Available online at www.sciencedirect.com

ScienceDirect

Acta Materialia 88 (2015) 74–82

Acta MATERIALIA

www.elsevier.com/locate/actamat

Reactive air brazing for sealing mixed ionic electronic conducting hollow fibre membranes

Hong Chen,[a] Leijun Li,[b] Raymond Kemps,[a] Bart Michielsen,[a] Marijke Jacobs,[a] Frans Snijkers[a] and Vesna Middelkoop[a,*]

[a]*Flemish Institute for Technological Research – VITO, Boeretang 200, B-2400 Mol, Belgium*
[b]*Department of Chemical and Materials Engineering, University of Alberta, Edmonton T6G 2V4, Canada*

Received 6 November 2014; accepted 17 January 2015

Abstract—Mixed ionic–electronic conducting (MIEC) ceramic membranes and high-temperature alloys are candidate materials for applications in high-temperature gas separation systems and solid oxide fuel cells (SOFCs). Ensuring a gas-tight seal between the components is of paramount importance in the operation of such devices. This paper investigates the wettability and joining of representative ceramic-to-ceramic and ceramic-to-metal components by reactive air brazing (RAB) using Ag–Cu alloys. The correlation of the interfacial reaction (including wettability) to the hermeticity of the joints has been demonstrated by elemental mapping using Electron Probe Micro-Analysis with wavelength dispersive spectrometry (EPMA-WDS). The wettability studies described herein demonstrate that RAB is a reliable method to achieve strong, gas-tight bonding between the dissimilar materials. These are the first reported results of successful air-brazed joints between $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) and $BaCo_{0.4}Fe_{0.4}Zr_{0.2}O_{3-\delta}$ (BCFZ) hollow fibre membranes to FeCrAlloy components using a 4 mol.% Cu in Ag filler metal composition which delivered an impressive runtime of up to 2000 h (for LSCF). It has been demonstrated that these RAB joints are hermetic and resistant to thermal ageing, making them suitable for membrane-based gas-separation applications. Post-operation EPMA-WDS analysis of the microstructures and compositional distribution of the brazed seals has revealed that their performance is largely dependent upon a reaction zone and an interfacial oxide layer adherent to the FeCrAlloy surface.

Keywords: Reactive air brazing; Ceramic-metal interfacial bonding; High-temperature joining and sealing; Gas-separation systems; Mixed ionic–electronic conducting hollow fibre membranes

1. Introduction

High temperature oxygen separation with mixed ionic and electronic conducting (MIEC) membranes is considered a technology with great potential in the pre- and oxy-combustion routes for future energy production from fossil fuels as well as chemical production and solid-state electrochemical applications. To use such membranes in real applications, gas-tight joining of membrane materials has to be achieved under high temperature conditions [1,2]. Examples of MIEC membrane materials include $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, $Ba_{0.5}Sr_{0.5}(Co_{0.8-x}Zr_x)Fe_{0.2}O_{3-\delta}$, $BaCo_{0.4}Fe_{0.4}Zr_{0.2}O_{3-\delta}$ and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (hereafter abbreviated to BSCF, BSCFZ, BCFZ and LSCF respectively). These perovskite structures provide either high oxygen fluxes (typically the Ba-containing ones) or superior stability under operating conditions. The metallic interconnectors and gas containing manifolds of the fuel cell and gas separation systems are made of Cr-containing ferritic or nickel-based alloys.

Various joining technologies have been developed to hermetically seal the interfaces between the ceramic membranes and metallic high-temperature alloys, including glass-sealing [3–5]. welding, active metal brazing, and reactive air brazing. First developed by Kim, Hardy, and Weil, reactive air brazing (RAB) has been identified as one of the most promising methods to meet the requirements for ceramic to metal joining in solid oxide fuel cells (SOFCs) [6–9] Using binary metallic brazing alloys, RAB is conducted in air, so stability issues of ceramics in vacuum or environments are avoided [10].

The joint is usually achieved at temperatures above 900 °C, and is therefore suitable for high temperature service. In order to prevent oxidation in air, a noble metal, such as silver, is used as the major component; a reactive element, such as copper, is used as the second component of the braze alloy to form oxide. Reactive air brazing using Ag–Cu (or Ag–CuO) binary filler metal systems for gas-tight ceramic-to-ceramic and ceramic-to-metal joints at high temperatures have been developed to bond alumina (Al_2O_3) [11,12] yttria-stabilized zirconia (YSZ) [13], LSCF 6 [14], BSCF [15], and stainless steel types such as FeCrAlloy, CroFer-22 APU and NiCrofer 6025 HT [16–18].

* Corresponding author; e-mail: vesna.middelkoop@vito.be

http://dx.doi.org/10.1016/j.actamat.2015.01.029
1359-6462/

The wetting behaviour of Ag–Cu filler metals on BSCF and LSCF membrane materials has already been studied. Kaletsch et al. recently conducted a study of the effects of copper oxide content on the microstructure and mechanical properties of reactive air-brazed BSCF [12]. For the wettability measurements, they used mixed Cu and Ag powder as the braze filler metal and the brazing temperature and time were selected to be 955 °C and 0.1 h, respectively. However, a more comprehensive study of the effects of Cu content would need to include a wider selection of ceramics and adjacent metal components, as well as a wider range of brazing temperature and time. Wetting can be defined as the contact and spreading of a molten brazing material over a solid substrate surface. Good wettability of a material is a prerequisite for ensuring gas-tight joining. This paper outlines the effect of the Ag–Cu braze compositions on the surface wettability for a range of materials of interest to MIEC-based membrane technology but it does not further dwell on the wetting behaviour. It focuses rather on the formation of the characteristic microstructure of selected MIEC ceramic-to-metal joints suited to withstand direct integration into practical devices and their operating conditions. For the purpose of this study LSCF–FeCrAlloy and BCFZ–FeCrAlloy were selected as the model joining systems, with FeCrAlloy as the metal component being relatively inexpensive, commercially available ferritic stainless steel. The current study presents the first account of the development of the RAB joint between the LSCF hollow fibre membrane and FeCrAlloy components and its continuous operation of up to 2000 h. Furthermore, this is the first report of a BCFZ hollow fibre joined with FeCrAlloy connectors using the Ag–Cu filler metal alloys. To the best of the authors' knowledge, there have been no studies on RAB joints between BCFZ membranes, either in a disc or tubular form or as ceramic or metallic components.

2. Experimental procedure

2.1. Materials and brazing procedure

All the perovskite powders were obtained from CerPoTechAS (Norway) except the BSCFZ powder, which was purchased from Treibacher Industrie AG (Austria). FeCrAlloy steel samples were purchased from Resistalloy Trading Ltd. and Crofer 22 APU and NiCrofer 6025 HT were obtained from ThyssenKrup VDM GmbH. Steel compositions are shown in Table 1. 8 wt.% YSZ and Al_2O_3 (97% purity) samples were commercially obtained from MTC Haldenwanger. The ceramic substrates were custom-made discs with diameters between 5 and 12 mm, and thickness of 3–5 mm. The steel substrates were commercially obtained plate with a thickness of 5 mm, prepared as 12 mm × 12 mm squares. Ag–Cu pellets were prepared by mixing analytically pure silver (Ag, purchased from Aldrich) with different mole fractions of pure copper (Cu, purchased from Merck) powder (2%, 4%, 8% 20% and 50%), cold pressed under a hydraulic press to a 0.15–0.20 mm thickness. The LSCF hollow fibre membrane that was brazed to FeCrAlloy hollow cylinders and thermally cycled had a length of 49.17 mm and diameters of $d_{out} = 3{,}24$ mm and $d_{in} = 2{,}46$ mm. The BCFZ hollow fibre membrane brazed to FeCrAlloy hollow cylinders had a length of 49 mm and diameters of $d_{out} = 3.85$ mm and $d_{in} = 3.05$ mm. These FeCrAlloy pieces were further brazed to alumina gas supply tubes for seal leak and membrane permeation testing.

Thin Ag–Cu brazing pellets were placed on the cleaned surfaces of BSCF, BSCFZ, BCFZ, LSCF, 8YSZ, Al_2O_3 discs and steel plates for the wetting experiments. The effect of thermal cycling was studied on LSCF hollow fibres brazed to alumina and FeCrAlloy tubular pieces and BCFZ brazed to FeCrAlloy pieces using Ag - 4 mol.% Cu braze. The brazing was conducted in high temperature furnaces under air atmosphere. The MIEC hollow fibre membranes for hermeticity and thermal cycling tests of the joints were manufactured from the perovskite powders by phase-inversion spinning, followed by sintering as described previously [19]. All the samples described herein were heated at a maximum rate of 300 °C/h up to a desired RAB temperature (selected to be 1020 °C but higher temperatures, 1050 °C, 1080 °C or 1100 °C were also tested). Once this temperature had been reached the samples were held for periods of from 30 min to 3 h to allow the molten braze (Ag–Cu pellet) to reach its equilibrium shape. The wettability samples were then cooled down to room temperature at a rate of 200 °C/h and joint samples were tested for gas-tightness at the temperature range of 750–950 °C. Table 2 provides an overview of the experiments conducted in this study.

2.2. Characterisation

Wettability of a brazing alloy is generally assessed by the contact angle the braze makes with the substrate. In the experiments presented here, contact angles were measured using sessile drop method with contact angle system OCA (DataPhysics Instruments). For a drop (molten pellet) of Ag–Cu braze deposited and spread on the substrate, the macroscopic contact angle is defined as the angle between the tangent to the drop outline at the contact location and the surface line of the solid substrate [20]. Two contact angle measurements were taken for each of the samples and averaged, to ensure the reliability of the results.

Table 1. Composition of metallic alloys used for wetting experiments (wt.%).

	FeCrAlloy	NiCrofer 6025HT	Crofer 22 APU
Fe	Bal.	8–11	Bal.
Cr	22	24–26	22
Ni		Bal.	
Al	5	1.8–2.4	0.5
Mn		0.5	0.6–0.8

Table 2. Summary of experiments.

Substrates	Braze composition (mol.% Cu in Ag)	Experiment
BSCF	20	Reactive wetting
BSCFZ	20	Reactive wetting
BCFZ	4 and 20	Reactive wetting
FeCrAlloy	4 and 20	Non-reactive wetting*
LSCF	4 and 20	Non-reactive wetting
LSCF + Al_2O_3	4	Hermetic joint
LSCF + FeCrAlloy	4	Hermetic joint
BCFZ + FeCrAlloy	4	Hermetic joint

* Wetting behaviour of FeCrAlloy is classified as non-reactive wetting because the wetting of the brazing alloys onto the substrate does not occur.