentrations, respectively, for the test with the Ti_2AlC by PVD while the other coatings showed 100% reduction of Cr and Mn in the salt. None of the tests showed decomposition of the coating (Ti or Zr) into the salt.

MAX Phase Materials and Coatings for High Temperature Heat Transfer Applications

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Molten salts have been used as heat transfer fluids in a variety of applications within proposed Gen IV nuclear designs and in advanced power system such as Concentrating Solar Power (CSP). However, operating at elevated temperatures can cause corrosion in many materials. This work developed coating technologies for MAX phase materials on Haynes-230 and characterized the corrosion of the coatings in the presence of commercial $MgCl_2$-KCl molten salt. Cold spraying of Ti_2AlC and physical vapor deposition (PVD) of Ti_2AlC or Zr_2AlC were tested to determine the most effective form of coating MAX phases on structural substrates. Corrosion testing at 850°C for 100 hrs showed that 3.9 μm Ti_2AlC by PVD was slightly protective while 117 μm Ti_2AlC by cold spray and 3.6 μm Zr_2AlC by PVD were completely protective. None of the tests showed decomposition of the coating (Ti or Zr) into the salt.

FY2015 Objectives

- Perform thermodynamic modeling of MAX phase materials in molten salts.
- Develop MAX phase coating technology.
- Perform corrosion testing in high temperature molten salts.
- Analyze and characterize samples after testing.

Introduction

DOE NE and EERE programs have increasingly come to the conclusion that power production efficiency from nuclear and concentrating solar power applications is limited by reliance on low temperature thermodynamic power cycles. High temperature power cycles such as the Brayton cycle or superheated Rankine cycle have the ability to make significant improvements on lower temperature steam driven cycles. However, the high temperature power cycles require efficient high temperature heat transfer and materials that have high durability under these conditions. Molten salts are one of the main classes of proposed heat transfer media at these temperature due to high volumetric heat capacity and other heat transfer characteristics, but high temperature molten salts can cause significant corrosion.

SRNL researchers have investigated the corrosion of advanced alloys in molten fluoride salts such as a LiF-NaF-KF eutectic mixture (FLiNaK) [1-5]. Figure 1 shows EDS images for Hastelloy metals that have significant changes in composition after being exposed to FLiNaK salts. These materials and other high strength Ni-Fe-Cr superalloys show leaching of Cr at these conditions that eliminates the passive layer on the material surface that prevents corrosion in most applications.

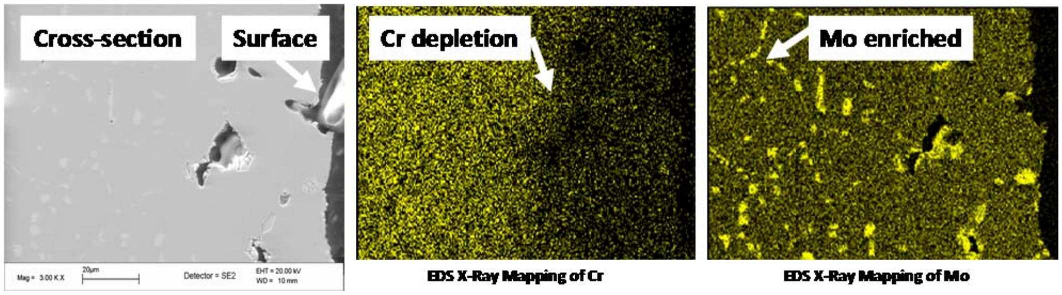

Figure 1. SEM of Hastelloy-N cross-section (left) with EDS x-ray maps of chromium (center), and molybdenum (right). Reproduced from [1].

Use of many ceramic materials for heat transfer applications with molten salts is complicated both by their lack of chemical compatibility and by their low thermal conductivity. MAX phase materials (layered structure with the chemical formula $M_{n+1}AX_n$, where n = 1, 2, or 3, M is an early transition metal, A is an A-group element, and X is carbon and/or nitrogen) have metallic electrical conductivity, thermal conductivity, and mechanical strength while having the chemical resistance of ceramics. These properties make it ideal for heat transfer applications. Coatings of MAX phase materials on high temperature alloys would be a low cost method to create heat transfer systems for high temperature power cycles. Due to their relatively new development that started in the mid-1990's, little research on MAX phase coatings or compatibility with molten salts has been performed. This project seeks to develop expertise in developing and characterizing MAX phase coatings at SRNL.

Approach

The stable corrosion products from expose of MAX phase materials in molten $MgCl_2$-KCl salt at high temperatures were calculated using the minimization of Gibbs Energy. These calculations were performed using FACTSage thermodynamic modeling software. Results from these models were used to understand the stability of selected MAX phase compositions and to identify if the materials would be resistant to corrosion. Cold spraying and physical vapor deposition (PVD) were tested to determine the most effective form of coating MAX phases on structural substrates. SRNL worked with partners at the University of Wisconsin-Madison (UW) to cold spray MAX phase materials on Ni-Fe-Cr alloys. UW and SRNL have jointly developed MAX cold-spraying techniques for Zr alloys and adapted these techniques for much harder Fe-Ni-Cr alloys. SRNL synthesized MAX coatings using a combination of PVD and annealing to create a nano-laminate structure. With PVD, coatings can be made less than 1 micron while cold-spray coatings need to be at least 25 microns.

Haynes-230 was used as the base alloy for testing. Coated samples with the selected MAX phase materials were subjected to corrosion testing in commercial $MgCl_2$-KCl molten salt. These tests consisted of long-term exposure (100 hrs) to the molten salt at 850°C to measure weight loss as the primary metrics of the corrosion rate. The amorphous film conversion to the MAX phase was evaluated by XRD. Microscopic analysis of changes in coating morphology was characterized by SEM and EDS. The corrosion products were analyzed by ICP-OES.

Results/Discussion

Thermodynamic modeling for Ti_2AlC in $MgCl_2$-KCl at 850°C was performed using FACTSage. The thermodynamic properties for Ti_2AlC were obtained from literature [6, 7] while the properties for $MgCl_2$-KCl are included with the software database. Results from this simulation shows that the stable products for this system are $MgCl_2$, KCl, TiC_2 and TiAl. Although the simulation shows the apparent decomposition of Ti_2AlC, MAX materials have properties of metals and ceramics which make them more stable and resistant to oxidation. This means that the kinetics for this decomposition could be very slow. Therefore, Haynes-230 samples were coated with Ti_2AlC using cold spray and PVD techniques and tested under the actual conditions. Additional samples of Haynes-230, coated with Zr_2AlC by PVD, were also tested in $MgCl_2$-KCl molten salt at 850°C. MAX phases for Ti_2AlC and Zr_2AlC amorphous films were obtained by furnace annealing at 900°C for 20 min. XRD development for the two coating materials are shown in Figure 2. The presence of additional peaks in the region of 2θ = 40°, after furnace annealing, confirm the conversion to the MAX phase.

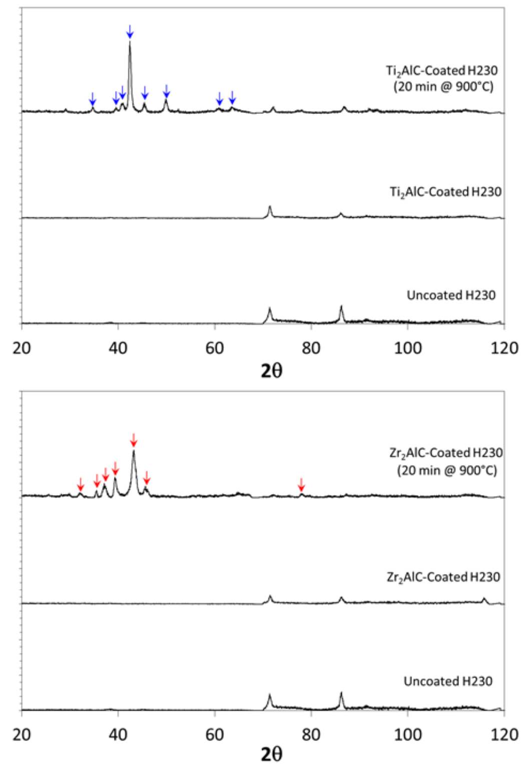

Figure 2. XRD development of Ti_2AlC and Zr_2AlC furnace annealing.

Corrosion rate results for the uncoated and coated samples are summarized in Table 1. Results for the coated samples are presented based on the total surface area of the coupons and normalized for the actual exposed or uncoated area. Based on the total area, it is expected that a sample for which the coating did not protect it will show a corrosion rate similar to the uncoated sample. Conversely, and still based on the total area, corrosion rates for samples which the coating protected the coated side will be lower than the corrosion rate of the uncoated samples. However, for the latter case, if the values are normalized for the actual exposed area, it is expected that the corrosion rates are similar to the uncoated samples. That is, the protected side (coated) will not corrode while the unprotected side (uncoated) will corrode at the rate of the base metal. Table 1 shows that the Ti_2AlC by PVD coating was slightly protective while the Ti_2AlC by cold spray and Zr_2AlC by PVD coatings were completely protective. This can be confirmed when the corrosion rates are normalized for the exposed area. For the samples coated with Ti_2AlC by cold spray the normalized corrosion rate is similar to the corrosion rate of the uncoated samples. However, for the samples coated with Zr_2AlC by PVD, the normalized corrosion rate is lower than the corrosion rate of the uncoated samples. This implies that the Zr_2AlC decreases weight loss from uncoated areas of the samples.

Table 1. Corrosion rates of uncoated and coated Haynes-230 exposed to $MgCl_2$-KCl at 850°C for 100 hrs.

Coating	Coating Thickness (μm)	Corrosion Rate (μm/yr ± 2σ)		
		Uncoated Sample	Coated Sample	
			Rate Base on Total Area	Rate Base on Exposed (Uncoated) Area
Ti_2AlC by PVD	3.9	550.2 ± 64.6	485.2 ± 29.8	1153.8 ± 70.2
Zr_2AlC by PVD	3.6	550.2 ± 64.6	114.3 ± 4.0	278.8 ± 10.3
Ti_2AlC by Cold Spray	117	550.2 ± 64.6	208.0 ± 7.6	521.0 ± 20.9

Main corrosion species concentrations of post-test salt analysis by ICP-OES are shown in Figure 3. Concentrations for the main corroding species, Cr and Mn, for the test with the uncoated Haynes-230 are 477 ppm and 337 ppm respectively. The test for the samples coated with the Ti_2AlC by PVD had significant reduction in the concentrations of Cr and Mn while the other coatings did not have readily detectable levels of Cr and Mn in the salt. In addition, decomposition of the coating (Ti or Zr) into the salt was not detected. However, some of the coating in direct contact with the salt may have been lost when the samples were separated from the frozen salt during post-test coupon removal. Cross-section SEM images of Haynes-230 coated with Ti_2AlC by cold spray before and after the immersion test are shown in Figure 4. Some reduction in the coating thickness after the test can be observed as previously explained. Also, an interfacial layer between the coating and substrate is attributed to carbide precipitation. More investigation is required to understand if this carbide formation acts as protective layer in conjunction with the MAX coating.

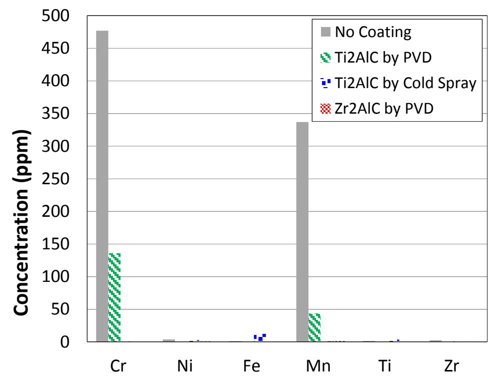

Figure 3. Post-test salt analysis by ICP-OES of 100 hrs immersion tests of uncoated and coated Haynes-230 coupons in commercial $MgCl_2$-KCl salt at 850°C.

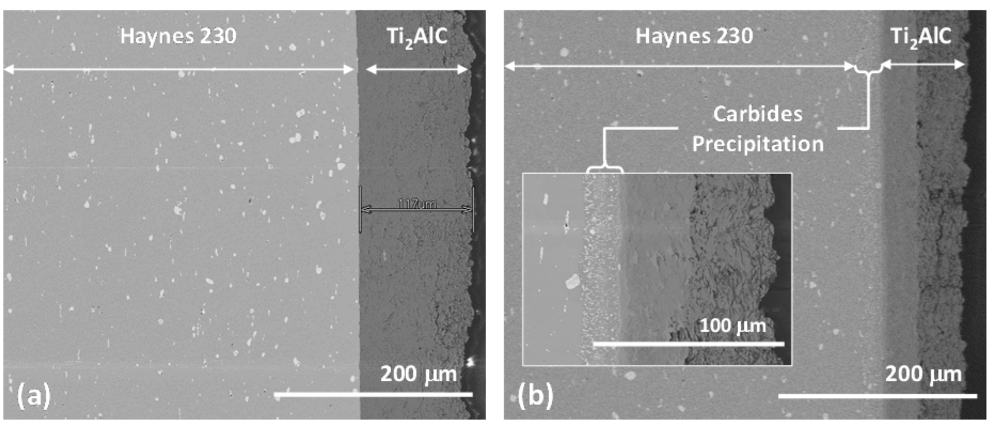

Figure 4. Cross-section SEM images of Haynes-230 coated with Ti_2AlC by cold spray (a) before and (b) after exposure to $MgCl_2$-KCl at 850°C for 100 hrs.

FY2015 Accomplishments

- Demonstrated that cold spraying and PVD technologies in combination with annealing can be used to coat Ti_2AlC and Zr_2AlC MAX phases on Haynes-230. XRD measurements show the amorphous film conversion to MAX phase.
- Corrosion testing of coated Haynes-230 for 100 hrs in commercial $MgCl_2$-KCl molten salt at 850°C demonstrated that 3.9 μm Ti_2AlC by PVD was slightly protective while 117 μm Ti_2AlC by cold spray and 3.6 μm Zr_2AlC by PVD were completely protective. Post-test salt analysis showed 71% and 87% reduction in the Cr and Mn concentrations, respectively, for the test with the Ti_2AlC by PVD while the other coatings showed 100% reduction of Cr and Mn in the salt.
- Post-test salt analysis showed no decomposition of the coatings (Ti or Zr) into the salt.

Future Directions

This project has developed a coating technology that has significant opportunity to be used for nuclear and CSP applications. The following path forward has been established from this work:

- Evaluate the opportunity to develop intellectual property around MAX phase coatings.
- Publish work results in a scientific journal.
- Leverage on the DOE SunShot program to present results from this LDRD work during SunShot project review.
- Use the outcome from this project to seek funding on DOE NE program, the DOE SunShot program, or programs in other federal agencies requiring materials that have high service temperatures.

FY 2015 Publications/Presentations

1. A publication in a scientific journal is expected from this work.

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Acronyms

CSP	Concentrated solar power
EDS	Energy dispersive spectroscopy
FACTSage	FACT stands for Facility for the Analysis of Chemical Thermodynamics. FACTSage is the fusion of two software packages in the field of computational thermochemistry: FACT-Win and ChemSage.
FLiNaK	Eutectic mixture of LiF-NaF-KF
ICP-OES	Inductively coupled plasma optical emission spectrometry

MAX	Material where M is an early transition metal, A is an A-group element, and X is carbon and/or nitrogen
PVD	Physical vapor deposition
SEM	Scanning electron microscopy
SRNL	Savannah River National Laboratory
UW	University of Wisconsin-Madison
XRD	X-ray diffraction

Intellectual Property

Outcome from this work will be evaluated for the opportunity of intellectual property.

Total Number of Post-Doctoral Researchers

One post-doctoral researcher was involved through a subcontractor.