MINIMIZING THE FUEL CLADDING CHEMICAL INTERACTION BETWEEN METALLIC FUEL AND ADVANCED FERRITIC MARTENSITIC CLADDINGS VIA VANADIUM BASED DIFFUSION BARRIER COATINGS

By

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This work is dedicated to God and my family, for their unconditional love and support.
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<tr>
<td>1-D</td>
<td>One Dimensional</td>
</tr>
<tr>
<td>ATR</td>
<td>Advanced Test Reactor</td>
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<tr>
<td>BSE</td>
<td>Back Scattered Electron</td>
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<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>Dpa</td>
<td>Displacement per atom</td>
</tr>
<tr>
<td>DPH</td>
<td>Diamond Pyramid Hardness</td>
</tr>
<tr>
<td>EBR-II</td>
<td>Experimental Breeder Reactor II</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>EPD</td>
<td>Electrophoretic Deposition</td>
</tr>
<tr>
<td>EPMA</td>
<td>Electron Probe Micro-Analyzer</td>
</tr>
<tr>
<td>FCCI</td>
<td>Fuel Cladding Chemical Interaction</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
</tr>
<tr>
<td>FFTF</td>
<td>Fast Flux Test Reactor</td>
</tr>
<tr>
<td>F/M</td>
<td>Ferritic/Martensitic</td>
</tr>
<tr>
<td>FNR</td>
<td>Fast Neutron Reactor</td>
</tr>
<tr>
<td>GHG</td>
<td>Greenhouse Gas</td>
</tr>
<tr>
<td>GIXD</td>
<td>Grazing Incidence X-ray Diffraction</td>
</tr>
<tr>
<td>IPFM</td>
<td>International Panel of Fissile Materials</td>
</tr>
<tr>
<td>LWR</td>
<td>Light Water Reactor</td>
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<tr>
<td>MOCVD</td>
<td>Metal Organic Chemical Vapor Deposition</td>
</tr>
<tr>
<td>MOX</td>
<td>Mixed Oxide Fuel</td>
</tr>
<tr>
<td>ODS</td>
<td>Oxide Dispersion Strengthened</td>
</tr>
<tr>
<td>OM</td>
<td>Optical Microscope</td>
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<td>PCDC</td>
<td>Pack Cementation Diffusion Coating</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<td>--------------</td>
<td>----------------------------------------------------</td>
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<tr>
<td>PLC</td>
<td>Programmable Logic Controller</td>
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<tr>
<td>PWM</td>
<td>Pulse-Width Modulation</td>
</tr>
<tr>
<td>RF</td>
<td>Radio Frequency</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary Electron</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscope</td>
</tr>
<tr>
<td>SFR</td>
<td>Sodium-cooled Fast-neutron Reactor</td>
</tr>
<tr>
<td>TD</td>
<td>Thermal Diffusion or Toyota Diffusion</td>
</tr>
<tr>
<td>TRISO</td>
<td>Tristructural Isotropic</td>
</tr>
<tr>
<td>WDS</td>
<td>Wavelength Dispersive Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
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<tr>
<td>YSZ</td>
<td>Yttria-Stabilized Zirconia</td>
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MINIMIZING THE FUEL CLADDING CHEMICAL INTERACTION BETWEEN METALLIC FUEL AND ADVANCED FERRITIC MARTENSITIC CLADDINGS VIA VANADIUM BASED DIFFUSION BARRIER COATINGS

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Major: Nuclear Engineering Sciences (NES)

FCCI has been a critical issue when developing the F/M steel claddings for metallic fuels in a fast nuclear reactor. The elevated operating temperature and accumulated lanthanides over fuel burn-up will aggravate the FCCI, due to eutectic formation. To mitigate the FCCI, vanadium-based diffusion barrier coating was deposited using PCDC. The resultant coating displayed excellent uniformity and structures. The compositional analyses show that the coating is V$_2$C. Diffusion couple experiments further demonstrate that the coating of less than 5 µm can effectively eliminate the interaction between cerium and steels. The PCDC was showed as an effective method to produce coating with excellent metallurgical bonding. However, the grains from diffusion coating have a columnar structure with specific crystalline orientations, which tends to become significant at higher temperatures. This oriented microstructure could promote the diffusion at a postulated accidental temperature above 800 °C. In addition, high temperature annealing from the coating process could transform the martensitic microstructure of claddings. Therefore, an alternative method using the metal-organic precursor was further investigated. The microstructural
characterizations show that a V$_2$C coating with equiaxed grain structures has been obtained by using MOCVD.

The FCCI is strongly related to interdiffusion. Although the FCCI has been extensively studied and improved by doping the fuels, employing advanced claddings, or applying coatings on the cladding, there are still knowledge gaps in understanding FCCI. For example, effects of the major alloying element (chromium) on interdiffusion between lanthanides and steel are not yet fully studied. In an attempt to understand the interdiffusion behavior, systematic studies of interdiffusion between cerium and Fe-Cr binary alloys with different Cr contents were also conducted. Following the thermal annealing at 560 °C, detailed microstructural characterizations were performed to determine the interdiffusion microstructures, compositions, diffusion mechanisms, and phase structures in the interdiffusion zone. The results unambiguously disclose that, as the Ce diffuses into Fe-Cr alloys, Cr segregates and precipitates into Cr-rich $\sigma$ phase consisted of Fe and Cr, instead of forming a ternary phase together with Fe and Ce. The precipitation of those $\sigma$ phase particles at the Ce diffusion front can effectively slow down the interdiffusion.
CHAPTER 1
INTRODUCTION

1.1 Motivation and Overview

Nuclear energy is considered as an energy source with near-zero greenhouse gas (GHG) emission as compared with fossil fuels [1]. However, debates over its safety and long-term disposal of spent fuels containing actinides and long-lived fission products have significantly impeded the anticipated development in nuclear industry, particularly in the United States [2]. In most cases, the spent fuels which come from light water reactors (LWRs) are stored on site or at dedicated repositories. According to the international panel of fissile materials (IPFM), there would be about 490 tons of separated plutonium around the world to be disposed, even if assuming that we decided to shut down all nuclear power facilities today [3]. The concerns about spent fuels will still remain. Nevertheless, nuclear energy is one of the primary sources for electricity generation, while the prospective renewable resources such as the wind or solar are not yet ready to serve as a base load power [4], let alone to fully replace nuclear energy. Figure 1-1 shows the world total required energy [5] and electricity generation by different sources [1, 6]. Based on the growth rate of energy demands, it will be unlikely to give up using nuclear energy, without consumption of more fossil fuels (i.e. coal, natural gas, oil) and generating more GHG. Therefore, further development of the spent-fuel processing technology - the fast neutron reactor (FNR) becomes an essential option in order to sustain a closed-loop fuel cycle and to reduce the spent fuel stocks [7].

The fast-neutron reactor operates with fission reactions induced by fast neutrons (E>0.1MeV), as compared with LWRs (E~1eV). Because of burn-up of actinides and
better utilization of uranium in FNR, the total radiation toxicity and lifetime of nuclear waste can be reduced [7]. Fast-neutron reactor development programs have been conducted in the United States over the past 50 years. The sodium-cooled fast-neutron reactor (SFR) is considered as a promising candidate for Generation IV reactors which are designed to operate with enhanced safety, to generate less radioactive waste, and to relieve the nonproliferation concerns. One of the major goals in the SFR development is to provide a mechanism to close up the nuclear fuel cycle, and a solution to disposal of long-lived actinide products generated from LWRs. In the United State, substantial experiences in the SFR [8] using mixed oxide (>50,000 rods), metal (>130,000 rods), and mixed carbide fuels (600 rods) were obtained from irradiation experiments in EBR-II (Experimental Breeder Reactor-II) and FFTF (Fast Flux Test Facility). In these experiments, the metal fuel and mixed oxide fuel were favored because of both historical and experimental reasons. In general, metal fuel is capable of having a high fissile density and a good chemical stability with sodium. The metal fuel also demonstrates high thermal conductivity, excellent compatibility with pyro-processing techniques [9], and proliferation resistance. Mixed oxide (MOX) fuel can operate at a higher temperature for a deeper burn-up. However, future development in the SFR fuel system should involve thorough consideration, including the fuel fabrication cost, post processing compatibility, and reliability.

Among the above considerations, it is especially critical to sustain an economical operation in the SFR, which relies on many factors. One of them is the fuel burn-up capability which can be improved through fuel assembly designs. For example, to accommodate the irradiation induced fuel growth or swelling, the optimal smear density
for the metal fuel-cladding is selected to be 75%. To increase the melting point of the fuel, the composition of metal fuels can be modified with addition of zirconium. The Zr can also help to stabilize the metallic phases of U and U-Pu, thus minimizing the swelling due to phase changes. Based on the past experiences from EBR-II and FFTF, all three types of fuel have been shown to achieve fuel burn-up capability of 200 GWd/tHM (~20 at.% of burn-up). Another factor contributing to the economical operation is the reactor thermal efficiency which can be improved by increasing the operating temperature [10]. However, the penalties from a higher operating temperature include the concerns about centerline melting for MOX fuels and exacerbated fuel-cladding chemical interaction (FCCI) for metal fuels.

The FCCI has long been acknowledged as a critical factor for the metal fuel-cladding system in a SFR. The mechanism is different in the MOX fuel system, where the FCCI effects are attributed to volatile fission products, e.g. Cs, Te, as well as oxygen from the excess oxygen-to-metal ratio of UO₂ [11]. Although these fission products from the MOX fuel could lead to potential cladding breach, the FCCI is not considered as a life-limiting factor in the MOX fuel system. In the metal fuel system, however, the major attribution in the FCCI comes from lanthanide fission products which migrate to the periphery of the fuel and eventually contact with the cladding due to fuel swelling. The subsequent interdiffusion and intermetallic formation will reduce the effective thickness of cladding by forming regions with degraded mechanical strength, especially when operating at a higher burn-up and an elevated temperature.

In this dissertation, I focused on the FCCI in a metal fuel system and its mitigating methodology through diffusion barrier mechanism by applying a coating on
the cladding inner surface. The interdiffusion behaviors between the lanthanide fission products and cladding constituents were also fundamentally investigated.

### 1.2 Challenge and Innovation

Stainless steels are the primary cladding materials in the SFR. As compared with the zirconium alloy in a LWR, the stainless steel claddings are more resistant to the severe operating conditions anticipated in a SFR. For example, the nominal coolant temperature in the SFR is about 550°C, and this temperature could be elevated to 600-700°C if it is attempted to achieve a better thermal efficiency. The radiation doses on claddings are also expected to be much higher in the SFR than in the LWR, due to a higher neutron energy and much more cumulative displacement-per-atom (dpa). The ferritic/martensitic (F/M) steels such as HT9, T91, and NF616 have been considered as the candidate cladding materials for the SFR, because of compatibility with sodium coolant and low radiation swelling rate. However, the constituents from stainless steels are prone to react with actinide and lanthanide elements from the fuel, especially at an elevated temperature. The chemical interactions will eventually compromise the mechanical integrity of fuel-cladding system.

To apply a physical coating layer on the inner surface of cladding tubes is one of the possible solutions to mitigating the FCCI. The coating material is expected to work as a diffusion barrier to reduce interdiffusion, and as a chemical isolating layer to prevent eutectic formation between the fuel or fission products and cladding constituents. However, to deposit a uniform and thin coating on the inner surface of a meter long cladding with a diameter of 6 mm could be very challenging by using conventional CVD method because of that inefficient precursor delivery can cause
thickness variation in the tube axis direction [12, 13]. Therefore, the geometric limitation is one of the major challenges when it comes to coating inner surface of fuel-cladding tubes. A strong metallurgical bonding between coating and cladding, good thermal and radiation stabilities of the coating layer are also desired.

In addition, the diffusion coating temperature is another limiting factor for developing a practical coating process. The conventional chemical vapor deposition (CVD) of vanadium-based materials requires an elevated temperature (900-1100 °C) in order to sustain an efficient deposition rate [14]. However, the elevated-temperature environment on the F/M steels can potentially ruin the specially-tailored lath microstructures due to over tempering [15], which causes carbon segregation, carbide precipitation, and recrystallization of martensites and dislocations. The vanadium chlorides used in conventional CVD processes could also cause decarburization, resulting in a vanadium carbide coating layer and a underneath substrate zone which has a degraded yield strength [16].

The grain structures of the coating layer can also be critical in mitigating the interdiffusion. In the previous study of TRISO coatings [17], it shows that the small equiaxed grain structure (Figure 1-2A) of SiC outperforms the larger columnar grain with a through-depth structure (Figure 1-2B). The diffusivity of cesium through the columnar structured SiC layer was found an order of magnitude greater than that in a SiC with a laminar grain structure. The difference in diffusivity could be due to that the smaller-grained SiC contains a higher tortuosity which retains metallic fission products more efficiently than the large columnar SiC (with more direct grain boundary pathways). This grain structure difference is believed to be primarily caused by different temperatures
used in the SiC coating process. Although different elements (i.e. lanthanides) are involved in the FCCI as compared with cesium in the case of TRISO fuel, an equiaxed grain structure in the diffusion barrier is still expected to perform better against the FCCI.

In this dissertation, in addition to the conventional diffusion coating process, a metal-organic chemical vapor deposition (MOCVD) method was further developed to obtain a nano-structured equiaxed grain microstructure. Since the deposition mechanism in the MOCVD is primarily through thermal decomposition of organic precursors, the required processing temperature is usually much lower than that in the diffusion coating. Therefore, interdiffusion between the deposited material and substrate compositions is much less likely to happen, reducing the formation of columnar grain structures.

1.3 Outline of Dissertation

In Chapter 2, past studies in analyses and characterizations of FCCI are critically reviewed. Pros and cons of several FCCI mitigation methods are summarized, which leads to my current methodology. The mechanical properties and irradiation tolerance of the proposed coating material are also evaluated.

In Chapter 3, theories and mechanisms of the proposed coating processes are reviewed. Critical phenomena from the FCCI, such as interdiffusion, compositional formation, and precipitation are also analyzed.

In Chapter 4, the experimental details of PCDC, MOCVD, and diffusion couples are discussed. In addition, the techniques for materials characterization are introduced.

In Chapter 5, the experimental results are presented. Analyses and interpretations of these results are also discussed.
Figure 1-1. Breakdown of the world total required energy and electricity generation by different energy sources during the past 40 years [1, 5, 6].

Figure 1-2. Comparison of the grain microstructure of SiC in the TRISO fuel. A) the laminar and B) columnar SiC diffusion barrier layers [17].
2.1 Fuel Cladding Chemical Interaction (FCCI)

2.1.1 Description of the FCCI

The typical SFR fuel assembly consists of fuel elements and structural materials such as the cladding, spacer wire, and duct. A simplified schematic for the setup of metal fuel with a cladding tube is shown in Figure 2-1, where the metal fuel rods are immersed in sodium at the lower section of the cladding tube and the gas plenum is located at the upper section [18, 19]. The sodium bonding between the fuel and cladding provides an excellent thermal conduction path by which heat can be efficiently transferred from the fuel rod to the cladding and then coolant. The specification and operating condition for the metal fuel assembly (X425 and X441) were summarized in Table 2-1 [20]. X425 and X441 were the fuel assemblies of metallic fuel U-19Pu-Zr for the EBR-II.

During the reactor operation, the metallic fuel element swells and eventually contacts with the inner cladding wall due to fission gas release [21]. The interdiffusion occurs between actinide elements and cladding steel, resulting in the formation of intermetallic phases which are brittle and have low melting points. The lanthanides (as the fission products) migrate to the fuel slug peripheral surface driven by the temperature gradient, where they participate in the interdiffusion and intermetallic formation with claddings. The mechanical properties of cladding are compromised due to the formation of cladding wastage layer from the interdiffusion. For example, cracks can be observed in the interdiffusion layer, which provides a localized fast diffusion path for fission products. The typical metallic fuel of U-10Zr after 8% burn-up contains
elements of U: 82.2 (wt.%), Zr: 11.0, Nd: 0.9, Xe: 0.88, Cs: 0.8, Mo: 0.74, Ce: 0.53, and Pu: 0.41 [20, 22]. Table 2-2 summarizes the eutectic melting temperature of phases between the primary actinides, lanthanides, and cladding constituents [23]. Binary phases which are formed between Ce, Pu from the metal fuel, and Fe, Ni from the cladding exhibit relatively low eutectic melting points as compared with the operating temperature in a fast reactor. Figure 2-2 shows the binary phase diagram between Fe and Ce, indicating the formation of eutectic phases Fe$_2$Ce and Fe$_{17}$Ce$_2$. Table 2-3 lists the elemental fraction (i.e. fission yield) among lanthanide fission products. The cerium (22.3 at.%) plays a critical role in the FCCI, not only because of its significant fraction, but also because of its capability of forming low melting phases.

Impacts from the FCCI can be shown in terms of the strength reduced interdiffusion zone, inter-granular penetration, and eutectic melting [24]. Figure 2-3 is an example of FCCI. The ODS and HCM12A were used to interact with metal fuel U-19Pu-9Zr, which was also added with Nd, Ru representing the fission product, and noble metal. In Figure 2-3, the backscattered image shows the interaction zone between the ODS and metal fuel is of the size beyond 200 µm [25]. Large voids were also found to suggest that melting potentially took place during the annealing. In addition, long cracks can also be observed implying the mechanical property of brittleness.

### 2.1.1.1 Eutectic melting in cladding

In general, the inter-granular penetration becomes worse with the formation of low melting-point eutectic phases. However, lowering in the metal fuel (primarily the uranium) melting point does not significantly interfere with the steady-state operation, since the U-Fe and U-Ni eutectic points are 719°C and 740°C (Table 2-2), respectively.
These temperature are well above the normal temperature near the cladding surface (Table 2-1). More concerns should be laid on the cladding and lanthanides. The cladding could be eroded and penetrated rapidly, if the temperature at cladding approaches 720°C during off-normal operations. Furthermore, lanthanides are accumulated along with the fuel burn-up, and they tend to migrate toward the cladding because of their insolubilities in metal fuels and the radial temperature gradient in the fuel rod. Lanthanides are known to harden (i.e. 1100 DPH) and embrittle the cladding, which could entirely change the mechanical integrity of the interdiffusion layer [18].

2.1.1.2 Compositional formation

The Figure 2-4 is an example showing that fuel/cladding (HT9) interface is impacted by the lanthanide concentration under different burn-up levels [26]. The interaction region becomes more observable as the burn-up progresses. In Figure 2-5, the back-scattered electron (BSE) image reveals a more detailed microstructure in the interaction region. A layered structure including the lanthanide-rich layer, the two-phase region at either cladding or fuel side, and the zirconium-iron rich layer can clearly be identified under the Z-contrast imaging from BSE. The composition of the two-phase regions on either the cladding or fuel side was also summarized in Figure 2-5. On the cladding side, the two-phase region consists of (Fe,Cr)$_2$(U, Pu) as the primary phase, and (Fe,Cr)(U,Pu)$_6$ as the matrix, approximately. The compositional results are compared with the U-Fe binary system, which has two eutectic phases, Fe$_2$U and FeU$_6$. On the fuel side, the two-phase region consists of a significant amount of iron either in the primary phase or the matrix. Interestingly, the zirconium was found enriched, but the plutonium depleted in the primary phase (i.e. 41U-6Pu-36Zr-16Fe), as compared with
the un-irradiated fuel U-19Pu-10Zr. This phenomenon is compared to Cr-rich precipitation [27, 28] between metal fuel and stainless steel claddings, and this Cr-rich precipitation behavior will be discussed in Chapter 5. The compositional profiles discussed above were based on the SEM-EDS analysis.

2.1.1.3 Decarburization and grain growth

A carbide or carbon denuded region (“A” in Figure 2-4B [26]) was also found in the cladding next to the interaction region as compared with the non-denuded region from the substrate. One of the differences between the denuded and non-denuded region is the hardness of 150 and 190 DPH, respectively. The DPH (diamond pyramid hardness) is a hardness unit, similar to HV (Vickers pyramid number). The grain size in the denuded region also increased as shown in Figure 2-6, and the carbides in the HT9 were also found being coarsened. These phenomena were attributed to decarburization since the carbides that function as the grain boundary stabilizer were dissolved or consumed.

2.1.2 Analysis and Characterization

Based on the discussion in previous section 2.1.1, the FCCI is complicated since it involves interdiffusion and compositional formation among multiple elements from the cladding, fuel, and fission products. The interaction between the cladding and lanthanide fission products is especially critical due to the formation of low melting eutectic phases from them. Therefore, the analysis of the FCCI is challenging and requires a combination of several different characterization techniques. In general, the FCCI can be characterized in terms of a) diffusion of lanthanide fission products into cladding, resulting in a brittle interdiffusion layer, or b) formation of a low melting alloy created from interaction of the cladding constituents and fission products (e.g. Ce) [10].
The observation of FCCI can be performed in an actual fuel cladding or using out-of-reactor diffusion couple experiments. The in-reactor experiments with metal fuels have been conducted in EBR-II, FFTF, and IFR [18, 26]. As compared with the out-of-reactor diffusion couples, the in-reactor experiments include the effects [29] from irradiation, and the temperature gradient. The out-of-reactor diffusion couples are usually performed in an isothermal condition [30]. However, diffusion couple experiments provide the flexibility of choosing the fuel and cladding materials. Therefore, diffusion couple experiments (as shown in Table 2-4) have been extensively conducted to study the interaction between fuel and cladding elements.

Table 2-4 summarizes the important diffusion couple experiments that have been performed in the past. In these experiments, the cladding material was coupled with either metal fuels such as U-Zr, U-Pu-Zr, or lanthanide fission products such as Ce. The cladding materials were chosen as commercial steels such as the HT9 or simplified alloys such as the binary Fe-Cr alloy. Although pure metals or Ni-based alloys have also been studied in the past, they are not the primary focus in this research. High-Cr steels (e.g. HT9) are the primary focus in this research, so the results from pure metals or Ni-based alloys are not included in the summarized table. The annealing condition was selected based on the operating condition (650-700 °C) in a fast reactor, or postulated accidental scenarios (around 800 °C). In some cases, relatively lower temperature (420-600 °C) was selected to study the interdiffusion process without the interference from severe eutectic melting.

The characterizations of the diffusion couples are based on cross-sectional analyses. The OM and SEM are the most commonly used to investigate the cross-
sectional interdiffusion structures. The BSE imaging in an electron microscope is also useful for showing an atomic contrast in the interdiffusion zone, since the fuel usually contains high-Z elements as compared with the cladding constituents. The EDS or EPMA (based on WDS) were used to study the compositional profiles in a diffusion couple. The spatial resolution of these two techniques would be insufficient if the size of the intermetallic formation or precipitations (e.g. sigma phase precipitation in [30]) is smaller than 1 µm. The minimal diameter of the interaction spot is about 1µm, given an electron beam energy of 15 kV in a SEM or EPMA [31].

2.1.2.1 Effects from the cladding alloying elements

The alloying elements of cladding steels such iron and nickel react with the actinides and lanthanides to form eutectic phases which have melting points lower than the operating temperature in a fast reactor, resulting in severe degradation of the reliability in a fuel cladding system [32]. The chromium, as a major alloying element in advanced stainless steel claddings, is not expected to form eutectic phases e.g. Cr$_2$Ce or (Fe,Cr)$_2$Ce together with the lanthanides (or actinides) at the operating temperature of fast reactor [23]. Nevertheless, many previous studies mentioned that ternary phases, e.g. (Fe,Cr)$_2$U or (Fe,Cr)$_2$Ln (Ln: lanthanides) could form during the interdiffusion process [33-35] and their arguments were usually ambiguous.

Tortorici and Dayananda [33] performed the diffusion couple experiments using cerium and Fe-10Ni (or Fe-20Cr) at 425 °C, and they estimated the interdiffusion coefficients using a scanning electron microscope (SEM) and energy dispersive X-ray spectroscope (EDS). Binary intermetallic phases of Fe$_2$Ce and Ni$_3$Ce$_7$ were identified in the interdiffusion zone. Ternary phases of (Fe,Ni)$_2$Ce, (Ni,Fe)$_3$Ce$_7$, and (Fe,Cr)$_7$Ce$_3$
were also claimed to be formed during the interdiffusion. Recently, Inagaki and Ogata [34] performed similar diffusion couple studies using the Fe-12Cr and 39Nd-24Ce-13La-12Pr, and they concluded that \((\text{Fe,Cr})_3\text{Ln}\) precipitated in the \((\text{Fe,Cr})_{17}\text{Ln}_2\) matrix at 500-650 °C. These two studies [33, 34] implied that chromium could participate in the interdiffusion zone to form ternary intermetallic phases. Another previous study [35] mentioned that Cr-rich precipitation took place due to the depletion of iron, instead of forming intermetallic phases. The concentration of chromium appeared to build up in the steel substrate to form a Cr-rich layer, which was also observed during the interdiffusion between U-Zr and Fe-Cr alloys [27]. However, the above studies were all based on the SEM/EDS observations, which have a limited resolution for compositional analyses. In this study, further investigation in the formation of Cr-rich layer and the effects from Cr on the interdiffusion would be performed using a scanning transmission electron microscope (STEM) and X-ray diffraction (XRD).

2.1.2.2 Interdiffusion coefficients

The effective interdiffusion coefficients have been obtained from the diffusion couples [33, 36] between metallic actinide, lanthanide fuel surrogate, and Fe, Fe-Cr alloys. The estimation of interdiffusion coefficients was based on the dimension and composition of diffusion zone. The interdiffusion between Ni and Ce is significantly faster than that between Fe and Ce. The eutectic phases of \(\text{Ni}_3\text{Ce}_7\) and \(\text{Fe}_2\text{Ce}\) form at 477 and 592 °C, respectively.

In the other case of using U-23Zr as the fuel [36], the interdiffusion coefficients are about two order of magnitude higher than those in the case of Ce, because of much higher annealing temperatures. It should also be noted that the interdiffusion
coefficients of U, Ni in Ni-16Cr are much higher than those of U, Fe in Fe-20Cr, because of the difference in eutectic melting temperatures.

2.1.3 Strategies in the Mitigation of FCCI

Mitigation of the FCCI is usually conducted through the following two approaches. One approach is to modify the fuel, while the other is to improve the cladding material, which is usually conducted by applying a physical diffusion barrier between the inner cladding surface and fuel. The candidate barrier materials are chosen based on the thermodynamic phase stability between the metal fuel and claddings (or between the coating and cladding).

2.1.3.1 Modification of the fuel composition

Since the FCCI involves interdiffusion between the fuel (including fission products) and cladding materials, to reduce the migration of these materials can in principle minimize the fuel-cladding interaction. During the early development of metal fuels for EBR-II, several alloying elements were considered for addition into the fuel matrix, in order to raise the solidus temperature. For example, zirconium was added to the metal fuel U-Pu-Zr because it could reduce FCCI by increasing the solidus temperature and stabilizing the fuel phases [37]. The lanthanide concentration increases as the fuel burns up, and the lanthanide elements migrate to the fuel periphery due to the temperature gradient and their relatively low solubility in the metal fuel matrix. A recent study [38] also proposed to stabilize the lanthanides by doping the fuel with palladium (Pd), since Pd can form intermetallic compounds (e.g. Nd₃Pd₇) with lanthanides as shown in Figure 2-7. The diffusion couple results show that reaction layers at interfaces of Ln-Pd/Fe (Ln:Pd=1:1) can be substantially reduced, except for
cerium which shows spinodal decomposition suggesting a considerable solubility of iron in cerium.

Zirconium molding is a technique using zirconium as the casting sheath (mold) material for the pyrometallurgical reprocessing. The original concept is to cast metal fuels into quartz, but the quartz residue remains as an issue of contamination. Zirconium was chosen as the sheath material because it is compatible with the U-Pu-Zr fuel alloy. The solidus temperature is expected to increase with addition of Zr, providing potentially better resistance against FCCI. However, a previous study [39] showed that Zr sheaths might not be a perfect barrier against FCCI, since the equivalent amount of fission gas could still trigger a fast release if extend of cracks in the fuel slug exists, as shown in Figure 2-8. Therefore, using the Zr casting sheaths against FCCI may not be a reliable approach.

2.1.3.2 Modification of the cladding tube

Similar to the concept of using Zr casting sheath, the cladding tube can be modified by applying a liner (duplex) on the cladding [40]. Vanadium was chosen for this purpose because in-reactor tests indicated that vanadium alloyed cladding had excellent metallurgical compatibility with the U-Pu-Zr fuel. The process used the Fenn hydraulic draw bench to pull a gripper with an outer diameter of 0.187”. The cladding tube HT9 has an inner diameter of 0.194”, and vanadium inner tube has an outer diameter of 0.183”, tube wall thickness of 0.005”. Based on the calculation, it was expected that the vanadium tube would expand into plastic range and the HT9 tube would shrink back, then the gap would be minimized. However, the gap of about 5-10 µm is still inevitable, as shown in Figure 2-9. The gapping could lead to localized high temperature spots due to a poor thermal conduction. In addition, decarburization in the
cladding could occur because vanadium tends to react with carbon (or oxygen) at an elevated temperature.

In addition to the vanadium liner techniques, many other mitigation methods were proposed. For example, Lee et al. [41] claimed that the oxide coating layer (e.g. Cr$_2$O$_3$, V$_2$O$_3$, or ZrO$_2$) formed in an acid on the inner surface of the cladding can help to prevent the FCCI. Yang et al. [42] developed a Cr electroplating technique which were performed in an electrolyte bath (250g/l CrO$_3$, 2.5g/l H$_2$SO$_4$) at 80°C. In Figure 2-10, an electroplated Cr of about 10 μm in thickness was obtained, and subsequent diffusion couple experiments demonstrate the effectiveness of coating against the FCCI. However, these two techniques (oxidation by acid, and electroplating) could involve formation of cracks (see Figure 2-10) and poor adhesion between the coating and substrate.

Another method is using nanofluid-based electrophoretic deposition (EPD) process [43] to deposit coatings of titanium oxide (TiO$_2$), yttria-stabilized zirconia (YSZ), and vanadium oxide (V$_2$O$_3$). A subsequent high-temperature (1050 °C for 4 hours) sintering process is performed to improve the density and bonding to substrate. To avoid a severe grain growth in the substrate steel, lower sintering temperature (850 °C for 15 hours) was suggested [44] in the case of sintering of titanium oxide coating. However, since the sintering temperature (850 °C) could be detrimental to the specially-tailored microstructures in ferritic-martensitic steels, this method cannot be practically applied on a F/M cladding.

Based on the previous diffusion couple studies, Ti, V, Cr, Zr, Nb and Mo were identified as the candidate diffusion barrier materials, while vanadium exhibited the most
promising performance [45-47]. In this research, vanadium-based material will be used as the diffusion barrier material. Chemical vapor deposition (CVD) was proposed to apply the vanadium-based (e.g. vanadium carbide) diffusion barrier, and the pack cementation diffusion coating (PCDC) method was used as a prototype methodology.

2.2 Development of Coating Method

2.2.1 Prototype Experiment: Pack Cementation Diffusion Coating (PCDC)

Compared with the mitigating methods discussed in the previous section, the PCDC method offers several advantages including superior bonding between the cladding substrate and coating layer, no significant residual stress or axial texture from cold-drawing, thinner coating layer, and versatile process with capability of coating large objects such as long pipes.

In general, the PCDC process is a surface treatment procedure that has been widely used for aluminizing, chromizing, or siliconizing the components in gas turbines, in order to increase lifetime of components in a high-temperature environment. PCDC is a relatively simple method by burying the to-be-coated components in a powder mixture within an alumina crucible container loaded into a high-temperature inert atmosphere for a sufficient period of time. The powder mixture (i.e. the pack) consists of the metal elements to be coated, a halide activator salt, and an inert filler material as shown in Figure 2-11. The simple setup makes the PCDC process repeatable, and its “non-line-of-sight” characteristic especially suitable for coatings on the inner surface of cladding tubes.

Historically, the application of PCDC can be dated back to early 20th century [48], when steels were chromized for the purpose of preventing high-temperature corrosion or oxidation. This purpose can be fulfilled because the Cr$_2$O$_3$ oxidized from Cr
coating in a high-temperature environment will further reduce the oxygen activity at the coating/substrate interface, therefore reducing oxidation. On the other hand, siliconizing of Fe-based alloy substrate has much less industrial applications since a nonporous coating with higher than 11 w.t.% of Si cannot be formed on this substrate. However, simultaneous deposition of Cr and Si (i.e. co-deposition) has been performed and proved to inhibit the chromium carbide formation by thermodynamic repulsion between Si and C, therefore to improve the Cr diffusion [49]. A lot more recent developments in the PCDC for high-temperature applications can be found in aluminizing Fe-based alloys or stainless steels [50-54], since iron aluminides exhibit an excellent high-temperature corrosion resistance. The typical aluminisation temperature in these researches was originally performed at a minimum temperature of 900 °C, which would degrade the microstructures of the substrate and the related mechanical properties such as creep resistance. Recently, by using alternative activator salts such as AlCl₃, the aluminisation temperature was reduced to less than 700 °C [51-53].

The published literature on deposition of vanadium coating using the PCDC is much less than those on chromium and aluminum PCDC coating. It might be because that most of industrial applications actually prefers vanadium carbide (or nitride) which exhibits great toughness and wear resistance. And the vanadium carbide coating is usually prepared by the TD (thermal diffusion) in a salt bath, as discussed previously. Nevertheless, there is one available report which suggested a powder mixture of V, NH₄Cl, and Al₂O₃. In addition, there is an U.S. patent [55] which claims to use V, vanadium nitride, and iodine. More recently, it was reported that the similar powder mixture with addition of naphthalene (C₁₀H₈) can produce a vanadium carbide coating
[56]. Unfortunately, the processing temperatures are all above 900°C in those three reported processes. For this study, the procedure with a processing temperature around 730 °C will be developed for the prototypic stage of coating development. The decarburization of the substrate and its impact on the mechanical properties should be evaluated, since pure vanadium is known to have a great affinity to carbon or nitrogen. Therefore, to use a vanadium-based material such as vanadium carbide or nitride can prevent the decarburization.

2.2.2 Metal-organic Chemical Vapor Deposition (MOCVD)

As discussed in the previous section, processes for deposition of vanadium usually involve high temperature, which requires extremely expensive processing equipment. In addition to the cost, high deposition temperatures also cause undesirable structural alterations such as coarse grain structures and decarburization of steel substrates. It is only at lower temperatures that fine-grained (instead of single-crystal) deposits can be obtained. The low temperature deposition process can be achieved in a conventional CVD apparatus using less stable precursors such as organometallic compounds. This process is known as the metal-organic chemical vapor deposition (MOCVD).

The MOCVD is a technique that is used to deposit very thin layers of atoms onto a substrate. The MOCVD has wide applications in manufacturing semiconductor thin film such as the gallium nitride (GaN). To deposit the thin films, the precursors are vaporized and transported into the reactor together with other gases. There, the critical chemical reaction takes place that turns the precursors into the desired crystal structures through thermal decomposition.
In order to deposit a vanadium-based (vanadium carbide) material onto the substrate, volatile precursors carrying vanadium should be identified. In an earlier development [57], it suggested vanadium carbide can be deposited at 550-600 °C. Subsequently, the deposition temperature at substrate can be further lowered to 200-400 °C [58] when using dicyclopentadienyl vanadium (Vanadocene, Cp₂V) as a precursor shown in Figure 2-12. Therefore, an innovative low temperature coating process can be developed. Compared with mechanical lining and conventional CVD technologies, the proposed low temperature process can offer several advantages: 1) no significant residual stress or axial texture from cold-drawing, 2) no detrimental effects on the martensitic substrate, and 3) a strongly bonded thin and uniform vanadium carbide coating can be readily obtained.

2.3 Functionality of Developed Diffusion Coating Barriers

2.3.1 Performance of the Diffusion Barrier: Diffusion Couple Method

Diffusion couple experiments were widely performed in the past, to study the interdiffusion and intermetallic formation between lanthanides (or actinides) and the claddings [25, 45, 46]. Cerium is used as a surrogate material for metal fuels, since it resembles the actinides, and cerium is also a dominant lanthanide element which forms low-melting eutectic phase with cladding compositions. The following Figure 2-13 shows the cross sectional analysis on the T91/cerium/sintered titanium coated T91 diffusion couple [44]. As it can be seen in the BSE images, on the bare side (left) severe interaction between iron and cerium happened and Fe₂Ce is formed. The width of the interaction zone is up to 63 μm. On the coated side (right), no evidence of interaction between cerium and iron is observed, which indicates an excellent diffusion barrier.
characteristic of the sintered titanium coating. The chemical compositional profile from the EDS line-scan (Figure 2-13B) shows an abrupt transition across the original interface at cerium/coating/steel boundary. Coating region is primarily composed of titanium indicating the negligible dissolution of cerium into it. In my research, similar experiments and analyses using diffusion couples between steel and cerium will be performed.

Due to fuel swelling, the normal stress between fuel-cladding cannot be ignored at a high fuel burn-up. This normal stress is difficult to be measured; however, the simulation code of FEAST-METAL [59] can estimate the stress. The FEAST-METAL code is equipped with physics based semi-empirical models to describe various phenomena such as fission gas swelling, release and hot pressing, fuel constituent redistribution, fuel clad chemical interaction, and transient creep fracture of the cladding. The code predicted EBR-II low zirconium fuel behavior satisfactorily for steady state and transients. As shown in Figure 2-14, the normal stress can reach 15 MPa with a 15 at.% burn-up of the low-Zr fuel. For the fuel with a higher content of Zr, to reach the same stress level (15 MPa) can sustain 20-30 at.% of burn-up.

2.3.2 Mechanical Integrity of the Deposited Thin Film

To evaluate the mechanical integrity of the coatings, micro scratch tests can be conducted. During the test, a standard Rockwell indenter (20° cone with 0.2 mm radius) is slowly plunged into the coating by a constant force (e.g. 150 g) while the sample is firmly clamped onto a moving stage. The stage starts to move with the constant speed of about 1.5 inch/min to make scratch. The width of the scratch is then measured using SEM and used as a criterion for mechanical properties of the coatings.
To evaluate the mechanical integrity of the coatings a scratch test can be performed on the diffusion barrier coatings. Figure 2-15 shows the SEM SE plane views of the scratch marks on the coatings. No full indenter penetration observed in the micrographs even on the as deposited coating (Figure 2-15A). Furthermore, the width of the scratch marks decreases by increasing the sintering temperature which is consistent with density measurement results. In the coating sintered at 850 °C for 15 h (shown in Figure 2-15B), the width of the scratch mark is almost the same as the one sintered at 1050 °C for 4 hours, even though the sintering temperature is significantly lower. On the other hand, some micro cracks can be seen close to the scratch marks in the latter despite their similar density. This suggests a higher toughness were achieved by sintering at a lower temperature (850 °C) but longer time.

2.3.3 Irradiation Tolerance of the Deposited Thin Film

To ensure the integrity of coating in the fuel cladding during reactor operations, irradiation response of the coating and the interfaces of the cladding/coating/fuel needs to be evaluated. There are two major objectives in evaluation of the irradiation performance of the fuel-cladding system. The first objective is to study the irradiation response of deposited materials (i.e. vanadium carbide) and the coating-cladding interface. The vanadium carbide could exhibit different swelling rate as compared with the cladding under radiation. The difference in swelling rate could introduce stress at the interface, causing de-lamination or spallation. The second objective is to understand the interdiffusion behavior under radiation. The irradiation could enhance the interdiffusion at the cladding/coating (e.g. decarburization) or coating/fuel interfaces.

Overall, the vanadium-based materials demonstrate great irradiation response. Historically, vanadium-based alloys were considered as the candidate materials for the
first wall and blanket materials in a fusion reactor, or for the fuel claddings in a SFR.
The vanadium alloys (e.g. V-7.5Cr-15Ti, V-4Cr-4Ti) show great void swelling resistance, according to the neutron and ion irradiation data [60-62]. The V-Cr-Ti alloys exhibit even lower swelling rate (~0.1% per dpa) as compared with the typical HT9 cladding (~0.2% per dpa). The swelling behavior of vanadium-based alloys can also be changed by alloying elements. In general, undersized alloying elements (e.g. Fe, Cr, Ni) increase the swelling rate, while oversized elements (e.g. W, Mo, Ti) decrease it. The atomic radii of the some common elements are summarized in Table 2-6. The size of vanadium atom is about 134 pm in radius, smaller than tungsten of 139 pm, but larger than chromium of 128 pm. These results provide a general idea about the irradiation capability of the vanadium-based coating.

In this research, ceramic vanadium carbide is the proposed coating material. The irradiation response of vanadium carbide can be compared to other carbides. The radiation effects in ceramics such as zirconium carbide (ZrC), nitride (ZrN), or titanium carbide (TiC) have been widely studied [63-66]. Although studies directly about the irradiation response of the vanadium carbide are rare, it is expected that vanadium carbide (VxCy) should be able to tolerate high irradiation at elevated temperature, based on the previous studies on zirconium and titanium carbides.

The primary irradiation effects in ceramics include dimensional instability, changes in transport properties, and changes in mechanical properties [67]. In Figure 2-16, the volume increase in most carbide [68] is less than 3% at 2-3×10^{21} n/cm^{2}, which corresponds to 3-4 dpa. Compared with HT9 (0.2% per dpa), carbides exhibit acceptable dimensional stabilities. Ion irradiation experiments were performed on
zirconium carbide with 2.6 MeV protons. The ZrC samples were irradiated at 800°C to doses of 0.7 and 1.5 dpa. High density of nano-sized faulted Frank loops was identified. Slight lattice expansion was also observed, consistent with previous neutron irradiation results [68]. Besides, the irradiated ZrC samples were found hardened after irradiation using the indentation technique. The increase in hardness can most likely be attributed to point defects. But, no irradiation induced amorphization, void, or precipitates were observed during proton irradiation. Similarly, irradiation on ZrN shows that high density of nano-sized defects, particularly identified as vacancy-type pyramidal dislocation loops in Figure 2-17. However, due to small total dose (dpa) in the above experiments, lattice expansion effect might not be fully revealed.
Figure 2-1. Schematic of a metallic, sodium bonded, fast reactor fuel element [18].

Table 2-1. Specification for the metal fuel assembly [20].

<table>
<thead>
<tr>
<th>Assembly #</th>
<th>X441</th>
<th>X425</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cladding material</td>
<td>HT9</td>
<td>HT9</td>
</tr>
<tr>
<td>Clad OD (mm)</td>
<td>5.84</td>
<td>5.84</td>
</tr>
<tr>
<td>Clad wall thick (mm)</td>
<td>0.38</td>
<td>0.38</td>
</tr>
<tr>
<td>Fuel alloy (w.t.%</td>
<td>U-19Pu-10Zr</td>
<td>U-19Pu-10Zr</td>
</tr>
<tr>
<td>Fuel slug length (mm)</td>
<td>343</td>
<td>343</td>
</tr>
<tr>
<td>Fuel OD (mm)</td>
<td>4.67</td>
<td>4.32</td>
</tr>
<tr>
<td>Smear density (%)</td>
<td>~85</td>
<td>~72</td>
</tr>
<tr>
<td>Linear power (W/cm)</td>
<td>~510</td>
<td>~400</td>
</tr>
<tr>
<td>Cladding Temp. (°C)</td>
<td>~600</td>
<td>~590</td>
</tr>
</tbody>
</table>
Table 2-2. Eutectic melting points for selected phases [23].

<table>
<thead>
<tr>
<th>Origin</th>
<th>Binary phase</th>
<th>Melting point (in °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actinide fuel</td>
<td>U-Fe</td>
<td>719</td>
</tr>
<tr>
<td></td>
<td>U-Ni</td>
<td>740</td>
</tr>
<tr>
<td></td>
<td>Pu-Fe</td>
<td>425</td>
</tr>
<tr>
<td></td>
<td>Pu-Ni</td>
<td>465</td>
</tr>
<tr>
<td>Lanthanide fission</td>
<td>Ce-Fe</td>
<td>592</td>
</tr>
<tr>
<td>products</td>
<td>Ce-Ni</td>
<td>477</td>
</tr>
<tr>
<td></td>
<td>Nd-Fe</td>
<td>685</td>
</tr>
<tr>
<td></td>
<td>Nd-Ni</td>
<td>561</td>
</tr>
</tbody>
</table>

![Figure 2-2. Binary phase diagram of Fe-Ce [23].](image-url)
Table 2-3. Fraction of lanthanide fission products generated in irradiated metal fuel [34].

<table>
<thead>
<tr>
<th>Elements</th>
<th>Fission Yield (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd</td>
<td>35.9</td>
</tr>
<tr>
<td>Ce</td>
<td>22.3</td>
</tr>
<tr>
<td>La</td>
<td>12.5</td>
</tr>
<tr>
<td>Pr</td>
<td>11.4</td>
</tr>
<tr>
<td>Sm</td>
<td>10.4</td>
</tr>
<tr>
<td>Y</td>
<td>4.0</td>
</tr>
<tr>
<td>Pm</td>
<td>1.2</td>
</tr>
<tr>
<td>Eu</td>
<td>1.2</td>
</tr>
<tr>
<td>Gd</td>
<td>1.1</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Figure 2-3. The cross-section of diffusion couples between fuel and claddings by using BSE imaging. The materials include the cladding A) ODS, B) HCM12A (12Cr) and the fuel of 65U-19Pu-9Zr-2Nd-2.5Mo-2.5Ru (wt.%) that were annealed at 700°C for 25 hours [25].
Figure 2-4. Typical fuel/cladding interaction cross-section. A) 5.6 at.\% of burn-up, and B) 11 at.\%. Both was annealed 800°C for 1h. The dark region represents the lanthanide elements [26].

Figure 2-5. The BSE image and compositional profile from Figure 2-4(B). It shows the zone-A (cladding), zone-B (lanthanide-rich layer), zone-C (two-phase region on the cladding side), zone-D (Zr, Fe rich layer), zone-E (two-phase region on the fuel side). The compositional profile was summarized in the table [26].
Figure 2-6. The denuded cladding after etching, showing large ferrite grains. The lanthanide rich layer is the dark region at the bottom [26].

### Table 2-4. Diffusion couple experiments.

<table>
<thead>
<tr>
<th>Alloys Composition</th>
<th>Annealing Conditions</th>
<th>Characterization techniques</th>
<th>Compositional Formation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-20.1Cr. (U-23Zr)</td>
<td>700C 4 days.</td>
<td>SEM/EDS</td>
<td>(Fe,Cr)$_2$U and Zr-rich phase</td>
<td>[36]</td>
</tr>
<tr>
<td>HT9 (U-21Pu-23Zr)</td>
<td>650C 100 hrs.</td>
<td>SEM/EDS</td>
<td>(Fe,Cr)$_2$(U,Pu,Zr), (Fe,Cr)(U,Pu,Zr)$_6$, and (Fe,Cr)$_2$(Zr,U,Pu)</td>
<td>[30]</td>
</tr>
<tr>
<td>Fe-12Cr (U-23Zr)</td>
<td>680-715C 1.6, 4, 14 d.</td>
<td>SEM/EPMA</td>
<td>Fe$_2$U, Fe$_6$U, and Fe$_2$Zr $\varepsilon$, $\chi$, $\gamma$, $\lambda$, $\beta$U (Fe,Cr)$_7$Ce$_3$ and Fe$_2$Ce were identified.</td>
<td>[27]</td>
</tr>
<tr>
<td>Fe-20.1Cr. (Ce)</td>
<td>425C 4 days.</td>
<td>SEM/EDS</td>
<td>Cr appears to build up in the (Fe,Cr)$_7$Ce$_3$ layer. (Fe,Cr)$_7$Ce$_3$ was stated as a new ternary phase.</td>
<td>[33]</td>
</tr>
<tr>
<td>Fe-9Cr-2W. (70Ce-30La)</td>
<td>660, 800C 25, 48 hrs.</td>
<td>SEM/EDS</td>
<td>The region (i.e. steel) near interface shows Cr-rich precipitation.</td>
<td>[35]</td>
</tr>
<tr>
<td>Fe-12Cr. (39Nd-24Ce-13La-12Pr)</td>
<td>650-420C. 20, 50, 170 hrs.</td>
<td>SEM/EPMA</td>
<td>At 500-650C, (Fe,Cr)$_3$RE precipitates in the (Fe,Cr)$_7$RE matrix.</td>
<td>[34]</td>
</tr>
</tbody>
</table>
Table 2-5. The effective interdiffusion coefficients for the diffusion couples from previous studies [33, 36].

<table>
<thead>
<tr>
<th>Diffusion couple (L vs. R)</th>
<th>$D_{\text{eff}, \text{L}}$ (m²/sec)</th>
<th>$D_{\text{eff}, \text{R}}$ (m²/sec)</th>
<th>Annealing condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe vs. Ce</td>
<td>$D_{\text{Fe or Ce}, \text{L}}=2.7 \times 10^{-16}$</td>
<td>$D_{\text{Fe or Ce}, \text{R}}=8.4 \times 10^{-17}$</td>
<td>425 °C for 4 days.</td>
</tr>
<tr>
<td>Ni vs. Ce</td>
<td>$D_{\text{Ni or Ce}, \text{L}}=7.3 \times 10^{-15}$</td>
<td>$D_{\text{Fe or Ce}, \text{R}}=4.9 \times 10^{-14}$</td>
<td>425 °C for 4 days.</td>
</tr>
<tr>
<td>Fe-20Cr vs. Ce</td>
<td>$D_{\text{Fe}, \text{L}}=7.5 \times 10^{-16}$</td>
<td>$D_{\text{Fe}, \text{R}}=8.1 \times 10^{-17}$</td>
<td>425 °C for 4 days.</td>
</tr>
<tr>
<td></td>
<td>$D_{\text{Ce}, \text{L}}=2.9 \times 10^{-16}$</td>
<td>$D_{\text{Ce}, \text{R}}=7.7 \times 10^{-17}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_{\text{Cr}, \text{L}}=6.7 \times 10^{-17}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-20Cr vs. U-23Zr</td>
<td>$D_{\text{Fe}, \text{L}}=5.33 \times 10^{-14}$</td>
<td>Not available.</td>
<td>700 °C for 4 days.</td>
</tr>
<tr>
<td></td>
<td>$D_{\text{U}, \text{L}}=4.1 \times 10^{-14}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_{\text{Cr}, \text{L}}=1.57 \times 10^{-14}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-16Cr vs. U-23Zr</td>
<td>$D_{\text{Ni}, \text{L}}=1.73 \times 10^{-11}$</td>
<td>Not available.</td>
<td>700 °C for 4 days.</td>
</tr>
<tr>
<td></td>
<td>$D_{\text{U}, \text{L}}=8.21 \times 10^{-12}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Not available.

Figure 2-7. Binary phase diagrams of A) Nd-Pd and B) Ce-Pd [23].
Figure 2-8. Longitudinal cross-section of a Zr-sheathed U-Pu-Zr element. The upper arrow indicates the original interface between the fuel slug and cladding. The bottom arrow points to a fuel-Zr sheath interaction region [39].

Figure 2-9. Vanadium liner obtained in the duplex tube drawing process, showing the gap between the cladding and vanadium liner [40].
Figure 2-10. Diffusion couples between Cr-plated HT9 and metal fuel after annealing at 800 °C for 48 hours. Penetration of uranium was found in the low density of the Cr-plating [42].

Figure 2-11. The typical content for a laboratory scale diffusion coating pack. Photo courtesy of Vilupanur A. Ravi.
Figure 2-12. Structure and thermolysis properties of the bis-cyclopentadienyl vanadium (Vanadocene or Cp₂V) precursor. The solid and gas phase transformation of the Cp₂V is about 130 °C [58].
Figure 2-13. Cross-sectional image and EDS line-scan from the EPD titanium diffusion barrier. A) The cross-sectional image of the diffusion couple experiment showing the interfaces at bare steel/cerium and cerium/coated-and-sintered steel. Severe interactions were observed at the bare steel/cerium interface. B) The EDS line-scan across the cerium/coated steel interface showing no interdiffusion [44].
Figure 2-14. Simulated contact pressure between the metal fuels of different compositions and claddings. A) U-15Pu-6Zr and B) U-50Pu-4Am-2Np-30Zr. About 10-15 MPa of contact pressure is expected after 15 at.% of burn-up [59].

Figure 2-15. SEM images of the scratched areas on the coatings made with 80 nm titanium particles. A) as deposited, and B) sintered at 850 °C for 15 hours [44].

Table 2-6. Comparison of the atomic size of the alloys or ceramics forming elements.

<table>
<thead>
<tr>
<th>Elements (At. Number)</th>
<th>Atomic radius (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (28)</td>
<td>124</td>
</tr>
<tr>
<td>Fe (26)</td>
<td>126</td>
</tr>
<tr>
<td>Cr (24)</td>
<td>128</td>
</tr>
<tr>
<td>V (23)</td>
<td>134</td>
</tr>
<tr>
<td>C (6)</td>
<td>69-77 (Covalent radius)</td>
</tr>
<tr>
<td>W (74)</td>
<td>139</td>
</tr>
<tr>
<td>Mo (42)</td>
<td>139</td>
</tr>
<tr>
<td>Ti (22)</td>
<td>147</td>
</tr>
<tr>
<td>Zr (40)</td>
<td>160</td>
</tr>
</tbody>
</table>
Figure 2-16. Gross volume increase of mono carbides of Ti, Zr, Ta, Nb, and W, irradiated at 300-700 °C as a function of fast neutron dose [67].
Figure 2-17. Planar defect and dislocation loop in proton irradiated ZrN. A) [0 1 1] lattice image of planar defect. B) Pyramidal dislocation loop revealed by Fourier-filter (2 0 0) diffraction lattice image [64].
CHAPTER 3
THEORETICAL ANALYSIS

3.1 Thin Film Deposition

3.1.1 Mechanisms in the PCDC Process

The pack cementation diffusion coating (PCDC) is essentially a chemical vapor deposition (CVD) process activated by halide salts such as ammonium chloride (NH₄Cl) or sodium chloride (NaCl). As shown in Figure 3-1, two inter-related processes take place simultaneously in the pack at an elevated temperature [53]. One process is about the chemical reactions to form metal halide vapors that subsequently migrate to the steel substrate. This process is called “activation/migration”. The other process is about the deposition of coating materials through the reduction reaction of metal halides at the steel surface, and the interdiffusion occurs between the deposited elements and substrate. This is called “deposition/interdiffusion”. The formation mechanism, growth kinetics, phase and microstructure of the coatings are closely related to the above two processes. In the following discussion, I will include the pack aluminization as an example to explain the critical processes in PCDC of vanadium. I will further discuss the differences between vanadization and aluminization.

3.1.1.1 Pack activation

In the halide activation for aluminization process, Levin and Caves [69] have pointed out that activation capabilities of halides ranked as F ≡ Cl > Br > I. In general, if the pack is highly activated (e.g. using the fluoride-activated pack), the dominant step for the entire PCDC process will be the solid-state diffusion (i.e. outward diffusion of nickel from steel substrate), which is known as a solid-state diffusion controlled process.
Contrastingly, if the pack is less activated, it might become a gaseous diffusion controlled process.

\[
\begin{align*}
HCl(\text{g}) + V(s) & \rightarrow VCl(\text{g}) + \frac{1}{2}H_2, \quad \Delta G_{730\,^\circ\text{C}} = 194.3 \, \text{kJ/mol} \\
HCl(\text{g}) + \frac{1}{2}V(s) & \rightarrow \frac{1}{2}VCl_2(\text{g}) + \frac{1}{2}H_2, \quad \Delta G_{730\,^\circ\text{C}} = 8.5 \, \text{kJ/mol} \\
HCl(\text{g}) + \frac{1}{3}V(s) & \rightarrow \frac{1}{3}VCl_3(\text{g}) + \frac{1}{2}H_2, \quad \Delta G_{730\,^\circ\text{C}} = -10.8 \, \text{kJ/mol} \\
HCl(\text{g}) + V(g) & \rightarrow VCl(\text{g}) + \frac{1}{2}H_2, \quad \Delta G_{730\,^\circ\text{C}} = -168.8 \, \text{kJ/mol} \\
HCl(\text{g}) + \frac{1}{2}V(g) & \rightarrow \frac{1}{2}VCl_2(\text{g}) + \frac{1}{2}H_2, \quad \Delta G_{730\,^\circ\text{C}} = -173.1 \, \text{kJ/mol}
\end{align*}
\]

To further understand the activation process, critical reactions between the halide activator and master alloy need to be analyzed. The Gibbs free energy change \( \Delta G \) in each reaction can be calculated based on tabulated thermochemical data. The chloride salt (e.g. \( \text{NH}_4\text{Cl} \)) is used as a primary activator for vanadium, and critical reactions for activation are listed as above equations. The \( \text{NH}_4\text{Cl} \) decomposes into \( \text{NH}_3(\text{g}) \) and \( HCl(\text{g}) \) at temperature above 338 °C. Four vanadium chlorides (\( VCl, VCl_2, VCl_3, \) and \( VCl_4 \)) could possibly be formed during the activation process. The corresponding \( \Delta G \) in the above reactions were calculated at 730 °C, the maximum temperature below which the microstructures in F/M steel should remain stable. The calculation of \( \Delta G \) was based on the JANAF thermochemical tables [70], and the detailed calculation procedures are discussed in Appendix A. Based on the calculation results of \( \Delta G \), only \( VCl_3(\text{g}) \) can be formed by reacting \( HCl(\text{g}) \) and \( V(s) \). Formation of \( VCl(\text{g}) \) and \( VCl_2(\text{g}) \) would require the reactions between \( HCl \) and gaseous vanadium \( V(g) \). Vanadium has an extremely low vapor pressure of about \( 10^{-20} \) atm as compared with Al (\(~10^{-10} \) atm), or Cr (\( 10^{-14} \) atm) calculated at 700 °C [71].
\[ VCl_2 \rightarrow \frac{1}{2}V + \frac{1}{2}VCl_4 \]
\[ VCl_2 \rightarrow \frac{1}{3}V + \frac{2}{3}VCl_3 \]
\[ VCl_2 + H_2 \rightarrow V + 2HCl \]
\[ VCl_3 \rightarrow \frac{1}{4}V + \frac{3}{4}VCl_4 \]
\[ VCl_3 + \frac{3}{2}H_2 \rightarrow V + 3HCl \]

Reduction reactions of the vanadium chlorides lead to deposition of vanadium, and different vanadium chlorides show different levels of potentials for reduction reactions. As a further analysis, five possible reduction reactions using \(VCl_2\) and \(VCl_3\) are listed as above. In Figure 3-1, the Gibbs free energy change \(\Delta G\) was also calculated for the above reactions. The results show that only the reduction reactions of \(VCl_2(g)\) is thermodynamically feasible as \(\Delta G < 0\). Therefore, without the presence of vapor phase \(VCl_2\), the deposition process cannot proceed based on the reduction reactions. However, the \(VCl_2(s)\) could be synthesized by the disproportionation of \(VCl_3\) at the temperature above 350 °C.

\[ 2VCl_3 \rightarrow VCl_2(s) + VCl_4(g) \]

Depending on the \(HCl/H_2\) ratio, solid \(VCl_2(s)\) could further be transformed into vapor phase. According to the previous study [14], \(VCl_2(g)\) vapor becomes significant only at above 900 °C, implying that the deposition efficiency could be significantly reduced as the temperature is below 900 °C. Therefore, the temperature becomes a rate-controlling factor for the PCDC process.
3.1.1.2 Migration

For the halide migration process, Levin and Caves [69] have formulated the relation (3-1) between the amount of deposited material \( m \) [mg] per unit area and total coating time of \( t \) [sec].

\[
m = k_g \sqrt{t}
\]  

(3-1)

where \( k_g \) is the parabolic rate constant of halide vapor migration, which can be expressed as

\[
k_g = \left[ \frac{2n \varepsilon M_{Al}}{lRT} \sum D_i (p_i - p_{i0}) \right]^{1/2}
\]  

(3-2)

where \( n \) [g/cm\(^3\)] is the Al concentration in the pack; \( \varepsilon \) and \( l \) are the unitless correction factors for porosity and pore length; \( M_{Al} \) [g] is the atomic weight; \( R \) [atm-cm\(^3\)/K-mole] is the gas constant; \( T \) [°K] is the temperature; \( D_i \) [cm\(^2\)/sec] denotes the diffusivity constant, and \( p_i \) [atm] is the partial pressure of the \( i \)-th species. The rate of aluminum transport in the halide-activated aluminizing pack can be calculated based on the assumption that gaseous aluminum halides diffuse through an aluminum-depleted zone adjacent to the substrate [72]. A detailed derivation for the above rate constant \( k_g \) is discussed as follows.

Firstly, the instantaneous flux [mole/sec-cm] of halides per unit area can be written as

\[
\frac{N_{Al}d}{A} = \frac{\sum D_i (p_i - p_{i0})}{RT}
\]  

(3-3)

\( N_{Al} \) [mole/sec] is the Al flow; \( d \) [cm] is diffusion distance; \( A \) [cm\(^2\)] is the unit area, based on the ideal gas law. The deposition rate \( \frac{dm}{dt} \) [mg/cm\(^2\)-sec] is proportional to \( n \) (the Al pack concentration), the instantaneous flux \( \frac{N_{Al}d}{A} \), and the atomic weight \( M_{Al} \); but is
inversely proportional to the deposited material $m$. In addition, porosity and porous length $\varepsilon$ and $l$ are considered.

$$\frac{dm}{dt} = \frac{n \varepsilon}{m l} M_{\text{Al}} \frac{N_{\text{Al}} d}{A}$$

(3-4)

Integrating over the above equation gives the relation between the deposited material $m$ and time interval $t$.

$$\int_0^m m' dm' = \frac{n e M_{\text{Al}} N_{\text{Al}} d}{l A} \int_0^t dt'$$

(3-5)

$$\frac{1}{2} m^2 = \frac{n e M_{\text{Al}} N_{\text{Al}} d}{l A} t$$

(3-6)

$$m^2 = \frac{2n e M_{\text{Al}}}{l} \sum D_i (p_i - p_{i0}) t$$

(3-7)

$$m = k_g \sqrt{t}$$

(3-8)

$$k_g = \left[ \frac{2n e M_{\text{Al}}}{lRT} \sum D_i (p_i - p_{i0}) \right]^{1/2}$$

(3-9)

According to the above equations, the driving force for transporting Al by migration of halides through the bulk pack to the substrate comes from the difference in partial pressure $(p_i - p_{i0})$.

In general, the above formalism is correct for using relatively weaker activators, such as NH$_4$Cl, NH$_4$Br, NH$_4$I, which do not involve a condensed phase in the pack. However, in the case of stronger activators, such as AlF$_3$, NH$_4$F, NaCl, NaF, condensation of activators on the substrate should be considered [72], as illustrated in Figure 3-3.

3.1.1.3 Deposition

The reactions accounted for depositing vanadium by reduction of vanadium chlorides are listed as follows ($\Delta G$ graphed in Figure 3-2).

$$VCl_2 \rightarrow \frac{1}{3} V + \frac{2}{3} VCl_3$$

$$VCl_2 \rightarrow 0.5V + 0.5VCl_4$$

$$VCl_2 + H_2 \rightarrow V + 2HCl$$
The vanadium after being deposited on the substrate surface could further interact with the substrate elements. Since vanadium does not form intermetallics with Fe or Cr at the coating temperature (700-1000 °C), the deposited vanadium will unlikely be reacting with them. However, vanadium could form stable phases with carbon, as shown in Figure 3-4.

3.1.1.4 Interdiffusion

Here is an example which shows the interdiffusion process will impact the phase and composition of the coating. In the case of Ni-based alloys, it was observed [73] that the coating grows via an outward Ni diffusion mechanism and the resulted phase is NiAl. This phase is a result of Al deficiency when the temperature is sufficiently high and the partial pressure of Al halide vapor is low. However, if the coating temperature is relatively low, or the partial pressure of Al halides is sufficiently high, the coating mechanism is controlled by an inward Al diffusion. The resultant phase will become Ni$_2$Al$_3$.

In addition, it was known that carbide could be formed during the PCDC process, according to the binary phase diagram. In the case of carbide coating, the growth rate of carbide layer could be controlled by either the diffusion coefficient of carbon or vanadium. However, since carbon diffuses faster than vanadium in a carbide layer, the continuous growth of carbide happens at the newly formed surface (i.e. the top surface of carbide). Therefore, the diffusion process of carbon through the carbide layer becomes critical.

3.1.2 Mechanisms in the MOCVD Process

As mentioned in Chapter 2, thermal decomposition is the primary mechanism for the CVD process using metal organic precursors. The entire MOCVD process includes
sublimation of precursor (e.g. Cp₂V in the research), transport of precursors onto the tube inner surface, surface reaction, and transport of by-products out from the reaction surface [74], as shown in the Figure 3-5. In general, the kinematics of reaction near the substrate is controlled by two processes. One is the molecular flux $J_1$ from the flowing gas to substrate; the other is the consumption flux $J_2$ of precursors (surface reaction). Many factors can alter the balance between $J_1$ and $J_2$. For example, if the consumption flux $J_2$ is much lower than molecular flux $J_1$ because of relatively low temperature, the kinematics should be “reaction limited growth”. But, if the molecular flux $J_1$ is much smaller than consumption flux $J_2$ because of scarcity of precursors or non-uniform flow pattern, the kinematics become “transport limited growth”.

In the case of inner tubular coating, assuming that there exists a laminar flow (i.e. Reynolds number $Re \approx 10$), the gas residence time $\tau_{res}$ over the sample, and precursor pump rate $\frac{dV_p}{dt}$ can be expressed as follows [74].

$$\tau_{res} = \frac{\pi PW_c d^2 l}{4RT \frac{dm_c}{dt}}$$  \hspace{1cm} (3-10)

$$\frac{dV_p}{dt} = \frac{W_p C_0 RT \frac{dm_c}{dt}}{\rho_p W_c (P - RT C_0)}$$ \hspace{1cm} (3-11)

In Equation 3-10, $P$ is pressure; $m_c$ and $W_c$ is the mass and molecular weight of the carrier gas; $\frac{dm_c}{dt}$ is the mass flow rate of carrier; $d$ is tube diameter; $l$ is the desired length to be coated. In the second equation, $C_0$ is the molar concentration; $\rho_p$ and $W_p$ is the density and molecule weight of the precursor gas. During a coating process, all the parameters except temperature remain constant, and the temperature changes as a function of distance from the heater. The gas residence time $\tau_{res}$ (3-10) indicates that increase of temperature will decrease the residence time. However, higher temperature
could also increase the deposition rate. There exists an optimized $\tau_{res}$ which can be
determined experimentally. On the other hand, the precursor pump rate $\frac{dV_p}{dt}$ has an
inverse relation to $\tau_{res}$, if the $RTC_0$ is negligible at a lower temperature. The precursor
pump rate is determined by pressure and temperature.

3.2 Phenomena in the FCCI

The interdiffusion phenomenon in FCCI usually involves multiple elements and is
difficult to be analyzed. In this section, the interdiffusion phenomenon will be discussed
based on Fick’s law. A closed-form expression for interdiffusion coefficients is derived
by using the Boltzmann-transformation of Fick’s equation, and the interdiffusion
coefficients were calculated based on the compositional profiles measured from SEM-
EDS line-scans.

During the interdiffusion, eutectic formation cannot be neglected since the
actinide fuels and lanthanide fission products tend to form low-melting phases with
cladding materials. As a result, interdiffusion and eutectic formation take place at the
same time. Precipitations of intermetallic phases within the cladding should be analyzed
because of abrupt compositional changes in the interaction zone.

3.2.1 Interdiffusion and Intermetallic Phases Formation

The occurrence of composition-dependent diffusivity is encountered in many
practical diffusion problems. The fuel-cladding system in a fast reactor is a great
example to demonstrate the relation between diffusivity and composition because of
abrupt compositional changes due to eutectic formation. Interdiffusion between fuel and
cladding can usually be interfered by new phase formations (e.g. eutectic phases or
precipitates). Conventional analyses for a diffusion problem starting with the diffusion
coefficient of each element are not practical here. As a result, it is necessary to use an
inversed analysis strategy to calculate the diffusivity given the concentration profile,
instead of calculating the concentration profile from the diffusivity [75].

The following analysis is based on the Onsager’s formalism of Fick’s second law [76]. The objective is to determine the interdiffusion coefficients and fluxes. The Fick’s
second law for time-dependent linear flow can be given by the continuity equation (i.e.
mass conservation). For simplicity, the diffusion couple can be assumed as a 1-D (one
dimensional) problem.

\[
J_x = -D \frac{\partial c}{\partial x} \tag{3-12}
\]

\[
\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right) \tag{3-13}
\]

Since the FCCI involves multiple elements, the subscript \( i \) corresponds to each
individual element.

\[
\left[ \frac{\partial c_i}{\partial t} \right]_x = - \left[ \frac{\partial J_i}{\partial x} \right]_t \tag{3-14}
\]

Apply chain rule to the continuity equation,

\[
\left[ \frac{\partial c_i}{\partial t} \right]_x = - \left[ \frac{\partial x}{\partial t} c_i \right] \left[ \frac{\partial c_i}{\partial x} \right]_t \tag{3-15}
\]

\[
\left[ \frac{\partial J_i}{\partial x} \right]_t \left[ \frac{\partial c_i}{\partial x} \right]_t \tag{3-16}
\]

Substitution of the Boltzmann transformation parameter \( \lambda \)

\[
\lambda = \frac{x-x_0}{\sqrt{t}} \tag{3-17}
\]

\[
\frac{\partial x}{\partial t} = \frac{1}{2} \frac{\lambda}{\sqrt{t}} \tag{3-18}
\]

\[
\left[ \frac{\partial J_i}{\partial x} \right]_t = \frac{1}{2} \frac{\lambda}{\sqrt{t}} \left[ \frac{\partial c_i}{\partial x} \right]_t \tag{3-19}
\]

\[
dJ_i = \frac{1}{2} \frac{\lambda}{\sqrt{t}} dC_i \tag{3-20}
\]

Apply indefinite integral to the interdiffusion flux \( J_i \)

\[
J_i = \int dJ_i = \frac{1}{2t} \int (X - X_0) dC_i \tag{3-21}
\]
Integrate from $C_i^-$ to $C_i(X)$

$$J_i(X) = \frac{1}{2t} \int_{C_i^-}^{C_i(X)} (X - X_0) dC_i$$ (3-22)

The interdiffusion flux at location $X$ can be calculated directly from the concentration profile from the above relation.

The Matano plane $X_0$ is defined as a plane within the diffusion couple, across which equal amount of mass have diffused to the left and right. The location of Matano interface can be determined through a mass-conservation condition.

$$\int_{C_i^-}^{C_i^+(X - X_0)} dC_i = 0$$ (3-23)
$$\sum_{k=1}^{n} (X_k - X_0)(C_{k+1} - C_k) = 0$$ (3-24)

The interdiffusion coefficients can be derived by integrating the interdiffusion fluxes [36]. $X_{i,R}$ is the effective penetration depth of component-$i$ on the right side of the Matano plane. $(X - X_0)_{i,R}^2$ is the mean squared distance from the Matano plane over the concentration range $C_i^-$ to $C_i^+$.

$$X_{i,R} = \sqrt{(X - X_0)_{i,R}^2} = \sqrt{2D_i t}$$ (3-25)
$$\frac{(X - X_0)^2}{(X - X_0)_{i,R}^2} = \frac{\int_{C_i^-}^{C_i^+(X - X_0)} dC_i}{C_i^+ - C_i^-}$$ (3-26)

### 3.2.2 Precipitation

Precipitation processes in the stainless steels (e.g. duplex stainless steel) usually refer to formation of various intermetallic phases (e.g. $\sigma$ or $\chi$) or carbides. Among these precipitates, the brittle $\sigma$ phase can drastically decrease the toughness properties, and it can also deteriorate the corrosion resistance due to the Cr segregation. It is usually difficult to prevent the precipitation of the $\sigma$ phase when the Cr concentration is above a certain level (e.g. 20 w.t.%) in stainless steels. The formation of $\sigma$ phase is attributed to
the phase transformation of $\delta \rightarrow \sigma$ ($\delta$-ferrite to $\sigma$ phase). When the $\delta \rightarrow \sigma$ phase transformation occurs, the $\sigma$ phase will precipitate in the high Cr-concentrated region of $\delta$-ferrite and form directly inside the $\delta$-ferrite particles. The $\sigma$ phase has a tetragonal crystal structure, and its precipitation temperature is between 600 and 1000 °C [77].

In this dissertation, interdiffusion between the F/M steels and lanthanide fission products is one of the primary interests. The Binary Fe-Cr alloys (with 6, 9, 12 w.t.% of Cr) which have ferritic microstructure are coupled with lanthanide cerium. The precipitation of the $\sigma$ phase was also explained by using the Thermo-Calc software as shown in Figure 3-7. Public binary alloys database (PBIN) is the selected database. The Thermal-Calc results indicate that $\sigma$ phase is formed with higher mole fraction as the relative Cr concentration increase in Fe-Cr alloys. The $\sigma$ phase is expected to be formed at temperatures above 510 °C for the Fe-Cr (ferritic) alloys. This thermodynamic simulation only requires the input of the element contents and experimental temperatures to produce the phase diagrams. The determination of phases in Thermal-Calc is based on minimization of Gibbs free energy. In addition to the Thermal-Calc results, ternary phase diagram of Fe-Cr-Ce (Figure 3-9) was also compared [78], since the cerium was the primary surrogate for fission products. The primary phases as shown in the ternary phase diagram are Ce, Fe$_2$Ce Fe$_{17}$Ce$_2$, and (Cr,Fe). The (Cr,Fe) refers to $\alpha$-Cr or $\alpha$-Fe. In general, the solubility of Ce is insignificant in Cr as shown in the Ce-Cr binary phase diagram (Figure 3-10). Cerium is therefore prohibited from forming ternary phases at the temperature around 600 °C. At higher temperature (e.g. 700 °C), Ce$_{0.08}$Cr$_{0.45}$Fe$_{0.47}$ and Ce$_{1.56}$Cr$_{2.60}$Fe$_{8.84}$ could possibly be formed based on
thermodynamic calculations. However, the ternary phase of (Fe,Cr)$_2$Ce is certainly not a favored phase in the Fe-Cr-Ce ternary system.
Figure 3-1. The PCDC for inner cladding wall, critical reactions, and mechanisms.

Figure 3-2. Gibbs free energy change $\Delta G$ of the critical reactions for $V_{(s)}$ deposition. All the vanadium chlorides $VCl_2$, $VCl_3$, $VCl_4$ are calculated in vapor phase.
Figure 3-3. Aluminum transport in the presence of both activator-depleted and aluminum-depleted zones due to condensation of activator. △: condensed AlF$_3$; O: Al(l). [72]

Figure 3-4. V-C phase diagram indicates the formation of various V-C phases [23].
Figure 3-5. Schematic diagram of the CVD process steps. (1) bulk transport, (2) transport to tube surface, (3) adsorption, (4) surface reaction (thermal decomposition), (5) desorption of by products, (6) transport out of surface, (7) bulk transport [74].

Figure 3-6. Relation between the concentration profile and interdiffusion flux. A) the schematic concentration profile, B) interdiffusion flux of component-i for a solid-solid diffusion couple [75].
Figure 3-7. Phase fraction in binary Fe-Cr alloy versus temperature. A) Fe-12Cr, B) Fe-20Cr, C) Fe-30Cr, D) Fe-50Cr binary alloys. (Courtesy of Billy Valderrama)
Figure 3-8. The Fe-Cr phase diagram versus temperature [23].

Figure 3-9. The ternary phase diagram of Fe-Cr-Ce.
Figure 3-10. Binary phase diagram of Ce-Cr [23].
CHAPTER 4
EXPERIMENTAL APPROACH

4.1 Sample Preparation

4.1.1 Materials Selection

The vanadium-based material is selected as the diffusion barrier to mitigate the FCCI. Metallic vanadium as the cladding liner material has been studied by several other researchers, and the results demonstrate that vanadium is an excellent diffusion barrier material against FCCI [40, 45, 46]. Based on binary phase diagrams, there are no low-melting intermetallic phases to be formed between the actinides (or lanthanides) and vanadium at the temperature below 1000 °C. The solubility of uranium in vanadium is less than 4 w.t.% at 800 °C. From the past diffusion couple experiments, the width of interdiffusion zone with a vanadium liner was also observed to be twelve times smaller than that with a zirconium liner [46].

The F/M (ferritic/martensitic) stainless steel is one of the promising candidate cladding materials for fast reactors. In this dissertation, a hexagonal duct of HT9 steel from the EBR-II is our primary source of substrate material for coating and diffusion couple experiments. The ODS (Y2O3 dispersion strengthened) ferritic steel which exhibits excellent high-temperature strength and creep resistance as another candidate cladding material is also used in some of the experiments. The elemental compositions of HT9 and ODS are listed as follows. In addition to commercial steels, model binary alloys of Fe-Cr were also prepared for studying Cr effects on the fuel-cladding interdiffusion process. The Fe-Cr model alloys were obtained from the Ames Laboratory (Ames, IA 50011). The Fe-Cr alloys with chromium contents of 6, 9, and 12 at.% were
fabricated using arc-melting and then subsequently rolled to 2 mm in thickness at 750°C.

HT9: Fe-11.92Cr-1.01Mo-0.92Ni-0.76Mn-1.04W-0.22V-0.39Si-0.22C wt.%
ODS: Fe-9.2Cr-2.0W-0.3Ti-0.36Y₂O₃-0.15C wt.%

For the diffusion couple annealing tests, pure cerium foil was used. As a nonradioactive material, cerium has been widely used as stand-ins for transuranic element, e.g. plutonium, and it is also one of the major lanthanide fission products that diffuse from fuel into the cladding when a steady state FCCI formed. The cerium sheet (0.8 mm in thickness) was procured from ESPI Metals (Ashland, OR 97520) with a material purity of 3N.

4.1.2 Surface Preparation

Before the coating deposition, the HT9 flat coupons were mechanically grinded and polished to a mirror surface finish using a 50 nm silica colloid solution, and the specimens were then thoroughly cleaned using acetone and methanol in an ultrasonic bath.

Grinding is a sample preparation procedure to ground the surface progressively using abrasive papers, e.g. 240, 400, 600, 800 grit in this research. Normally, an abrasive grit size of 180 or 240 is coarse enough to apply on surfaces sectioned by an abrasive cut-off wheel, while hack-sawed or band-sawed requires abrasive grit sizes in the range from 120 to 180 grit. In principle, each grinding step, while producing damage itself, must remove the damage from the previous step. The depth of damage decreases with the abrasive size but so does the metal removal rate.
Polishing is the final process in producing a scratch-free, and mirror-like finish. This step is critical for subsequent metallographic interpretation. In my experiments, polishing is usually conducted in two stages which are the rough polishing using water-based polycrystalline diamond suspension (3 µm) and the final colloidal silica suspension (0.06 or 0.02 µm). The water-based alumina suspension (0.05 µm) is alternatively added to the final polish stages since to wash off colloidal silica could sometime be difficult. As a rule of thumb form less residual silica, it is suggested to stop adding abrasive at about 15-20 sec remaining in the polishing step, and to introduce a water jet onto the polishing cloth at about 10 sec remaining.

4.2 Experimental Details of PCDC

4.2.1 Furnace System Configuration

The objective of the first experiment is to develop a prototype coating process using the PCDC method, which requires an inert gas and high-temperature environment. A single heat zone tube furnace with controlled environment was used, and the inert gas environment is aimed to prevent oxidation of steel samples at an elevated temperature during the coating process. To contain the sample and chemical powder mixture, alumina crucible boats were used. To monitor the temperature and to maintain a more uniform temperature profile inside the tube furnace, a thermocouple and alumina heat blocks are inserted in the reaction tube.

The block diagram of Figure 4-1 shows the experimental setup of the PCDC coating system. The furnace and its accessory tubing system were flowed with inert gas (i.e. argon) and the chamber pressure was maintained at slightly over 1 atm, to keep the gas flowing outward. The rotary vacuum pump was operated at the initial stage (pumping down and refilling argon) to help reduce oxygen level inside the furnace tube.
To further eliminate oxidation, an oxygen getter material such as tantalum foil was placed nearby the crucible. Figure 4-2 shows the tube furnace used in the PCDC coating process. The exhaust of the tubing system and the rotary pump were guided into fume hood for a health and safety reason.

4.2.2 Experimental Procedure

During the PCDC experiments, a uniform mixture of the chemical powders is critical in the PCDC experiments. However, because of a relatively low fraction of activator (i.e. 1-2% in this case), it is difficult to mix the powders. The mixing process can be assisted with a shaker (e.g. SPEX 8000).

The weight change of the coated sample was measured before/after the PCDC process. After the process, surface morphology was observed with SEM. The coating composition and formation of phases were studied by using EDS, WDS, and XRD. The microstructure in the coating was further examined using cross-sectional SEM, as well as TEM. The TEM samples were prepared by using in-situ FIB lift-out.

4.2.3 Experimental Test Matrix

The PCDC experiments were designed to study the factors listed in Table 4-1. The substrates HT9 and ODS are two representative cladding materials for a fast reactor, and they contain 12 % and 9 w.t.% of chromium, respectively. The 410 stainless steel contains 12 w.t.% of chromium and other different alloying elements (e.g. Si, P). The coating temperature was kept below 900 °C, since the microstructure of F/M steels becomes significantly unstable at a higher temperature. Effects from the pack chemistry are critical in either obtaining coating or corrosion. The compositional profile (of master alloy, activator, and inert filler), and type of activators (e.g. NaCl, NH₄Cl,
AlCl$_3$) were analyzed. Coating time was also extended to study the evolution of deposition rate.

4.3 Experimental Details of MOCVD

4.3.1 CVD System Setup

Figure 4-3 shows a simplified design concept for the MOCVD system. The sample to be coated is placed in a vacuum chamber, while the metal-organic precursors and carrier gas flow through the sample. In this research, since the stainless steel sample is ferromagnetic material, a RF induction heater can be applied to increase the substrate temperature by eddy current heating.

To study the kinetics of the MOCVD process, a flat coupon sample is used in the initial experiments. The benefits of using flat coupons include ease of performing the cross-sectional analyses, XRD and diffusion couple experiments. Figure 4-4 shows that the reaction chamber is a custom-made of quartz tube that is attached with a temperature observation port (i.e. window) as well as a precursor supplying port. The germanium temperature observation window is specifically selected as it allows infrared transmission.

Figure 4-5 shows the diagram of experimental setup including a RF heater, an infrared temperature detector, Pirani pressure sensor, flow meter, and the safety shut off mechanism that is controlled by a programmable device. The temperature from infrared detection provides a feedback signal to control the RF heater, to maintain a constant temperature in the heated zone. Since the MOCVD system occasionally involves using hydrogen as a carrier gas, a safety shut off mechanism could respond to accidental situations and shut off the gas supply. The safety shut off mechanism includes a solenoid valve that will automatically turn off during power outage. In
addition, the pressure is monitored, which responds to loss of vacuum caused by unexpected leakage. For example, when the pressure increases to more than 100 Torr, the power supply for the solenoid valve will be turned off, which shuts off the gas supply automatically. A more detailed description of the signal interfaces and programming for the above MOCVD system can be found in APPENDIX B.

4.3.2 Experimental Procedure

Before the coating experiment, it is suggested [58] to pump down and bake the reaction chamber (using the chamber heater as shown in Figure 4-6) for at least 8 hours, in order to reduce the residual moisture and oxygen in the chamber. During the experiment, the temperature of chamber and precursor is maintained at 150 and 90-100 °C, respectively. The pressure is maintained at around 1 Torr, while the flow rate of carrier gas is suggested to be at least 300 sccm. However, the expected flow rate is different based on individual chamber design. For example, the tubular chamber with smaller inner diameter requires relatively less flow rate.

4.4 Diffusion Couple Experiments

4.4.1 Diffusion Couple Fixture

The diffusion couple experiment was used to verify functionality of the vanadium coating as a diffusion barrier. It was also used to study the interdiffusion and intermetallic formation between lanthanides and model alloys. The diffusion couple fixture as shown in Figure 4-7 and 4-8 is the key component for my experiments. The material of the fixture is Kovar alloy, which exhibits a similar thermal expansion coefficient with those of HT9, and cerium metal. The fixture was custom made by Shular Tool (Oak Ridge, TN 37830) using EDM (electrical discharge machining).
4.4.2 Experimental Procedure

Before the diffusion couple experiments, the as-received fixture should be annealed in 800 °C for 8 hours to relax the stress from machining. After the initial heat treatment, the thread on bolt and body should be re-threaded with a tap and die. The load and torque was measured by using load cell and torque wrench, respectively. Figure 4-9 shows the calibration setup and the linear torque-load relation.

4.5 Characterization Method

4.5.1 Cross-sectional Analysis Procedure

The cross-sectional analyses were performed to examine the samples from coating and diffusion couple experiments. Depending on the thickness of region to be analyzed, several techniques can be used.

The FIB (Focused Ion Beam) is a technique which simultaneously employs the electron (i.e. SEM) and gallium ion beam on the sample surface. In the case of relatively thin film deposition (≤10 µm), the FIB can used to assist the cross-section analysis procedure. By milling out a trench on the coated sample surface at 45°, the thickness and grain structure of the coating can be observed by using a SEM. The compositional profile can also be measured by using the EDS linescan.

In the case of relatively thick structure such as the interdiffusion (≥ 100 µm), the epoxy set from Allied High Tech (Rancho Dominguez, CA 90220) is currently used as the cold mounting procedure in our lab. Although this product claims to have virtually no shrinkage after the epoxy cured, gapping can still easily be observed if the epoxy cured at an incorrect temperature or over-cured. Gapping can be a serious issue, as the edge preservation is critical in the material characterization. Charging and out-gassing are
other issues if the mounted sample is observed in a SEM, where a certain level of vacuum should be reached. To coat the sample (after grinding/polishing) with a thin layer of evaporated carbon (~30 nm) and establish a proper conduction path for current dissipation can effectively eliminate the problem of charging. Out-gassing can be reduced by letting the sample in vacuum for at least 2 hours. In the future, access to other mounting procedure such as the compression hot-pressing system using the EpoMet from Buehler (Lake Bluff, Illinois 60044) could be considered if the edge preservation becomes more critical.

4.5.2 Microstructural Analysis

In this research, microstructural analyses were primarily performed by using TEM. The samples for TEM were prepared by FIB, since it is easier to lift out the lamella from a specific location such as the coating/substrate interface.

Bright-field imaging was the most frequently used to observe the grain microstructure in the PCDC coating. The formation of intermetallic phases and precipitation in the diffusion couple experiments were also observed with the bright-field imaging. Since the high-resolution TEM is not required for the above applications, much of the microstructural analysis was performed by using JOEL 200CX located at MAIC. Occasionally, JOEL 2010F and a more advanced JOEL JEM-ARM 200F which are located at the NHMFL (Tallahassee, FL 32310) were used as supplemental resources.
Figure 4-1. Experimental setup for coating of the steels using the PCDC method.

Figure 4-2. The tube furnace system used for the PCDC process. Photo courtesy of author.
Table 4-1. Summary of experimental conditions used in the PCDC experiments.

<table>
<thead>
<tr>
<th>Experimental factors</th>
<th>HT9</th>
<th>ODS</th>
<th>410</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>730-860 °C</td>
<td>730-800 °C</td>
<td>730-800 °C</td>
</tr>
<tr>
<td>Pack composition</td>
<td>50V-1.5NaCl</td>
<td>50V-1.5NaCl</td>
<td>50V-1.5NaCl</td>
</tr>
<tr>
<td></td>
<td>50V-2NaCl</td>
<td>50V-1.5NaCl</td>
<td>50V-2NaCl</td>
</tr>
<tr>
<td></td>
<td>50V-4NaCl</td>
<td>50V-2NaCl</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60V-2NaCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activator</td>
<td>NaCl, NH4Cl,</td>
<td>NaCl</td>
<td>NaCl, AlCl3</td>
</tr>
<tr>
<td>Coating time</td>
<td>8-120 hours</td>
<td>24-72 hours</td>
<td>24 hours</td>
</tr>
</tbody>
</table>
Figure 4-3. The schematic of a simplified MOCVD reaction chamber.

Figure 4-4. Detailed MOCVD reaction chamber design.
Figure 4-5. The diagram of system level signal integration.

Figure 4-6. The MOCVD system. Photo courtesy of author.
Figure 4-7. Diffusion couple fixture and the sample configuration.

Figure 4-8. The diffusion couple assembly made of Kovar alloy. Photo courtesy of author.
Figure 4-9. Calibration of the diffusion couple assembly. A) Setup of calibration for the load and torque. B) The measured torque-loading curve.
5.1 PCDC Experiments

5.1.1 Kinetics of the Coating Process

To study the kinetics of coating process, systematic experiments with different factors of coating temperature, time, and pack chemistry have been performed. As shown in Figure 5-1, the growth rate measured by weight gain (per unit area) is a function of both coating temperature and time, and the corresponding film thickness on HT9 can grow up to 5 µm at 860 °C in 24 hours. Since the growth of coating depends on the outward carbon diffusion through the film, the unit weight gain ($m$) should be proportional to a parabolic function of coating time ($t$), based on the classic mechanism of reaction kinetics. Based on the previous theoretical discussion, the parabolic relation comes from the assumption of $\frac{dm}{dt} \propto \frac{1}{m^\alpha}$. When $\alpha \to 1$, the coating growth follows the relation of a square root of time (5-1).

$$m = K\sqrt{t}$$

(5-1)

where $m$ is the unit weight gain [$\mu g/cm^2$], $K$ is the parabolic growth rate constant which depends on the diffusion coefficient of carbon in the vanadium carbide coating, and $t$ is the coating time [hours]. Figure 5-1(B) shows a linear fitting between the unit weight gain and the square root of time. For HT9, the experimental results can be fit to (5-1), while for the ODS the fitting is good with small delay time (i.e. $m = K\sqrt{t - t_0}$). The growth rate constant $K$ is a function of the activation energy and processing temperature, as shown in the Arrhenius Equation (5-2).

$$\ln K = -\frac{Q}{RT} + A = -\frac{Q}{1000R} \frac{1000}{T} + A$$

(5-2)
where $A$ is a constant, $Q$ is the diffusion activation energy of carbon in vanadium carbide layer, $R$ is the gas constant (8.3145 J/K/mol) and $T$ is temperature in Kelvin. The least-square fitting of the data points in Figure 5-1(A) gives:

$$Q_{HT9} = 221.9 \text{ [kJ/mol]}$$

$$Q_{ODS} = 179.4 \text{ [kJ/mol]}$$

from which an activation energy of 221.9 kJ/mol can be obtained for the coating process on HT9 in the temperature range of 740–860 °C. For the ODS, the activation energy is around 179.4 kJ/mol. It should be noted that $Q$ may vary with the stoichiometry and the point defect concentration of the coating layer and the substrate as well. The activation energies associated with carbon (interstitial) diffusion in different substrates such as BCC-Fe and FCC-Fe are 84.1 and 148 kJ/mol, respectively [79]. This difference in substrate could most likely be the cause of different activation energies for HT9 and ODS. Nevertheless, both the resultant activation energies fall in the range of reported values of 173-227 kJ/mol [80].

The Figure 5-1(B) shows that the coating process slows down along with time. However, the reason for the slowing down of process needs to be confirmed. In the PCDC experiments, two factors may contribute to the slow-down process. One could be the outward diffusion of carbon through the coated layer as pointed out previously. The diffusion process can be slowed down while the deposited film grows thicker. It could also be because of the depletion of reactants in the pack along with the process. To evaluate the second factor caused by depletion of reactants, the PCDC experiment for a series of time segments was specifically performed. At the end of each time segment, the pack of powder was renewed (i.e. replaced with fresh powder). Figure 5-2 shows
the cumulative weight gain of the same sample in the PCDC experiments performed for 4-5 days (i.e. 4-5 segments of 24 hours) using NH₄Cl and NaCl as activators. The result shows that the slowed-down PCDC process is not caused by depletion of pack reactants. It is assumed that continuous supply of carbon from the bulk will not change along with time given the relatively low activation energy for carbon diffusion in steels and the sufficient bulk thickness. Therefore, the outward diffused carbon through the deposited vanadium carbide is the most possible controlling factor for the entire PCDC process.

5.1.2 Surface Morphology

Figure 5-3(A) and (B) show the SEM images of the surface morphology of vanadium-based diffusion coating on HT9 at 730 and 860 ºC, respectively. It clearly shows that higher coating temperature promotes grain growth. Figure 5-4(A) shows the surface morphology of a coated sample using a relatively weaker activator NH₄Cl, as compared with Figure 5-3(A) using NaCl. The porosity in the coating was minimized in Figure 5-4(A), which is consistent with the theoretical discussion [69] that a relatively weaker pack may improve the uniform film growth because of better match with the weak outward diffusion of carbon.

The EDS spectrum in Figure 5-4(B) was measured from the vanadium-based diffusion coating. The spectrum shows the content of vanadium (Kα: 4.95 keV, Kβ: 5.43, Lα: 0.51), as well as minor trace of carbon (Kα: 0.28 keV). To further confirm the compositional profile of coating, the WDS and XRD results will be discussed in the following sections.
In summary, a uniform coating which contains pure vanadium and a certain level of carbon has been obtained from the PCDC method. Surface morphology of the sample from diffusion coating shows less porosity as compared with the EPD method (see Figure 5-5) which starts with a colloidal material containing particles of about 80nm in size. The starting material in the vapor-phase deposition such as the diffusion coating or MOCVD is about the size of precursor molecule, which is much smaller than the colloidal nano particles. The involvement of using high temperature in coating process or subsequent heat treatment can further densify the deposited material as well as promote the grain growth.

5.1.3 Coating Thickness and Cross-sections

The cross-sectional analysis of the coating was examined by using SEM and TEM techniques.

The cross-sectional SEM image of Figure 5-6 shows that the coating has nearly 100% density and no porosities were observed. The coating thickness is fairly uniform. The coated layer has a solid metallurgical bonding with the substrate, and it is free from any cracks after being cooled down from as high as 860 °C to room temperature. This mechanical integrity is attributed to the strong bonding between the coating and substrate, nanostructured grains and small thickness. In Figure 5-6(B), the gapping can be observed between the epoxy resin and coated substrate. However, the edge of coating was nearly intact after grinding and polishing, which shows its excellent mechanical integrities. The EDS line-scan in Figure 5-6(C) clearly shows that the coating is rich in vanadium while scarce in iron. Certainly, the coating layer contains a higher content of carbon than the substrate, which was from decarburization of the
substrate. Iron (or chromium) apparently does not inter-diffuse with vanadium, while carbon does. The possible chromium peak ($K_{\alpha}$: 5.412 keV) is due to an overlapping with that from vanadium ($K_\beta$: 5.427 keV). Based on the EDS result, the PCDC process renders a similar elemental composition to that of vanadium carbide coating prepared in a molten salt bath where the carbon was also supplied by the substrate [80].

The cross-sectional TEM images in Figure 5-7 reveal more details about the microstructures. The columnar structure orientated normal to the substrate can clearly be seen in the TEM images. The cementite interlayer ($Fe_3C$) can be observed in between the columnar structure and the steel substrate, which is consistent with the ternary C-Fe-V phase diagram. The formation of the cementite interlayer is an evidence of decarburization [81].

5.1.4 Phase and Compositional Study

In order to more accurately determine the compositional profile and phase formation in the coating, XRD and WDS were also performed.

Figure 5-8 shows the XRD results from samples prepared at different temperatures. By comparing the spectra to the standard diffraction peaks, the peaks from the coating can be matched at $2\theta = 39.4^\circ$, 41.2$^\circ$, 54.3$^\circ$, and 72.7$^\circ$, which belongs to $V_2C$. These peaks correspond to Miller indices $(h k l) = (2 0 0)$, $(1 2 1)$, $(2 2 1)$, and $(3 2 1)$, respectively. It can also be observed that higher temperature promotes a single orientation $(2 0 0)$ crystal growth, while lower temperature makes the coating contains more equally oriented grains. Also, the signal from substrate (HT9) is absent in the spectra of coated samples as shown in Figure 5-8, which confirms a sufficient thickness and a good coverage of coating on the substrate.
The WDS result shown in Table 5-1 is a further evidence to support the determination of $V_2C$ from XRD measurement. The WDS measurement provides better resolution, which can generate more precise compositional profile of the coating, especially for lighter elements such as carbon. The WDS result in Table 5-1 was measured out of 10 points from each sample, and the data were expressed with a 95% confidence interval calculated from the following equation (5-3). The Cr concentration was also measured, but it dropped due to less than 1.5 at.%. Based on the WDS result, the composition of the coating can be concluded as the $V_2C$.

$$\bar{X} \pm 1.96 \frac{\sigma}{\sqrt{N}}$$

(5-3)

where $\bar{X}$: average, $\sigma$: standard deviation, $N$: sample size.

5.1.5 Performance against FCCI

Diffusion couple experiments were conducted to verify the performance of $V_2C$ coating against interdiffusion of cerium and HT9 substrate. As shown in Figure 5-9, the interdiffusion between pure cerium and HT9 steel without diffusion coating barrier was characterized using SEM imaging and EDS mapping on the cross-section. The width of interdiffusion zone is nearly 100 µm and it mainly consists of Ce and Fe. A more detailed analysis of the interdiffusion and intermetallic formation will be discussed in the coming sections. From the EDS mapping, it can be clearly observed that Ce actively diffuses into HT9 steel. A minimal eutectic-melted structure on the Ce side was observed due to a relatively low annealing temperature of 660 °C. Figure 5-10 shows the diffusion couple experiment using the HT9 substrate coated with $V_2C$, and it shows that the Fe-Ce interaction zone completely vanishes. However, due to a much higher hardness of the $V_2C$ layer as compared with that of HT9 steel, metal debris piles up on
both sides of the coating layer formed from smearing of HT9. In the future, ion beam milling will be pursued to eliminate the smearing effects.

To further confirm the functionality of the V\(_2\)C coating layer as FCCI diffusion barrier, the cross-sectional structure and elemental compositions of diffusion couple were studied using TEM, as shown in Figure 5-11. Clearly, the layered structure and interfaces are preserved after the diffusion couple annealing. Not only the V\(_2\)C layer is immune to chemical reactions with HT9 substrate or cerium, but the V\(_2\)C also inhibits the interdiffusion between HT9 and cerium. The STEM/EDS linescan across the V\(_2\)C layer shows only vanadium while copper is from the grid. That is, no cerium, iron or chromium was detected in the V\(_2\)C coating layer, which demonstrates that V\(_2\)C could be an excellent diffusion barrier material for mitigating the FCCI in a metallic fuel and F/M steel cladding system. This result is consistent with experiments done by Ryu et al. [45] indicating that vanadium appeared to be the most promising diffusion barrier material among Ti, V, Cr, Zr, Nb and Mo by conducting the foil-inserted diffusion couple of U-10Zr-4Ce with T91.

To verify the bulk performance of vanadium carbide as a diffusion barrier, an additional diffusion couple experiment was performed using the VC disk, cerium, and HT9. The configuration of the diffusion couple was Ce/VC/HT9. The VC disk was purchased from Kurt J. Lesker, which was prepared by using hot isostatic pressing (HIP). The annealing condition was at 780 °C for 100 hours. The annealed sample was then characterized by SEM/EDS at the diffusion couple interface. TEM was also performed on a cross-sectional sample lifted out by FIB from near the interface. Figure 5-12 shows the BSE image of VC near the diffusion couple interface with Ce. Cerium
can be found at the grain boundaries, instead of within the VC grain. The EDS results from spot 1 and 2 in Figure 5-12 indicate that the composition are C: 24.2 at.%, O: 43.1%, Ce: 32.7% and C: 45.8%, V: 54.2%, respectively. The bulk VC does not react with Ce, but the Ce apparently moves freely through the grain boundaries. A more detailed investigation on the VC/Ce interface was performed by using the TEM. Figure 5-13 shows the TEM image which was lifted out by FIB at the microstructural interface between VC and Ce. The TEM image shows no inter-mixing can be found between VC grain and Ce. On the other hand, Figure 5-14 shows the interface between HT9 and VC, indicating the compatibility between HT9 and VC. Based on these results, vanadium carbide has been verified as an excellent barrier material against Ce. As long as the grain boundaries between VC can be minimized, the VC can effectively eliminate the FCCI.

5.1.6 Decarburization Study

Figure 5-15 shows the grain structures and carbide precipitates of the HT9 cross sections after diffusion coating process at 730 °C (120 hours) and 740 °C (72 hours). The grains close to the coating layer appear to contain slightly less nano-sized carbide precipitates, while the large carbide particles at the grain boundaries remain intact. The results from 730 and 740 °C are basically similar. The grain coarsening is not apparent in this range of coating temperature. However, the coarsening becomes more evident at a higher temperature of 800 °C, as shown in Figure 5-15.

A more quantitative analysis of the decarburization can be done by performing micro hardness tests. In Figure 5-17, the results from micro hardness tests show that the softening of substrate nearby the coating layer is not severe. However, the overall
decrease of hardness of the substrate was observed, and it could be attributed to annealing of the dislocations which were formed during rapid cooling in F/M steel processing. The data in Figure 5-17 emphasize the overall decrease in hardness, instead of hardness change close to surface, so the error bar on each point is not shown. Therefore, decarburization may not be the cause of softening. The micro hardness can be calculated by the following Equation (5-4). For a fresh HT9 sample, the measured hardness is supposed to be about 260.

\[ HV = \frac{F}{A} \approx \frac{1.8544F}{d^2} \]  

(5-4) 

where \( F \) is the loading in gram; \( d \) is the measured diagonal length in mm.

5.2 Experiments of Cr Effects on Interdiffusion

5.2.1 Cross-sectional SEM and EDS analysis

Figure 5-18(A)-(C) shows the cross-sectional SEM images of the diffusion couples between cerium and Fe-Cr alloys annealed for 100 hours. The widths of interdiffusion zone (indicated between the arrows) were measured from multiple locations, and the results are summarized in Figure 5-18(D). It can be seen that as the concentration of Cr in Fe-Cr model alloy decreases, the width of interdiffusion zone increases. To analyze the compositional distribution, the EDS line-scans were performed across the interdiffusion zones along the blue lines in Figure 5-18(A) and (B). The Fe, Cr and Ce elemental profiles in Figure 5-19 indicate that the interdiffusion zone consists of two distinct regions separated by the Matano interface labeled using a blue vertical line. Both regions contain Fe and Ce with an atomic ratio of approximately 2 between Fe and Ce, while there is nearly zero concentration of Cr in the cerium part. Moreover, the chromium concentration is found to fluctuate between 5 and 30 at.% in
the Fe-12Cr alloy near the Motano interface, which implies that Cr segregates and forms Cr-rich precipitates during the interdiffusion.

The EDS mappings shown in Figure 5-20(B)-(D) were performed at the interdiffusion zone of Fe-12Cr/Ce diffusion couple, and the BSE image of Figure 5-20(A) shows the area of interest. Consistent with the EDS line-scan profile shown in Figure 5-18(A), iron and cerium inter-diffuse and form a compositional region across the original diffusion interface (Matano interface). Chromium segregates and forms a localized Cr-rich layer slightly away from the original diffusion interface into the Fe-12Cr substrate, while no Cr diffuses into the Ce. The integral elemental distribution was analyzed by vertically integrating the brightness of pixels of the elemental mapping and the profiles are plotted on the top of image. As shown in Figure 5-20(D), the concentration of Cr largely varies at the interdiffusion direction with a slightly depletion at and near the Matano interface. In addition, Figure 5-20(A) clearly shows a dendrite structure of diffusion front as Ce diffuses into Fe-Cr alloy, which is coincidently reflected by the variation in chromium counts from the EDS line-scan.

The BSE images of Figure 5-21(A) and (B) reveal detailed microstructures of interdiffusion zone in the Fe-12Cr alloy, and the dark areas represent low Ce content. Table 5-2 of SEM-EDS spot analysis shows that the dark areas (the spot 2,4,5) consist of Fe, Cr, and Ce, while the bright areas (spots 1 and 3) contain nearly zero of Cr and are identified as Fe₂Ce. This analysis clearly shows that the Cr tends to segregate to locations at or near grain boundaries. However, due to the spatial resolution limit of SEM-EDS (~1µm), the exact size and chemical compositions of Cr-rich phases cannot
be determined, and it is no applicable to conclude whether ternary phases of Fe-Cr-Ce could form in the interdiffusion by solely using the SEM-EDS analysis.

5.2.2 Composition and Phase Analyses using STEM and X-ray Diffraction

The STEM EDS was used for the 2-D compositional mapping on the Cr-rich precipitates. Figure 5-22(A) is a bright-field TEM image of the sample lifted out from the interface between Fe-12Cr substrate and Ce. It is clearly shown that the Cr-rich precipitates can only be observed in the Fe-12Cr. Figure 5-22(B) is a more detailed TEM image of the precipitates and it shows that the normal size of the precipitates is about 200nm. The STEM EDS mapping results in Figure 5-22(C) show that the precipitates consist of only chromium and iron, while the matrix contains iron and cerium with nearly zero Cr. The STEM EDS spot analyses in Figure 5-22(D) also demonstrate that cerium is not present in the Cr-rich precipitates while chromium is not detectable in the matrix. Therefore, it can be concluded that the ternary phase of (Fe, Cr)\textsubscript{2}Ce is not formed during the interdiffusion process at 560 °C. This result is consistent with the ternary phase diagram of Fe-Cr-Ce, as discussed in Chapter 3.

The XRD results from the interfacial surfaces are shown in Figure 5-23. The spectrum from the Fe-9Cr/Ce interdiffusion (red line) indicates the presence of Fe\textsubscript{2}Ce and the α Fe-Cr substrate, while the spectrum from Fe-12Cr/Ce diffusion couple shows several additional peaks at 2θ = 46.1, 47.0 and 76°. Those additional peaks are identified as reflections of [212], [411] and [532] from σ phase. Fe\textsubscript{17}Ce\textsubscript{2} was not detected in either Fe-9Cr/Ce or Fe-12Cr/Ce diffusion couple annealed at 560 °C in this study. The identified Cr-rich precipitates have a similar crystal structure to that of σ-phase precipitate in a duplex stainless steel [20, 21]. Although the diffraction peaks of
Cr-rich precipitates did not appear in the spectrum from the Fe-9Cr/Ce diffusion couple, they were clearly observed in a cross-sectional SEM specimen. As shown in Figure 5-24, the mole fraction of σ-phase in a Fe-Cr alloy was obtained from simulations using Thermo-Calc (Figure 3-7) by varying the Cr concentration from 20 to 50 wt.%. It indicates that when the chromium concentration increases to 20%, the proportion of σ-phase becomes significant as temperature approaches 512.7 °C or above.

5.2.3 Interdiffusion Kinetics Analysis

To study the interdiffusion reaction kinetics, thermal annealing for less than 100 hours were performed. BSE images of Figure 5-25 (A) and (B) show the cross-sections of the diffusion couple annealed at 560°C for 12 and 50 hours, respectively. As compared with the 100 hours annealing shown in Figure 5-20(A), the samples of 12 and 50 hours annealing clearly display the diffusion initiation path of cerium into the Fe-Cr alloy. The diffusion starts at the grain boundaries of Fe-Cr alloy and then engulfs the grains progressively. The STEM EDS mapping was also performed on a TEM sample lifted out from the diffusion path as indicated (yellow bar) in Figure 5-25(A). The STEM image of Figure 5-26(A) shows that cerium diffuses along the grain boundary and also starts to precipitate into the grains as particle clusters. The EDS mapping of Figure 5-26(B) further discloses that a Cr-rich shell forms around the cerium particle as the eutectic reaction between Fe and Ce proceeds and it depletes Fe from the bulk surrounding cerium particle.

The interdiffusion fluxes of elements Cr, Fe, and Ce are calculated for Fe-12Cr/Ce and Fe-9Cr/Ce diffusion couples by using the Equation (5-5) derived by Dayananda [75]. The calculations are based on the concentration profiles in Figure 5-
The positive value of flux corresponds to the diffusion into Ce (right direction), and the negative value indicates the diffusion into Fe-Cr alloy (left direction). Averagely, the interdiffusion flux $\dot{J}_{Fe}$ and $\dot{J}_{Ce}$ are higher in Fe-9Cr/Ce diffusion couple of than those in Fe-12Cr/Ce. This is consistent with the observation that high Cr content in the alloy substrate can slow down the interdiffusion. For both 9 and 12 Cr model alloys, it is clearly shown that the flux $\dot{J}_{Cr}$ is closely running against the flux $\dot{J}_{Ce}$ by following the exactly opposite trend, and this synchronization indicates that the Ce is diffusing against Cr into Fe-Cr alloy. In addition, the flux $\dot{J}_{Cr}$ at Matano interface is nearly zero for both cases, which implies that Cr does not diffuse across the alloy surface into Ce. The fluctuation of $\dot{J}_{Cr}$ becomes evident since at about 10 μm away from the Matano interface, which corresponds to Cr segregating and clustering. This observation is consistent with the microstructural characterization results in Figure 5-21, where more Cr-rich phases are found at the Ce diffusion front.

$$\dot{J}_i(X) = \frac{1}{2t} \int_{X_o}^{C_i(x)} (X - X_o) dC_i$$

$$X_i = \sqrt{2D_i^{eff} t}$$

The effective interdiffusion coefficient $D_i^{eff}$ were calculated using the Equation (5-6), where $X_i$ is the effective interdiffusion width of component i in Fe-Cr (L) or in Ce (R) and $t$ is total annealing time. The results are summarized in Table 5-3. Consistently, Ce has a much lower effective interdiffusion coefficient in Fe-12Cr that that in Fe-9Cr, as highlighted in Table 5-3. The formation of layer of Cr-rich precipitates shall be the mechanism for slowing down the interdiffusion process, and chromium has been shown as an excellent barrier material against FCCI [42, 45].
5.3 MOCVD Experiments

5.3.1 Microstructural and Compositional Characterization

Figure 5-28 shows the surface morphology of the coating obtained by using the Cp₂V as precursor at different temperatures. The averaged grain size is reduced from 0.55 to 0.12 µm as the deposition temperature decreased from 600 to 300 °C. The porosity in the coating is much less than those reported in previous studies [42, 44] which use electroplating of Cr and electrophoretic deposition of Ti, respectively. The extensive porosity in the coating would require high temperature (> 800 °C) post treatment. However, high temperature treatment could cause tempering and grain growth for ferritic/martensitic steels, as mentioned in the PCDC result sections. The nano-sized grain structure formed at lower temperature can eliminate the necessity of using high temperature post treatment.

The EDS spectrum in Figure 5-28(C) indicates that the compositional profile of the coating in Figure 5-28(B), which consists of vanadium, carbon, and oxygen. The accurate concentration of carbon and oxygen cannot be decided only by SEM/EDS. The X-ray diffraction that used a grazing incidence angle (α<1°) (GIXD) was employed to determine the phase structures of the thin film. Figure 5-30 is the GIXD result showing that the composition of the coating is primarily VC₆O₆ and V₂C. The intensity of VC₆O₆ is significant as compared with V₂C, which implies oxygen is presented in the coating.

The cross-sectional structure of the coating such as thickness was characterized by using FIB milling. Unlike the coating obtained by using PCDC, the vanadium carbide by MOCVD could show weaker mechanical strength compared with the substrate. Using epoxy resin with the grinding/polishing procedure could end up damaging the
edge of coating. Alternatively, the ion beam milling at a 45° to the surface was used to produce a clean cross-section cut without damaging the edge. To determine the thickness simply requires using the SEM to measure the size of coating layer (from the top view). The Figure 5-29 indicates the thickness of coating in Figure 5-28(B) is about 2.3 µm. The cross-sectional TEM was also prepared by using FIB, which was shown in Figure 5-31. The cross-sectional TEM image shows that the microstructures such as the grain and carbide in HT9 substrate remain intact.

5.3.2 Performance against FCCI

Similarly, diffusion couples of Ce/coating/HT9 and Ce/HT9 were performed to verify the performance of the MOCVD vanadium carbide. After annealing at 660 °C for 24 hours, the cross sections of these samples were characterized by using OM, SEM/BSE, and EDS. In Figure 5-32(A) and (B) show the OM images of Ce/coating/HT9 and Ce/HT9, respectively. Although there is still cerium diffused into HT9 (at the top side), the HT9 surface is protected compared with the Ce/HT9 interface. Under the SEM/BSE of Figure 5-32(C) and (D), the interdiffusion microstructure can be more clearly observed. The dark spots in the BSE image correspond to Cr rich precipitates. The precipitation mechanism is expected to be the same as previous experiments which use Fe-Cr alloys. That is, as the intermetallic formation proceeds, the relative Cr concentration rises so that the Fe-Cr intermetallic phase starts to precipitate.
Figure 5-1. The diffusion coating kinetics of $V_2C$ on HT9 and ODS substrate. A) The dependence of unit weight gain on temperature, and B) the dependence on hours.
Figure 5-2. The unit weight gain versus coating time for HT9 substrate using different activators. The experiments were performed in 4 segments of day, while the pack was renewed after each day.

Figure 5-3. Surface morphology of the deposited vanadium coating at different processing conditions. A) 730 °C and 120 h and B) 860 °C and 8 h.
Figure 5-4. Surface morphology and compositional profile of the coating using NH4Cl as the activator. A) The SEM image of the deposited vanadium processed at 730 °C, compared with Figure 5-3(A) using NaCl. B) The EDS spectrum obtained from the coating sample.

Figure 5-5. Surface morphology of the sample obtained from the EPD method [44]. A) The as-coated sample, and B) the same sample after annealed at 850 °C for 15 hours.
Figure 5-6. Cross-sectional imaging and compositional profile of the sample from Figure 5-3(B). A) The cross-sectional SEM image, B) zoomed-out cross-section shows uniformity, and C) EDS line-scan elemental analysis results.
Figure 5-7. The cross-sectional microstructures by TEM. A) The sample from Figure 5-3(A) prepared by FIB. B) The cementite interlayer can be found between the coating and HT9 steel substrate.
Figure 5-8. X-ray diffraction patterns of the vanadium carbide coating layers prepared at different temperatures.

Table 5-1. Elemental profiles of the samples prepared at different coating temperatures.

<table>
<thead>
<tr>
<th>Coating temperature vs. Elemental composition</th>
<th>860 °C</th>
<th>730 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>V (at.%)</td>
<td>63.7 ± 1.4</td>
<td>65.0 ± 1.3</td>
</tr>
<tr>
<td>C</td>
<td>33.8 ± 2.0</td>
<td>30.6 ± 1.2</td>
</tr>
<tr>
<td>O</td>
<td>1.2 ± 1.1</td>
<td>3.0 ± 1.6</td>
</tr>
</tbody>
</table>
Figure 5-9. Interdiffusion structures from the cross-section of diffusion couple without coating. A) The SEM image, B) and C) the 2-D elemental mappings of Fe and Ce were performed by SEM-EDS.
Figure 5-10. Interdiffusion structures from the cross-section of diffusion couple with $V_2C$ coating. A) The SEM image, B)-D) the 2-D elemental mappings of Fe, Ce and V were also performed, as compared with Figure 5-9.

Figure 5-11. Cross-sectional TEM image of the annealed diffusion couple structure (centered at $V_2C$), and the EDS line-scanned spectrum at the $V_2C$ coating.
Figure 5-12. BSE image of the vanadium carbide (VC) near the diffusion couple interface with Ce.

Figure 5-13. TEM image at the interface between the Ce and the grain of VC.
Figure 5-14. BSE image at the interface of diffusion couple between HT9 and VC.

Figure 5-15. Cross-sectional SEM images of the coated HT9 samples with different conditions. A) 730 C (120 hours) and B) 740 C (72 hours). The sample were polished and etched to reveal the grain structures.
Figure 5-16. Cross-sectional SEM images of the coated HT9 samples which were processed at 800 °C for 24 hours. The polished/etched sample shows grain coarsening as compared with Figure 5-15.

Figure 5-17. Micro hardness test results on the samples coated at 860 C (8 hours) and 730 C (100 hours).
Figure 5-18. Cross-sectional images of the interdiffusion zones. Between Ce and A) Fe-12Cr using the BSE detector, B) 9Cr, and C) 6Cr using the SE detector. The BSE image reveals the original interface of 12Cr/Ce. D) The size of the interdiffusion zone versus Cr (w.t. %) is graphed.

Figure 5-19. The EDS line-scan elemental analysis results. A) Ce vs. Fe-12Cr, and B) Fe-9Cr vs. Ce. The solid (blue) lines indicate the Matano interface ($X_0$).
Figure 5-20. The BSE images and EDS elemental mappings in terms of Ce, Fe, Cr. The elemental concentration distribution is also demonstrated with the profiles of averaged brightness (EDS counts of Ce, Fe, Cr) obtained by integrating the brightness of pixels vertically in each elemental mapping.

Figure 5-21. Cross-sectional microstructures in the interdiffusion zone of Fe-12Cr alloy.
Table 5-2. EDS elemental analyses of the spots labeled in Figure 5-21(B)

<table>
<thead>
<tr>
<th>At. %</th>
<th>Fe</th>
<th>Cr</th>
<th>Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>68.0</td>
<td>~ 0</td>
<td>32.0</td>
</tr>
<tr>
<td>2</td>
<td>70.3</td>
<td>22.5</td>
<td>7.2</td>
</tr>
<tr>
<td>3</td>
<td>68.7</td>
<td>~ 0</td>
<td>31.3</td>
</tr>
<tr>
<td>4</td>
<td>52.7</td>
<td>25.5</td>
<td>21.8</td>
</tr>
<tr>
<td>5</td>
<td>51.9</td>
<td>30.2</td>
<td>17.9</td>
</tr>
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</table>
Figure 5-22. Cross-sectional microstructures and compositional analyses in the interdiffusion zone of Figure 5-21. A) The cross-sectional TEM image across the original interface (dash line), B) TEM image on precipitates, C) STEM EDS elemental mapping, D) EDS spectra from spot 1, 2 in the mapping.
Figure 5-23. X-ray diffraction results from the interdiffusion zone of 9Cr/Ce and 12Cr/Ce.

Figure 5-24. Phase fraction versus temperature for Fe-20Cr, Fe-30Cr, Fe-50Cr binary alloys. The fraction of σ phase increases in a lower temperature with a higher Cr concentration.
Figure 5-25. Cross-sectional BSE images from Fe-12Cr/Ce with reduced annealing time  
A) 12 hours and B) 50 hours.

Figure 5-26. Cross-sectional microstructures and compositional mappings in the  
interdiffusion zone of Figure 5-25(A). The bright-field STEM image A) from  
Fe-12Cr/Ce after 12 hours of annealing, and B) STEM EDS element mapping  
from the selected area (dashed line).
Figure 5-27. The calculated diffusion flux $\dot{J}(X)$ of Fe, Cr, Ce in the diffusion couples. A) The diffusion couple of Ce vs. Fe-12Cr, and B) Fe-9Cr vs. Ce, corresponding to Figure 5-18.

Table 5-3. The effective interdiffusion coefficients and effective penetration depths for the diffusion couples of Fe-12Cr / Ce and Fe-9Cr / Ce. The subscript L is the Fe-Cr side, and the R is the Ce side.

<table>
<thead>
<tr>
<th>Diffusion couple assembly</th>
<th>$D_{Fe,L}^{eff}$ (m$^2$/sec)</th>
<th>$D_{Fe,R}^{eff}$ (m$^2$/sec)</th>
<th>$X_{Fe,L}$ (µm)</th>
<th>$X_{Fe,R}$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-12Cr vs. Ce</td>
<td>$7.8 \times 10^{-16}$</td>
<td>$3.0 \times 10^{-16}$</td>
<td>23.8</td>
<td>14.7</td>
</tr>
<tr>
<td>Fe-9Cr vs. Ce</td>
<td>$1.6 \times 10^{-15}$</td>
<td>$5.1 \times 10^{-16}$</td>
<td>34.2</td>
<td>19.1</td>
</tr>
</tbody>
</table>
Figure 5-28. Surface morphology and EDS spectrum of the vanadium carbide coated at different temperatures. A) 300 °C and B) 600 °C. The EDS spectrum of (B) indicates the composition of V, C, O.

Figure 5-29. The SEM of cross section of Figure 5-28(B) prepared by using FIB.
Figure 5-30. Grazing incidence X-ray diffraction (GIXD) on Figure 5-28(B) where $\alpha = 0.5^\circ$ at the bottom spectrum, and $\alpha = 3^\circ$ at the top.

Figure 5-31. Cross sectional TEM image of the coated HT9 substrate in Figure 5-28(A).
Figure 5-32. Cross-sections of the diffusion couples of Ce/coating/HT9 and Ce/HT9. A) The OM image of Ce/coating/HT9, B) OM image of Ce/HT9, C) BSE image of Ce/coating/HT9, D) BSE image of Ce/HT9.
Mitigation of the fuel-cladding chemical interaction between the metallic fuels and F/M steel cladding has been demonstrated by applying a vanadium-based diffusion barrier coating. A solid metallurgical bonding between the coating and substrate and a coating structure free from through-depth cracks were achieved by using the pack cementation diffusion coating process. Growth kinetics study shows that the growth rate follows a parabolic law and is regulated by the outward diffusion of carbon from the steel substrate. Diffusion couple tests demonstrate that a V_2C layer with a thickness of less than 5 µm can effectively slow down the interdiffusion between lanthanide cerium and HT9 steel at 660 °C for 100 hours. However, as inherited from the diffusion coating process, decarburization or tempering of the HT9 substrate under high temperature for extended period of time could become an issue. In addition, a columnar grain structure for diffusion coating process is difficult to be avoided, which might lead to fast diffusion path by promoting the interdiffusion. Therefore, a modified CVD process which employs an organic precursor (dicyclopentadienyl vanadium) was being developed.

The effects from Cr concentration in steel on the interdiffusion of Ce and the Fe-Cr alloys have also been studied in this dissertation. This portion of research helps the understanding of interdiffusion process and Cr-rich precipitation. The width of interdiffusion zone increases with decreasing Cr content, and it has been shown that Cr can effective slow down the interdiffusion process for mitigating FCCI in a metallic fuel system. The composition distributions in the interdiffusion zone have been analyzed by EDS using SEM and STEM. In addition, the phases of compositions were also determined by using XRD. The interdiffusion zone in the Fe-Cr alloy consists of
localized Cr-rich $\sigma$ phase and Fe$_2$Ce. Chromium does not form ternary phases together with Fe and Ce, which is consistent with the Ce-Cr phase diagram that no intermetallic phases will be formed at the temperature below 1000 °C. The interdiffusion kinetics studies show that the diffusion of Ce into Fe-Cr is initiated through the grain boundaries and then engulfs the grains along with the segregation and precipitation of Cr from the Fe-Cr matrix. The interdiffusion coefficient analysis quantitatively show that the diffusion rate of Ce in Fe-Cr was nearly reduced into half by increasing the Cr concentration from 9 to 12 at.%.

The future work which could be extended from this dissertation is discussed as follows. Based on the preliminary MOCVD experimental results, a nano-sized ~0.12 μm and equiaxed grain structure has been obtained at a low temperature. The coating process which was experimented on flat sample would be transferred and optimized in an inner tubular surface. Mechanical properties such as the adhesion between coating and substrate should be evaluated by micro-scratch tests. Irradiation experiments can be performed on the as-coated sample and diffusion couples to study the radiation induced swelling in the coating and radiation-enhanced interdiffusion. Beside, electronic structure calculations at the level of density-functional theory can also be performed to determine the diffusion behavior through the vanadium carbide. These results will be used to optimize vanadium carbide coating processes for a desired microstructure.
APPENDIX
A. CALCULATION OF GIBBS FREE ENERGY CHANGE

The JANAF thermochemical tables were used as a primary data source for the following thermochemical analyses. Supplemental data for the vanadium chlorides VCl, VCl₂, VCl₃, and VCl₄ were referred to a recent study [82], because the JANAF table simply didn’t include them. The use of tabulated thermochemical data and calculation of critical parameters such as Gibbs free energy will be discussed [83].

The chemical reaction which reactants \( R_i \) react and generate the products \( P_j \) can be expressed as

\[
\eta_1 R_1 + \eta_2 R_2 + \cdots + \eta_i R_i \rightarrow \nu_1 P_1 + \nu_2 P_2 + \cdots + \nu_j P_j
\]

here the \( \eta_i \) and \( \nu_j \) are stoichiometric coefficients of the reactants and products, respectively.

The enthalpy is usually expressed as a difference. In the JANAF table, the parameters are listed as in the standard state pressure of 0.1 MPa, and the enthalpy reference temperature of 298 K. The difference in enthalpy, e.g. the sensible heat \( H(T) - H(298) \), is a JANAF parameter.

\[
H(T) - H(298) = \int_{298}^{T} C_p(T) \, dT
\]

For the above chemical reaction, the change in enthalpy can be written as the heat of formation

\[
\Delta_{\text{rxn}} H(T) = \sum_j \nu(j) \Delta_f H(T, j) - \sum_i \eta(i) \Delta_f H(T, i)
\]

Alternatively, we can refer to the sensible heat
\[
\sum_j v(j)[H(T, j) - H(298, j)] - \sum_i \eta(i)[H(T, i) - H(298, i)] + \sum_j v(j) \Delta_f H(298, j)
\]
\[
- \sum_i \eta(i) \Delta_f H(298, i)
\]

Note that the heat of formation of the compounds can be found in the JANAF table, or written in terms of elemental enthalpy function \( H(T) \).

At \( T = 298 \) K,
\[
\Delta_{rxn} H(298) = \sum_j v(j) \Delta_f H(298, j) - \sum_i \eta(i) \Delta_f H(298, i)
\]

Now, consider the formation of a compound (\( B \)) in terms of elements (\( E_i \)):
\[
\eta_1 E_1 + \eta_2 E_2 + \cdots + \eta_i E_i \rightarrow B
\]

Similarly, the enthalpy of formation for the compound can be expressed as
\[
\Delta_f H(T, B) = H(T, B) - \sum_i \eta(i) H(T, E_i)
\]

The enthalpy function \( H(T, E_i) \) is referenced to \( T = 298 \) K, so \( H(298, E_i) = 0 \) at \( T = 298 \) K.
\[
\Delta_f H(298, B) = H(298, B) - \sum_i \eta(i) H(298, E_i)
\]
\[
\Delta_f H(298, B) = H(298, B)
\]

After rearrangement of the equation,
\[
H(T, B) = \Delta_f H(298, B) + [H(T, B) - H(298, B)]
\]

We have discussed the change in enthalpy \( \Delta_{rxn} H(T) \) for a chemical reaction, the enthalpy function \( H(T, B) \), and the heat of formation \( \Delta_f H(T, B) \) for a compound, which can all be expressed in terms of the JANAF parameters.

The change of Gibbs free energy associated with the reaction can also be expressed as
\[ \Delta_{rxn} G(T) = \sum_j v(j) G(T,j) - \sum_i \eta(i) G(T,i) \]

Similarly, the free energy of formation for the compound can be expressed as

\[ \Delta_f G(T,B) = G(T,B) - \sum_i \eta(i) G(T,E_i) \]

Another useful information from the JANAF table is the Free energy function (FEF) based on \( T= 298 \text{ K} \)

\[ FEF_{298}(T) = \frac{G(T) - H(298)}{T} \]

\[ G(T) = T \times FEF_{298}(T) + H(298) \]

\[ \Delta_{rxn} G(T) = T \left[ \sum_j v(j) FEF_{298}(T,j) - \sum_i \eta(j) FEF_{298}(T,i) \right] + \Delta_{rxn} H(298) \]

This equation allows us to calculate the free energy change of a reaction, from FEF (at \( T= 298 \text{ K} \)) and \( \Delta_f H(298) \).
B. DESCRIPTION OF SIGNAL INTERFACES IN THE MOCVD SYSTEM

As shown in Figure 4-5, the MOCVD system contains multiple singles. For example, the temperature is detected by an infrared sensor (Raytek MI3, D:S= 22:1, T=0-1000 °C). The pressure is detected by a Pirani gauge (A&N MicroPirani™ 925). The detected signals are fed to a programmable logic controller (PLC, Arduino Leonardo) which will then integrate these environmental signals and generate the control signals for the induction heater and solenoid valve. It is important to understand the interface of these signals in terms of signal types, amplitudes, and signal processing speed. The details are described as follows.

The output signal from the infrared sensor is a current of 0-20 mA, which should be convert into a voltage signal of 0-5 V before entering the PLC. The induction heater receives a voltage signal 0-10 V which corresponds to the minimal and maximal output RF power. In my current setup, the output signal from the PLC is a 0-5 V PWM (Pulse-Width Modulation) signal which is enough for applications since I am targeting at low-temperature (300-600 °C) experiments. The pressure gauge generates a voltage signal of 0-5 V which is used to control the solenoid valve for emergency shutdown.

The temperature control in the PLC is based on the loop control. A segment of the Arduino programming code is listed as here as an example.

/*
Analog input, analog output, and serial output:

Reads an analog input pin, maps the result to a range from 0 to 255 and uses the result to set the pulse-width modulation (PWM) of an output pin. Also, print the results to the serial monitor.
The circuit:

* Potentiometer connected to analog pin 0. Center pin of the potentiometer goes to the analog pin. Side pins of the potentiometer go to +5V and ground

* LED connected from digital pin 9 to ground

*/

// these constants won't change. They're used to give names
const int analogInPin = A0; // Analog input pin that the potentiometer is attached to
const int analogOutPin = 9; // Analog output pin that the LED is attached to
const int indicatorLedPin = 13; // pin that the built-in LED is attached to

//
int sensorValue = 0; // value read from the pot
int outputValue = 0; // value output to the PWM (analog out)
int targetTemp = 400; // 435 C = 3.4 V ; 696/1024 ; 5/18: 500

//
void setup()
{
    // initialize serial communications at 9600 bps:
    serial.begin(9600);
    sensorValue = analogRead(analogInPin);
    // outputValue = map(sensorValue, 0, 1023, 0, 255);
    outputValue = 150;
}

//

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void loop()
{
    // read the analog in value:
    sensorValue = analogRead(analogInPin);

    // map it to the range of the analog out:
    //outputValue = map(sensorValue, 0, 1023, 0, 255);

    if (sensorValue < targetTemp) {
        outputValue = outputValue + 1;
    }

    if (sensorValue > targetTemp) {
        outputValue = outputValue - 1;
    }

    // in case the sensor value is outside the range seen during calibration
    outputValue = constrain(outputValue, 0, 255);

    // change the analog out value:
    analogWrite(analogOutPin, outputValue);

    delay(1500);

    digitalWrite(indicatorLedPin, HIGH);

    // print the results to the serial monitor:
    Serial.print("sensor = ");
    Serial.print(sensorValue);
    Serial.print("t output = ");
}
Serial.println(outputValue);

// wait 1000 milliseconds before the next loop
// for the analog-to-digital converter to settle
// after the last reading:

delay(1500);
digitalWrite(indicatorLedPin, LOW);

}

In the future work, the code can be continually developed. More sophisticated control scheme integrating multiple temperature signals is suggested to be built, to achieve a more uniform temperature. Motion control (position signal) of the induction heater will also need to be integrated. The PLC coding provides a basic idea for future developers to continually work on this project.
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Mr. Wei-Yang Lo was born in Taiwan. He obtained his bachelor and master's degree in electrical engineering, from Nation Tsing-Hua University (Hsinchu, Taiwan). Before joining the University of Florida, he was a senior semiconductor engineer responsible for CMOS processes integration, failure analysis, and memory products development in Taiwan. His current research interests are extended to nuclear structural materials, chemical vapor deposition of ceramics, and material characterizations using SEM, STEM, and XRD.