

APPLICATION OF BE-FREE ZR-BASED AMORPHOUS SPUTTER COATINGS AS A BRAZING FILLER METAL IN CANDU FUEL BUNDLE MANUFACTURE

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ABSTRACT – Amorphous sputter coatings of Be-free multi-component Zr-based alloys were applied as a novel brazing filler metal for Zircaloy-4 brazing. By applying homogeneous and amorphous-structured layers coated by sputtering the crystalline targets, highly reliable joints were obtained with the formation of predominantly grown α -Zr grains owing to a complete isothermal solidification, exhibiting high tensile strength as well as excellent corrosion resistance, which were comparable to those of Zircaloy-4 base metal. The present investigation showed that Be-free and Zr-based multi-component amorphous sputter coatings can offer great potential for brazing Zr alloys and manufacturing fuel rods in a CANDU fuel bundle system.

Introduction

In manufacturing CANDU fuel bundles, various appendages (spacers and bearing pads) are joined by a brazing process onto the surface of the thin-walled (≈ 0.38 mm) cladding tubes made of Zircaloy-4 (1.38Sn-0.2Fe-0.1Cr-balance Zr in wt.%). For the brazing filler metal (BFM), physically vapor-deposited (PVD) metallic beryllium (Be) has currently been used, since Be has a very low neutron absorption cross section ($\sigma_a \approx 0.0092$ barns), and it readily reacts with a surrounding Zircaloy-4 to form a Zr-Be molten alloy, thereby enabling a brazing therebetween by eutectic melting (i.e., 965 °C at 65Zr-35Be in at.%) [1]. Unfortunately, the utilization of Be as a BFM requires very complicated physical protection and safety systems and its exposure levels are strictly monitored by legislation, as its metallic vapor is highly toxic to the human body and is extremely harmful to the environment [1,2]. This hazard of airborne Be has been a primary trigger for our recent studies to find a new BFM as a substitute for pure Be [2-4].

During the brazing cycle, in addition, an undue penetration of the Be BFM into the tube wall, as well as an excessive reduction in the tube thickness, not infrequently generates defective products owing to the nature of Be-diffusion brazing [5]. In a joint structure, a ZrBe₂ intermetallic phase produced typically by a eutectic reaction ($L \rightarrow \alpha\text{-Zr} + \text{ZrBe}_2$) can impair the mechanical strength of the joints and is likely to cause galvanic corrosion as coupled to a highly corrosion-resistive α -Zr phase. These additional issues can be more significant for an advanced pressurized heavy water reactor (PHWR) characterized by a high burn-up and long operation period with thinner cladding tubes.

Among the various candidates for the Be-free BFM for Zircaloy-4, Zr-based multi-component systems can be considered as the best choice to operate at high temperatures as well as in highly corrosive environments [6]. Not only are these Zr-based filler metals highly compatible with Zr alloys as noticed naturally from their main constituent of Zr, but they also provide considerably low brazing temperatures below 900 °C owing to their deep eutectic characteristics [3,6]. In practice,

several Zr-based filler metals have been applied for joining Ti as well as Zr alloys and have yielded a high strength and excellent corrosion resistance of the resultant joints [2-4,6]. However, the employed alloy fillers have been mostly tested by their amorphous ribbon form produced by rapidly solidified (RS) technology, which is not easy to introduce directly to a brazing procedure of the fuel bundle components because of an insertion problem between the fuel cladding and appendages.

In our recent researches [2-4], several amorphous sputter coatings of Zr-based multi-component alloys without containing Be were proposed, not only as a novel BFM for Zr alloys but also as a feasible application method of the filler for a brazing procedure of the nuclear fuel bundle components. In a brazing, a sputter coating was expected to offer a great potential, because it can provide an easier introduction of the filler to the base metal, an atomically perfect interfacial contact with the base metal, an excellent composition uniformity over the area to be joined, and an accurate control of the filler amount.

This paper will summarize the results on Zircaloy-4 brazing when using the Be-free Zr-based amorphous sputter coatings as a filler, being structured in the following sections: Selection of filler compositions (Section 1), Sputtering of multi-component Zr-based alloys (Section 2), Structure of the brazed joints (Section 3), Properties of the brazed joints (Section 4), and Prototype manufacture of CANDU fuel rods (Section 5). Finally, the applicability of the Be-free and Zr-based multi-component amorphous sputter coatings will be discussed for brazing Zr alloys and manufacturing fuel rods in a CANDU fuel bundle system.

1. Selection of filler compositions

The Zr-based multi-component systems have been widely investigated for a study of metallic glasses as well as a development of brazing filler alloys due to their deep eutectic characteristics. Based on a number of the reported Zr-based alloys, practical considerations have been addressed to determine suitable constituent elements of a BFM for CANDU fuel bundle manufacture. First, the Be should be excluded from the filler composition, and the elements of the filler need to have a low neutron absorption cross section ($\sigma_a < 10$ barns), a low possibility of hydrogen uptake, and an adequate ability to reduce melting temperatures of the filler alloys. According to these criteria, the alloying elements of Ti, Cu, Fe, and Al were selected properly, and the two Zr-rich ternary systems of Zr-Cu-Fe and Zr-Cu-Al were determined primarily by considering their low eutectic temperatures. The lowest liquidus temperatures were reported at about 880 °C and 930 °C in these systems, with the compositions of $Zr_{74}Cu_{13}Fe_{13}$ and $Zr_{60}Cu_{30}Al_{10}$ in at.%, respectively [4,7]. By a partial substitution of Zr with Ti, and Cu with Fe, the liquidus temperatures of the alloys could be further reduced to about 850 °C and 880 °C at the compositions of $Zr_{58}Ti_{16}Cu_{10}Fe_{16}$ and $Zr_{57}Ti_{13}Cu_{25}Fe_5Al_{10}$, respectively [4]. The compositions of the filler alloys used in our studies are summarized in Table 1. The first four alloys were based on the primary Zr-Cu-Fe and Zr-Cu-Al systems, but the last alloy (Ni-1) was also tested owing to its relatively low melting temperature despite containing the hydrogen-absorptive Ni element. In terms of the melting temperatures, it was quite promising that the brazing temperature could be reduced below 900 °C by applying these Zr-based alloy fillers. This brazing temperature was substantially low as compared to the relevant studies and practical procedures where the brazing required is at least more than 1050 °C [1,5].

Table 1 Compositions of the filler alloys used in our studies (at.%)

Filler	Zr	Ti	Cu	Fe	Al	Ni	Liquidus (°C)
Fe-1	74	-	13	13	-	-	880
Fe-2	58	16	10	16	-	-	850
Al-1	60	-	30	-	10	-	930
Al-2	57	3	25	5	10	-	880
Ni-1	50	17	15	-	-	18	830

2. Sputtering of multi-component Zr-based alloys

The sputtering bulk targets of the multi-component Zr-based alloys (Table 1) were fabricated by two typical methods, i.e. vacuum arc melting and powder metallurgical process. As shown in Figure 1, the circular disc targets with a diameter of 76.2 mm and a thickness of 6.3 mm were prepared by vacuum arc melting under a high-purity argon atmosphere, while the rectangular disc targets with a dimension of 63 mm × 100 mm and a thickness of 5 mm were produced by hot pressing of gas-atomized alloy powders. All the targets showed the intact surfaces without any defects such as cracks.

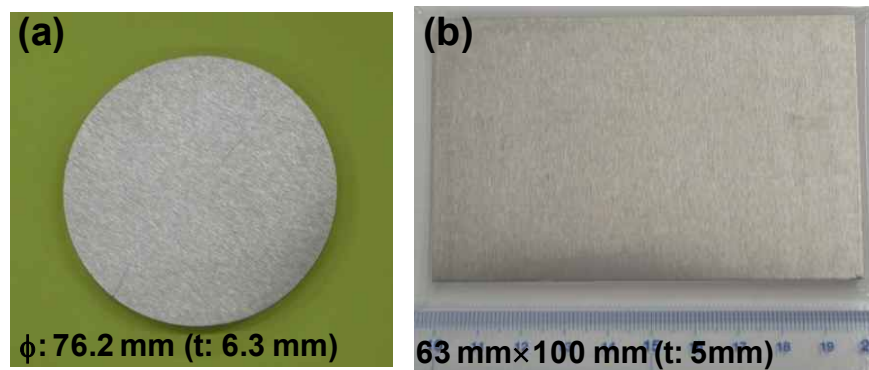


Figure 1 Sputtering targets fabricated by (a) vacuum arc melting and (b) powder metallurgical process

Figures 2(a) and (b) show the scanning electron microscope (SEM) images for the as-fabricated Ni-1 bulk target and the cross-section of the coating on the Zircaloy-4 base metal prepared by sputtering, respectively, and their corresponding X-ray diffraction (XRD) patterns are represented in Figures 3(a) and (b) [2]. The as-fabricated bulk target revealed a complicated structural characteristic with various crystallized phases, as shown in Figures 2(a) and 3(a). On the contrary, a

homogeneous coating was produced by sputtering a crystalline Ni-1 bulk target (Figure 2(b)), and its structure was evidently amorphous without any distinguishable diffracted peaks in the XRD pattern (Figure 3(b)). From the viewpoint of brazing application, this phenomenon was worthy of notice in that the amorphous alloy filler with multi-components could be coated simply by sputtering its crystalline bulk target fabricated by the conventional metallurgical processes. Based on the inductively coupled plasma atomic emission spectrometry (ICP-AES), furthermore, the composition of the target was estimated to be $Zr_{47.6}Ti_{19.9}Cu_{15.1}Ni_{17.4}$ showing a small variation as compared to its nominal composition.

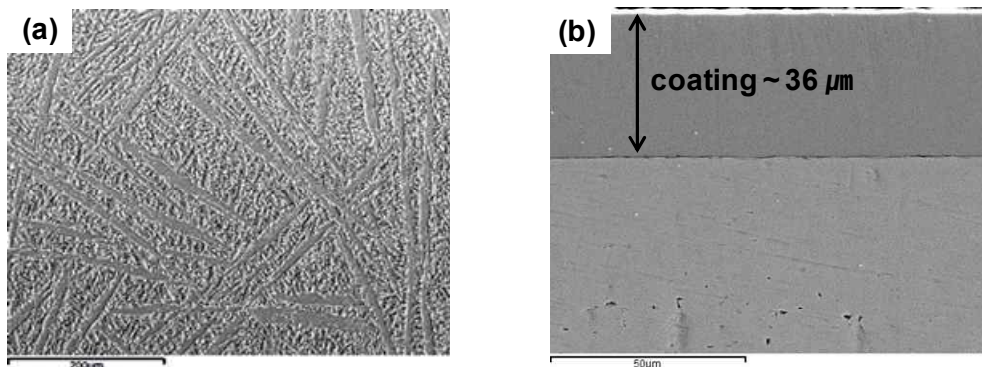


Figure 2 SEM images for (a) the as-fabricated Ni-1 bulk target and (b) the cross-section of the coating on the Zircaloy-4 base metal

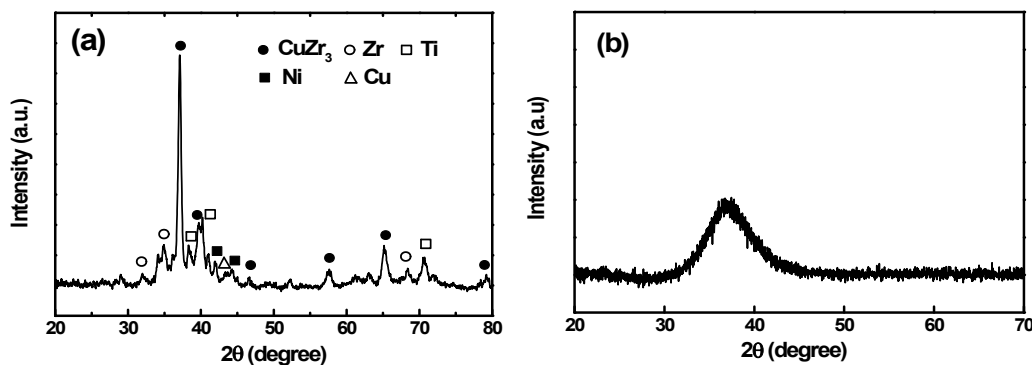


Figure 3 XRD patterns for (a) the as-fabricated Ni-1 bulk target and (b) the coating on the Zircaloy-4 base metal

In order to evaluate the spatial composition homogeneity of the produced coating layer, the composition analyses by the energy dispersive spectrometry (EDS) were comprehensively carried out for both the surface and cross-section of the coating. As can be seen in Figure 4, the measured

elemental compositions of the amorphous-structured coating were highly uniform for both the surface and cross-section of the coating [2]. For instance, the measured variation of the Zr concentration was only within 1 at.% over 10 mm × 10 mm square surface area, and it was also less than 1~2 at.% for the cross-section. For the surface, the measured average elemental compositions were 47.6, 18.4, 14.8, and 19.2 at.%, and for the cross-section, they were 48.0, 18.3, 14.6, and 19.1 at.% in the order of Zr, Ti, Cu, and Ni. They were almost identical to that of the $Zr_{47.6}Ti_{19.9}Cu_{15.1}Ni_{17.4}$ target based on the EDS chemical composition. From the viewpoint of brazing application, it was noteworthy that the multi-component alloy filler could be coated with an equivalent target alloy composition by simple sputtering.

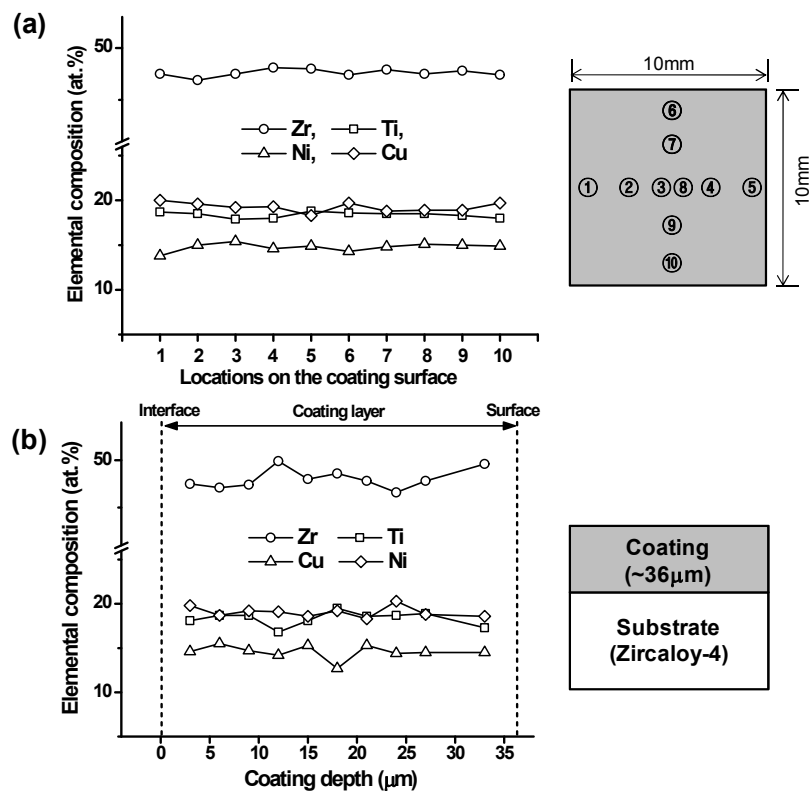


Figure 4 (a) EDS chemical compositions taken from a 10 mm × 10 mm square surface area and (b) the ones from the cross-section of the coating with the thickness of 36 μm

3. Structure of the brazed joints

Figure 5 shows the optical microscope (OM) images for the Zircaloy-4 joints, which were brazed for 10 min at different temperatures using Fe-2, Al-2, and Ni-1 amorphous sputter coatings, respectively [2-4]. In this case, the base metals were hot-rolled and annealed rectangular Zircaloy-4

blocks with dimensions of 10 mm × 13 mm × 26 mm. Regardless of the filler compositions, two distinctive zones, specifically named a dendritic growth zone (D) and a segregated center zone (S), respectively, were produced in the joints brazed at relatively low temperatures (Figures 5(a), (c), and (e)). When the brazing temperatures increased, however, the segregated center zones completely disappeared from the joints by forming fully coarse dendritic structures (Figures 5(b), (d), and (f)).

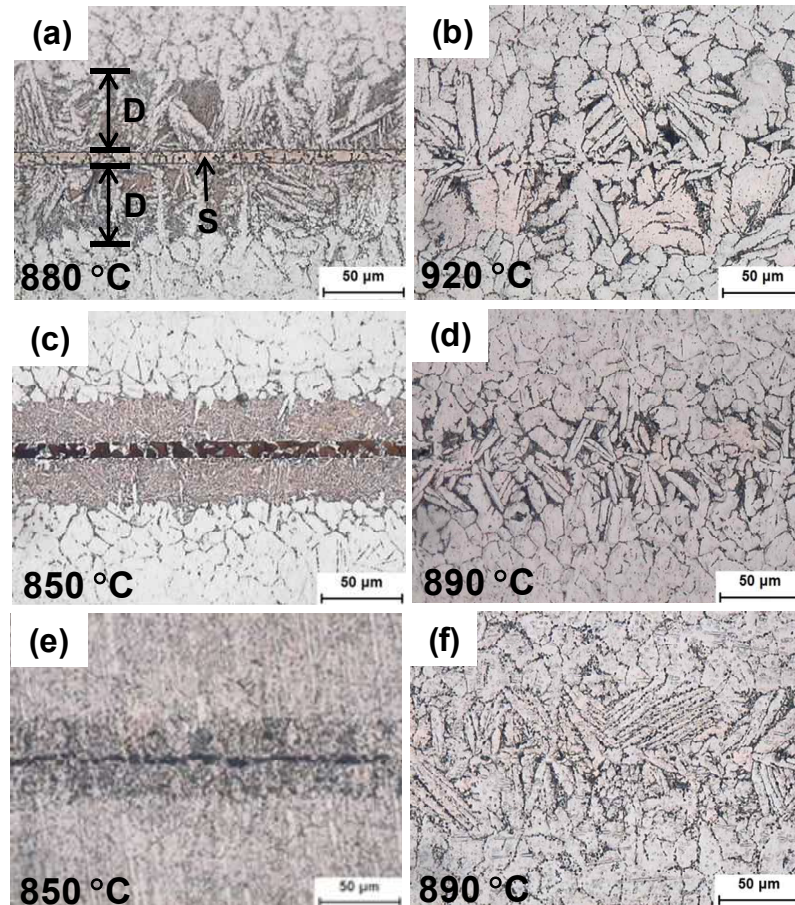


Figure 5 OM images of the Zircaloy-4 joints brazed at different temperatures for 10 min using (a)-(b) Fe-2, (c)-(d) Al-2, and (e)-(f) Ni-1 amorphous sputter coatings

Based on the observed microstructural features, the structural evolution of the Zircaloy-4 joints brazed by Zr-based amorphous sputter coatings can be explained by isothermal solidification through the diffusion reaction between the molten filler and Zircaloy-4 base metal [2-4]. Upon heating to the brazing temperature (850 to 920 °C), a thin liquid layer formed because the melting point of the filler metal used was exceeded. Just after the filler metal began to melt, the Zircaloy-4 base metal dissolved rapidly by the molten filler. As a result, the molten filler in the vicinity of the

Zircaloy-4 base metal became richer in Zr. Such a compositional change at the solid/liquid interface initiated an isothermal solidification of the Zr-rich molten filler. The primarily solidified phase was α -Zr rather than β -Zr because the brazing temperature (850 to 920 °C) did not go much beyond the α - β transformation temperature of the pure Zr (863 °C), where the α - β transition kinetics was very sluggish.

From Figure 5, it was noted that the isothermally solidified α -Zr phase grew into the joints with a dendritic structure, which is a typical growth morphology during alloy solidification containing solute atoms. When these α -Zr dendrites nucleated to grow into the joints, excessive Cu, Fe and Ni elements beyond their solubility in α -Zr were expelled from the growing α -Zr phase. According to the binary phase diagrams, the solubility of Cu, Fe and Ni in α -Zr is almost negligible, and thus these elements were saturated at an interdendritic region. Furthermore, this interdendritic region was acted as a primary atomic path for the outward diffusion of the solute elements, thereby being enriched more with the Cu, Fe and Ni elements. As a result, transformed β -Zr phase with a higher content of Cu, Fe and Ni formed at an interdendritic region, as Cu, Fe and Ni are β -Zr stabilizers. Finally, these interdendritic β -Zr phase was decomposed into fine lamellar α -Zr and γ phases by the eutectoid reaction of β -Zr $\rightarrow$ α -Zr + γ at the subsequent cooling stage, as noted from the Zr-X (X: Cu, Fe, and Ni) binary phase diagrams.

Since such isothermal solidification of the molten filler to form the α -Zr was accompanied by a large compositional change, a considerable amount of the filler elements (Ti, Cu, Fe, Ni, and Al), which were employed as a melting point depressant (MPD) in this study, should be taken away from the solidification front into the growing α -Zr and base metal. It was deduced that the atomic transport of these solute elements was dependent on their solubility in α -Zr, i.e., Ti is completely soluble with Zr and Al is slightly soluble in α -Zr, but the others have almost a negligible solubility in α -Zr based on the binary phase diagrams. Accordingly, the amount of Cu, Fe and Ni transported away toward the base metal was considered to be highly limited compared to that of Ti and Al, leading to a segregation of the supersaturated Cu, Fe and Ni in the central zones. For this reason, the central zones were compositionally preferable to be crystallized into the (Cu,Fe,Ni)-rich intermetallics such as a Zr_2Ni or Zr_2Fe phase ('S' in Figure 5).

There was no doubt that a homogenization of the joints including a disappearance of the segregated center zones was rate-controlled by the diffusion of the filler elements into the isothermally solidified Zr phases and Zircaloy-4 base metal. The sluggish homogenization at relatively low brazing temperatures resulted in the continuous formation of the central segregated phases (Figures 5(a), (c), and (e)), while these segregated phases were completely eliminated at higher brazing temperatures owing to an increased diffusion rate of filler elements (Figures 5(b), (d), and (f)). This enhanced diffusion also attenuated the concentration of the β -Zr stabilizers (Cu, Fe, and Ni) in the joints, and thus the β -Zr area, which subsequently transformed into a α -Zr + γ lamellar structure upon cooling, diminished considerably with an increase in the brazing temperatures, as shown in Figures 5(b), (d), and (f). Consequently, quite homogeneous joints were obtained as shown in the SEM images (Figure 6), which were dominated by the coarse dendritic structure of the α -Zr phase slightly holding the two-phase lamellar region of the α -Zr + γ phases.

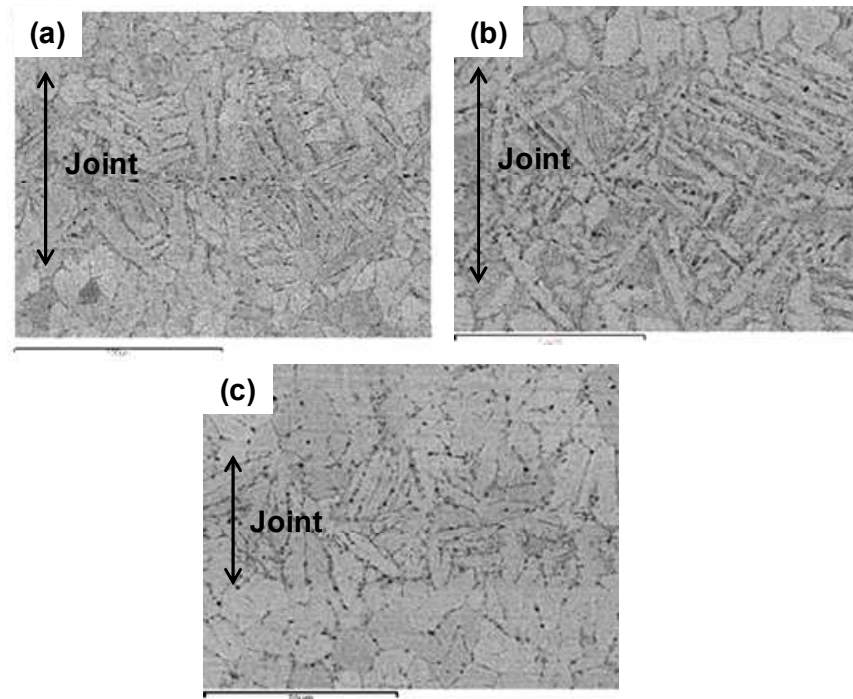


Figure 6 SEM images of the homogenous joints brazed by (a) Fe-2, (b) Al-2, and (c) Ni-1 amorphous sputter coatings

4. Properties of the brazed joints

4.1 Bonding strength of the joints

Figure 7(a) shows the stress-strain curves obtained by tensile tests at elevated temperatures (100 to 400 °C) as well as at room temperature for the samples brazed at 890 °C for 10 min using an Al-2 amorphous sputter coating (joint structure of Figure 5(d)). Analogous to the results of the bulk Zircaloy-4 (Figure 7(b)), fully developed stress-strain curves were obtained regardless of the testing temperatures, indicating that a fracturing did not occur in the joint areas, but in the base metal with a considerable plastic deformation. This can be clearly seen in the fracture images of the tested samples in Figure 8, where the joint areas remained stable. It is obvious that the tensile strengths presented in 7(a) are those for the base metal; moreover, the bonding strengths of the joints were higher than those of the bulk Zircaloy-4. In our studies [2-4], the detrimental intermetallic phases were eliminated properly from all the investigated joints by the controlled isothermal solidification during brazing, as shown in Figure 6. Moreover, the resultant joints were hardened by not only the solute atoms coming from the BFM but also by the interdendritic second phases (γ phases), thereby remaining quite stable after the tensile tests. All these results signified an excellent durability of the present joints at a high operating temperature of a PHWR (250 to 350 °C).

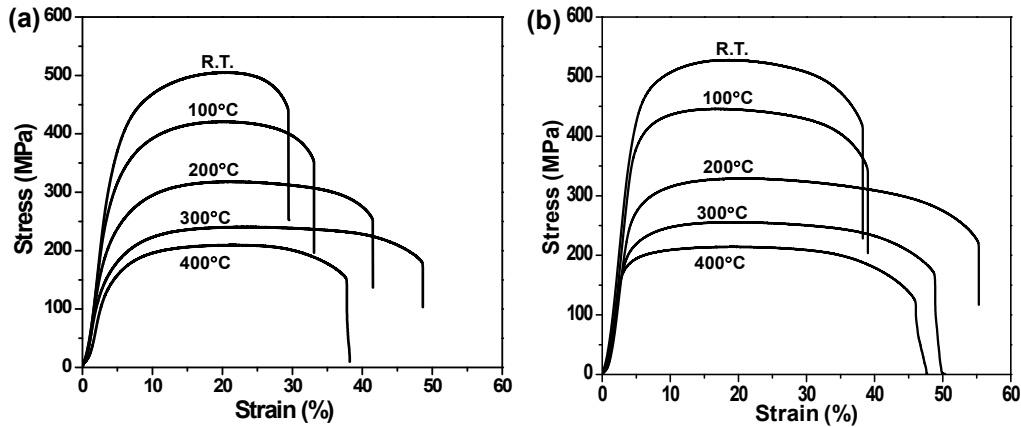


Figure 7 Stress-strain curves obtained by tensile tests at elevated temperatures as well as at room temperature (a) for the samples brazed at 890 °C for 10 min using an Al-2 amorphous sputter coating (joint structure of Figure 5(d)), and (b) for the bulk Zircaloy-4

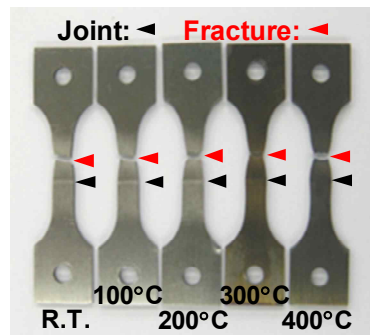


Figure 8 Fractured samples brazed by an Al-2 amorphous sputter coating after the tensile tests

4.2 Corrosion resistance of the joints

In order to investigate the corrosion resistance of the Zircaloy-4 joints, the experimental joints were prepared using ribbon-type filler metals with the same compositions as the Zr-based amorphous sputter coatings in Table 1. For comparison, an additional joint was brazed at 1050 °C for 20 s using a $Zr_{63}Be_{37}$ amorphous alloy ribbon as an alternative to the conventional joint brazed by pure Be [3]. Then the prepared specimens were tested in autoclave with 360 °C saturated water according to ASTM G2 specification.

In contrast with the tensile properties in Section 4.1, the corrosion resistance of the joints was sensitively affected by the compositions of the applied filler metals. Some elements in the filler metals caused the selective leaching in the joint area, but the others showed little effect on the

corrosion resistance of the brazed joints. Now, we are investigating the detailed effect of each element in the filler metals on the corrosion resistance of the brazed joints to optimize the filler composition for brazing Zircaloy-4 in CANDU fuel bundle manufacture.

Figure 9 shows the corrosion rate of the joined Zircaloy-4 specimen brazed by one of the optimized Zr-based amorphous filler metals together with the results of the joined specimen brazed by the $Zr_{63}Be_{37}$ amorphous alloy ribbon as well as the bulk Zircaloy-4. The results indicate that the corrosion rate of the present joined specimen was almost same as that of the bulk Zircaloy-4, and even lower than that of the specimen brazed by the $Zr_{63}Be_{37}$ filler metal. Furthermore, the present joint remained quite stable after the corrosion test in autoclave as shown in Figure 10(a), while the selective corrosion was observed clearly in the conventional joint based by the $Zr_{63}Be_{37}$ filler metal (Figure 10(b)). All these results demonstrated an excellent corrosion resistance of the present joints in a PHWR operating environment.

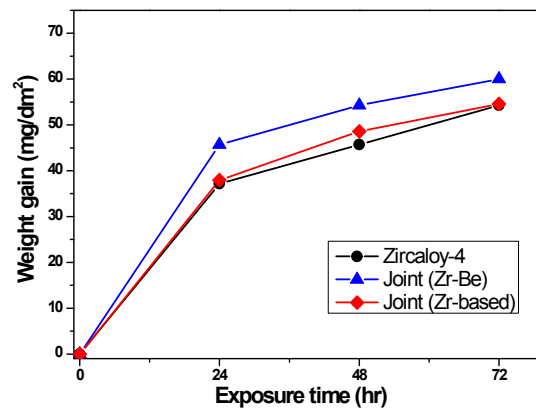


Figure 9 Weight gains of the brazed specimens together with the result of the bulk Zircaloy-4

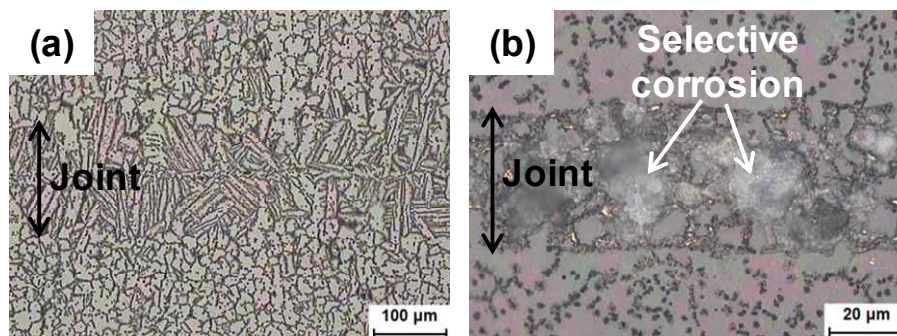


Figure 10 OM images of the joints brazed (a) by the Zr-based multi-component filler metal, and (b) by the $Zr_{63}Be_{37}$ filler metal after the corrosion tests in autoclave

5. Prototype manufacture of CANDU fuel rods

Based on the fundamental studies above, we tried to braze the appendages onto the cladding tubes using the Zr-based amorphous sputter coatings for CANDU fuel rod manufacture. As shown in Figure 11, a coating layer of Zr-based multi-component amorphous alloys was applied to a Zircaloy-4 strip by sputtering technique and appendages were punched from the sputter-coated strip. During punching, any flakes of the coating layer were not generated, since the sputter coating layer was strongly held to the Zircaloy-4 strip. Then the cladding was assembled by tack-welding the sputter-coated appendages in position on the tube. Once the appendages were tacked in place, the joints were finally brazed by heating the tube, under vacuum or inert Ar gas, to a predetermined temperature. Brazing conditions were set up based on the standard fuel fabrication process used at KEPCO NF in Republic of Korea. The result was quite promising, as such that the appendages were successfully brazed without any defects such as pore or void in the entire joint area (Figure 11). In some brazing conditions, however, a considerable amount of pores were generated, and the further study is necessary to find the optimum brazing conditions when using the Zr-based amorphous sputter coatings as a brazing filler.

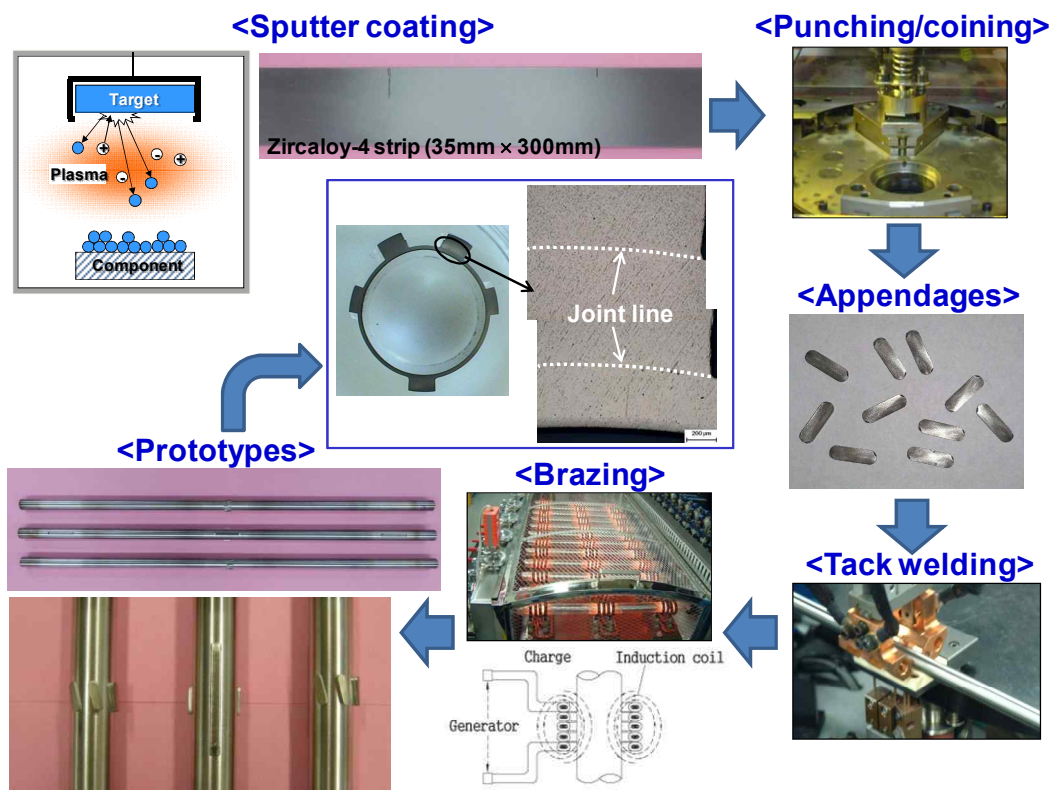


Figure 11 Brazing procedures using the Zr-based amorphous sputter coatings for prototype manufacture of CANDU fuel rods

6. Conclusions

This paper provided a summary of our progress in Zircaloy-4 brazing using Zr-based amorphous sputter coatings for CANDU fuel bundle manufacture. It was noteworthy that the homogeneous and amorphous-structured Zr-based coatings with low melting temperatures below 900 °C were obtained by sputtering the multi-component crystalline bulk targets. Together with the compositions nearly consistent with those of the targets, the sputter coatings were highly uniform in elemental composition distributions. In the application of the Zr-based amorphous sputter coatings for Zircaloy-4 brazing, the strengths of the resultant joints at room temperature, as well as at elevated temperatures (up to 400 °C), were high enough to cause yielding and fracture in the base Zircaloy-4. Furthermore, the corrosion resistance of the present joints was higher than that of the conventional joint brazed by the Zr-Be filler, and even comparable to that of the bulk Zircaloy-4. By applying the Zr-based amorphous sputter coatings, the real appendages were joined to the fuel cladding tubes using the standard CANDU fuel brazing process, and the result was quite promising, as such that the appendages were successfully brazed without any defects such as pore or void in the entire joint area.

The present investigation showed that the Be-free and Zr-based multi-component amorphous sputter coatings can offer great potential for brazing and manufacturing a Zircaloy-4 CANDU fuel bundle system. Nevertheless, several issues should be further addressed for the actual application, such as an irradiation resistance of the joints, an effect of the filler elements on the neutron efficiency, a possibility of hydrogen uptake, a determination of optimum brazing conditions, and an economics of the new process.

7. References

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