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Compositional effects of Zr-rich multi-component brazing alloys on the corrosion of Zr alloy joints

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ABSTRACT

High-temperature corrosion of Zircaloy-4 joints brazed by various Zr(Ti)–Cu–Ni-based multi-component alloys was studied to draw up the compositional guideline of the brazing alloy. From the compositional and microstructural effects of the joints on the corrosion, there was strong evidence for galvanic corrosion susceptibility of primary α-Zr grains (usually Sn-containing) owing to alloying of nobler Ti and its concentration gradient in a joint, inducing a microgalvanic corrosion. The Ti concentration for corrosion inhibition was proposed to be less than about 1.0 at.%. The results clearly demonstrate that the exclusion of Ti is needed for the use of Zr-rich multi-component brazing alloys.

1. Introduction

Owing to the possession of deep eutectics characterized by considerably low-melting-point and narrow-melting-range, multi-component amorphous alloys or metallic glasses have attracted increasing attention for their potential applications to brazing alloys [1,2]. This is greatly encouraged by recent developments of a wide variety of metallic glass forming compositions (e.g. Zr-, Ti-, Cu-, Fe-, Pd-, Ni- and Co-based systems) [3], making it possible to join various structural or functional alloys at temperatures much lower than their original melting points by a proper choice of chemically compatible alloy system.

To date, the most widely investigated brazing alloy systems are Zr-rich ternary and quaternary alloys in which Ti is generally contained and Cu and/or Ni are added as a melting point depressant [1,4]. From Ti–Cu, Ti–Ni, Zr–Cu, and Zr–Ni binary eutectic systems, the extended Zr–Ti–Ni [5] and Zr–Ti–Cu [6] ternary systems with lower eutectic and peritectic points have been developed for use as brazing alloys. On this basis, more advanced Zr–Ti–Cu–Ni quaternary systems have been developed with a recent discovery of novel quaternary eutectic points where the melting point decreases to about 800 °C [7]. Because of their excellent chemical compatibilities with Ti and Zr, investigations have been conducted on the brazing of Ti-based alloys for aerospace, nuclear and chemical plant applications [1,6–8], and are recently extending toward the brazing of Zr-based alloys for nuclear applications [9–11]. One of the main purposes of such activities must be to improve the mechanical properties of Ti- and Zr-alloy joints, especially for use in high-temperature environments.

In spite of good mechanical properties achieved, however, of more serious concern might be the corrosion performance of the joints, which should operate under highly corrosive conditions, since the joints usually remain very susceptible to corrosion. As this is a very critical issue in many nuclear and chemical plant environments [12,13], the foremost criterion is that brazed joints must possess corrosion resistance comparable to the level of the virgin base metals. Nevertheless, most brazing studies reveal with great consistency that the evaluation and understanding of structure-strength characteristics of bonded joints have been the main research topic along with routine processes [6,8–11], leaving such a big issue out of scope. Virtually, the corrosion properties of the joints brazed by these promising multi-component alloys are little known and compositional guidelines of brazing alloys based on the corrosion resistance remain tenuous.

Presumably, an understanding of the influence of many compositional variants of amorphous brazing alloys on the corrosion behavior of the joints is difficult owing to the compositional and microstructural heterogeneities of the resulting joints, caused by complex reactions among the brazing alloy constituents and base metal [14,15]. For instance, the use of Zr-rich multi-component brazing alloys with compositions different from the base metal

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may lead to an electrochemical potential difference by making some alloying regions in a joint more active or passive. In addition, a multi-phase microstructure may exist with essential alloying elements (e.g. Cu and Ni) partitioning into specific intermetallic compounds (IMCs) owing to their limited solubilities in major Zr [11,16], resulting in local variations of the galvanic corrosion susceptibility [17,18]. Since these structure-related corrosion phenomena are all closely relevant to the intrinsic material property, i.e., the composition of chemistry of the brazing alloy chosen, it is necessary to select candidate brazing alloys on the basis of the probable effects of the alloying constituents on the corrosion resistance.

The research objective of this study is to provide insight into the effects of Zr(Ti)–Cu–Ni-based multi-component brazing alloy systems on the corrosion mechanism of Zr alloy joints, elucidating the relation between the corrosion resistance and the structural and compositional variation of the joints as a function of brazing alloy. Four Zr-rich metallic glass alloys with different alloying compositions in Ti, Cu, and Ni were introduced as brazing alloys, which are ternary $Zr_{43}Ti_{17}Cu_{40}$, $Zr_{55}Ti_{25}Ni_{20}$, and $Zr_{67}Cu_{17}Ni_{16}$, and quaternary $Zr_{50}Ti_{17}Cu_{17}Ni_{16}$. For a base metal, a chemically compatible Zircaloy-4 alloy (1.32Sn–0.22Fe–0.12Cr–bal. Zr in wt.%) was used, which is widely used as nuclear fuel cladding materials in pressurized water reactor environment (temperature 280–350 °C; pressure 10–15 MPa; pH ~6.8; dissolved oxygen <5 ppb; Li ~2.2 ppm; B ~650 ppm). The corrosion characteristics of the joints were examined in high-temperature pressurized water environment. Various model materials simulating the joint phases were also prepared to support discussions of the galvanic corrosion phenomena of the joint.

2. Experimental procedure

2.1. Materials

Zircaloy-4 used as the base material was provided in a hot-rolled and annealed bar (ATI Wah Chang, USA, ASTM B351) and its yield and tensile strengths were 380 MPa and 507 MPa, respectively, according to the ASTM E8 specification at room temperature. The samples for brazing were machined into rectangular cubes with dimensions of 10 mm × 10 mm × 15 mm, and their surfaces to be joined were abraded using SiC papers of 800 and 2000 grit and cleaned ultrasonically in ethanol and acetone.

The brazing alloys were in the form of ribbons prepared by a melt spinning technique in a quartz crucible under Ar gas, followed by ejection with an excessive Ar pressure of about 40 mbar onto a Cu wheel rotating at a surface speed of 20 m/s in an enclosed chamber with an atmosphere of 200 mbar Ar. The ribbons were 7 mm wide, 8 mm long, and 30 μm thick in a flexible form, and they were cleaned ultrasonically in ethanol and acetone prior to brazing. Their chemical compositions and melting temperatures, i.e. solidus T_S and liquidus T_L, based on a differential scanning calorimetry (DSC; SETARAM Setsys Evo. TG-DSC/DTA), are presented in Table 1.

Table 1
Chemical compositions and melting temperatures of Zr-rich brazing alloys.

Brazing alloy	Composition (at.%)*				T_S (°C)*	T_L (°C)*
	Zr	Ti	Cu	Ni		
Zr–Ti–Cu–Ni	50	17	17	16	795	835
Zr–Ti–Cu	43	17	40	–	828	890
Zr–Ti–Ni	55	25	–	20	795	820
Zr–Cu–Ni	67	–	17	16	915	950

* The accuracy is ±1 at.% for compositions and ±2 °C for temperatures.

2.2. Brazing

An infrared heating technique was used to braze the Zircaloy-4 samples. The chamber was evacuated up to 6.6×10^{-3} Pa and then purged with Ar gas at a flow rate of 4 l/min. The infrared heating then began at a heating rate of 100 °C/min and was isothermally held at a fixed temperature (T_B) for a constant time (t_B), finally followed by cooling at 100 °C/min. During brazing, the Zircaloy-4 samples were compressively loaded at 0.13 MPa.

In this work, a diffusion brazing technique was employed to obtain homogenized joints induced by isothermal solidification at T_B (usually, above T_L), and thus the microstructure and mechanical properties of the joint can resemble those of the base metal. Otherwise, the macro-segregation of unwanted brittle Zr-based IMCs generally formed by a eutectic reaction of the liquid filler negatively affect the final properties of the joints [9,11,16]. Therefore, preliminary brazing studies were undertaken to establish the processing conditions eliminating macro-segregation with regard to four brazing alloys. The optimized brazing conditions were T_B = 960 °C and t_B = 30 min, which were commonly applied for all brazing alloys.

2.3. Structure analysis

The as-joined samples were subjected to chemical etching in a solution of 10 mL HF, 45 mL HNO_3, and 45 mL H_2O for microscopic analyses using an optical microscope (OM; OLYMPUS B202). The detailed phase and compositional properties in a joint, dependent on the chemical composition of brazing alloy, have been characterized using both a field-emission scanning electron microscope (FE-SEM; JEOL, JSM-7000F) coupled with an energy dispersive spectroscope (EDS) with an operating voltage of 20 kV and a spot size of 1 μm and a field-emission transmission electron microscope (FE-TEM; JEOL 2100F) with an EDS operating at 200 kV, including selected area electron diffraction (SAED).

Since diffusion brazing generally produces fine second-phase particles, i.e., IMC, in a joint owing to the limited solubility of alloying elements in Zr [11,16], quantifications of the size and number density of the IMC particles were carried out using a statistical image analysis (iMT, iSolution DT) based on the SEM and TEM micrographs. Particles smaller than 300 nm were determined from TEM results, while the SEM results were used for the larger ones. About 150–920 particles were analyzed for each joint.

2.4. Corrosion tests

For the corrosion test, the brazed samples were machined into rectangular cubes with dimensions of 7 mm × 7 mm × 5 mm. Their surfaces were mirror-polished at up to a 1 μm diamond suspension, and then cleaned in ultrasonic baths using acetone and ethanol. The immersion tests were performed in a static isothermal autoclave operating at 360 °C and 18.6 MPa according to the ASTM G2-88 specifications. The surface morphology for each sample was evaluated using a FE-SEM after the corrosion test. The immersion test was carried out three times for each joint to assure the confidence of the resulting data.

To explore the nature of the galvanic corrosion phenomena of the joints, various model alloys and IMCs simulating the phases present in each joint were prepared using an arc-melting technique. For the electrochemical experiments, the nickel wire was spot-welded to the model alloy samples, which was shielded by a heat-shrinkable polytetrafluoroethylene (PTFE) tubing. Open circuit potential (OCP) measurements (i.e. corrosion potential versus time) were carried out using a two-electrode electrochemical system connected with a multi-channel potentiostat (VMP, Bio-logic)