

CONCEPTS FOR SMART PROTECTIVE HIGH-TEMPERATURE COATINGS

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ABSTRACT

Design of smart protective coatings is envisioned as a means to overcome materials barriers imposed by the environments associated with advanced fossil energy systems. To this end, short-term sulfidation behavior over a range of temperature was studied for baseline stainless steels and an iron aluminide as a step toward addressing corrosion resistance at lower sulfur activities and temperatures in terms of the implications for alloy/coating design for such conditions. The superior sulfidation resistance of an iron aluminide in a H₂-H₂S-H₂O gas mixture (relative to steels), previously established by extensive studies at 800°C, appeared to be maintained at lower temperatures (400 and 600°C).

INTRODUCTION

All fossil fuel-derived processes contain reactive species such as sulfur, water vapor, oxygen, carbon, etc. Consequently, high-temperature degradation of many alloys or ceramics limits performance or materials lifetimes in fossil, particularly coal-based, systems such that efficiency, emission, and/or economic requirements are not realized. Therefore, resistance to this degradation is a critical material barrier to the operation of advanced fossil energy systems. Achievement of high-temperature corrosion resistance for a particular material is predicated on the formation of stable, protective (slowly reacting, mechanically sound, adherent) surface products. Factors affecting the establishment and stability of such layers have been studied for many years, yet the selection or development of materials to withstand the harsh operating conditions of advanced fossil-fuel-based technologies is still an imposing technical challenge given multiple reactive species, high temperatures and pressures, and variations in operating conditions. Consequently, to seek solutions that have the most far-ranging impact on this difficult, wide-ranging problem, new approaches to corrosion resistance in multiple or changing high-temperature environments (such as the smart corrosion-resistant coatings proposed by Nicholls¹) are needed.

The long-range aim of this work is to assess the feasibility of different material and design approaches to smart protective coatings by exploring new alloying and microstructural routes to improved high-temperature environmental resistance of metallic materials. As such, this work supports the overarching goal of the Department of Energy's Fossil Energy Advanced Research (AR) Materials Program to provide a materials technology base to assure the success of coal-based fuels and advanced power generation systems. This specific project is motivated by needs for materials with improved high-temperature environmental resistance that could be used as protective coatings under the harsh conditions encountered in advanced fossil systems. The focus is on coating concepts because coatings offer possibilities for corrosion protection under aggressive (and changing) environmental conditions while the substrate provides strength or other desired properties. The project's goal is not to develop coatings per se. Rather, it is to examine concepts that can then be translated into coatings by further developmental efforts if promising high-temperature corrosion results are found for a particular composition/microstructure combination and possible synthesis routes can be identified. This approach can hopefully lead to concepts for "smart" coatings or materials that have the ability to sense and respond appropriately to a particular set or series of environmental conditions in order to provide high-temperature corrosion protection.

The current effort is focused on concept definition and exploratory experimentation aimed at proof-of-principle. (The most successful concepts can transition to a more comprehensive project within the AR Materials Program or graduate to a technology development project.) The strategies previously explored in this work involved cooperative or in-place oxidation or sulfidation reactions of multiphase alloys.²⁻⁴ Alloy systems based on Mo-Si-B and TiAlCr(-X) compositions (X = Nb, Ta, or both) were investigated. More recently, the project has focused on lower, more realistic sulfidation temperatures relative to previous work in simulated coal syngas mixtures (H₂-H₂S-H₂O) which primarily involved investigations of behavior at 800°C. The present experiments allow exploration and understanding of how compositions and structures react in various ways determined by not only the nature of the reactive species but also by temperature and partial pressure so as to define routes to establishing effective protective barrier layers can form under different environmental conditions.

The present set of lower-temperature experiments involved conventional types 410, 430, 446, and 316L stainless steel formed by powder metallurgy (P/M) techniques as well as a P/M iron-aluminide. Iron aluminide was included as a benchmark for excellent high-temperature sulfidation resistance, at 700- 800°C.^{5,6} Results from these exposures are used to (1) directly address whether the superior sulfidation resistance of iron aluminide is maintained at lower temperatures and sulfur pressures and (2) form a basis for exploring more advanced alloy systems (as was previously done with Mo-Si-B and Ti-Al-CR-X, see above).

RESULTS AND DISCUSSION

Table 1 shows the nominal compositions of the alloys used in this study. Specimens were exposed to 79%H₂-5.5%H₂S-1.5%H₂O-Ar (vol%) at 400, 600, and 800°C. During most of the exposures to this mixed gas, specimen mass was continually monitored using a Cahn microbalance. Post-exposure characterization of selected specimens was by scanning electron microscopy and x-ray diffraction.

The partial pressures of oxygen and sulfur for 79% H_2 -5.5% H_2S -1.5% H_2O -Ar at 400, 600, and 800°C are shown in Table 2. These pressures are calculated using equilibrium thermodynamics, which yield fairly accurate values at higher temperatures, but may be unrealistic at lower temperatures, where kinetic limitations may produce nonequilibrium conditions. At equilibrium, alumina would be expected to form on the iron aluminide under all three exposure conditions; this previously has been experimentally observed at 800°C in this mixed gas⁷ and accounts for its sulfidation resistance. However, given possible kinetic limitations and nonequilibrium gas compositions at lower temperatures, it is therefore important to conduct experimental screening to determine whether iron aluminide still has better sulfidation resistance relative to conventional stainless steels under these conditions.

Table 1. Nominal Compositions of Alloys Used in This Study

Type	Wt%				
	Fe	Cr	Ni	C	Other
316L	65	17	12	0.03	2Mo, 2Mn, 1Si
410	86	12		0.1	<1Mn
430	83	16		0.1	<1Mn, <1Si
446	75	25	<0.2	<0.2	<1Si
FeAlCr	82	2			16Al

Table 2. Temperatures and Calculated Partial Pressures for 79% H_2 -5.5% H_2S -1.5% H_2O -Ar

Temp. (°C)	P_{O_2} (atm)	P_{S_2} (atm)
400	10^{-37}	10^{-11}
600	10^{-28}	10^{-8}
800	10^{-22}	10^{-6}

Significant reactions of the steels were observed at all temperatures. X-ray diffraction revealed that the principal corrosion products were iron and chromium sulfides. Type 316L stainless steel showed the extent of sulfidation. For example, after only a 1-h exposure at 800°C, a type 316L stainless steel specimen showed a relative mass gain of 13% in contrast to ~22% in 3 h for types 430 and 446 and 1.4% for the iron aluminide after 72 h. (Relative, rather than specific, mass changes are reported because the P/M materials were not fully dense.) The high susceptibility of a Ni-containing austenitic stainless steel in this specific environment at 800°C was first reported by DeVan⁷ for a model type 310 steel. This is presumably due to the presence of the Ni, which readily forms sulfide (which should be molten at 800°C), although the in-plan diffraction analyses did not detect such at any of the exposure temperatures. The more extensive sulfidation of type 316L relative to the ferritic steels was also observed at the lower exposure temperatures, as shown by the mass change data in Figs. 1 (1 h, 600°C) and 2 (72 h, 400°C).

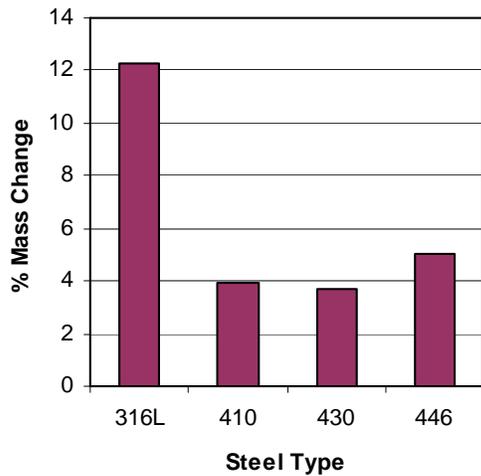


Fig. 1. Mass change for 1-h exposures to 79% H_2 -5.5% H_2S -1.5% H_2O -Ar at 600°C

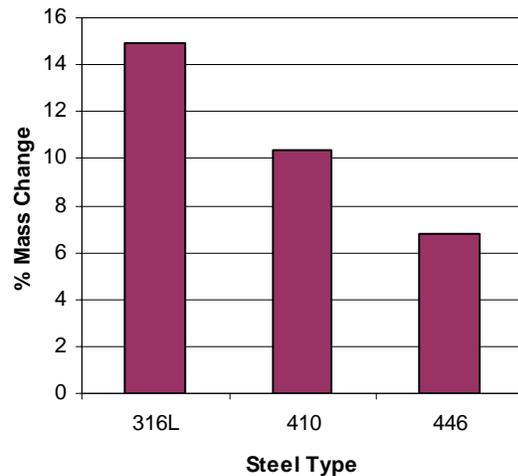


Fig. 2. Mass change for 72-h exposures to 79% H_2 -5.5% H_2S -1.5% H_2O -Ar at 400°C

Gravimetric results as a function of time for the type 446 steel are presented in Fig.3, which shows the expected increase in the extent of sulfidation with exposure temperature (and increasing sulfur partial pressure, see Table 2). Representative micrographs of the type 446 steel corresponding to each exposure temperature are also shown in Fig. 3. At 800°C, relatively thick, blocky sulfides were observed., much like what was observed under the same exposure conditions for Fe-Al alloys when their protective alumina surface layer failed to provide protection (due to inadequate levels of aluminum either generally or locally).⁸ Present data are insufficient to definitively conclude that one ferritic steel is more sulfidation resistant than the others, but there was some indication that the higher-Cr type 446 stainless steel sulfidized less than types 410 and 430, although at a much greater rate than iron aluminide – see Fig. 4. This is consistent with general trends that higher chromium alloys are more sulfidation resistant.⁹

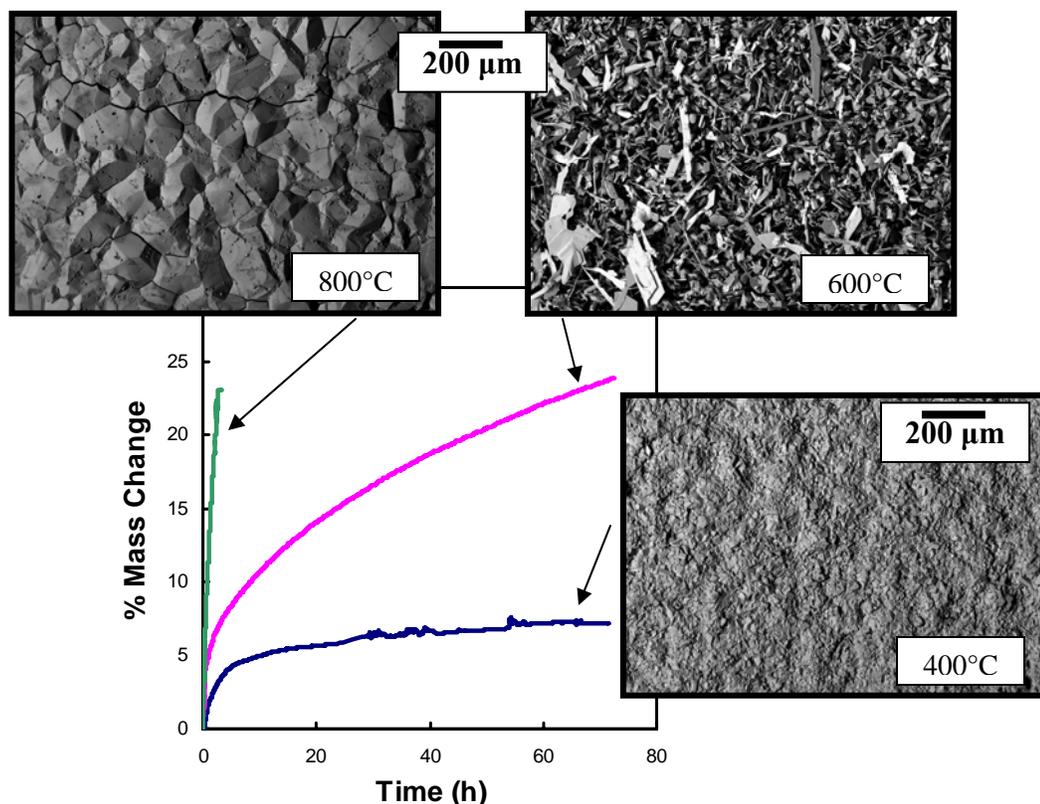


Fig. 3. Type 446 stainless steel exposed to 79% H_2 -5.5% H_2S -1.5% H_2O -Ar

While it is possible that an iron aluminide would actually sulfidize to a much greater extent at lower temperatures if a protective alumina couldn't form, the present data do not yield evidence for this. The mass changes at all three temperatures were much lower than the steels (see, for example, Fig. 4) and, at 400°C, it was difficult to obtain a good measurement of mass change. X-ray diffraction of the exposed surfaces did not reveal any reaction products. Therefore, even though kinetics to form alumina at these lower temperatures are presumably sluggish, there must be a protective effect of the native, pre-existing oxide or there is still sufficient near-surface mobility to establish a barrier layer. Other work with iron aluminides in an actual syngas environment at approximately 400-450°C showed that preoxidation at 800°C was critical to assure longer-term corrosion resistance,¹⁰ but the much greater complexity of that environment makes the relevance of these observations to the present case problematical.

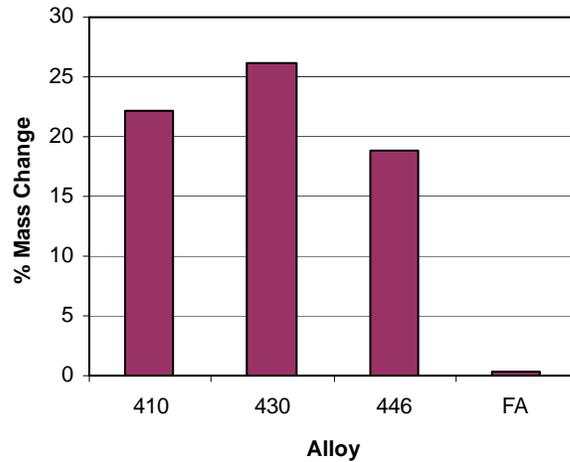


Fig. 4. Mass change for 27-h (type 410) or 72-h exposures (types 430, 446 and iron aluminide, FA) to 79% H_2 -5.5% H_2S -1.5% H_2O -Ar at 600°C

SUMMARY

For type 316L and 400-series steels exposed to a simulated syngas (79% H_2 -5.5% H_2S -1.5% H_2O -Ar, vol%), significant sulfidation was observed at 400, 600, and 800°C with formation of iron and chromium sulfides. Relatively little differences in sulfidation resistance were found between the 300-series and the 400-series steels at 400°C, but 316L was substantially more susceptible at 600 and 800°C. An iron aluminide composition showed superior sulfidation resistance at 800°C (as shown previously) as well as at lower temperatures where alumina growth is sluggish: almost negligible mass changes were found in short-term exposures (up to 72 h) at all temperatures and no reaction products were detected by conventional x-ray diffraction.

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