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DIP-COATING PROCESS OF ZIRCALOY-2 FUEL CLADDING WITH COLLOIDAL GRAPHITE

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ABSTRACT

DIP-COATING PROCESS OF ZIRCALOY-2 FUEL CLADDING WITH COLLOIDAL GRAPHITE. The intensive researchs on high discharge burn-up of Light Water Reactor (LWR) fuel element have been continously performed due to the extension of fuel element's utility life. One of these researches was allowing for alteration of the existing zirconium-based clad system through coating. A coating technique with the coating layer thickness of 10 - 30 µm will improve the corrosion resistance of cladding without changing the dimension of cladding. The scope of this current research is to obtain the zircaloy-2 cladding coated with ZrC layer by dipping process of zircaloy-2 specimens in colloidal graphite at room temperature. The dip-coated specimens undergo heating process at 700 ^oC, 900 ^oC and 1100 ^oC respectively in Argon gas atmosphere for 1 hour and are subsequently characterized by optical microscope and XRD. The optical microscope images show that the coating layers thickness are increased as the heating temperature increased. The coating layers thickness are 10 µm, 20 - 40 µm and 100 µm for the specimens heated at 700 ^oC, 900 ^oC and 1100 ^oC respectively. The calculated diffusivity of carbon into zircaloy-2 cladding for the coated specimens at 700 ^oC, 900 ^oC and 1100 ^oC are 3,10216E-11 cm^2s^{-1}; 3,60479E-11 cm^2s^{-1} and 4,00613E-11 cm^2s^{-1} respectively. From XRD examination analysis reveals that the ZrC phase appears in the specimens heated at 1100 ^oC but it is not the case for specimens heated at both 700 ^oC and 900 ^oC. The coating layer of specimens heated at both 700 ^oC and 900 ^oC mostly consists of carbon. At these heating temperatures, carbon atoms have diffused into zircaloy-2 and substituted the zirconium atoms with a limited occupation to form C-Zr solid solution. At the temperature of 1100 ^oC, due to the increase in vibration energy, the carbon atoms have enough energy to diffuse to form the carbide phase. Heating process at higher than 700 ^oC, however, will degrade the zircaloy-2 cladding.. It is concluded that the dip-coating process of zircaloy-2 cladding in graphite colloid with subsequent high temperature heating is not the proper method to gain the ZrC-coated zircaloy-2 cladding. Therefore, as for the future works of this research, the others method should be searched and investigated to obtain the proper ZrC coating process on LWR zircaloy cladding which fulfills the dimension and quality requirements.

Keywords: zircaloy, cladding, dip-coating, colloidal graphite, ZrC

ABSTRAK

PELAPISAN ZrC PADA KELONGSONG ELEMEN BAKAR NUKLIR ZIRKALOI-2*. Penelitian intensif pada elemen bakar reaktor berpendingin air dengan fraksi bakar tinggi terus dilakukan dalam rangka memperpanjang umur operasi elemen bakar. Salah satu penelitian adalah proses mengubah kelongsong berbasis zirkonium yang ada saat ini dengan cara pelapisan dengan unsur carbon. Proses pelapisan carbon dengan ketebalan lapisan 10 - 30 µm akan memperbaiki ketahanan korosi kelongsong tanpa mengubah dimensi kelongsong. Penelitian ini bertujuan untuk memperoleh kelongsong zirkaloi-2 berlapis ZrC. Lapisan ZrC berada pada daerah antarmuka kelongsong dengan lapisan karbon yang diperoleh melalui proses pencelupan (dipping) spesimen zirkaloi-2 dalam koloid grafit pada temperatur kamar. Spesimen, selanjutkan dipanaskan pada temperatur 700 ^{o}C, 900 ^{o}C dan 1100 ^{o}C dalam media gas Argon selama 1 jam. Spesimen hasil pemanasan, kemudian dikarakterisasi menggunakan mikroskop optik dan uji difraksi sinar-X. Pengujian dengan mikroskop optik memperlihatkan terjadinya penebalan lapisan seiring dengan kenaikan temperatur pemanasan. Ketebalan lapisan diperoleh masing-masing 10 µm, 20 - 40 µm dan 100 µm untuk spesimen yang dipanaskan pada 700 ^{o}C, 900 ^{o}C dan 1100 ^{o}C. Ketebalan lapisan akibat pemanasan dikorelasikan dengan hasil perhitungan diffusivitas karbon. Besarnya diffusivitas karbon ke dalam kelongsong zirkaloi-2 diperoleh masing-masing sebesar 3,10216E-11 cm^2s^{-1}; 3,60479E-11 cm^2s^{-1} dan 4,00613E-11 cm^2s^{-1} yang bersesuaian dengan kenaikan temperatur pemanasan. Sementara itu, hasil analisis uji dengan XRD mengungkapkan bahwa struktur ZrC terbentuk pada permukaan spesimen kelongsong zirkaloi-2 yang dipanasi pada temperatur 1100 ^{o}C. Fasa ini tidak muncul pada pemanasan dengan temperatur 700 ^{o}C and 900^{o}C walaupun terjadi kenaikan difusivitas atom karbon. Pada pemanasan 700 ^{o}C dan 900 ^{o}C diperkirakan sebagian atom-atom karbon dalam lapisan mampu mendifusi ke dalam zirkaloi-2 dan mensubstitusi atom zirkonium membentuk larutan padat C-Zr tetapi bukan fasa ZrC. Pada temperatur 1100 ^{o}C, dengan naiknya energi vibrasi karena agitasi termal maka sebagian atom karbon mempunyai energi yang cukup untuk mendifusi ke permukaan kelongsong membentuk fasa ZrC. Walaupun demikian, proses pemanasan yang dilakukan pada temperatur tinggi di atas 700 ^{o}C akan merusak kelongsong zirkaloi. Dari hasil ini dapat disimpulkan bahwa proses pencelupan kelongsong zirkaloi dalam koloid grafit yang diikuti dengan pemanasan pada temperatur tinggi bukanlah cara yang tepat untuk memperoleh kelongsong zirkaloi-2 berlapis ZrC. Penelitian lebih lanjut perlu dilakukan untuk mencari dan meneliti metode lain yang tepat untuk memperoleh kelongsong zirkaloi LWR yang berlapis ZrC yang memenuhi persyaratan dimensi dan kualitas sebagai kelongsong bahan bakar nuklir.*

Kata Kunci*: zirkaloi, kelongsong, pelapisan dengan pencelupan, koloid grafit, ZrC.*

INTRODUCTION

Recently, the Nuclear Power Plant (NPP) especially Light Water Reactors (LWRs) have been operated with power uprates and increasing fuel discharged burnup in order to improve reactor core economics[1]. The increasing fuel discharged burn up gives the consequences of longer fuel operating cycles and placed additional stress on the fuel[2]. This results in the degradation of the mechanical properties of the zirconium cladding due to the increased radiation damage, corrosion and hydrogen uptake, as well as increased fission gas inventory[3]. To allow more efficient operation during normal reactor operating conditions with higher safety margins, nuclear fuel research and development (R&D) work focus on the development of an advanced fuel cladding system [1] with slower oxidation rates, reduced hydrogen pick-up, and limited irradiation growth as well as creep of the cladding during the long-term normal operation[4-5].

One of the improvement concepts that can be deployed in existing LWRs is surface-modified fuel cladding concept [5-6] using a thin protective coating on the zirconium-based cladding exterior [1, 4-7]. The major benefit of the surface-modified fuel cladding concept is the economics because in the commercial Zr-based alloy and manufacturing facility can be continuously operated by developing the surface-modified cladding [5]. Thin ceramic coatings provide a protective layer for the zirconium alloy that will reduce oxidation and hydrogen pick-up during normal operating conditions while significantly retarding oxidation kinetics and hydrogen production during Beyond Design Based Accident (BDBA) conditions[2,4,7]. The ceramics considered as additional coating of incorrodible (corrosion resistance) materials on the zirconium-based cladding exterior are oxides, carbides and nitrides of early transition metals such as Y_2O_3, SiO_2, Cr_2O_3, Al_2O_3, ZrO_2, Cr_2C_3, SiC, ZrC and ZrN [8]. Findings show that ceramic coatings should remain 10 - 30 µm thick to limit the neutronic penalty[4]. Under normal operating conditions of LWRs, coatings on zircaloy cladding must meet stringent safety constraints[6] such as adhere to the zirconium alloy, self-heal if defected, remain stable with respect to spalling and grid-to-rod fretting, and provide stable properties under irradiation[4].

The coating technology is widely applied to reduce the corrosion damage as the corrosion resistance can be easily obtained by a coating technology without a base material change. However, the optimized coating technology related to the materials and methods must be developed, since the chemical and mechanical failures of the coating layer are a serious concern in coating technology[8]. Various of the coating technologies, such as a plasma spray, Chemical Vapor Deposition (CVD) or Physical Vapor Deposition (PVD) and laser cladding have been applied in the commercial industry to control the surface properties of components [5].

Carbide film in general and zirconium carbide film in particular have preeminent properties such as chemical resistance, heat conductivity, good thermal shock resistance, and high melting point (3450ºC)[9-10]. It is used in some hi-tech areas such as coating layer of High Temperature Gas-cooled Reactor (HTGR) nuclear fuel[9-10], used in aerospace industry and coating of fire line shell in all the long-range missiles[10]. Based on ZrC phase diagram in Figure 1 and yield of ZrC deposition in Figure 2 show that ZrC film will be formed at temperature ranging of 500 ºC to 3500 ºC[11-12].

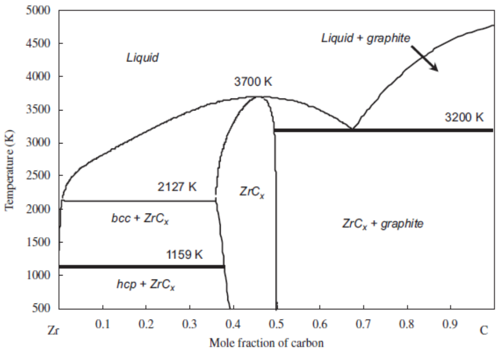


Figure 1. The calculated Zr-C phase diagrams[11].

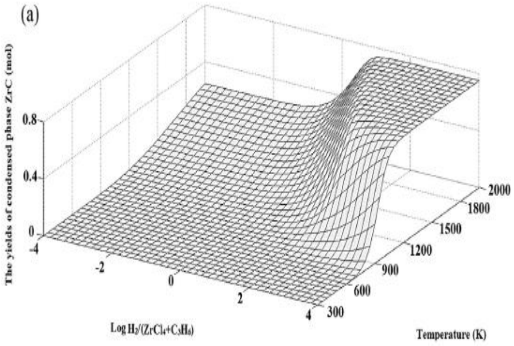


Figure 2. Production of the condensed phases ZrC as the function of inject reactants ratios [12].

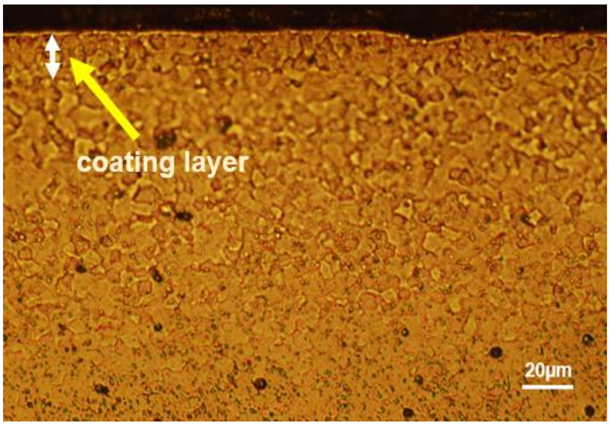
By using Chemical Vapor Deposition (CVD) process, the synthesis of ZrC film on graphite substrates has been investigated at temperature 1200 °C with H_2 flow at 20 mL/min and Ar, gas CH_4 flows at 30, 80 mL/min with 8 g of $ZrCl_4$ for 1 hour process[10]. ZrC film obtained on the substrat is composed of two main phases, ZrC phase and carbon phase with the film thickness is about 10.5 - 15.5 µm. The coating layer is relatively uniform, flat, non-crack and high compact crystals in average size of 5 - 7 µm. Boundary between ZrC film and graphite substrat has no space and coating layer peeling[10].

So far, the publications of researches on ZrC as protective coating on zircaloy cladding of LWR fuel element are unavailable. In this research, synthesis of zirconium carbide phase on zircaloy-2 cladding was performed by dip-coating process of zircaloy-2 specimens in colloidal graphite[13] with subsequent high heating temperature to force carbon atoms to diffuse onto zircaloy surface to form ZrC layer. The microstructure and crystal structure of the coated cladding zircaloy specimens were characterized by optical microscope and XRD to evaluate the microstructure and to assure that the coated film on zircaloy cladding was ZrC.

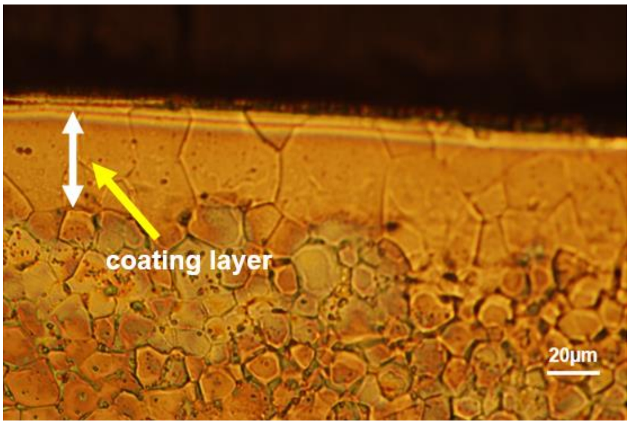
METHODOLOGY

The test specimens for dip-coating process were zircaloy-2 tube with 19.87 to 20.13 mm of outer diameter, 0.5 mm of thickness and 10 mm in length[13]. The specimens were washed with alcohol in ultrasonic pit for 30 minutes prior coating process and dried using hot air.

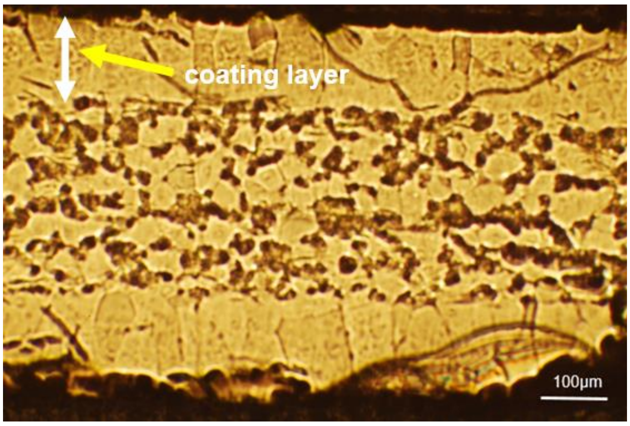
The coating of process were performed at room temperature by the immersion (dipping) of test specimens in precursor solution for about 15 seconds for complete wetting. The precursor solution was colloidal graphite with the optimum density of 0.9195 g/cm^3[13]. By pulling the test specimen upward, a thin layer of precursor solution (colloidal graphite) is deposited, and the excess liquid will drain from the specimen surface. To evaporate the solvent of the colloidal graphite, the test specimens were dried at room temperature for 24 hours. The thin coating layer on the specimens is subsequently subject to further heat treatment to burn out residual organics and induce crystallization of the carbide. In this experiment, in order to force carbon atoms in thin coating layer to diffuse into zircaloy surface to form ZrC layer, the specimens were heated in a furnace at a temperature variation of 700 °C, 900 °C and 1100 °C for 1 hour with argon gas as the heating medium[13].



a. Zircaloy-2 specimen heated at 700 ^{o}C with coating layer thickness of 10 µm.



b. Zircaloy-2 specimen heated at 900 ^{o}C with coating layer thickness of 20 – 40 µm.



c. Zircaloy-2 specimen heated at 1100 ^{o}C with coating layer thickness of 100 µm.

Figure 3. Optical microscope images of cross sectional view of dip-coated zircaloy-2 cladding specimens which undergoes heating process.

To evaluate the microstructure of the coated layer on the specimen, metallographic test done with an optical microscope, while to reveal the crystal structure, the coated layer was tested using XRD equipment. The thickness of the coated layer was observed from optical microscope images.

RESULTS AND DISCUSSION

The microstructure images of dip-coated zircaloy-2 cladding specimens which heated at temperature of 700 ºC, 900 ºC and 1100 ºC are presented in Figure 3.

In Figure 3 (a), it is rather difficult to distinguish between the outer graphite coating layer and the zircaloy-2 surface for specimen heated at 700 ºC. The coating layer is relatively flat with the thickness of about 10 µm and has smaller grain size than the grain size of the zircaloy-2 cladding. The image for the specimen heated at 900 ºC shows that the thickness and the grain size of coating layer increased significantly. As shown in Figure 3 (b), the thickness of coating layer heated at 900 ºC is about 40 µm. If it is compared to the ZrC film obtained by chemical vapor deposition (CVD) method in process at temperature of 1300 ºC[10], the thickness of the coating layer in the current research is much thicker. Using CVD process, the obtained coating layer thickness is about 8 - 14 µm[10] and this value is in the range of the coating thickness requirement of zircaloy cladding from economically neutronic consideration of LWR[4]. As explained previously, ceramic coatings of LWR fuel of zircaloy cladding should remain 10 - 30 µm thick to limit the neutronic penalty[4]. This dip-coating layer thickness is obtained at lower temperature than that obtained in CVD process.

By dip-coating process, the coated layer tends to be thickened and the grain size develops bigger as the heating temperature increases. When heating temperature is raised up to 1100 ºC, the specimens show the thickest and reaches more than 100 µm. At 1100 ºC, the heating process reaches the sintering temperature of zirconium. At this temperature, beside grain growth of carbon layer occurs, the rate of carbon atoms diffusion into zircaloy-2 cladding increases due to higher vibration energy of carbon atoms and zirconium atoms, which results in the softening of zircaloy-2 cladding. It shows that zircaloy-2 grain becomes much larger and there is some cracks in the coating layer. This fenomena also occurs in coating process using CVD[10]. CVD process conducted at 1300 ºC gives results in the decline in uniformness and reduction in compactness of coating layer.

The experiments done by Sugondo et al show that the diffusivities of carbon into zircaloy-2 cladding at heating temperature of 450 ºC, 500 ºC and 550 ºC are 2,5079E-12 cm^2s^{-1} ; 5,3439E-12 cm^2s^{-1} and 6,6647E-12 cm^2s^{-1} respectively[14]. Based on these data, the calculated values of diffusivities of carbon into zircaloy-2 cladding for the coated specimens at 700 ºC, 900 ºC and 1100 ºC are listed in the Table 1. In this Table, the coating layer thickness obtained at each heating temperature is also listed. The diffusivity of carbon increases with heating temperature.

Table 1. Coating layer thickness and calculated diffusivity of carbon atom into zircaloy-2 cladding at heating temperature of 700 ºC, 900 ºC and 1100 ºC[14].

No	Heating temperature (ºC)	Coating layer thickness (µm)	Carbon diffusivity (cm^2s^{-1})
1	700	10	3,10216E-11
2	900	20 – 40	3,60479E-11
3	1100	100	4,00613E-11

The X-ray diffraction (XRD) patterns of ZrC and dip-coated zircaloy-2 cladding specimens at different heating temperatures of 700ºC, 900 ºC and 1100 ºC are presented in Figure 4. The XRD peaks of coated specimens heated at 700 ºC and 900 ºC do not match with any peak of ZrC, indicating that ZrC phases do not appear in the zircaloy surface of coated specimens, as shown in Figure 5(a) and 5(b). The coating layer is composed of amorphous carbon. At this temperature, carbon atoms difuse into zircaloy-2 and substitute the zirconium atoms with a limited occupancy, which results in the solid solution of carbon in zircaloy at the interface of carbon layer and zircaloy-2 cladding surface. Although the diffusivity increases at heating temperature of 700 °C and 900 °C as shown in Table 1. The carbon atoms vibration energy from thermal agitation are insufficient to form ZrC phase. The XRD pattern of these two heated specimens do not show ZrC phases, and this indicates that ZrC phase has not been formed. ZrC phase will be formed at low temperature up to 500 °C if high energetic carbon atoms involved in the process, such as in laser cladding process or reactive magnetron sputtering process.

At the heating process of 1100 °C, ZrC phase appears in coating layer as shown in Figure 5(c). The layer is composed of ZrC (COD 96-900-8778) and amorphous carbon. In the comparison with the research done by Yan Zhu et al.[12], ZrC will start to be formed at the temperature of 750 K (500 °C). Below 1100 °C, it seems that the carbon atoms in the coating layer gains insufficient energy to diffuse into zircaloy surface for the formation of carbide phase. By CVD process, on the other hand, ZrC phase is obtained at the temperatures in the range of 1000 °C to 1300 °C[9-10].

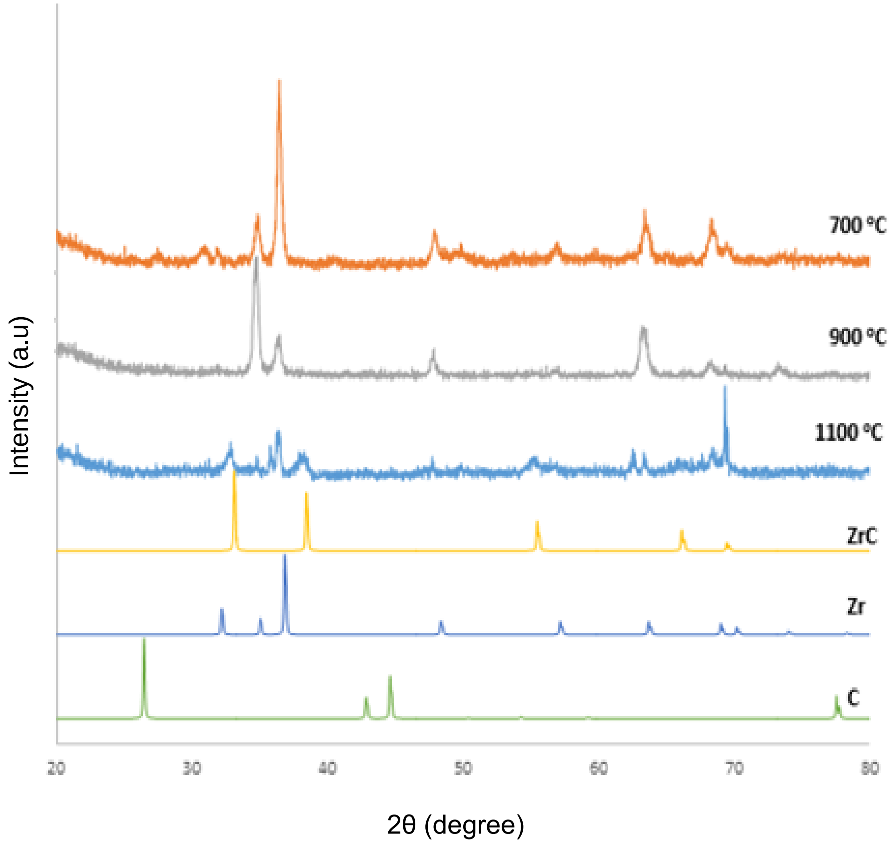
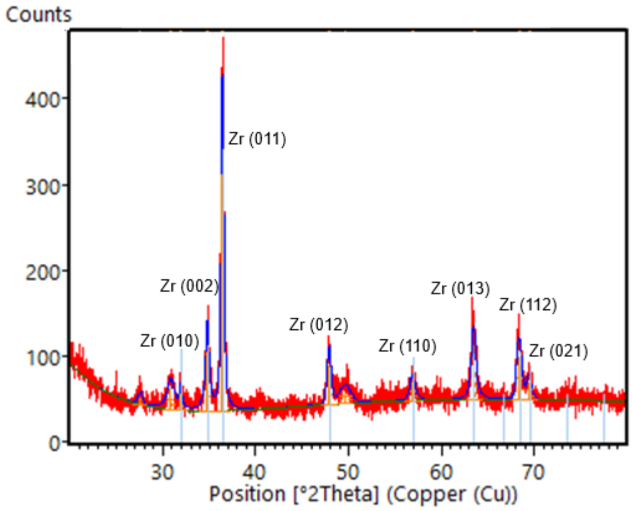
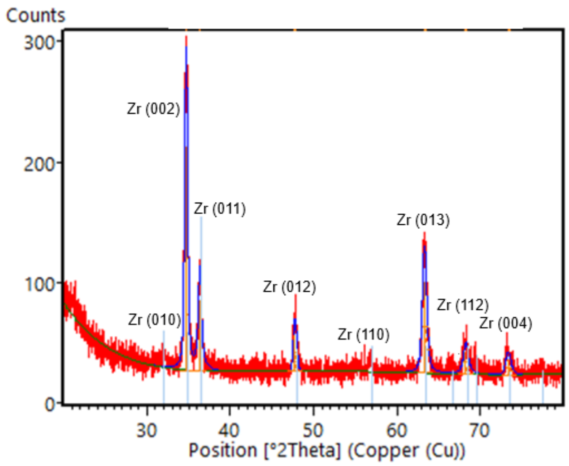


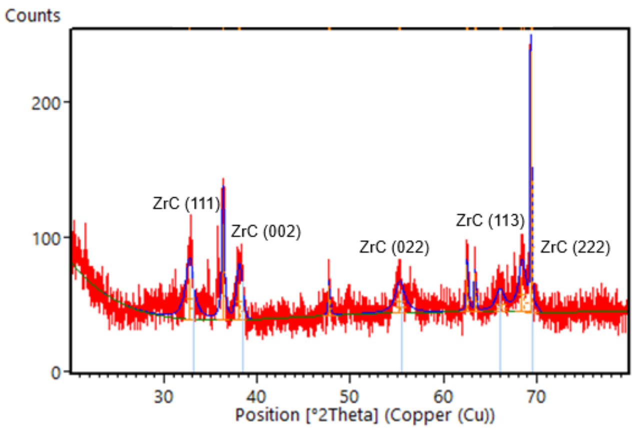
Figure 4. XRD pattern of coated zircaloy-2 specimens at different heating temperatures (700 °C, 900 °C and 1100 °C).



a. XRD peaks matching for coated zircaloy-2 specimens heated at 700 ^{o}C.



b. XRD peaks matching for coated zircaloy-2 specimens heated at 900 ^{o}C.



c. XRD peaks matching for coated zircaloy-2 specimens heated at 1100^{o}C.

Figure 5. XRD peaks matching of coated zircaloy-2 specimens at different heating temperatures (700 ^{o}C, 900^{o}C and 1100 ^{o}C).

As explained before, using dip-coating prosess and subsequently heating at 1100 °C, the carbon atoms have enough energy to diffuse to form carbide phase on zircaloy surface due to the increase of vibration energy of carbon atoms and the softening of zircaloy-2 cladding at its sintering temperature. Unfortunately, heating at 1100 °C yielded a very thick coating layer and degraded the zircaloy-2 cladding. The coating layer thickness and the existence of ZrC phase at each heating temperature are listed in Table 2. The thickness and the imperfection of the coating layer obtained at heating temperature of 1100 °C by this dip-coating process do not meet the requirements of coating on zircaloy cladding of LWR fuel element..

Table2. Coating layer thickness and existence of ZrC phase on zircaloy-2 cladding coated specimens at heating temperature of 700 °C, 900°C and 1100 °C.

No	Heating temperature (°C)	Coating layer thickness (µm)	The existence of ZrC phase
1	700	10	Not exist
2	900	20 – 40	Not exist
3	1100	100	Exist

CONCLUSION

Dip-coating process in colloidal graphite with subsequent heating at 1100 °C resulted in the formation of ZrC phase on zircaloy-2 cladding with carbon layer thickness of 100 µm. The requirement for ceramic coating thickness of LWR fuel element should remain 10 - 30 µm to limit the neutronic penalty. In this research, the coating layer thickness which meets the requirement was obtained for the coated zircaloy-2 cladding heated at 700 °C and 900 °C. Nevertheless, the coating layer of zircaloy-2 cladding specimens heated at 700°C and 900 °C mostly consists of carbon and does not consist of ZrC phase. At these heating temperatures, it is supposed that carbon atoms have diffused into zircaloy-2 and substituted the zirconium atoms with a limited occupancy to form C-Zr solid solution. However, heating process at higher temperature than 700 °C will degrade the zircaloy-2 cladding. It is concluded that the dip-coating process of zircaloy-2 cladding in graphite colloid with high temperature subsequent heating is not the proper method to gain the ZrC-coated zircaloy-2 cladding. Therefore, as future works of this research, other methods should be studied and investigated to obtain proper ZrC coating process on LWR zircaloy cladding.

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