技術論文

비정질 이원계 합금 Zr-Be 용가재를 이용한 지르칼로이-4의 브레이징 타당성 검토

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A Feasibility Study on the Brazing of Zircaloy-4 with Zr-Be Binary Amorphous Filler Metals

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Key Words : Binary amorphous filler metals(이원계 비정질 용가재), Zircaloy-4(지르칼로이-4), Eutectic composition(공정조성), Physical vapor deposition, PVD(물리증착), Hypo-eutectic composition(아공정조성), Hyper-eutectic composition(과공정조성), Corrosion resistance(내식성), Microstructure(미세조직), Dendritic structure(수지상정조직)

Abstract

An attempt was made in this study to investigate the brazing characteristics of Zr-Be binary amorphous alloys for the development of a new brazing filler metal for joining Zircaloy-4 nuclear fuel cladding tubes. This study was also aimed at the feasibility study of rapidly solidified amorphous alloys to substitute the conventional physical vapor-deposited(PVD) metallic beryllium.

The Zr_{1-x} Be_x($0.3 \leq x \leq 0.5$) binary amorphous alloys were produced in the ribbon form by the melt-spinning method. It was confirmed by x-ray diffraction that the ribbons were amorphous. The amorphous alloys were used to join bearing pads on Zircaloy-4 nuclear fuel cladding tubes. Using Zr-Be amorphous alloys as filler metals, it was found that the reduction in the tube wall thickness caused by erosion was prevented. Especially, in the case of using $Zr_{0.65}Be_{0.35}$ and $Zr_{0.7}Be_{0.3}$ amorphous alloys, the smooth and spherical primary α-Zr particles appeared in the brazed layer, which was the most desirable microstructure from the corrosion-resistance standpoint.

1. Introduction

In the manufacturing process of HWR(Heavy Water Reactor) fuel bundles for Wolsung type nuclear power plant, various components such as spacer and bearing pads are joined on the surface of Zircaloy-4 cladding tubes by brazing process.[1] At present, the metallic beryllium is coated on the surface of Zircaloy-4 components by the physical vapor deposition(PVD), in which the coated metallic beryllium is used as

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a brazing filler metal.[2] However, in the process of deposition of metallic beryllium on the components, a somewhat complicated PVD process for physical protection is required due to the chemical toxicity of beryllium vapor.[3] In addition, the brazement made by the metallic beryllium with PVD process results in the reduction of the tube wall thickness and difficulty of microstructural control due to the nature of diffusion brazing.[4,5] The zirconium-beryllium(Zr-Be) binary crystalline alloys which are being used as brazing filler metals have some shortcomings such as brittleness and difficulty in handling in the process of brazing and cause the unsound brazing.[6] Therefore, other filler metals such as Zr-Be amorphous alloys should be developed to substitute for the metallic beryllium. Above all, the Zr-Be alloy has an eutectic composition (Be=35a/o), so that it has a low melting temperature and the good amorphous formability.[7]

There have been numerous studies on the applications of amorphous alloys for brazing filler metals because the rapidly solidified amorphous alloys offer the superior chemical and microstructural homogeneity.[8] In brazing, the amorphous filler metals are put as an interlayer between the base metals. This can not only eliminate the dependence on capillary action to convey filler metal throughout the joint areas but also prevent the erosion of the base metals.[9]

In this study, the joints brazed by using PVD Be metal and Zr-Be amorphous alloys are compared from the microstructural standpoints. Also, it is hoped that the Zr-Be amorphous alloys are applicable to the brazing of Zircaloy-4 and overcome the shortcomings caused by the conventional PVD beryllium metals.

2. Experimental

Metallic beryllium fillers made by PVD and $Zr_{1-x}Be_x$(x=0.3, 0.35, 0.4, 0.45 and 0.5) amorphous alloys were used as filler metals. They were prepared from materials with 99.9w/o purity by means of arc-melting under an inert atmosphere of argon. These alloys were melted three times for homogeneity. These were from hypo-eutectic to hyper-eutectic composition of Zr-Be binary alloy system.

Amorphous ribbons were prepared by the melt-spinning method in a low pressure of argon. The alloys were heated to about 1000℃ (above the corresponding liquidus temperature) in a quartz tube by a high frequency induction heating method and injected onto the copper wheel by the argon pressure of 0.7 atm, in which the wheel turned at a tangential speed of 32m/sec in argon atmosphere to prevent ribbons from oxidation. The thickness and width of the ribbons were about 40㎛ and about 2mm, respectively.

After the amorphous ribbon was located between a bearing pad (2.5×30×1.5mm) and a Zircaloy-4 cladding tube of 0.4mm in thickness and 13mm in diameter, the pad was tacked by a spot welder. And then brazing was carried out in the 10^{-5} torr atmosphere at 1050 ℃ for 20 seconds.

The amorphization of these ribbons was examined by an x-ray diffractometer (RIGAKUD/MAX-ⅢC) with Cu-Kα radiation and by a transmission electron microscopy (TEM:Phillips CM 20). The microstructures of the brazed layer were examined by optical and scanning electron microscopies.

3. Results and discussion

The x-ray diffraction(XRD) patterns of Zr-Be ribbons are shown in Figure 1. There are no distinguishable peaks in these patterns over all compositions except broad peaks in the vicinity of 36°. The TEM diffraction pattern of the ribbons shows the diffuse halo-ring as shown in Figure 2. From these, it is confirmed that

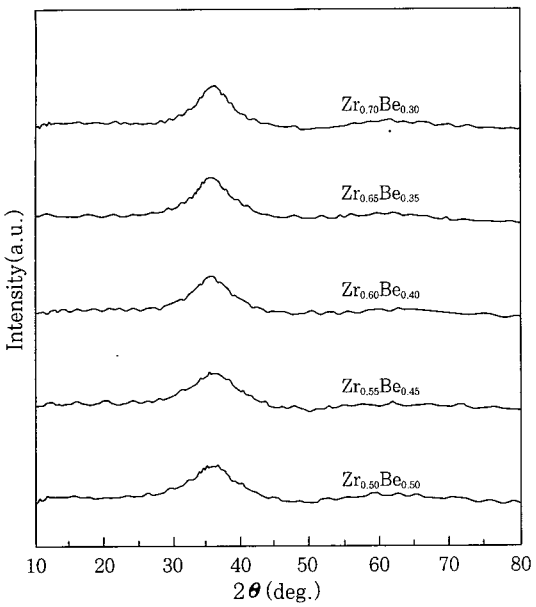


Fig. 1 X-ray diffraction patterns of Zr-Be amorphous alloys.

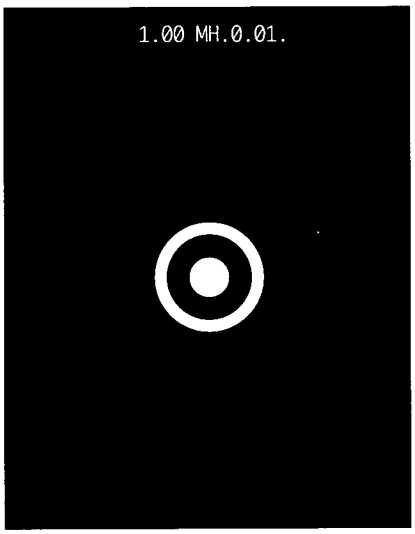


Fig. 2 TEM diffraction pattern of Zr-Be amorphous alloys

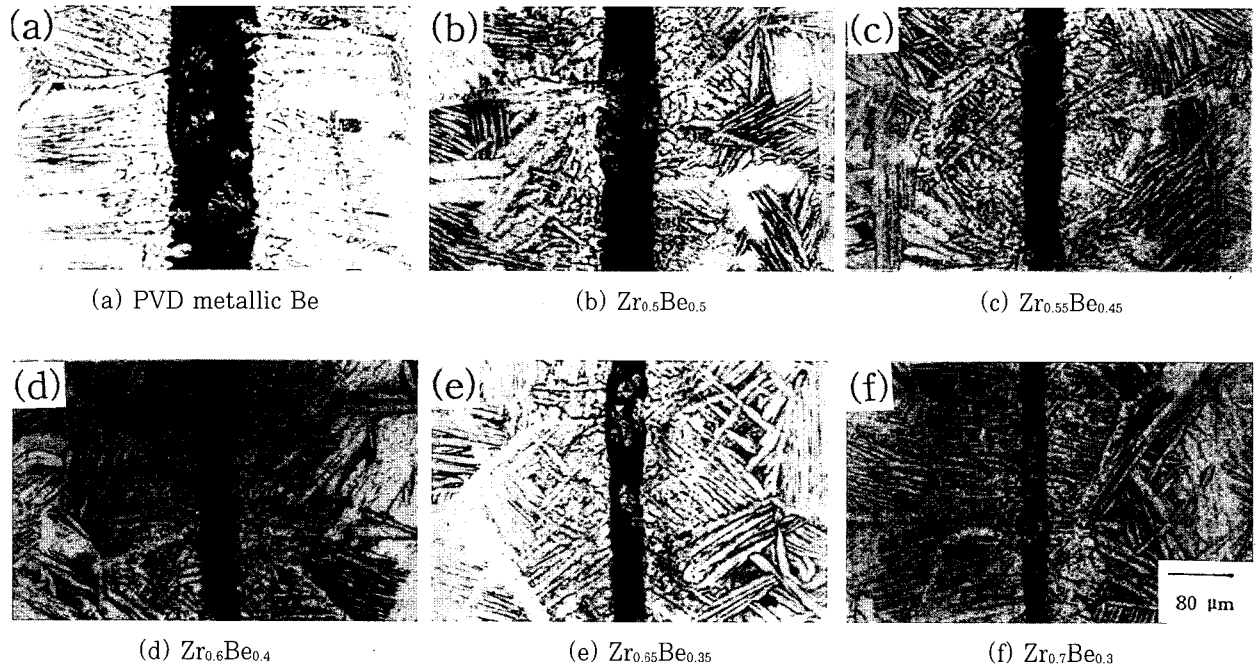
the ribbons are amorphous alloys.

Bearing pads were brazed on the surface of cladding tube with $Zr_{1-x}Be_x(0.3 \leq x \leq 0.5)$ amorphous ribbons of 40 μm thick as filler metals for 20 seconds at 1050℃. Figures 3 and 4 are the microstructures of the brazed layers. For the comparison, the microstructure of layers brazed with PVD metallic beryllium to join bearing pads on the Zircaloy-4 cladding tube are also shown in Figures 3 and 4.

The width of brazed layer with the PVD metallic Be of 40μm thick is about 80μm as shown in Figures 3(a) and 4(a). Although the melting temperatures of Be and Zr are 1289℃ and 1855℃, respectively, the eutectic temperature of the Zr-Be is 975℃ from the Zr-Be phase diagram as shown in Figure 5.[10] As the composition of the Zircaloy-4 cladding tube in contact with the PVD Be reaches to near the eutectic point by the diffusion of Be atoms into the tube, the alloys in the contact zone which has near the eutectic composition begin to melt into the liquid phase at 1050℃. The liquid fills up the brazing gap and solidifies by cooling. Solidification of the melt starts at the cladding tube wall and constructs the dendritic structure observed by light and scanning electron micrographs as shown in Figures 4(a) and 6.

On the other hand, in the case of the Zr-Be amorphous ribbons, there was no remarkable increase of the width in the brazed layer compared with the original thickness of the filler metals. Therefore, it can be inferred that the erosion of the cladding tube wall can be prevented by application of the Zr-Be amorphous filler metals in the brazing process compared with the PVD metallic Be[2]. There was only a little difference in the width of the brazed layer depending on the content of beryllium in the amorphous ribbons. With increasing the content of Be in the amorphous alloys, the concentration gradient of Be between the ribbon and the cladding tube became larger and the diffusion of Be atoms to the wall would be promoted. Therefore, in the case of the Zr-Be amorphous ribbons with relatively large amount of beryllium, the thickness of the brazed layer was relatively thick as shown in Figure 3.

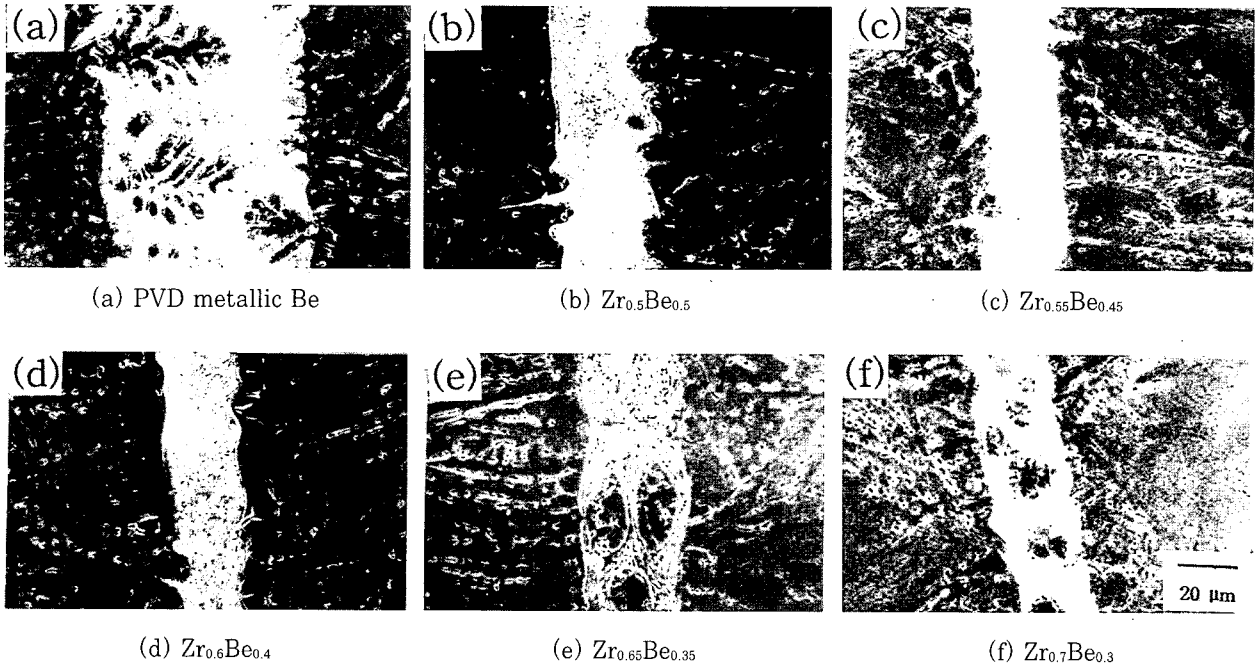
Brazed interface layers consisted of matrix and primary particles. According to the equilibrium phase diagram of Zr-Be binary system,[11] island particles in the eutectic bed were primary α-Zr for the hyper-eutectic composition as shown in Figure 7(a) and are



(a) PVD metallic Be (b) $Zr_{0.5}Be_{0.5}$ (c) $Zr_{0.55}Be_{0.45}$

(d) $Zr_{0.6}Be_{0.4}$ (e) $Zr_{0.55}Be_{0.35}$ (f) $Zr_{0.7}Be_{0.3}$

Fig. 3 Brazed layers of Zircaloy-4 by light microscopy



(a) PVD metallic Be (b) $Zr_{0.5}Be_{0.5}$ (c) $Zr_{0.55}Be_{0.45}$

(d) $Zr_{0.6}Be_{0.4}$ (e) $Zr_{0.65}Be_{0.35}$ (f) $Zr_{0.7}Be_{0.3}$

Fig. 4 Brazed layers of Zircaloy-4 by scanning electron microscopy

primary $ZrBe_2$ for the hypo-eutectic compositions as shown in Figure 7(b), respectively. When the PVD metallic Be was used as the filler material, there were well developed dendritic structures in the brazed layer as stated earlier.

In the case of hypo-eutectic compositional ribbons which contained relatively large amount of Be, the interface between the cladding tube and the brazed layer was rough and developed the dendritic structure in it. The dendritic structure growed from the interface into the brazed layer as shown in Figures 3(b), (c) and (d). The diffusion of beryllium atoms

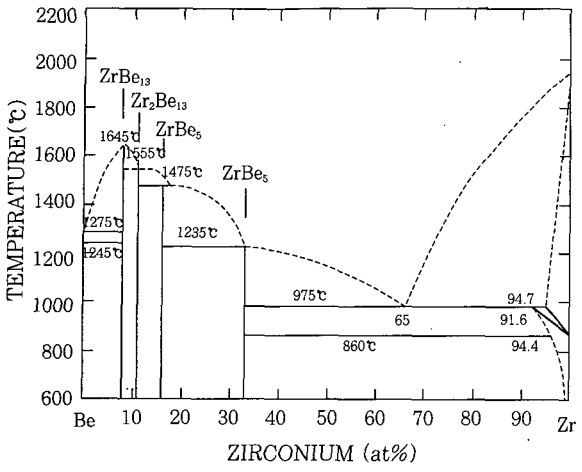


Fig. 5 Phase diagram of the zirconium-beryllium system.

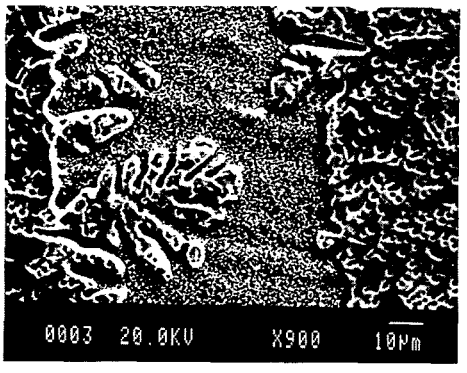
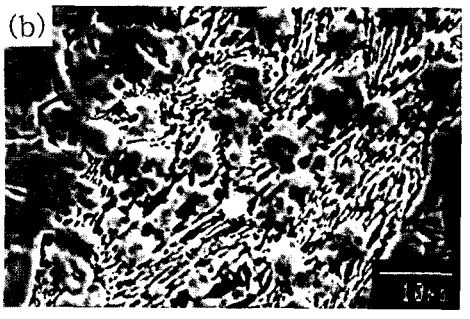


Fig. 6 SEM micrograph of brazed layer with PVD metallic beryllium.

toward the Zircaloy caused the formation of liquid alloy at 1050℃. As the solidification proceeded, the equilibrium primary particles would be produced from the liquid alloy in the brazed gap by nucleation at the interfaces of cladding tube/liquid and growed into the brazed gap.

By using the amorphous alloys with the hyper-eutectic compositions as filler materials, the smooth interface and spherical particles were formed in the eutectic bed as shown in Figures 3(e) and 3(f), as well as Figures 4(e) and 4(f). The thickness of the brazed layers of amorphous alloys with hyper-eutectic compositions was smaller than that of the brazed layers with hypo-eutectic compositions. Therefore, the decrease in the thickness of the cladding tube wall by brazing could be reduced by using the amorphous Zr-Be binary alloys with hyper-eutectic composition. In the case of $Zr_{0.7}Be_{0.3}$ and $Zr_{0.65}$ $Be_{0.35}$ amorphous alloys with hyper-eutectic compositions, the liquid phase was formed by melting the amorphous filler metals at 1050℃.

(a) $Zr_{0.65}Be_{0.35}$



(b) $Zr_{0.7}Be_{0.3}$

Fig. 7 SEM micrograph of brazed layers with Zr-Be amorphous alloys

From the microstructural evolution in the brazed joints with changing of the composition of in amorphous filler materials of $Zr_{1-x}Be_x(0.3 \leq x \leq 0.5)$, it was found that the morphology of brazed layers could be easily controlled without the change of other brazing parameters. Concerning the corrosion behavior of brazed layers, it was reported that the corrosion rate of $ZrBe_2$ was faster than that of α-Zr.[12] It could be drawn from this that the corrosion resistance of brazed joints of Zircaloy-4 cladding tubes would be enhanced if the brazed layer had primary α-Zr particles in the eutectic bed. Based on the results, it can be suggested that the $Zr_{0.7}Be_{0.3}$ amorphous alloy is the best filler metal for the joining of Zircaloy-4 nuclear fuel cladding tubes from the corrosion resistance standpoint.

4. Conclusions

$Zr_{1-x}Be_x$ binary amorphous alloys in the composition range of $0.3 \leq x \leq 0.5$ were produced by the melt-spinning method. The ribbons were amorphous alloys. The microstructure and brazing characteristics of brazed layers by using amorphous alloys were compared with those of brazed layers by using the conventional PVD Be metal.

The thickness of the brazed layer with the Zr-Be amorphous alloy was thinner than that of the brazed layer with the conventional PVD Be metal. In the case of using hypo-eutectic compositions of $Zr_{0.55}Be_{0.45}$ and $Zr_{0.5}Be_{0.5}$ alloys which contained relatively large amount of Be, the rough interface between the cladding tube and the brazed layer appeared and the dendritic structure grew from the interface into the brazed layer. In the meantime, in the hyper-eutectic compositional amorphous alloys such as $Zr_{0.7}Be_{0.3}$ and $Zr_{0.65}Be_{0.35}$, the smooth interface and spherical primary particles were formed in the eutectic bed. Morphologies of brazed layers could be controlled by changing the composition of amorphous filler metals. Based on this study, it seemed that the $Zr_{0.7}Be_{0.3}$ amorphous alloy was the most probable candidate for joining of Zircaloy-4 from the corrosion resistance standpoint.

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