Synthesis and characterization of binder-free Cr₃C₂ coatings on nickel-based alloys for molten fluoride salt corrosion resistance

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Abstract

Under various conditions, chromium carbides appear to be relatively stable in the presence of molten fluoride salts and this suggests that their use in corrosion resistant coatings for fluoride salt environments could be beneficial. One method for producing these coatings is the carburization of sprayed Cr coatings using methane-containing gaseous precursors. This process has been investigated for the synthesis of binder-free chromium carbide coatings on nickel-based alloy substrates for molten fluoride salt corrosion resistance. The effects of the carburization process on coating microstructure have been characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM) in conjunction with energy dispersive spectroscopy (EDS). Both plasma-sprayed and cold-sprayed Cr coatings have been successfully converted to Cr₃C₂, with the mechanism of conversion being strongly influenced by the initial porosity in the as-deposited coatings.

1. Introduction

Future designs for molten salt fast reactors (MSFRs) can pose significant challenges for materials selection since candidate materials for containment of secondary heat transfer media are required to have desirable mechanical properties and microstructural phase stability during prolonged exposure to dynamic, molten fluoride salts in the temperature range of 700-850°C [1]. While nickel-based alloys, in particular those derived from the Ni-Cr-W system, have demonstrated considerable microstructural phase stability and retention of mechanical properties after long-term exposure at temperature [2], there is concern regarding the microstructural stability of these alloys in molten fluoride salts [3, 4]. However, chromium carbides have been shown to form on graphite components used to investigate the corrosion resistance of nickel-based alloys [3], which suggests that this particular subset of refractory materials could be used as a corrosion barrier for alloys in molten fluoride salt environments. While chromium carbides may not be thermodynamically stable in molten fluoride salts, the kinetics of carbide coating dissolution could substantially increase the lifetime of nickel-based alloys. Consequently, modification of the surface of nickel-based alloys via the deposition of chromium carbide coatings offers a potential pathway to withstanding the extreme environment envisioned in the MSFR concept.

In previous work Cr_3C_2 , one of three stable carbide phases found in the Cr-C system, was deposited by means of physical vapor deposition (PVD), chemical vapor deposition (CVD) and spray techniques [5]. Of these processes spray techniques are especially suited for coating industrial-scale components. Spray techniques such as atmospheric plasma spray (APS), high velocity oxy-fuel (HVOF), high velocity air-fuel (HVOF), and, in particular, cold gas dynamic spray (CGDS) have all used a solid solution NiCr binder phase to promote bonding between the Cr_3C_2 spray material and the substrate during coating buildup. A considerable amount of work has been conducted in recent years to improve and to characterize the microstructure and resulting material properties of sprayed Cr_3C_2 -NiCr cermet coatings [6, 7]. Even so, the presence of the NiCr binder phase could present problems for sprayed Cr_3C_2 -NiCr cermet coatings used in applications requiring molten fluoride salt corrosion resistance.

Research has shown [3, 4] that the predominant mechanism of molten fluoride salt corrosion in nickel-based alloys with high Cr content is selective dealloying of Cr from the grain boundaries of the

matrix phase (a solid solution of Ni, Cr and other common alloying elements) [8]. Exposure of sprayed Cr_3C_2 -NiCr cermet coatings to a molten fluoride salt environment would likely result in the selective dealloying of Cr from the NiCr binder phase, followed by the formation of voids via vacancy diffusion and coalescence. The development of an interconnected network of voids, and subsequent exposure of the underlying nickel-based alloy to corrosion, would probably be facilitated by the complex pore structure characteristic of sprayed materials [9].

Also the effect of the NiCr binder phase on the long-term high-temperature microstructural phase stability of sprayed Cr_3C_2 -NiCr cermet coatings must be considered. The thermodynamically-driven transformation of Cr_3C_2 to Cr_7C_3 as a result of the direct interaction between Cr_3C_2 particles and the NiCr binder phase has been observed at temperatures slightly above the expected operating range of MSFRs [10, 11]. This transformation is unfavorable for applications requiring molten fluoride salt corrosion resistance since void formation related to Cr consumption in the NiCr binder phase and spallation due to specific volume change might occur over the service lifetime of the coating [11].

For these reasons, the formation of binder-free Cr_3C_2 coatings would be advantageous for applications requiring molten fluoride salt corrosion resistance. In the work described here, a two-stage process for the synthesis of binder-free Cr_3C_2 coatings on nickel-based alloy substrates has been investigated. The deposition of Cr coatings by means of APS and CGDS has been employed, followed by the conversion of these coatings to Cr_3C_2 via carburization with methane-containing gaseous precursors. Since APS and CGDS are at opposite extremes of the spray processing spectrum, these deposition techniques provide the opportunity to assess the effects of Cr coating microstructure on the resulting carbide coating characteristics. Microstructural characterization throughout the carburization process was performed to determine phase morphology and porosity evolution in the coating.

2. Experimental

2.1. Substrate materials and preparation

Nickel-based alloys derived from the Ni-Cr-W system are currently considered to be leading candidates for MSFR materials selection [1]. One of these, Haynes 230 (H230), exhibited the greatest weight loss per unit area in a recent molten fluoride salt corrosion study [3] and could benefit from the

use of a corrosion-resistant coating. Consequently, this particular alloy was chosen as a substrate material for the current study. Table 1 shows the nominal chemical composition of the H230 alloy [12].

Table 1. Nominal Chemical Composition (wt. %) of H230 alloy.

Ni	Cr	W	Mo	Fe	Co	Mn	Si	Al	C	La	B
57	22	14	2	3	5	0.5	0.4	0.3	0.10	0.02	0.015

This alloy was procured in sheet form (per AMS 5878 rev. C) with dimensions of 914.4 X 304.8 X 3.2 mm and was cut into coupons measuring 76.2 X 25.4 X 3.2 mm. These were grit blasted with 36 grit Al_2O_3 media and cleaned with compressed air prior to Cr deposition.

2.2. Cr coating deposition

Two different methods for Cr coating deposition were implemented in this work. For APS, a Metco 9MB plasma gun with a Bay State Surface Technologies Model 1200 powder feeder was used. For CGDS, a Cold Gas Technology Kinetiks 4000 cold gas gun/powder feeder was utilized. An SEM micrograph of the Cr feedstock powder used in this work is shown in Fig. 1 and its specifications are provided in Table 2 (Sulzer-Metco). Both methods used robotic movements to control deposition conditions and these are summarized in Tables 3 and 4.

Fig. 1. SEM micrograph of Cr feedstock powder showing a loosely controlled particle size distribution and particle agglomeration.

Table 2. Cr Feedstock Powder Specifications.

Feedstock Powder	Chemical Composition (wt. %)	Particle Size (μm)	Morphology
Amdry Chrome	99.5 % Cr	-45	Spherical

Table 3. Atmospheric Plasma Spray (APS) Deposition Conditions.

Feedstock Powder	Voltage (V)	Current (A)	Working Distance (mm)	Traverse Speed (mm/sec)	Step Size (mm)
Amdry Chrome	70	500	127	416.56	3.18

Table 4. Cold Gas Dynamic Spray (CGDS) Deposition Conditions.

Feedstock Powder	He Pressure (MPa)	He Temperature (K)	Working Distance (mm)	Traverse Speed (mm/sec)	Step Size (mm)
Amdry Chrome	4	873.15	25.4	100	0.5

2.3. Conversion of sprayed Cr coatings to Cr_3C_2

Sprayed Cr coatings were carburized using a flowing, methane-containing atmosphere (80 vol. % Ar with 20 vol. % CH_4 ; 250 SCCM) in a horizontal quartz tube (60 X 64 X 1300 mm) furnace for 6 and 12 h at 1000 °C. The system was purged for 3 h with 400 SCCM Ar prior to the initiation of the thermal cycle. Heating and cooling ramps were carried out at a rate of 400 °C/h and 200 °C/h respectively, with an atmosphere of 200 SCCM Ar. Ultra-high purity gas sources were used in conjunction with an in-line purifier (Matheson Nanochem Purifilter) to further reduce O_2 and H_2O impurity levels (<0.1 ppb O_2 and H_2O). Gas mixture composition was regulated through the use of mass flow controllers (Alicat Scientific Series MC) [13].

2.4. Microstructural characterization

2.4.1. Phase identification

XRD data used for phase identification throughout the carburization process were collected with a Philips X'Pert Pro MRD equipped with a Cu-K α X-ray source and a programmable divergence slit. The irradiated length was held constant at 8 mm throughout the full scan range.

2.4.2. Metallographic sample preparation, SEM and EDS

Secondary electron SEM imaging of sample cross sections was performed on a Hitachi TM3000 tabletop microscope. Samples were initially vacuum-impregnated with Buehler EpoThin low-viscosity epoxy at a pressure of 33.6 kPa. Sectioning and semi-automatic grinding/polishing were then performed on a Buehler IsoMet 1000 and a Buehler EcoMet 3000/AutoMet 2000 respectively, using the recommended procedures for the metallographic preparation of thermally-sprayed ceramics [14].

Additional secondary electron micrographs of free-standing sample cross sections were overlaid with qualitative EDS X-ray mapping results generated with a JEOL JSM-6700F field emission microscope equipped with an EDAX Apollo XL detector.

3. Results

Cross-sectional SEM micrographs of plasma-sprayed and cold-sprayed Cr are shown in Fig. 2a and Fig. 3a respectively. A Cr coating of relatively uniform thickness ($\sim 30\ \mu\text{m}$) is obtained via plasma spray, while significant coating thickness variations ($\sim 25\text{--}85\ \mu\text{m}$) are observed in cold-sprayed Cr. Both the plasma-sprayed and the cold-sprayed Cr coatings contain globular voids and interlamellar porosity. Intrallamellar microcracks oriented normal to the plane of the coating are only present in plasma-sprayed Cr. This result suggests substantial oxidation of plasma-sprayed Cr feedstock material prior to splat quenching since intralamellar microcracking is characteristic of brittle materials deposited via “hot” thermal spray processes [15]. Oxidation of feedstock material is confirmed by XRD measurements that indicate chromium oxide formation in plasma-sprayed Cr (Fig. 4). Further confirmation of oxidation is indicated by the varying electron contrast in the lamellae of the plasma-sprayed Cr deposit (Fig. 2a). No evidence of impurity phases resulting from the cold spray deposition process is identified in cold-sprayed Cr using SEM (Fig. 3a) or XRD (Fig. 4).

(a) Left

(b) Middle

(c) Right

Fig. 2. Cross-sectional SEM micrographs of: (a) plasma-sprayed Cr, (b) plasma-sprayed Cr after 6 h of carburization and (c) plasma-sprayed Cr after 12 h of carburization.

(a) Left

(b) Middle

(c) Right

Fig. 3. Cross-sectional SEM micrographs of: (a) cold-sprayed Cr, (b) cold-sprayed Cr after 6 h of carburization and (c) cold-sprayed Cr after 12 h of carburization.

Fig. 4. XRD patterns of sprayed Cr coatings showing locations of diffraction peaks associated with Cr and Cr_2O_3 . The top scan corresponds to cold gas dynamic spray (CGDS) and the bottom scan relates to atmospheric plasma spray (APS). Color online and in print.

Accounting for the presence of Cr_2O_3 in plasma-sprayed Cr, the conversion of sprayed Cr coatings to Cr_3C_2 via carburization with methane-containing gas is likely described by the following two reactions [16]:

Under the processing conditions used, this conversion to carbide occurred over extended periods of time and it was found that the rates for carbide formation depended on the nature of the Cr coating initially deposited on the H230 substrate. Fig. 5 shows the XRD patterns for plasma-sprayed and cold-sprayed

Cr after 6 h of carburization.

Fig. 5. XRD patterns of sprayed Cr coatings after 6 h of carburization showing locations of diffraction peaks associated with Cr_3C_2 , C and Cr. The top scan corresponds to cold gas dynamic spray (CGDS) and the bottom scan relates to atmospheric plasma spray (APS). Color online and in print.

Both plasma-sprayed and cold-sprayed Cr demonstrate successful conversion to Cr_3C_2 upon carburization, accompanied by a strong preference for development of carbide grains oriented with the [203] and [301] crystallographic directions normal to the coating surface. A broad low-angle diffraction peak corresponding to amorphous carbon deposition is identified in carburized plasma-sprayed Cr, with no such peak present in carburized cold-sprayed Cr. In the instance of carburized cold-sprayed Cr, a peak corresponding to unconverted Cr is present. These results should be compared to those shown in Fig. 6 where XRD patterns for plasma-sprayed and cold-sprayed Cr after 12 h of carburization are

presented.

Fig. 6. XRD patterns of sprayed Cr coatings after 12 h of carburization showing locations of diffraction peaks associated with Cr_3C_2 , C and Cr. The top scan corresponds to cold gas dynamic spray (CGDS) and the bottom scan relates to atmospheric plasma spray (APS). Color online and in print.

XRD measurements indicate that no structural change in the carbide coating originating from plasma-sprayed Cr occurred with additional carburization time. The most significant change is the increase in height of the peak for amorphous carbon. In contrast, additional carburization of cold-sprayed Cr yields an XRD pattern with relative peak intensities closely matching that of randomly-oriented Cr_3C_2 [17], along with a reduction in the intensity of the peak corresponding to unconverted Cr. Due to considerable microstructural differences in plasma-sprayed and cold-sprayed Cr it was expected that carburization would lead to correspondingly different carbide coating microstructures. These differences are indicated by the SEM micrographs of coating morphology and porosity evolution throughout the carburization process shown in Figs. 2 and 3.

Plasma-sprayed Cr contains an interconnected network of globular voids, interlamellar porosity and intralamellar microcracks oriented normal to plane of the coating (Fig. 2a). After 6 h of carburization (Fig. 2b) the corresponding carbide coating microstructure displays significant deviation from the size, shape and distribution of porosity in the as-deposited Cr coating. Inspection of Fig. 2b also indicates the presence of a second phase in the carbide coating and an effect of the carburization process along the grain boundaries of the substrate (to a depth of $\sim 90 \mu\text{m}$). SEM, in conjunction with

EDS, was performed to determine the chemical makeup of the second phase, as well as to investigate the effect of the carburization process along the grain boundaries of the substrate.

(a) Left

(b) Middle. Color online and in print.

(c) Right. Color online and in print.

Fig. 7. EDS X-ray mapping of carburized plasma-sprayed Cr: (a) Reference SEM cross-sectional micrograph, (b) Cr-K α and (c) O-K α .

The EDS mapping results in Fig. 7 reveal that the second phase is chromium deficient and oxygen rich relative to the carbide phase. It is possible that this second phase is an unconverted chromium oxide with insufficient mass fraction for identification by XRD. A uniform concentration of oxygen in the surrounding carbide phase is also unmistakable, suggesting that the carbide originating from plasma-sprayed Cr is an interstitial solid solution of carbon and oxygen in a Cr metal host lattice of the form $\text{Cr}_3(\text{C},\text{O})_2$. This interstitial oxygen impurity is often overlooked in the characterization of carbides [18], but has been recognized for the synthesis of zirconium carbide and hafnium carbide from their respective oxides [19]. Additionally, in this work, the abundance of oxygen in the Cr-rich grain boundaries of the substrate occurs only in the instance of plasma-sprayed Cr – presumably a result of the partially oxidized Cr coating – which serves as a solid-state source of oxygen for diffusion along the grain boundaries of the substrate prior to the conversion of the coating to carbide. In agreement with the XRD results presented in Figs. 5 and 6, no noteworthy microstructural changes in the carbide coating originating from plasma-sprayed Cr are observed with additional carburization time (Fig. 2c). The depth to which the grain boundaries of the substrate are affected by the carburization process is unchanged with additional carburization time.

In contrast to the through-thickness carbide formation in the instance of carburized plasma-sprayed Cr, the conversion of cold-sprayed Cr to carbide originates at the precursor-coating interface and proceeds along the thickness of the coating. As a result, surface carbide is formed with an underlying unconverted Cr layer after 6 h of carburization (Fig. 3b). This observation is in agreement with the XRD results presented in Figs. 5 and 6. Distinct concentrations of voids are evident at the interface between the surface carbide and the underlying Cr, as well as at the interface between the Cr and the substrate. In regions where the as-deposited Cr coating shows considerable variation in thickness and porosity, a coalescence of globular voids is observed. With additional carburization time, carbide and void formation has progressed through the coating thickness, and the underlying Cr layer is nearly consumed (Fig. 3c). Beyond void formation, after both 6 and 12 h of carburization the substrate does not show any indication of oxygen migration along its grain boundaries. This likely corresponds to the lack of a solid-state source of oxygen in cold-sprayed Cr for diffusion along the grain boundaries of the substrate.

4. Discussion

Although the conversion of both plasma-sprayed Cr and cold-sprayed Cr to carbide largely proceeds by way of Eq. 1, there is a clear distinction between the conversion mechanisms in these two systems. Through-thickness conversion is achieved in a relatively short reaction time (6h) in the instance of carburized plasma-sprayed Cr, whereas a relatively long reaction time (12 h) is needed to achieve the same effect in the example of carburized cold-sprayed Cr. This difference could be related to the ability, or in the instance of cold-sprayed Cr the inability, of methane gas to penetrate the pore structures of the as-deposited Cr coatings. It is possible that the infiltration of methane gas into the complex pore structure of plasma-sprayed Cr contributes to a rapid through-thickness conversion mechanism by providing an intralayer carbon source.

In cold-sprayed Cr, globular voids and interlamellar porosity were unexpected since metallic coatings deposited using this particular spray technique typically display negligible micron-scale porosity [20]. This finding might be due in part to a loosely controlled particle size distribution in the Cr feedstock powder and the agglomeration of finer particles on the surface of the larger particles (Fig. 1). It is conceivable that the sporadic breakup of agglomerations upon impact with the substrate could give rise to inadequate bonding and consequently intermittent, micron-scale porosity. Nevertheless, methane decomposition appears to be confined to the coating surface for the cold-sprayed Cr coatings in this work, suggesting some type of top-down conversion mechanism. While the observations in the instance of carburized cold-sprayed Cr support this notion, specific models are needed to confirm the details of this type of process. If a top-down conversion mechanism dominates in the carburization of cold-sprayed Cr, then the intermittent porosity observed in the as-deposited Cr coating might not play a significant, or more importantly, a beneficial role during carbide formation.

Qualitatively, an increase in coating porosity volume fraction appears to accompany the conversion of both plasma-sprayed and cold-sprayed Cr to carbide. This is a noteworthy observation when considering the specific volume increase associated with Eq. 1 (23.57 %). Although it looks to be inaccurate in this instance, a reaction with an associated specific volume increase ordinarily results in a decrease in porosity volume fraction when material dimensions are constrained. As such, both systems seem to follow a conversion mechanism which inherently involves the formation of voids. Future work should involve a quantitative study of porosity evolution throughout the carburization of fully-dense cold-sprayed Cr in hopes of gaining a better understanding of the conversion mechanism driving void formation.

5. Conclusion

In this work, a method has been presented for the synthesis of binder-free Cr_3C_2 coatings on nickel-based alloy substrates via the carburization of sprayed Cr coatings. Both plasma-sprayed and cold-sprayed Cr coatings have been successfully converted to Cr_3C_2 , with the mechanism of conversion being strongly influenced by the initial porosity in the as-deposited coatings. This preliminary work has focused on microstructural characterization of these carbide coatings and has qualitatively shown the evolution of the pore structure throughout the carburization process. This porosity might not be favorable for applications requiring molten fluoride salt corrosion resistance and a quantitative understanding of its development would be useful for future implementation of this processing approach. Even so, for applications that could benefit from binder-free Cr_3C_2 coatings, the carburization of sprayed Cr demonstrated in this work appears to be a promising technique for carbide coating formation.

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