Plasma sprayed coatings for containment of Cu-Mg-Si metallic phase change material

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Abstract

The performance of Y₂O₃-stabilized ZrO₂ (YSZ), Y₂O₃, and Al₂O₃ plasma sprayed coatings are investigated for their ability to prevent attack of Haynes 230 by a near-eutectic Cu-Mg-Si metallic phase change material (PCM) in a closed environment at 820 °C. Areas where coatings failed were identified with optical and scanning electron microscopy, while chemical interactions were clarified through elemental mapping using electron microprobe analysis. Despite its susceptibility to reduction by Mg, the Al₂O₃ coating performed well while the YSZ and Y₂O₃ coating showed clear signs of failure. Due to a lack of reliable melting in the PCM, these results are attributed to the evolution of gaseous Mg leading to the formation of MgO and MgAl₂O₄.

Keywords: phase change material, plasma spray, liquid metal containment, thermal energy storage

1. Introduction

Containment of liquid metal phase change materials (PCMs) is a necessity for adding thermal energy storage to Dish-Stirling concentrated solar power (CSP) systems. With this addition, these systems stand to become cost competitive with conventional forms of energy production, potentially meeting the U.S. Department of Energy (DOE) SunShot cost goal of \$0.06/kWh[1]. Recent work in this group has evaluated the feasibility of using Cu-21.1Mg-25.3Si (wt.%) near eutectic as the PCM in a redesigned Dish-Stirling system using sodium heat pipe technology for latent heat transport and Haynes 230 Ni alloy for PCM containment[2-5]. This alloy features high thermal conductivity, high heat of melting, and a melting temperature within the operating range of current Stirling engines making it a logical choice to provide thermal energy storage within practical weight limits.

The greatest challenge associated with using metallic Cu-Mg-Si alloys for thermal energy storage is containment of the liquid metal phase due to the high reactivity of Si and the volatility of magnesium. Containment of Mg alloys is typically accomplished in stainless steel vessels[6], with which Si would be highly reactive. Conversely, liquid Si can be contained in multiple materials, including SiN, SiO₂, Y₂O₃-stabilized ZrO₂ (YSZ), Al₂O₃, and graphite[7]; however, the reactivity of liquid Mg with these materials has not been well documented. A unique material to contain both elements in the liquid state has not been established. Containment of the Cu-Mg-Si eutectic in Haynes 230 presents several specific challenges. It is well known that Si forms multiple intermetallic compounds with Ni and Cr, two major components to Haynes 230, with an initial solubility of ~5 wt.% or more in both Ni and Cr[8, 9]. Additionally, the complete miscibility between Cu and Ni may lead to erosion of the Haynes 230 containment vessel by dissolution in the PCM.

Here we attempt to mitigate the compatibility issues between Haynes 230 and the Cu-Mg-Si PCM using three plasma sprayed metal-oxide coatings: ZrO₂-20 wt.% Y₂O₃, Y₂O₃, and Al₂O₃.

To understand the capability of these coatings as effective barriers against PCM attack of Haynes 230, sub-sized containment vessels were used to simulate the conditions of a single cycle of the thermal energy storage system.

The chosen coating materials are known to be stable oxides. As illustrated by the Ellingham diagram in Figure 1, only Y_2O_3 is expected to be stable against reduction by Mg[10].

Although YSZ and Al_2O_3 are expected to be partially, or fully, reduced by Mg according to the Ellingham diagram, the kinetics of these reactions are unknown. Reaction of the oxide coatings with the PCM, along with penetration of the coatings by one or more elements of the PCM, was found to determine failure in the investigated coatings.

2. Materials and Methods

2.1 Materials

2.1.1 Containment and Phase Change Alloys

Haynes 230 test boats were constructed by welding flat plates to the end of inch-long semi-circular pipe sections. Final dimensions of the boats were approximately 25 mm long by 25 mm wide by 12 mm deep with 1.5 mm wall thickness. Flat lids approximately 25 mm by 25 mm were cut from Haynes 230 sheet. All boats were grit blasted and cleaned before application of plasma sprayed coatings.

For the coated boats, a 2.5 kg heat of Cu-21.2Mg-25.3Si (wt.%) PCM was obtained in ingot form from Ames Laboratory (Ames, IA). Based on differential scanning calorimetry, the melting point of this alloy was 782°C. Prior to use, pieces of the PCM ingot were broken off and ball milled into powder form. For the uncoated boats, a smaller test batch was acquired previous to the large batch using the same procedures.

2.1.2 Plasma-Sprayed Coatings

Plasma sprayed coatings of Al_2O_3 , $20\text{Y}_2\text{O}_3\text{-ZrO}_2$ (wt.%) (YSZ), and Y_2O_3 were hand sprayed in air onto test boats and lids by Thermal Spray Technologies (Sun Prairie, WI). To improve adhesion, an initial bond layer of Ni-20%Cr (wt.%) was applied first below a transition layer mixing both Ni-20%Cr (wt.%) and ceramic coating materials used in order to help mitigate any issues arising from mismatched coefficients of thermal expansion (CTE). Each of these layers was approximately 100 μm thick. Ceramic coatings were sprayed 100-200 μm thick onto the surface of the transition layer. Final thickness of complete coatings was 300-400 μm . The as-sprayed structure of each coating is shown in Figure 2.

2.2 Testing and Characterization

Each boat was filled with 3g of PCM, covered with a corresponding lid, and wired shut using stainless steel wire. Closed boats were individually contained within a quartz capsule. Each capsule was evacuated to 10^{-6} Torr, back-filled with 200 Torr Ar, and sealed. This pressure allows for near atmospheric pressure in the capsule at 820 °C. Sealed capsules were placed in a box furnace and heated to 820 °C over 2 hours followed by an isothermal hold for 150 or 500 hours, after which they were furnace cooled to room temperature. Magnesium volatilization caused a darkening of the quartz through a reduction reaction with silica[11]. An optically clear capsule indicated failure of the hermetic seal during initial ramp since Mg readily reacts with oxygen, rather than the SiO_2 of the quartz to form MgO. The capsules were opened in an argon atmosphere and any remaining loose PCM removed before potting in epoxy. Potted boats were sectioned and polished for optical microscopy. For comparison, one uncoated boat was tested for 150 hours under the same conditions.

While the test temperature was well above the melting temperature of the PCM, there was limited evidence of melting in the majority of the coated boats when the capsules were opened. Variation among the PCM batches used is the likely culprit for the difference in melting behavior. Further work performed concurrently on changes in melting point of the Cu-Mg-Si can be found in [12]. Near the eutectic point of the Cu-Mg-Si system, the melting point of the alloy becomes sensitive to small changes in composition which may be present in the large ingot produced for the coated boats.

There are two likely causes for the elevated melting temperature of the PCM: 1) the formation of an oxide on the surface of the powder particles, and 2) the loss of Mg through volatilization. Evidence of the second source was illustrated by the black film on the inside surface of the quartz capsules, which results from the reaction of Mg with SiO_2 to form MgO. In the current work the possibility of coating and substrate degradation due to limited amounts of molten metal attack should not be discounted, as there is evidence to support a limited amount of liquid metal-substrate interaction. However due to the nature of the majority of PCM-coating interactions shown in Section 3, interactions observed between Mg and the coated boats will be discussed in terms of Mg gas. Despite the lack of melting in the PCM, the results from the current work are indicative of how the plasma-sprayed oxide coatings will respond to contact with the liquid PCM; and, are relevant to understanding their ability to protect Haynes 230.

Optical and scanning electron microscopies (SEM) were used to locate areas of interest within the polished cross-sections. Electron microprobe analysis (EMPA) using wavelength dispersive spectroscopy (WDS) was used to qualitatively evaluate the scope of attack in failed coatings and possible PCM-coating interactions in coatings where no attack was detected optically. In all EMPA elemental maps, the color scale has been normalized to the maximum amount of the element in the map. Maps do not indicate the relative amount of one element

with respect to the others. Warm colors (red) indicate larger amounts of an element while cooler colors (blue) represent less.

3. Results and Discussion

3.1 Uncoated Haynes 230

After 150 hours of exposure at 820 °C, the uncoated Haynes 230 boat was severely attacked by the Cu-Mg-Si PCM; nearly one quarter of the boat thickness was consumed, as seen in Figure 3a. It is clear from these images, that the PCM fully melted in this test. Back-scattered SEM (BSE) images of the areas of attack are shown in Figures 3 b-d. Qualitative elemental maps from the thin section indicated in Figure 3a are shown in Figure 4. At the areas of attack, a porous diffusion layer, rich in Si and Cr, 30-50 µm thick, has formed at the PCM-Haynes 230 interface. As the diffusion layer is traversed toward the Haynes 230 substrate, the amount of Si decreases stepwise to create a bilayer structure within the diffusion layer (Figure 4c). Porosity and the depletion of Ni within the diffusion layer indicate that Ni diffused out of the Haynes 230 substrate faster than Si diffused inward. Areas of higher Si concentrations overlap areas of higher Cr content supporting a strong interaction between the two elements as predicted [8, 9]. Copper and magnesium do not appear to directly interact with the substrate alloy according to Figures 4b and d. These elemental maps confirm the high affinity of Si to Ni and Cr and the incompatibility of Haynes 230 with the chosen PCM.

3.2 Yttria containing coatings

Both YSZ and Y₂O₃ coatings were able to protect the Haynes 230 alloy during the 150 hour exposure to the PCM at 820 °C. However, both coatings showed distinct areas of attack varying in severity after the 500 hour test, including areas of limited liquid metal attack. These areas are shown in Figure 5 with the severity of the interaction increasing in each coating from left to right. Increases in the severity of attack are assumed to correspond to

more mature interactions between the PCM and coating with the worst areas caused by liquid metal attack. At the largest area of failure in the YSZ cross-section shown in Figure 5d, the PCM consumed all but a small fraction of the boat thickness. The morphology and appearance of the attack in this area indicate the presence of molten PCM.

Compared to the YSZ coating, only a small portion of the substrate appears affected in the Y_2O_3 coated boat shown in Figures 5b and f-h. Based on the Ellingham diagram in Figure 1, ZrO_2 is thermodynamically predicted to be reduced to Zr in the presence of Mg in the temperature range of interest. Thus, it is expected that the YSZ coating may be considered metastable with respect to the strong oxidizing potential of Mg in the PCM. Since no attack was detected in the YSZ coating after 150 hours, the kinetics of the reaction between Mg and the coating may initially be slow, especially when no melting occurs. In contrast, Y_2O_3 is thermodynamically stable compared MgO . Thus, the degradation of the Y_2O_3 coating by Mg from the PCM was not anticipated. Regardless, the Y_2O_3 cross-section shows several areas of attack varying from discoloration of the coating to partial consumption of the Haynes 230 substrate as shown in Figures 5f-h, respectively.

Electron microprobe analysis was used to clarify the nature of PCM attack in the YSZ and Y_2O_3 coatings, where liquid metal attack was not the overt mechanism. Qualitative elemental maps for the areas of the Y_2O_3 cross-section shown in Figures 5f and g are given in Figures 6a and b, respectively. In the area showing the least amount of attack (Figure 6a) Mg fully penetrates the Y_2O_3 coating until reaching the transition layer. In Figure 5f this magnesium trace is only visible as a faint black outline near the Y_2O_3 -transition layer interface. Above the surface of the coating, areas of Mg are enriched with oxygen; the Mg trace through the coating overlaps oxygen enriched traces through the oxide coating and transition layers indicating the formation of MgO . There is no increase in Mg content of the Y_2O_3 coating itself, which implies Mg infiltrates the coating through open porosity inherent to the coating

structure versus attacking the bulk Y_2O_3 . Serial sectioning of the boat in Figure 6, would likely reveal a network of porosity infiltrated by Mg which subsequently reduced the nearby Y_2O_3 to form MgO.

In Figure 6b, Mg infiltrates the coating through to the bond layer-Haynes interface. From here Si becomes more invasive permeating the interface into the Haynes 230 substrate. Similar to the attack of the uncoated boat, Mg and Cu stop at the bond layer-Haynes 230 interface, and Ni is depleted in the area where Si has permeated the interface. This may indicate a small amount of liquid metal interaction with the coating and substrate interface after extensive interaction of the coating with Mg gas.

Despite the predicted thermodynamic stability of Y_2O_3 with respect to MgO (Figure 1), careful investigation of the elemental maps taken from both YSZ (not shown) and Y_2O_3 (Figure 6) cross-sections show the presence of yttrium without oxygen. In Figure 6a this is evidenced by the blue area in the yttrium map at the top right corner that does not overlap with oxygen in the same location. This is illustrated in Figure 6b by the blue area at the top of the yttrium map which is absent of oxygen in the corresponding map. Both of these areas correspond to locations rich in Cu and Si, and to a lesser degree Ni, all elements with which yttrium is known to form intermetallic compounds[13-15]. Similar observations were made for the YSZ cross-sections with respect to Zr and Y. Further discussion of the mechanisms involved in the reduction of these coatings is given in Section 3.4.

3.3 Alumina Coating

Initial optical and scanning electron microscopy of the 150-hour (not shown) and 500-hour (Figure 7) alumina coated-boats at multiple locations show no signs of failure during exposure to the PCM. Close examination of the SEM micrographs in Figure 7 reveals a surface layer along the top of the Al_2O_3 coating, which has broken away from the surface of the remaining coating. This surface layer was investigated further using EMPA. An electron back-

scattered image is shown in the top left corner of Figure 8 showing the edge of the coating (dark grey) in contact with the PCM (dark and light grey particles) at the left followed by the Al_2O_3 coating, the intermediate layer (marbled structure), bond layer (lighter grey), and Haynes 230 (lightest grey) to the right. The Mg map indicates that Mg overlaps with Al and oxygen up to the thin web of cracks that separate the permeated from the unalloyed Al_2O_3 coating. Beyond the thin web of cracks there is little if any Cu, Si, or Mg and the plasma sprayed layers, along with the Haynes 230, remain intact. Despite prediction by the Ellingham diagram in Figure 1, it is likely that the surface layer present is MgAl_2O_4 as will be discussed in Section 3.4.

3.4 Thermochemical Calculations

According to Figure 1, Y_2O_3 should be more stable and ZrO_2 and Al_2O_3 should be less stable than MgO throughout the temperature range of the current work. This Ellingham diagram considers the reaction between oxygen gas and solid metal constituents at 1 atm. However, the current experiments take place in a very low partial pressure of O_2 in Ar with a small amount of Mg gas present at the test temperature. To consider the possible equilibrium compositions of each of the oxides in contact with the test environment, the Equilibrium Compositions module of HSC Chemistry 8[10], a program developed to run basic thermodynamic calculations using an extensive thermochemical database, was used to conduct thermochemical analyses. Here we modeled our system with rough estimates of gas and solid oxide quantities looking specifically at the fractions of metal reduced from each oxide assuming a vapor pressure of Mg approximately equivalent to that above pure Mg, a near zero partial pressure of O_2 , and Ar as the balance to 1 atm. The YSZ coating was modelled in terms of ZrO_2 . The equilibrium amounts of the likely products from each reaction between Mg gas and the oxides were calculated along with the equilibrium amounts of remaining reactants. The results of these calculations are illustrated in Figure 9. The mole

fractions presented represent the amount of Zr, Y, Al, or O that was produced by the reaction or that remains in the oxide. For example, the $MgAl_2O_4$ line represents the amount of Al consumed producing $MgAl_2O_4$ when compared to the initial amount of Al present in Al_2O_3 .

At the testing temperature, 820°C, approximately 35% of the ZrO_2 is reduced to Zr, while only a trace amount of Y_2O_3 is reduced to Y. Considering the test environment is not at equilibrium, as Mg is consumed more Mg gas will evolve, it is likely that all of the ZrO_2 present will eventually be reduced to Zr. Alternatively, if the kinetics are similar, it will take a much longer time to reduce all of the Y_2O_3 . Based on the theoretical density of each species, reduction of Y_2O_3 by Mg is accompanied by a volume loss while the reduction of ZrO_2 is accompanied by a smaller volume increase. Therefore, the reduction of Y_2O_3 and YSZ coating species can create pathways for the surface transport of Si through the coatings along open porosity and splat boundaries. Attack of the coating by bulk diffusion of Si from the PCM through newly formed MgO or the Y_2O_3 coating is unlikely as both of these oxides have been shown to inhibit interdiffusion of Ni and Si[16-18]. In an environment where the PCM is present as a liquid, the kinetics of this reaction will increase likely causing more damage to the Y_2O_3 coating.

For the Al_2O_3 coating, the calculations predict the equilibrium product to be $MgAl_2O_4$ with some remaining elemental Al, while all of the available oxygen is consumed. Al_2O_3 should be reduced to form MgO and Al according to

Al_2O_3 can further combine with MgO from Equation 1 to form $MgAl_2O_4$ (magnesium aluminate) according to:

which is the most stable phase under the current conditions according to the calculations performed using the HSC software. Based on the rough estimate of the initial amount of oxide available, all of the oxide should be consumed during the reaction. In our experiment, only part of the Al_2O_3 coating was consumed during the reaction with Mg, in which case either the kinetics of the reaction are rather slow or the initial estimate of the amount of oxide is imprecise.

Both reactions occurring to form MgAl_2O_4 from Al_2O_3 result in a volume increase which would decrease Si transport through the coating and protect the Haynes 230. As noted above, this layer has broken away from the remaining Al_2O_3 coating parallel to the interface indicating a build-up of stress due to the volume expansion, or mismatch of the coefficient of thermal expansion manifested on cooling. This coating would likely fail under multiple charging (heating) and discharging (cooling) cycles in the Dish-Stirling thermal energy storage application due to this mechanical flaw. It may be possible to avoid spallation of an MgAl_2O_4 layer by directly applying MgAl_2O_4 as a plasma-sprayed coating in place of Al_2O_3 . However, the performance of a less dense MgAl_2O_4 layer may be less protective than that formed in the current experiments.

4. Conclusions

The failures of the Y_2O_3 and YSZ coatings are believed to have occurred through reaction of the coatings with Mg vapor causing a volumetric loss, which generated localized cracks in the coating and facilitated the transport of Si across the coatings to the substrate alloy.

Unexpectedly, Al_2O_3 prevented damage to the Haynes 230 substrate, but showed signs of mechanical degradation due to reaction with Mg. Elemental mapping illustrated the likely formation of MgO and/or MgAl_2O_4 , which did not allow the coating to be permeated by the PCM. The thermodynamic behavior of all three coatings was captured well with the HSC Chemistry 8 Equilibrium Compositions Module and the Ellingham diagram; however, the

Ellingham diagram served as only a partial indicator of oxide coating performance as kinetic behavior was the final factor in understanding performance.

This is evident in the failure of the Y_2O_3 coating to protect Haynes 230 from attack by the Cu-Mg-Si near eutectic PCM and the formation of protective layer of MgAl_2O_4 from the Al_2O_3 coating. However, the diagram accurately predicted the reduction of both the ZrO_2 coating and the inner surface of the SiO_2 capsules. Future work in this area should take advantage of this or similar software to more accurately predict the success of protective coatings.

Despite the lack of widespread melting in the PCM during testing of the oxide-coated boats, the results from the current work are suggestive of how the plasma-sprayed oxide coatings will respond to contact with the liquid PCM; and, are relevant to understanding their ability to protect Haynes 230.

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Figure Captions

Figure 1: Ellingham diagram showing the relative thermodynamic stability of chosen coating materials and possible oxides formed by the PCM. This diagram was created using HSC Chemistry 8 software produced by Outotec Technologies.

Figure 2: Optical micrographs of the cross-sections of as-sprayed lids coated with (a) YSZ, (b) Y_2O_3 , and (c) Al_2O_3 . In each image, the layers from the bottom up are Haynes 230, a Ni-20Cr (wt.%) bond layer, a cermet transition layer (marbled appearance), and the oxide coating (dark band).

Figure 3: (a) Optical overview and (b-d) BSE micrographs of attacked areas in the Haynes 230 boat tested for 150 hours at 820 °C.

Figure 4: EMPA elemental maps taken from a section of Figure 3c showing relative amounts of Cu, Si, Mg, Ni, and Cr. The electron-backscattered image is shown at the top. The Haynes 230 boat is located at the left edges of the images and the PCM at the right. The amount of each element is normalized relative to itself over the area shown. This does not reflect overall composition.

Figure 5: Optical overviews (a and b) and BSE images showing areas of attack by PCM in boats coated with YSZ (a,c-e) and Y_2O_3 (b,f-h) after 500-hours exposed to PCM.

Figure 6: EMPA elemental maps of the areas shown in Figures (a) 5f and (b) 5g. indicating initial infiltration of coating by magnesium and subsequent attack by silicon. The electron-backscattered images are shown at the left. The Haynes 230 boat is located at the bottom edges of the images and the PCM at the top. The amounts of each element are normalized relative to itself over the area shown, not in reference to overall composition.

Figure 7: (a) Optical overview and (b-d) BSE micrographs of the Al_2O_3 -coated boat tested for 500 hours.

Figure 8: EMPA elemental maps of Al_2O_3 coating after testing for 500 hours. The electron-backscattered image is shown at the left. The Haynes 230 boat is located at the bottom edges of the images and the PCM at the top. The amounts of each element are normalized relative to itself over the area shown, not in reference to overall composition.

Figure 9: Mole fractions of at equilibrium of pertinent reaction products and reactants with respect to initial amounts available in the system. MgAl_2O_4 fractions have been compared to the initial amount of Al present in Al_2O_3 .

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9