

## **EVALUATION OF IRON ALUMINIDES FOR HOT GAS FILTER APPLICATIONS**

P. F. Tortorelli (tortorellipf@ornl.gov; 423-574-5119)  
E. Lara-Curzio (laracurzioe@ornl.gov; 423-574-1749)  
C. G. McKamey (mckameycg@ornl.gov; 423-574-6917)  
B. A. Pint (pintba@ornl.gov; 423-574-2897)  
I. G. Wright (wrightig@ornl.gov; 423-574-4451)  
R. R. Judkins (judkinsrr@ornl.gov, 423-574-4572)  
Oak Ridge National Laboratory  
P. O. Box 2008  
Oak Ridge, Tennessee, U. S. A. 37831

### **INTRODUCTION**

Hot-gas filtration is a key enabling technology for advanced coal-based power plants using integrated gasification combined cycles (IGCC) and pressurized fluidized bed combustors (PFBC). The use of filters to remove particles from hot gases produced by coal gasification or combustion is vital to achieving the efficiency and emission goals of these systems as they protect the gas turbine and other downstream components from degradation by erosion, corrosion, or deposition. Consequently, reliability and durability of the hot-gas filtering devices are of special importance.

Materials used in hot-gas filters are required to withstand prolonged exposure to corrosive, high-temperature gaseous environments as well as to condensable vapors and solid species, some of which may have the potential for localized interaction with the filter material after extended times. The gas streams may be oxidizing (PFBCs) or reducing, in which the sulfur species are largely in the form of  $H_2S$  (in the case of the product gas from IGCC processes or from carbonizers). Degradation of metallic filter elements has been observed under oxidizing, sulfidizing, and/or carburizing conditions and acts as a driving force for the development of ceramic hot-gas filters, particularly for the higher temperatures associated with advanced gasification and combustion designs. However, iron aluminides can also be considered for such applications because they offer the reliability advantages of metallic filters and typically have good to exceptional high-temperature corrosion resistance in a variety of sulfur-bearing environments relevant to coal-derived energy production systems.<sup>1-11</sup>

In most cases, the results from laboratory corrosion studies with iron aluminides have been directly compared to those of austenitic stainless steels (particularly type 310). With respect to such alloys, iron aluminides with greater than about 20 at.% Al show exceptional corrosion resistance in coal-gasification environments (high  $p_{S_2}$ , low  $p_{O_2}$ , and sulfur present as  $H_2S$ ).<sup>1,3,5-11</sup> Alloys based on  $Fe_3Al$  also show better corrosion behavior under some coal-combustion-gas conditions (high  $p_{O_2}$ , low  $p_{S_2}$ , and sulfur as  $SO_2$ )<sup>2,4,7,8</sup> and in the presence of  $CaSO_4$  and ash deposits<sup>4,7</sup> up to at least 900°C. However, relative differences with stainless steels are not as pronounced as in the gasification environment. Therefore, because of their corrosion resistance in such environments,  $Fe_3Al$ -based alloys may offer distinct temperature and reliability advantages as materials of construction for hot-gas filters used in advanced coal plants. Consequently, metallurgical and mechanical evaluations of dense and porous  $Fe_3Al$ -based alloys exposed under environmental conditions appropriate to IGCCs and PFBCs are being performed.

## EXPERIMENTAL PROCEDURES

Cylindrical, sintered metal filter elements of Fe-28 at.% Al-2% Cr-0.1% Zr (FAS-Zr) were fabricated by Pall Corporation (Cortland, NY) from water-atomized alloy powder produced by Ametek, Inc. (Eighty-Four, PA). Two of the four filter elements used to provide specimens for this study, IA-191 and IA-141, were preoxidized (at Pall) for 7 h at 800 and 1000°C, respectively. O-ring specimens (nominal inner diameter of 56 mm and wall thickness of 2 mm) were cut from IA-141 and IA-191 as well as from the two as-fabricated cylinders (IA-187 and IA-188). Some of the o-rings from each of the four elements were further divided into eight sections along their circumference. Specimens were exposed to flowing air or air + SO<sub>2</sub> (approximately 100 cm/min, ambient pressure) at temperatures up to 900°C. Weight changes were measured before and after exposure or continuously at temperature using a recording microbalance. Post-exposure characterization consisted of microstructural analysis by optical and scanning electron microscopy, energy dispersive x-ray analysis (EDS), and mechanical testing of o-rings by internal pressurization to determine tangential (hoop) stress-strain behavior.

The internal pressurization tests were conducted in ambient air and by subjecting an elastomer insert to axial compression at a constant displacement rate of 2 mm/min. The o-ring specimens were either 12.7 or 25.4 mm long; strength values were independent of specimen length. The machined edges of the specimens were dry-sanded to a smooth finish using 400 grit silicon carbide paper.

Because of the interest in determining the mechanical properties of iron-aluminide and ceramic filters at elevated temperatures, part of the present work has been devoted to the design, demonstration, and use of an approach to measure the tangential strength of tubular components at temperatures up to 900°C. However, to date, only room-temperature measurements have been made. Efforts in this regard are described in the appendix.

## RESULTS AND DISCUSSION

### AS-FABRICATED MATERIALS

The as-fabricated materials contained numerous oxide particles on pore surfaces and at the

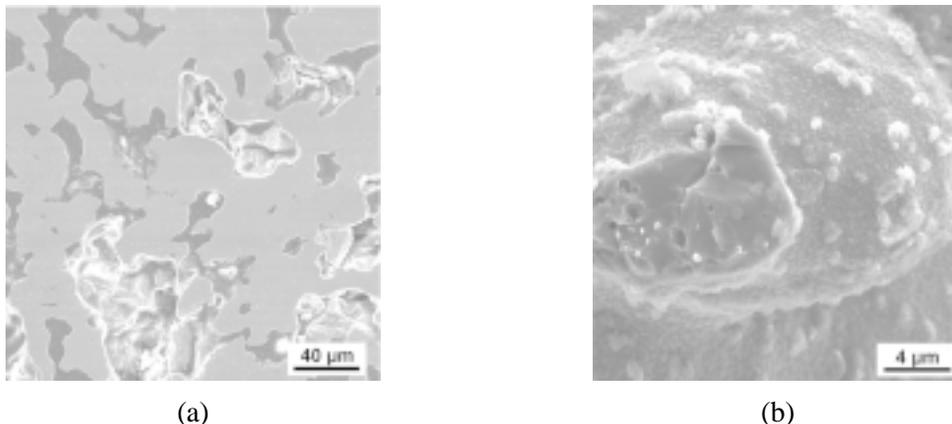


Fig. 1. As-fabricated FAS-Zr filter material. Oxide particles are found on pore surfaces (a) and at the boundaries of agglomerated powder particles (b).

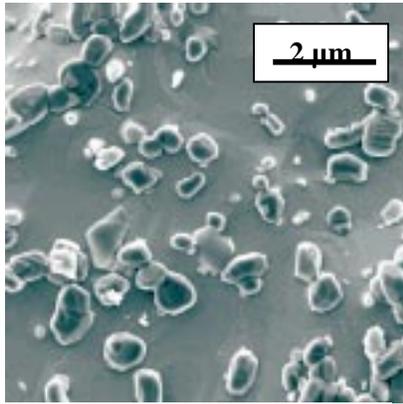


Fig. 2. As-fabricated FAS-Zr filter material.

boundaries of agglomerated powder particles (see Figs. 1 and 2). Qualitative analysis by EDS showed that these particles were most likely alumina and zirconia. These oxides form during the water atomization process and most likely coarsen during subsequent processing.

Determination of the room-temperature tangential stress - tangential strain curves using the rubber-insert-internal pressurization approach showed that the porous iron aluminides had reasonable strengths (see, for example, Fig. 3). The average hoop strengths for o-rings cut from two as-fabricated filter elements (IA-187, IA-188, three specimens each) were 112.1 and 112.3 MPa, respectively ( $\pm \sim 12\%$ ). As typified by the behavior shown in Fig. 3, the stress-strain

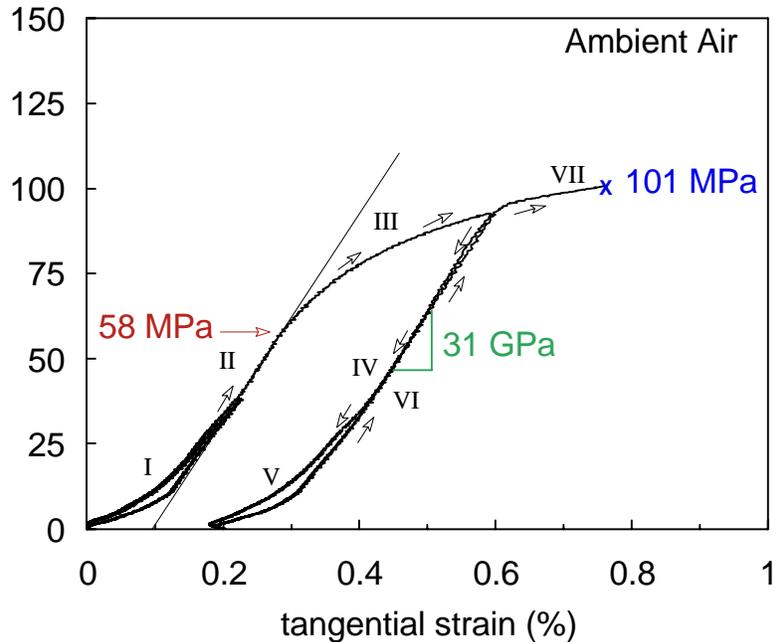


Fig. 3. Stress-strain curve for as-fabricated FAS-Zr filter material.

curves exhibited a linear region, a proportional limit, and a non-linear dependence up to failure. Loading/reloading experiments demonstrated that the proportional limit was associated with the onset of plastic deformation. The slope of the linear regions (modulus) was typically between 25 and 35 GPa. Microscopy of the ruptured o-rings showed transgranular failure through fully sintered material and that the transgranular fracture surfaces were free of oxide particles (Fig. 4). As such, the fracture surfaces were typical of the ductile failures observed for fully dense iron aluminide and, when allowance is made for the reduced load-bearing area, the measured strengths appear to be consistent with those for similar dense alloys.<sup>3</sup>

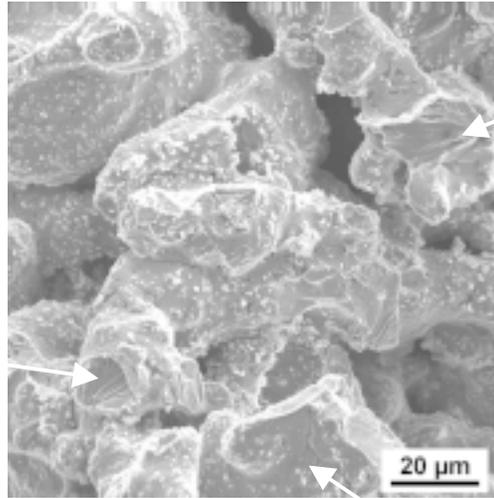


Fig. 4. Fracture surfaces of as-fabricated FAS-Zr filter material showing transgranular failure through fully sintered material. Examples of such are indicated by arrows. Note lack of oxide particles on fracture surfaces.

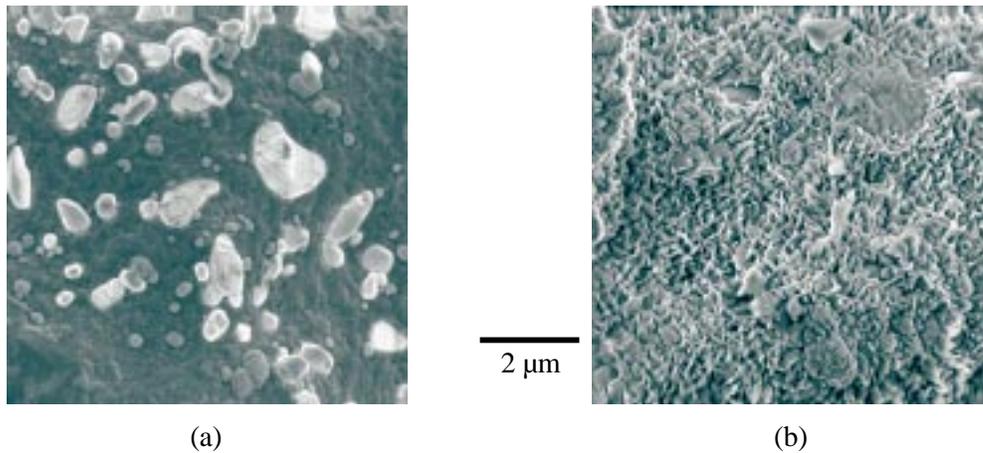


Fig. 5. FAS-Zr filter material after preoxidation for 7 h at temperatures of (a) 800°C and (b) 1000°C.

#### PREOXIDIZED MATERIAL

After preoxidation at 800°C, the original oxide particles (Fig. 2) are still clearly evident and a thin scale has formed on the metal surface (See Fig. 5a). High magnification examination of the scale indicated the grain size was ~30 nm. It is reasonable to assume that the scale was mainly alumina (an iron-containing oxide would grow much faster), but it was not possible to identify its phase or composition because it was so thin. Preoxidation at 1000°C led to the particles being nearly incorporated into the scale (see Fig. 5b). The rough protruding morphology is indicative of the less protective cubic alumina phases such as  $\theta$ -Al<sub>2</sub>O<sub>3</sub>. Previous work on alumina-formers oxidized at 1000°C indicated that ZrO<sub>2</sub> tends to stabilize these cubic alumina phases.<sup>12,13</sup> The presence of ZrO<sub>2</sub> has previously been found to be detrimental to the sulfidation resistance of pre-oxidized alumina-

formers.<sup>14</sup> In that study on FeCrAl, it appeared that  $ZrO_2$  either helped nucleate iron sulfides or the alumina scale that formed during preoxidation cracked in the vicinity of the particles. Since  $ZrO_2$  is known to stabilize  $\theta-Al_2O_3$  and the  $\theta$  to  $\alpha$  transformation involves oxide cracking,<sup>13,15</sup> this latter process seems likely. It may explain why a 1000°C preoxidation treatment did not lead to improved sulfidation resistance in more aggressive environments.<sup>16</sup>

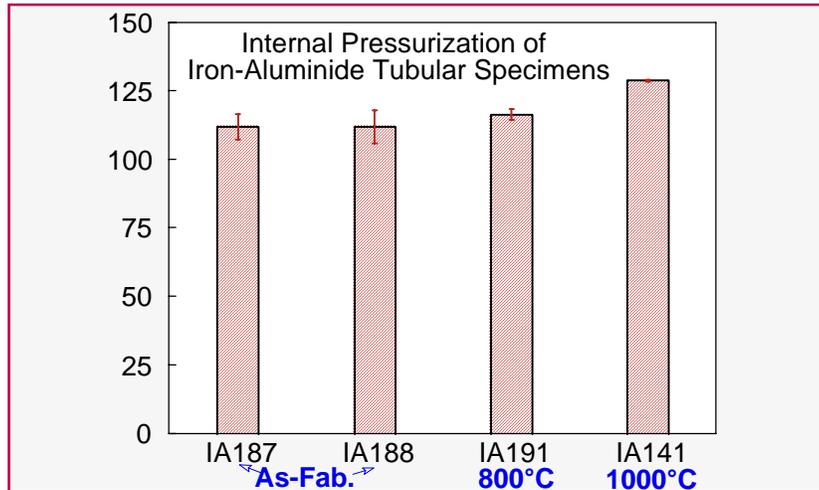


Fig. 6. Hoop strength of as-fabricated and preoxidized FAS-Zr.

Preoxidation at 1000°C for 7 h resulted in an increase in the hoop strength of the FAS-Zr filter material (IA-141), while an 800°C treatment (IA-191) had no influence. This effect is illustrated in Fig. 6, which compares the hoop strength of preoxidized o-rings to that of as-fabricated specimens (IA-187 and IA-188). The error bars in Fig. 7 bound the highest and lowest tangential strength values from 3, 3, 2 and 2 tests for specimens from tubes IA-187, IA-188, IA-141 and IA-191, respectively. The higher strength of the specimens preoxidized at 1000°C may be related to some densification of the material during the thermal treatment.

## EFFECTS OF CORROSION

### Gravimetric Results

Thermogravimetric analysis showed that, upon exposure to high-temperature gaseous environments, porous iron-aluminides displayed rapid initial weight gains followed by much more gradual mass increases with time. Examples of this behavior are shown by the microbalance traces in Figs. 7 and 8. This type of kinetic behavior is typical of most systems that form protective oxide layers during exposure (in this case, alumina) and is normally observed for iron aluminides.<sup>5,17</sup> However, the percent weight changes of the filter materials are always much higher than for companion fully dense  $Fe_3Al$  alloys because of the much greater exposed surface areas in the porous bodies (Fig. 7). Based on this surface area effect, the present results are consistent with

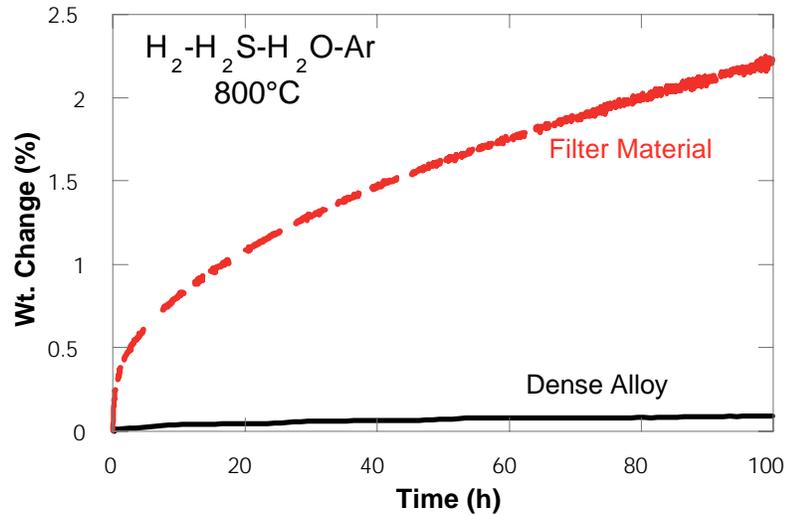


Fig. 7. Weight change versus time for FAS alloy exposed to  $H_2$ - $H_2S$ - $H_2O$  at  $800^\circ C$ . The higher weight change of the filter material simply reflects its much greater surface area rather than any significant difference in its corrosion resistance relative to dense FAS.

prior observations of good high-temperature corrosion resistance of iron aluminides in gaseous environments typically experienced by hot-gas filters used for IGCC and advanced PFBCs.

O-ring filter specimens exposed in a furnace to simulated combustion environments (flowing air or air + 1 vol%  $SO_2$ ) showed weight changes consistent with those measured in the microbalance experiments (compare Fig. 8 with the data in the first row of Table 1). The presence of  $SO_2$  did not degrade corrosion resistance at 800 or  $900^\circ C$ . In fact, these gravimetric measurements indicated that, at  $900^\circ C$ , measured corrosion weight gain was higher in air than in air + 1%  $SO_2$ . This is somewhat surprising as previous work with dense iron aluminides showed that  $SO_2$  slightly accelerated the oxidation<sup>2,8,18</sup> and, therefore, the presently observed trend will need to be examined in more detail.

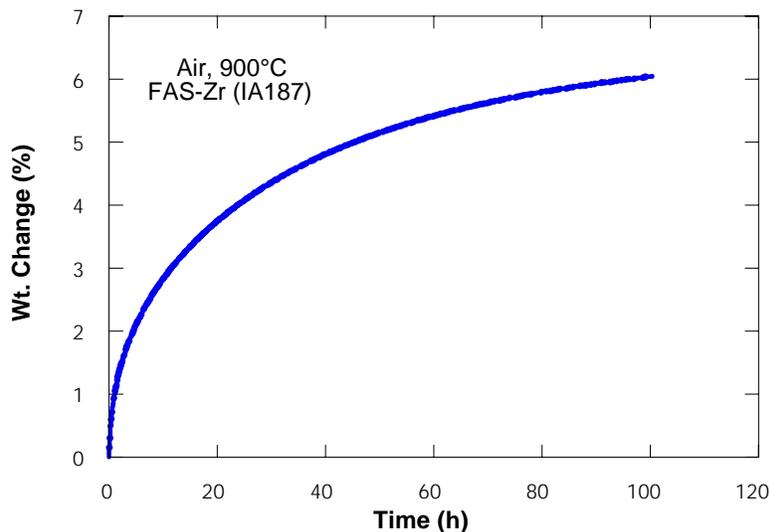


Fig. 8. Weight change versus time for as-fabricated FAS-Zr filter material exposed to air at  $900^\circ C$ .

The Pall preoxidation treatments reduced the subsequent effect of the air + SO<sub>2</sub> environment on mass gain of the FAS-Zr filter materials (Table 1). As shown in Fig. 8, much of the weight gain of these porous specimens occurs within the first few hours of exposure. Therefore, a preoxidation step of 7 h clearly should reduce the weight gain upon subsequent exposure to an oxidizing environment if the protective alumina scale formed during this treatment remains adherent. Based on the results shown in Table 1, this preoxidation treatment was effective in this regard and could be used for protection in more aggressive environments, where the surface alumina can still provide protection but any potential problems with its nucleation and initial growth are avoided. However, the beneficial effect of preoxidation is predicated on avoidance of any problems with scale cracking that may result from the presence of coarsened oxide particles, as discussed above (Fig. 5b).

Table 1. Weight changes of O-rings of FAS-Zr filter material exposed for 100 h<sup>a</sup>

Material Condition	Environment	% Wt. Change 100 h	% Wt. Change 200 h
	<u>900°C</u>		
as-fabricated	Air	5.2 ± 0.0	
as-fabricated	Air + 1% SO <sub>2</sub>	3.9 ± 0.2	11.4 ± 3.4
7 h at 800°C	Air + 1% SO <sub>2</sub>	2.3	
7 h at 1000°C	Air + 1% SO <sub>2</sub>	0.9	
	<u>800°C</u>		
as-fabricated	Air	3.5 ± 0.8	
as-fabricated	Air + 1% SO <sub>2</sub>	3.1	6.7
7 h at 800°C	Air + 1% SO <sub>2</sub>	1.9	
7 h at 1000°C	Air + 1% SO <sub>2</sub>	0.2	

<sup>a</sup>Absence of standard deviations indicate single measurements.

### O-ring Strength

Initial results from experiments to determine the effect of 100-h exposures in air and air + 1% SO<sub>2</sub> on the mechanical behavior of the FAS-Zr filter material indicated that the hoop strength increased after these treatments (Fig. 9). This finding is consistent with the above results for preoxidized specimen tubes that were exposed at 800°C and 1000°C in air for 7 h. Comparison of Figs. 7 and 10 shows that, while the 800°C exposures had essentially no effect on hoop strength, higher-temperature treatments (100 h at 900°C or 7 h at 1000°C) resulted in a small, but significant, strength increases (up to about 10%). At the same time, it appears that the stiffness increased after exposures (Fig. 9) and that the degree of stiffening was proportional to the treatment.

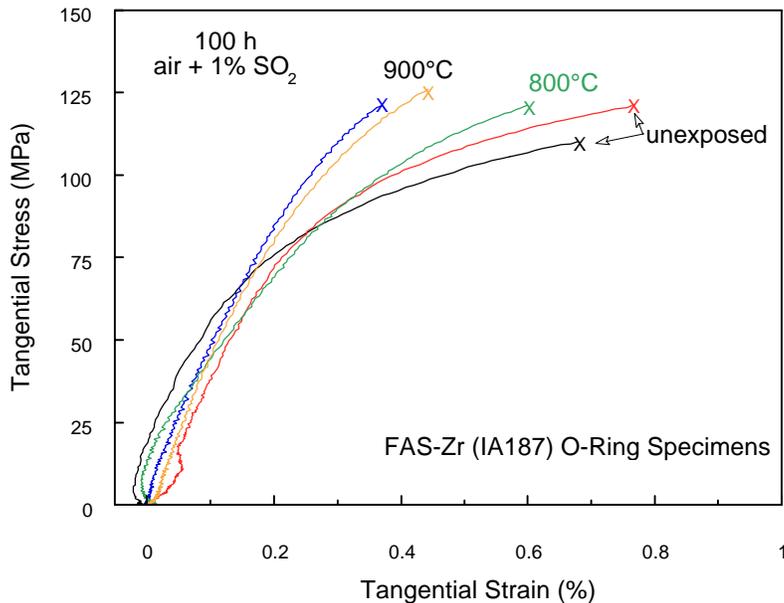


Fig. 9 Stress-strain curves for as-fabricated FAS-Zr filter material in the unexposed condition and after 100-h exposures in air + 1% SO<sub>2</sub> at the indicated temperatures.

The observed increase in strength must be considered preliminary pending further testing and microstructural analysis, but it is interesting to speculate that such an effect (albeit minor) may possibly be explained by an increase in density of the porous bodies during high-temperature exposure. Indeed, there is also some indication from the gravimetric data that some densification may be occurring. Specifically, examination of the thermogravimetric curve in Fig. 8 reveals that the kinetics are sub-parabolic at longer times:  $n < 0.5$  where  $\bullet w = (k \bullet t)^n$  and  $\bullet w$ ,  $k$ , and  $t$  are the total weight change per unit area, the associated rate constant, and the exposure time, respectively. Such behavior may possibly be explained by a decrease in the effective surface area (densification) over the course of the experiment simply as a result of further thermal aging/sintering. Based on preliminary analyses, there was not sufficient corrosion observed to explain this densification as being from closure of some pores by accumulation of reaction products in them.

While, in general, there was little effect of high-temperature exposures on the mechanical behavior of these filter materials, there was an exception to this trend. It was found that the IA191 o-rings (800°C preoxidation) exposed for 100 h to air + 1%SO<sub>2</sub> at 900°C suffered significant strength degradation (about 50%) compared to IA187 (not preoxidized) and IA141 (preoxidized at 1000°C). The lower hoop strengths were attributed to initiation of fracture at localized sulfur-containing corrosion products found at the o-ring edges (see Fig. 10). As these products were only observed at these edges, they may have formed during the 100-h exposure to air + 1%SO<sub>2</sub> because the oxide layer formed by preoxidation at 800°C was disrupted when the o-rings were cut from the filter element. As such, this environmental effect can be considered an artifact of the o-ring preparation procedure and not inherently problematic. However, a similar strength degradation was not observed after similar preparation and exposures of the o-rings from the iron-aluminide filter preoxidized at 1000°C (IA141), nor was there a sulfidation effect on the strength of the o-rings from the as-fabricated filter materials (IA-187, IA-188). Further examination of this effect is underway. This will include preoxidizing the o-rings after they have been cut from an as-processed tube.



Fig. 10. O-ring cut from FAS-Zr filter material preoxidized at 800°C and then exposed for 100 h in air + 1% SO<sub>2</sub> at 900°C.

### SUMMARY

Experiments with porous iron-aluminide filter materials fabricated by Pall Corporation showed good high-temperature corrosion resistance in air, air + SO<sub>2</sub>, and H<sub>2</sub>S-containing environments. As-fabricated iron-aluminide filter materials have a significant amount of incorporated alumina and zirconia, but their strength and failure are characteristic of typical Fe<sub>3</sub>Al alloy behavior. Preoxidation at 800 and 1000°C for 7 h or 100-h exposures in air and air + SO<sub>2</sub> at 800 and 900°C had little effect on hoop strength apart from a possible increase in load at failure due to densification at the higher temperatures.

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## APPENDIX: DEVELOPMENT OF A HIGH-TEMPERATURE INTERNAL PRESSURIZATION TECHNIQUE FOR DETERMINATION OF HOOP STRENGTH

Because of the interest in the mechanical properties of filter materials at elevated temperatures, some effort has been dedicated to the design and demonstration of an approach that would allow the determination of the tangential strength of tubular components up to 900°C while avoiding some of the technical problems associated with the use of gases or molten glass for high-temperature internal pressurization.<sup>A1,A2</sup> To this end, preliminary experiments conducted on clear extruded acrylic o-rings have demonstrated the viability of a mechanical loading approach. Clear extruded acrylic was chosen for the demonstration experiments because it is made with reproducible mechanical properties and tubes are very inexpensive and readily available with uniform dimensions. This material is therefore very appropriate for use in verifying the reproducibility of the data measured by this technique. Figure 11 shows the resulting load versus crosshead and radial displacement curves from four internal pressurization tests. These results

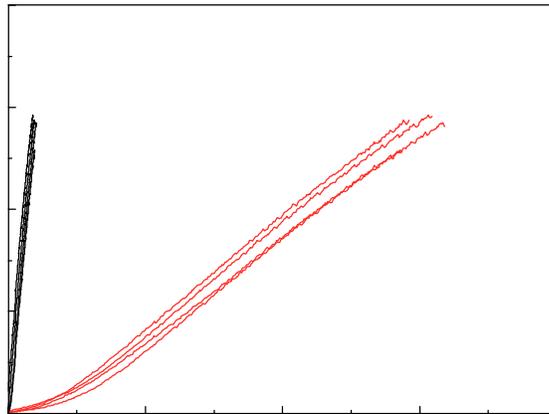


Fig. 11. Load versus cross-head and radial displacement curves obtained from the internal pressurization of four different extruded clear acrylic O-ring specimens using a developmental mechanical loading technique.

serve to demonstrate the uniformity in the properties of the acrylic specimens and the reproducibility of the test results.

To investigate the degree of strain uniformity, the tangential strain on the outer surface of o-ring specimens subjected to internal pressurization was monitored using adhesively bonded strain gauges and two linear variable differential transducers (LVDTs) positioned on opposite sides of the specimen. One strain gauge was placed at the same spot where one LVDT was contacting the specimen. Figure 12 shows a comparison of the tangential strain measurements using the strain gauges and the LVDTs. Although there are small deviations among the three tangential strain readings at the start of the test, the slope of the curves obtained by the strain gauges and by the

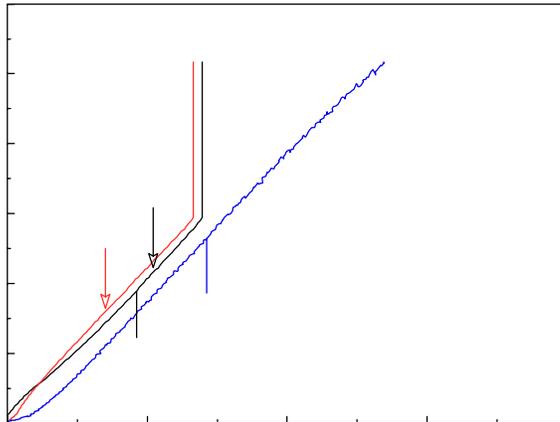


Fig. 12. Load versus tangential strain from the internal pressurization of acrylic O-rings using a developmental mechanical loading technique. Tangential strains were recorded using both adhesively bonded strain gauges and two LVDTs.

LVDTs are nearly identical afterwards. The discrepancies at the start of the test are attributed to slack in the load train.

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