CONF-970111--6

EFFECTS OF COAL SLAG CORROSION ON THE MECHANICAL PROPERTIES OF SINTERED α-SILICON CARBIDE

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ABSTRACT

Tubes of sintered SiC were exposed for 500 h in a laboratory furnace to three different coal slags at three temperatures. No corrosive attack or strength reduction was observed after exposure at 1090°C. At 1260°C the least viscous slag caused formation of corrosion pits and loss of strength. At 1430°C formation of iron silicides at the interface between the slag and the base material caused severe loss of strength for slags with the highest and the lowest viscosity, while the specimens exposed to the slag with medium viscosity and medium iron content survived quite well. The results show that mechanical strength can be retained for certain coal slag - temperature combinations.

INTRODUCTION

A new generation of coal fired power plants with increased efficiency, fewer emissions and lower costs is currently being developed.[1,2] Large improvements in efficiencies will require a change to gas turbines (Brayton Cycle) instead of exclusive reliance on steam turbines (Rankine Cycle). Extremely high working fluid temperature is required to boost the efficiency, and the result is that the power plant sub-systems will be exposed to much more corrosive environments than the present systems. The uses of ceramic heat exchangers are being investigated for those new power plants because of the potential for producing a clean, hot working fluid for the gas turbine.

The leading candidate materials for ceramic heat exchangers are silicon carbide-based materials in the form of sintered SiC, siliconized SiC, or a composite containing SiC. The thermal conductivity of this group of ceramics is high, and the retention of mechanical properties, as well as the thermal shock resistance, are presumed to be adequate for the application. However, relatively little is known about the behavior of these ceramics in the corrosive coal combustion environment. Some early studies indicated severe corrosion problems in a coal/oil burning rig[3-6] including influences of different coal

8

compositions. More recently modern SiC and a new SiC-particulate reinforced Al_2O_3 composite have been tested in a coal ash environment.[7-11]

The purposes of the present work are to evaluate the behavior of ceramic tube-components under coal ash corrosion, to measure the remaining mechanical properties, and to identify corrosion mechanisms. This study is being coordinated with ongoing work of several research groups using coals with comparable chemical compositions and temperatures.

EXPERIMENTAL PROCEDURE

Tubes of sintered α-SiC (Hexoloy, Carborundum Co.) of OD 52 mm, ID 43 mm and length 150 mm have been evaluated. For these experiments three different slags were gathered from the taps of three cyclone-fired utility boilers. One was an Illinois #6 from the Illinois Power Company Baldwin Plant (labeled Baldwin) and was a mixture of Illinois #6 and Illinois #5, resulting in a typical slag with less Ca and more Fe than "standard Illinois #6." The second slag was Illinois #6 from coal burned at the Central Illinois Public Service Coffeen Plant (labeled Coffeen) and was produced from a low sulfur producing mine. The low sulfur (in the form of low FeS_2 content) leads to high viscosity of the slag, so therefore 1.5% limestone was added at the power plant to reduce the viscosity. The third slag was collected from the Northern States Power Riverside Plant and was a sub-bituminous coal slag from a Powder River Basin coal produced from the Rochelle mine in Wyoming (labeled Rochelle). This slag was the least viscous and most basic of the three slags. The slag was analyzed at the University of North Dakota Energy and Environmental Research Center (UNDEERC)[12] and was split from the main barrel according to ASTM D 2013 "Standard Method of Preparing Coal Samples for Analysis." The chemical compositions of the three coal ashes are given in Table 1, and the viscosities are compared in Fig. 1.

The test temperatures were 1090°C to produce a condition of sintered ash, 1260°C for a viscous molten ash and 1430°C for a runny molten ash. Tube-sections were placed in a box furnace, an initial layer of coal slag was added and the furnace was brought up to temperature in 2 hours. In order to replenish the coal slag 75 ml was added to each tube length every 48 h through the top of the furnace, the goal being to keep a layer of about 5 g/cm^2 on the surface. Total exposure time was 500 h after which the furnace was slowly cooled to room temperature. After inspection each tube was cut into C-ring specimens for strength testing. The C-rings were placed in a mechanical test system containing a box furnace, heated back up to the exposure temperature and loaded in compression to failure at a fast (20 MPa/s) loading rate. The strength was evaluated using the appropriate formula for C-rings in compression.[5] Three tubes were cut into C-rings and tested in the as-received condition in order to provide base-line strength data at each test temperature. The strength data were analyzed using Weibull statistics.[13, 14] Fractography was performed by optical (100%) and

Scanning Electron Microscope (SEM) (selected specimens). After strength testing and fractography it was apparent that some of the specimens failed from an area outside the area of maximum tension, and also that for some of the exposure conditions there was a considerable amount of localized thinning in areas where the coal ash was applied. In both cases the basic C-ring formula would over-estimate the strength, and a Finite Element Analysis was incorporated in order to correct for this.[15] The strength results presented in this paper have been corrected accordingly.

Table 1. Chemical composition of the coal ashes.

Oxide, wt%	Baldwin	Coffeen	Rochelle
SiO_2	53.4	52.5	47.0
Al_2O_3	18.6	16.3	18.6
Fe_2O_3	17.6	13.5	5.3
TiO_2	0.7	0.7	1.4
P_2O_5	0.0	0.2	0.6
CaO	7.1	13.1	19.7
MgO	0.9	1.2	5.7
Na_2O	0.0	0.8	0.9
K_2O	1.7	1.6	0.4
SO_3	0.0	0.1	0.4
Basic Oxides/ Acidic Oxides	0.38	0.43	0.48

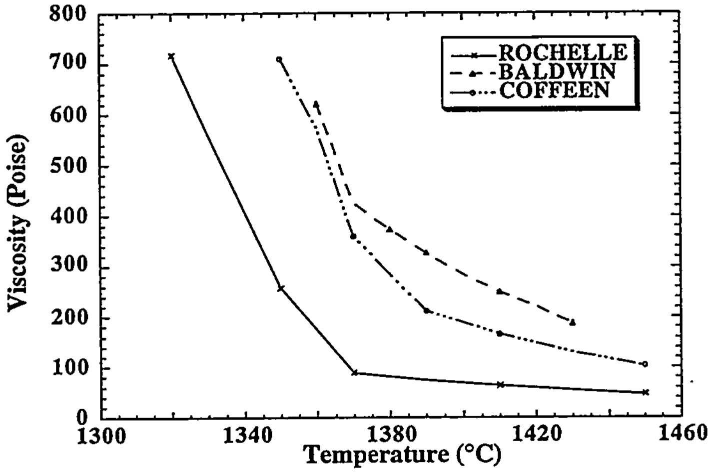


Fig. 1. Comparison of the viscosities of the three coal ashes.

Analysis of the slags, interfaces, and corrosion products was performed using a microanalytical probe. Both identification of major elements by x-ray and more detailed analysis by linescans were performed.

RESULTS AND DISCUSSION

The strengths were measured on an average of 14 specimens per condition. Each C-ring was inspected after the test in order to determine the fracture location and fracture origin. If the fracture location was off the maximum tensile region, or in the cases with localized thinning, the strengths were corrected appropriately with the aid of a finite element analysis. The complete Weibull graphs for the specimens are given in Figs. 2-4 for the three test temperatures respectively.

The first important observation was that the Weibull moduli were quite low with the as-received moduli being about 5 at all temperatures. The as-received strengths were determined from only 9 specimens at each temperature, and that results in a fairly low confidence in these m-values. The second observation was that the Weibull moduli remained almost unchanged throughout the experiments, with the exception of Rochelle exposed specimens which literally fell apart due to cracking after exposure at 1260 and 1430°C.

The fractography of the as-received specimens showed that the specimens generally failed from pores at or near to the surface, independent of test temperature. The results at 1090°C showed no significant change in strength as a result of the exposures. The fractography showed that the failures were from pores at and near the surface just as in the as-received case (consistent with the unchanged Weibull moduli).

The strength testing after exposure at 1260°C showed a much more differentiated picture. The strength of the Baldwin exposed specimens showed a significant increase in strength as compared to the as-received strength. The strength for the Coffeen exposed specimens remained unchanged while the Rochelle exposed specimens showed a significantly decreased strength. The fractography demonstrated that the Baldwin exposed specimens generally failed from surface connected pores as before, however, the pores were blunted by the viscous, glassy slag, see Fig 5. Similarly, it could be expected that the Rochelle slag would effectively blunt pores, but localized corrosive attack had occurred under the glassy slag, and these corrosion pits in combination with cracks acted as fracture initiation points, see Fig. 6.

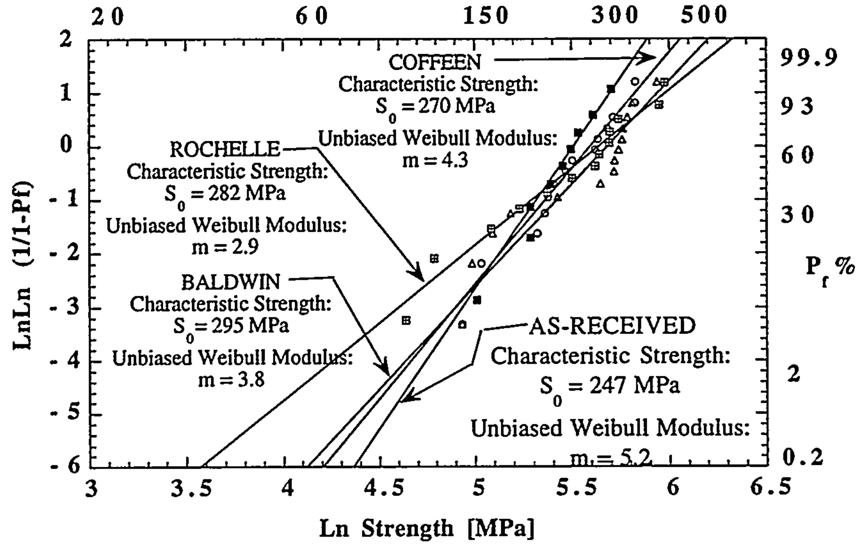


Fig. 2. Weibull analysis of C-rings exposed and tested at 1090°C.

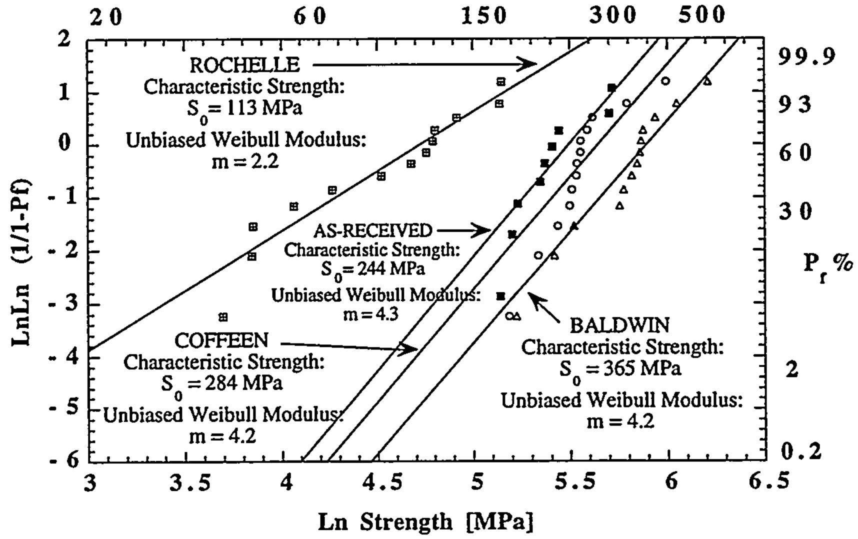


Fig. 3. Weibull analysis of C-rings exposed and tested at 1260°C.

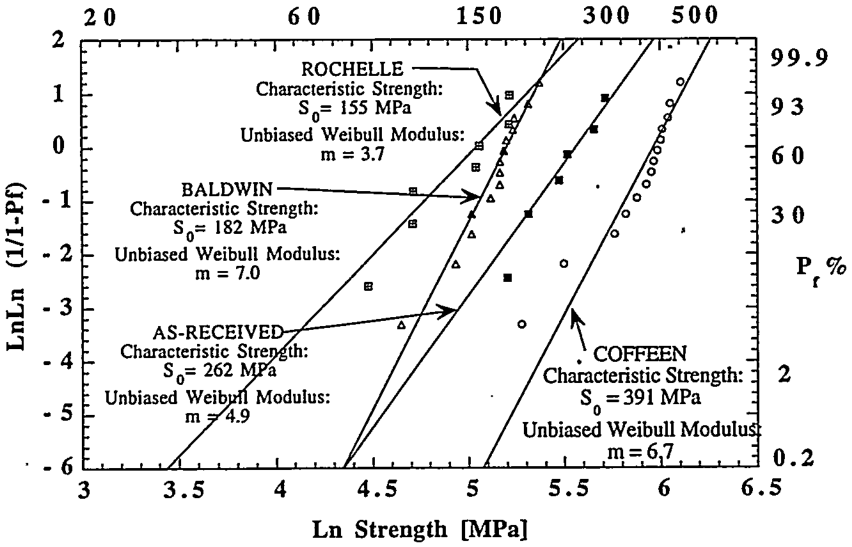
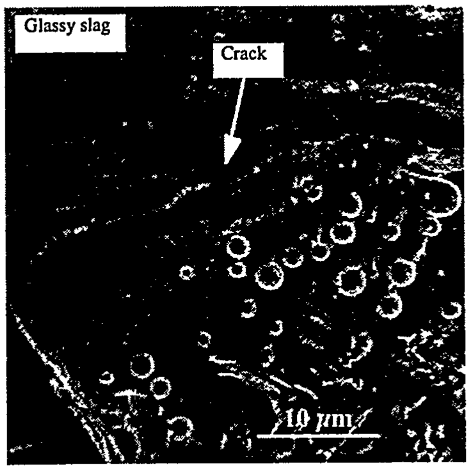


Fig. 4. Weibull analysis of C-rings exposed and tested at 1430°C.



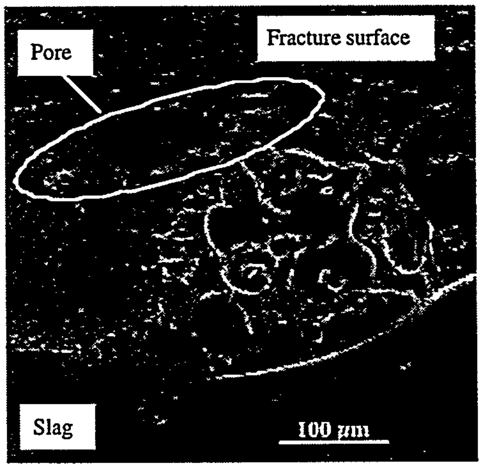


Fig. 5. Fracture origin in specimen exposed to Baldwin slag at 1260°C.

Fig 6. Fracture origin in a specimen exposed to Rochelle slag at 1260°C.

At 1430°C the Baldwin and Rochelle exposed specimens experienced a significant loss of strength, while the Coffeen exposed specimens increased somewhat in strength. The fractography showed that the weakened specimens generally failed from areas with corrosive attack. Especially in the case of the Rochelle exposed specimens a deep penetration and uniform thinning were observed, see Figs. 7 and 8. For the specimens exposed to Coffeen slag the fractography confirmed that the fracture origins were pores blunted by glassy slag.

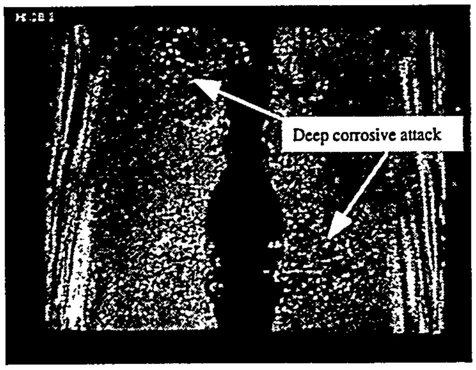


Fig 7. Fracture surfaces of a Rochelle exposed specimen at 1430°C showing material loss from the surface.

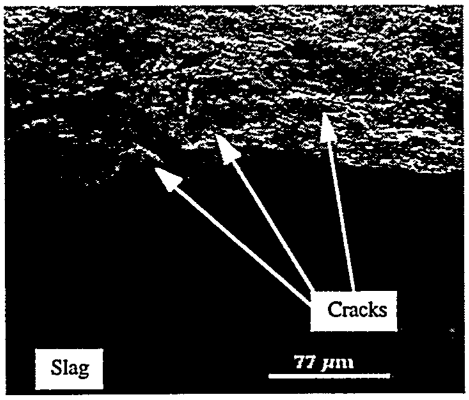


Fig. 8. Fracture origins in Rochelle exposed specimen at 1430°C were typically cracks at corrosion pits.

From the above discussion it is obvious that the degree of corrosive attack with subsequent loss of strength is a combination of coal slag chemical composition and viscosity. In order to investigate this further several specimens were studied using the microprobe. First it is important to emphasize that there were large local variations in the chemical composition as observed by the microprobe. This likely stemmed from the fact that there were large local variations in the composition of the coal slags, and that the coal slags were not sieved or treated in any way before the test. However, several general observations can be made to explain the differences in strength behavior.

As expected, there was little reaction at 1090°C. There was some coal slag stuck onto the surface of the specimens, and for the Baldwin and Coffeen exposed specimens some areas with 2-3 μm crystalline silica was observed. The Rochelle exposed specimens had a 60 μm thick glassy layer on the surface, but no general corrosive attack was observed.

At 1260°C the specimens exposed to Baldwin and Coffeen exhibited a relatively uniform glassy slag layer on top of a very thin (≈ 2 μm) layer of silica crystals, see Fig. 9. It is likely that the crystals protected the original surface from active corrosive attack. The Rochelle exposed specimens had experienced active corrosion at 1260°C, evidenced by the very uneven interface between the slag and the base material, see Fig. 10. The microprobe analysis showed segregation of iron to the interface resulting in formation of iron silicides consuming silicon from the substrate resulting in formation of corrosion pits.

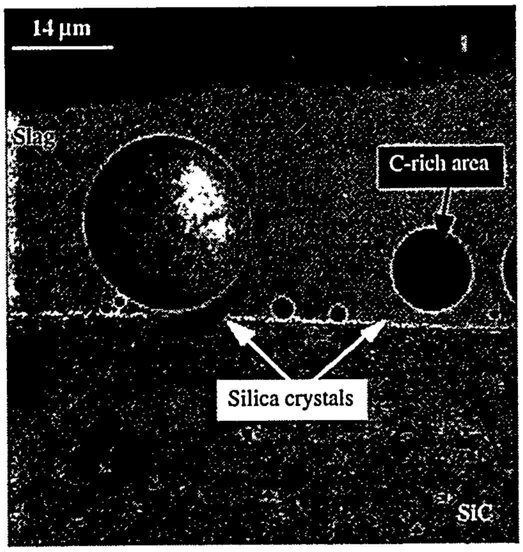


Fig. 9. Backscattered image of the slag/SiC interface for a specimen exposed to Baldwin slag at 1260°C.

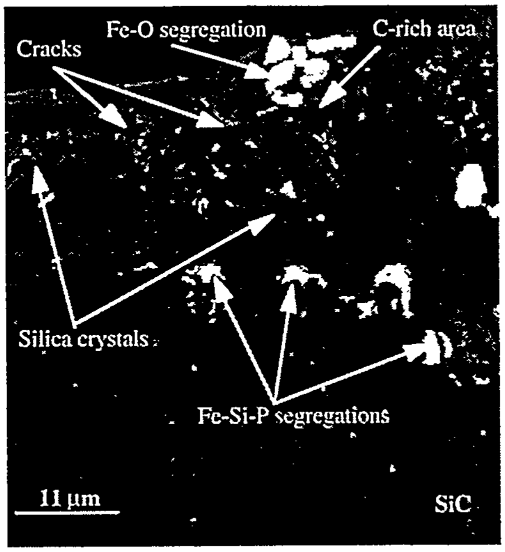


Fig. 10. Backscattered image of the slag/SiC interface for a specimen exposed to Rochelle slag at 1260°C.

A microprobe analysis of Rochelle exposed specimens at 1430°C was not performed. However, the significant loss of strength and cracking of specimens during exposure indicated that the process described above had progressed further.

The microprobe analysis of the specimens exposed to Baldwin (with strength loss) and Coffeen (with no strength loss) at 1430°C helped clarify the picture. The Baldwin exposed specimens had a glassy layer on top of a layer of silica crystals, but a segregation of Fe with subsequent formation of iron silicides had produced sizable corrosion pits, see Fig. 11. For the Coffeen exposed specimens the layer of silica crystals had protected the base material and no corrosion pits were observed.

It is possible to construct a diagram showing which SiC/temperature/coal slag combinations resulted in strength loss or gain. In Fig. 12 the strength is given relative to the as-received strength, and the coal slags are ranked according to increased viscosity. It is evident that for this 500 h exposure 1090°C was not a severe temperature for any of the coal slags. At 1260°C it is seen that the specimens exposed to the slag with the lowest viscosity experienced severe loss of strength due to the ease of transport of Fe to the interface. The two other slags could still be used at 1260°C where the lower viscosity of the Coffeen slag apparently was offset by the lower Fe-content. However, at 1430°C the viscosity of all the slags was low, and the higher Fe content in Baldwin was enough for iron silicides to form.

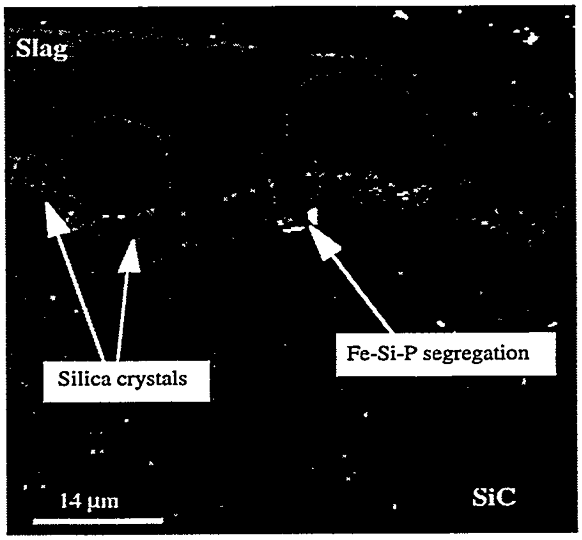


Fig. 11. Backscattered image of the slag/SiC interface for a specimen exposed to Baldwin slag at 1430°C.

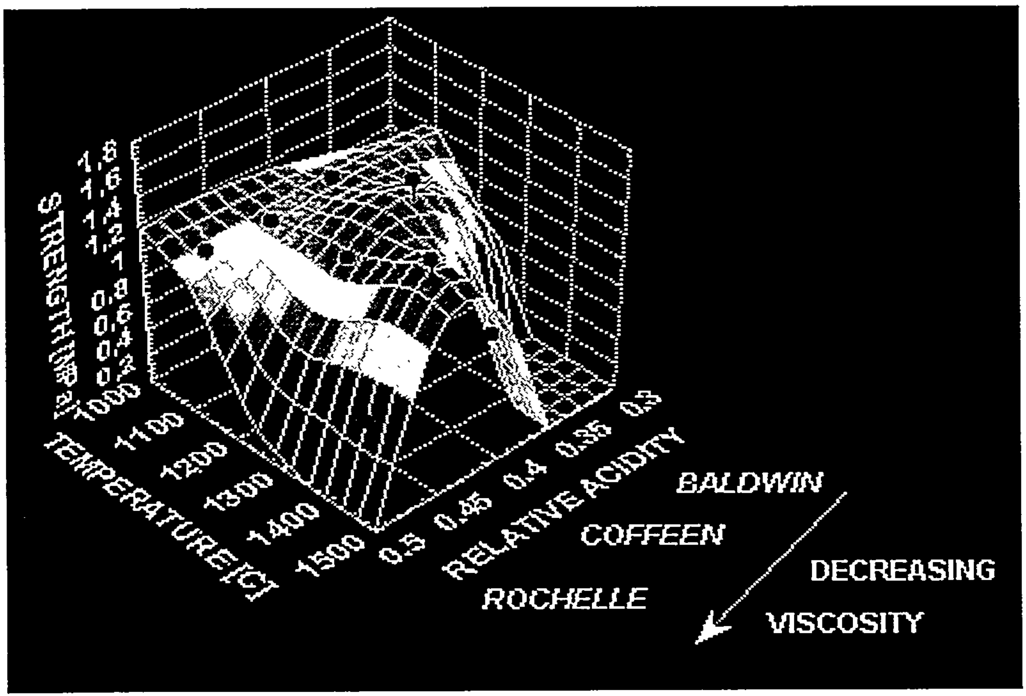


Fig. 12. Relative retained strength as a function of exposure temperature and coal slag type.

SUMMARY AND CONCLUSIONS

The 500 h laboratory exposure showed that it was possible to differentiate between the various coal slags and temperatures and their influence on retained strength. The important differences between the coal slags were the difference in the viscosity combined with the difference in chemical composition. At the lowest exposure temperature, 1090°C, the slag did not melt and consequently no significant reactions occurred. The strengths remained unchanged from the as-received strengths and the failure modes were similar. At the intermediate temperature, 1260°C, the slags had melted but remained relatively "sticky." The slag with the lowest viscosity (Rochelle) caused severe pitting accompanied by a significant loss of strength. In spite of this slag having lowest iron content, the corrosion was due to the formation of iron silicides, probably facilitated by the low viscosity. The two slags with higher iron content did not produce corrosive attack at 1260°C presumably due to slow iron transport in the more viscous slag. The slag with the highest viscosity experienced strengthening due to effective blunting of the surface pores. At 1430°C severe loss of strength was experienced in the specimens exposed to the slag with highest iron content and to the least viscous slag, while the slag with intermediate viscosity and intermediate iron content caused no strength reduction. The resulting map of relative retained strengths as a function of exposure temperature and coal slag type gave a good indication of where problems might occur, and in which direction to aim further efforts.

ACKNOWLEDGMENTS

Research sponsored by the U.S. Department of Energy, Office of Fossil Energy, Pittsburgh Energy Technology Center, Advanced Combustion Technology Program, DOE/FE AA 20 10 00 0, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

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