

Improved Austenitic Steels for Power Plant Applications

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Abstract

Using alloy design principles, an austenitic alloy, with base composition of Fe-16Cr-16Ni-2Mn-1Mo (in weight percent, wt%), was formulated to which up to 5 wt% Si and/or Al were added specifically to improve the oxidation resistance. *Cyclic oxidation* tests were carried out in air at 700 and 800°C for 1000 hours. For comparison, Fe-18Cr-8Ni type-304 stainless steel alloys was also tested. The results showed that at 700°C, all the alloys were twice as oxidation resistant as the type-304 alloy (i.e., the experimental alloys showed weight gains about half that of type-304). Surprisingly, at 800°C, alloys that contained both Al and Si additions were less oxidation resistant than the type-304 alloy. However, alloys containing only Si additions were significantly more oxidation resistant than the type 304 alloys (i.e., showed weight gains 4 times less than the type-304 alloy). Further, alloys with only Si additions pre-oxidized at 800°C, showed zero weight gain in subsequent testing for 1000 hours at 700°C. This implies the potential for producing in-situ protective coating for these alloys. Preliminary exposure tests (1% H₂S at 700°C for 360 hrs) indicated that the Si-modified alloys are more *sulfidation resistant* than type-304 alloy. The *mechanical properties* of the alloys, modified with carbide forming elements, were also evaluated; and at 600, 700 and 800°C the yield stresses of the carbide modified alloys were twice that of type-304 stainless steel. In this temperature range, the tensile properties of these alloys were comparable to literature values for type-347 stainless steel. It should be emphasized that the microstructures of the carbide forming alloys were not optimized with respect to grain size, carbide size and/or carbide distribution. Also, presented are initial results of vari-strain weld tests used to determine parameters for *joining* these alloys.

Introduction

Supercritical and ultra-supercritical fossil fuel power plants will require new materials for use at temperatures of 700°C and above [1,2]. Superheater and reheater tubes are likely to experience the most severe service conditions with respect to fire-side corrosion, steam-side oxidation and creep [2]. A material for this application must not only be: (i) creep resistant, (ii) oxidation resistant, and (iii) corrosion resistant at elevated temperatures; but also be, (iv) easily fabricated, (v) easily joined, and (vi) economical [2]. An austenitic ferrous alloy with enhanced elevated temperature performance characteristics would be attractive for this application, because such an alloy would be more cost effective and/or easier to join than nickel-base superalloys and ODS alloys.

Besides construction materials for advanced boilers, other power generation systems will benefit from the development of cost effective, creep resistant, oxidation/corrosion resistant alloys -- components and systems, such as recuperators for advanced turbine systems, tube sheets and liners for gas cleanup systems, and metallic inner-connects for solid oxide fuel cell technology. This paper focuses on the initial development of an austenitic stainless steel for potential power plant applications.

Alloy Design and Production

Using the principles of Cr and Ni equivalence, a base composition of Fe-16Cr-16Ni-2Mn-1Mo (in weight percent, wt%) was formulated, to which between 1 and 5 wt% Al and/or Si can be added and maintain an austenitic structure [3,4,5]. Chromium was added to provide oxidation resistance via formation of a protective Cr₂O₃ film; and Ni and Mn to stabilize the austenitic phase. Al and Si were added to enhance oxidation resistance of the alloy.

TABLE I. NOMINAL COMPOSITIONS (WT%) OF ALLOYS

Alloy	Fe	Cr	Ni	Mn	Mo	Si	Al
1	bal	16	16	2	1	0	0
2	bal	16	16	2	1	3	0
3	bal	16	16	2	1	3	1
4	bal	16	16	2	1	2	0
5	bal	16	16	2	1	2	1
6	bal	16	16	2	1	2	2
7	bal	16	16	2	1	1	1

Alloys were produced by vacuum induction melting 5 or 50kg charges of high purity (99.9 pct. +) material. For repeatability, multiple heats were produced. The ingots were forged and rolled to 12.7 mm sheet at 1075°C. The sheet material was annealed for 1 hour at 1200°C and air cooled. Table I shows the nominal composition of the alloys produced for oxidation testing.

Oxidation Resistance

Oxidation specimens with nominal dimensions of 25.4 x 25.4 x 7.6 mm were machined from the anneal sheets and polished to a 400 grit finish. Cyclic oxidation tests were carried out at 700°C and 800°C in a tube furnace. Specimens of a conventional type-304 (Fe-18Cr-8Ni-2Mn-1Si) stainless steel were included in testing as a standard. Weight changes were recorded at regular intervals after removing samples from the furnace and cooling to room temperature.

Figure 1 shows results for cyclic oxidation at 700°C. The baseline Fe-16Cr-16Ni-2Mn-1Mo composition shows the highest oxidation rate, significantly higher than the standard type-304 alloy. All the experimental alloys modified by Al and Si show an improvement (approximately 2 times in terms of weight gain) in oxidation resistance compared to the type-304 alloy. Figure 2 shows results for cyclic oxidation at 800°C. Surprisingly, the experimental alloys with both Al and Si combinations were less oxidation resistant than the standard type-304 alloy. However, the alloys with only Si addition were significantly more oxidation resistant compared to the type-304 alloy (approximately 4 times in terms of weight gain). It is interesting to note, the magnitude of the weight gain after 1000 hrs for the type-304 alloy doubles from 700 to 800°C; however, the magnitude of the weight gain for the experimental Si-alloys is the same at 700 and 800°C.

Figure 3 shows the oxide scales that formed at 800°C on the surfaces of a Si-only alloy and a Si plus Al alloy. Table II lists characteristics of these features. The scale on the Si-only alloy is considerably thinner than the scale on the Si plus Al alloy. In the Si plus Al alloy there are discrete pockets of internal oxidation in the base metal. ESCA analysis [see ref 3], revealed that in both alloy cases the scales are primarily Cr₂O₃; however, in the Si-only alloys, Si is concentrated near or at the oxide metal interface. A bromide etching technique allowed for the examination of the back surface of the oxide scale-base metal interface (Figure 4). The bromide etchant removed the base metal leaving oxide scale for analysis. In the Si-only alloys SiO₂ was detected at grain boundaries and triple points of the scale near the oxide scale-base metal interface (Figure 4). These were absent in the Al plus Si alloys.

The excellent oxidation resistance of Si-only alloys is attributed to the formation of SiO₂ along high diffusivity paths (grain boundaries and triple points) in the scale at or near the scale-base metal interface [3,4,5]. This impedes the outward diffusion of Cr ions and slows the growth of the Cr₂O₃ scale, leading to the excellent oxidation resistance. Al disrupts this mechanism by the formation of internal Al₂O₃ pockets, which does not protect the alloy.

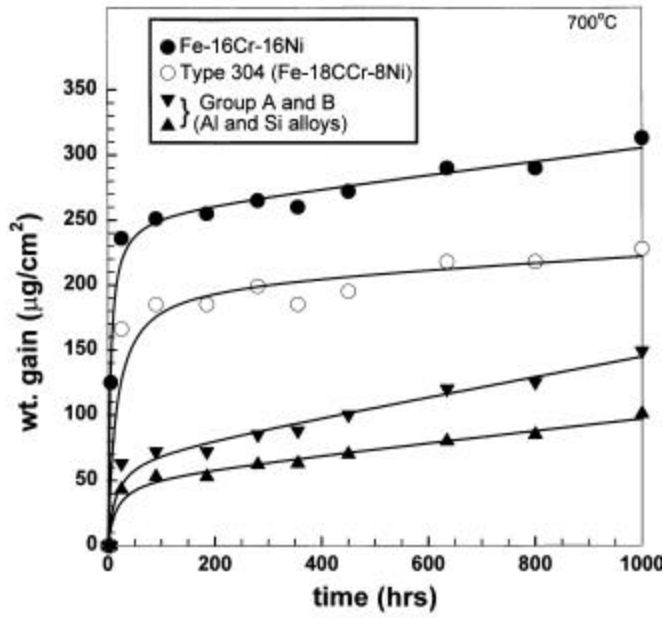


Figure 1. Oxidation behavior at 700°C.

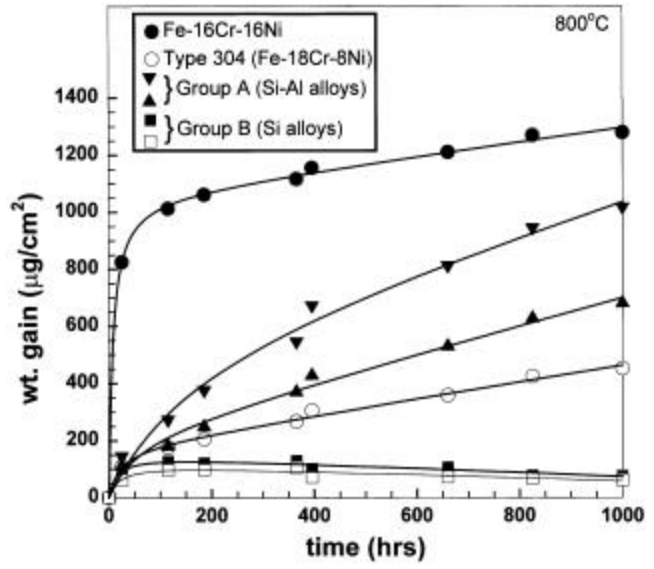
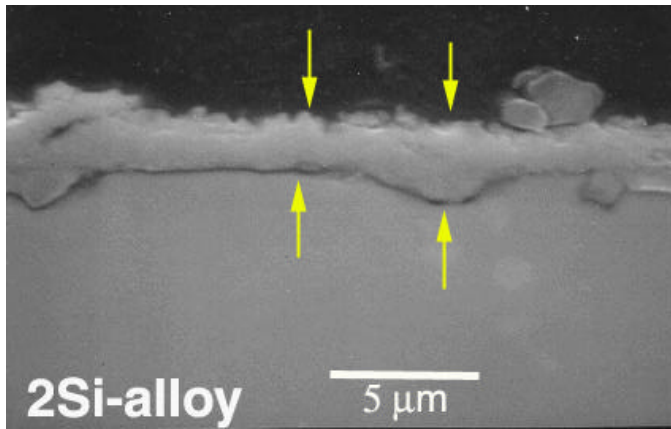
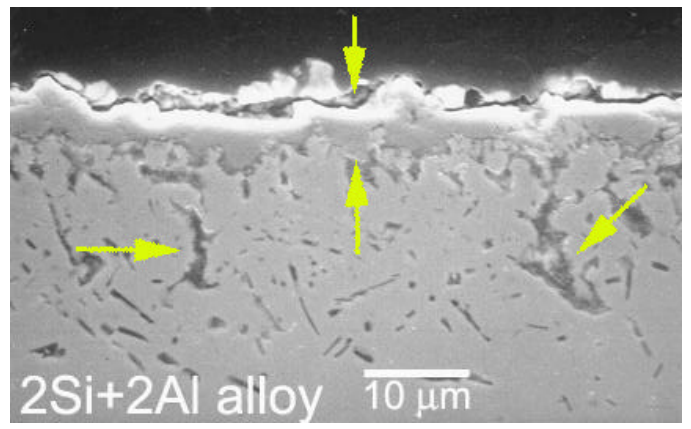


Figure 2. Oxidation behavior at 800°C.



(a)



(b)

Figure 3. Cross sections of the oxide surface scales that formed after 1000 hrs at 800°C on: (a) Fe-16Cr-16Ni-2Mn-1Mo-2Si, and (b) Fe-16Cr-16Ni-2Mn-1Mo-2Si-2Al alloys

TABLE II: Oxide Characteristics
(Formed after 1000 hrs at 800°C)

Alloy	Oxide Features	Penetration (thickness)
Fe-16Cr-16Ni-2Mn-1Mo-2Si	surface film	2-5 μm
Fe-16Cr-16Ni-2Mn-1Mo-2Si-2Al	surface film internal oxidation	7-15 μm 25-30 μm

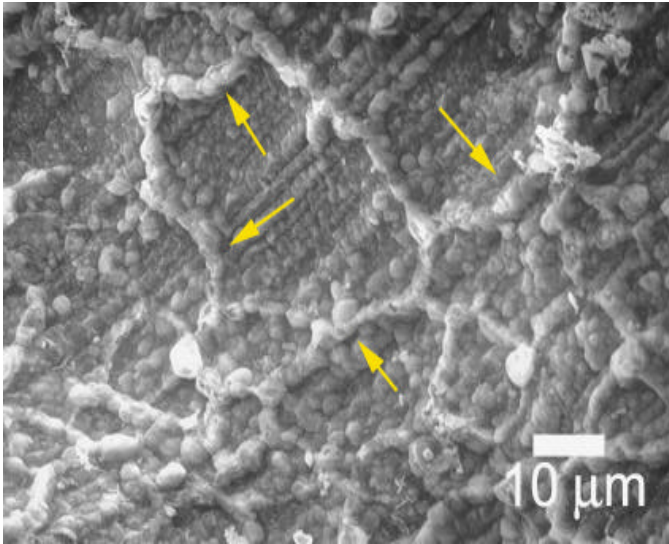


Figure 4. Oxide scale near oxide-metal interface of Fe-16Cr-16Ni-2Mn-1Mo-2Si alloy after 1000 hrs at 800°C. Arrows point to SiO₂ along grain boundaries and triple points.

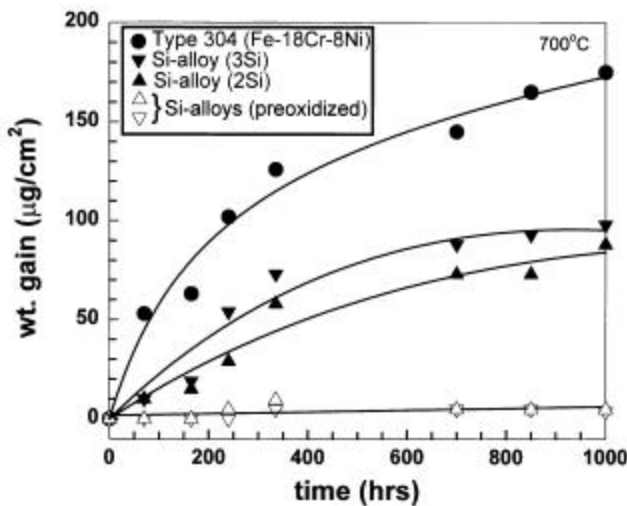


Figure 5. Oxidation behavior, at 700°C, for the Fe-16Cr-16Ni-2Mn-1Mo-2Si alloy. Specimens pre-oxidized at 800°C for 175 hrs show no subsequent weight gain upon further exposure at 700°C.

The 2 and 3 wt% Si alloys were oxidized for 175 hrs at 800°C prior to a 1000 hour exposure at 700°C. Data are shown in Figure 5. The not pre-oxidized and the type-304 standard showed the same relationship as the earlier 700°C tests (Figure 1). The pre-oxidized specimens showed zero weight gain after 1000 hours at 700°C. The implication of this result is that this may provide a method for producing in-situ protective coatings.

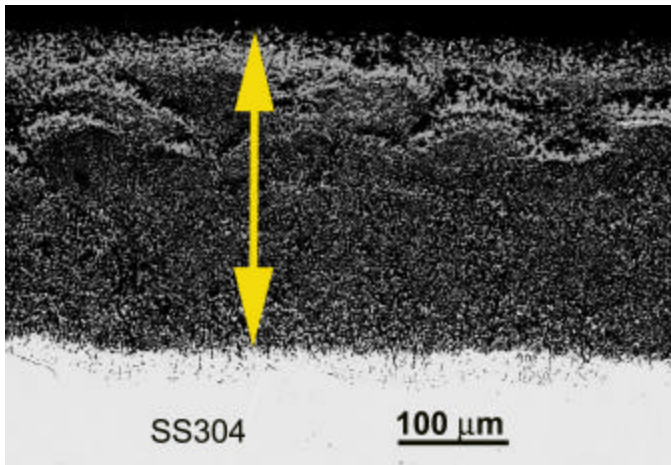
Sulfidation Resistance

Specimens of the experimental Fe-16Cr-16Ni-2Mn-1Mo-2Si alloy, as well as, a standard type-304 alloy were sent to IPST in Atlanta, Georgia, for sulfidation testing. Figures 6 and 7 show cross sections of the surfaces of the alloys after exposure to 1% H₂S at 700°C for 360 hrs (15 days). A thick and porous scale formed on the type-304 alloy (Fig. 6a). A much thinner scale formed on the surface of Fe-16Cr-16Ni-2Mn-1Mo-2Si alloy (Fig. 6b). Significant grain boundary attack occurred below the porous scale in the base metal of the type-304 alloy (Fig. 7a). By contrast, little or no base metal grain boundary attack occurred in experimental Fe-16Cr-16Ni-2Mn-1Mo-2Si alloy (Fig 7b).

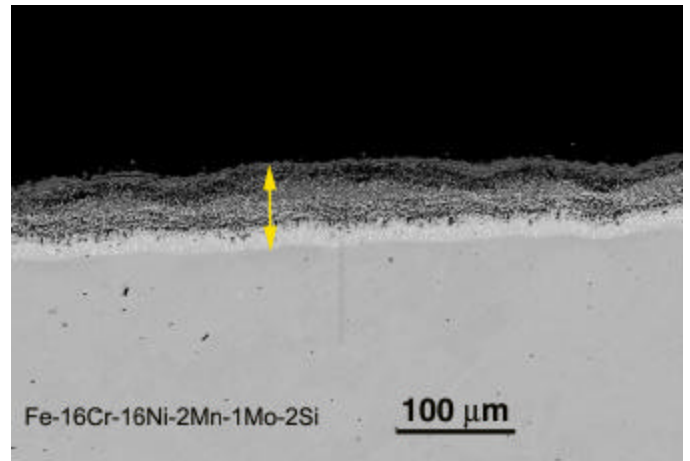
The results indicate that the experimental Si modified alloys can be designed to be more corrosion resistant than conventional alloys. It appears resistance to sulfidation attack of the experimental alloys is the formation of protective species along high diffusivity paths, such as grain boundaries and triple points, similar to what occurs during oxidation. This is suggested by the absence of significant grain boundary attack in the experimental alloys. These results are very preliminary in nature and more work is required to quantify the hot-corrosion behavior of these alloys. Such efforts are currently underway, utilizing ARC's newly built high temperature gaseous corrosion laboratory.

Mechanical Properties

Tensile tests were performed in air at 25, 600, 700 and 800°C. The experimental alloys were further modified by alloying with carbide forming elements (Ti, Nb, V added as 10 times the carbon content) to impart high temperature strength. The alloys were produced by VIM followed by hot-forging and hot-rolling into plate. Prior to testing the alloys were solution annealed at 1175°C for 1 hour followed by aging at 700°C for 1 hour.

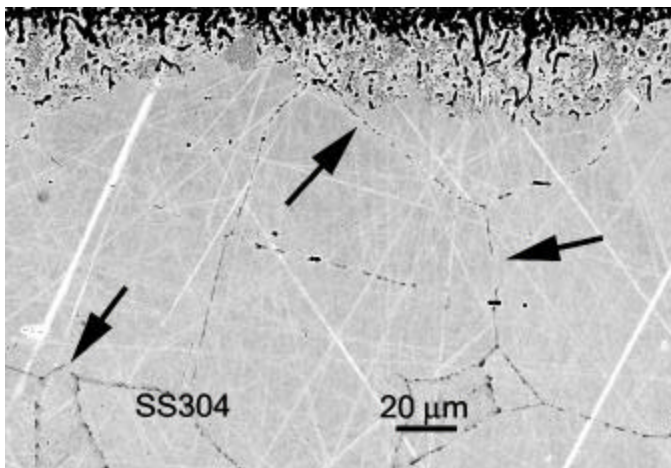


(a)

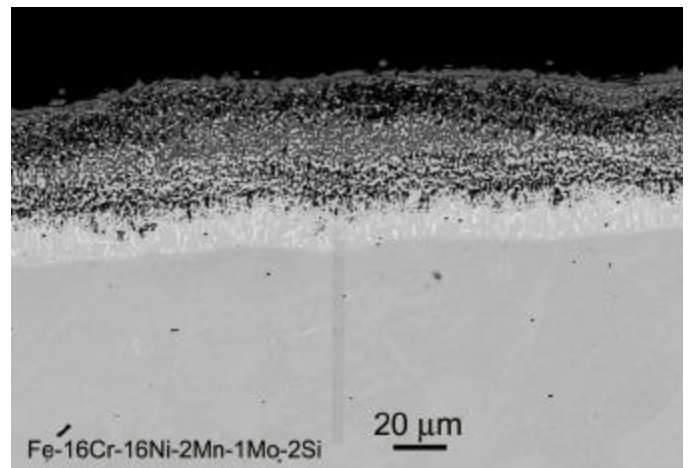


(b)

Figure 6. Cross section of scales on alloys after exposure to 1 pct. H_2S at $700^\circ C$ for 360 hrs: (a) type-304, and (b) Fe-16Cr-16Ni-2Mn-1Mo-2Si alloy



(a)



(b)

Figure 7. Cross section of alloys after exposure to 1 pct. H_2S at $700^\circ C$ for 360 hrs: (a) base metal below the scale of the type-304, and (b) Fe-16Cr-16Ni-2Mn-1Mo-2Si. Notice, significant grain boundary attack occurs in the base metal of the type-304 alloy. Limited grain boundary attack occurs in the Fe-16Cr-16Ni-2Si alloy.

Yield stress versus temperature for the alloys are plotted in Figure 8. At the elevated temperatures, the experimental alloys modified with carbides are about twice as strong as unreinforced experimental alloys and the commercial type-304 alloy. The tensile properties of these alloys compare favorably to literature values (from ref. 6) for type-347 stainless steel (Figure 9).

It should be mentioned that type-347H, the high carbon alloy, has higher strengths than the type-347 plotted on Figure 9. It also should be emphasized that the microstructures of the experimental alloys have not been optimized with respect to grain size, and carbide size, distribution and volume fraction. All these factors effect mechanical properties and can be controlled through heat-treatment and composition.

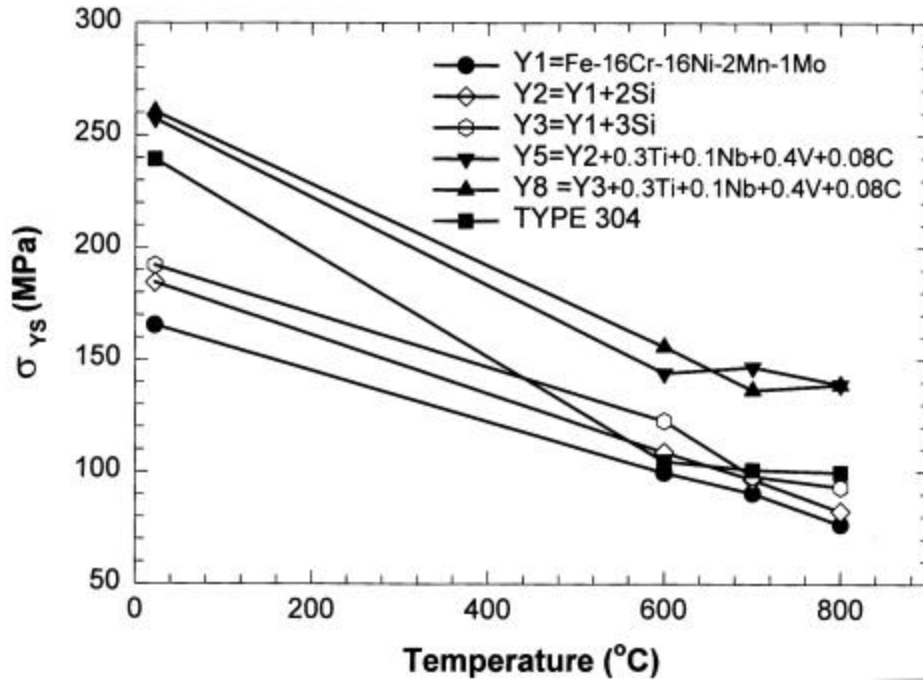


Figure 8. Tensile yield stress (σ_{ys}) versus test temperature.

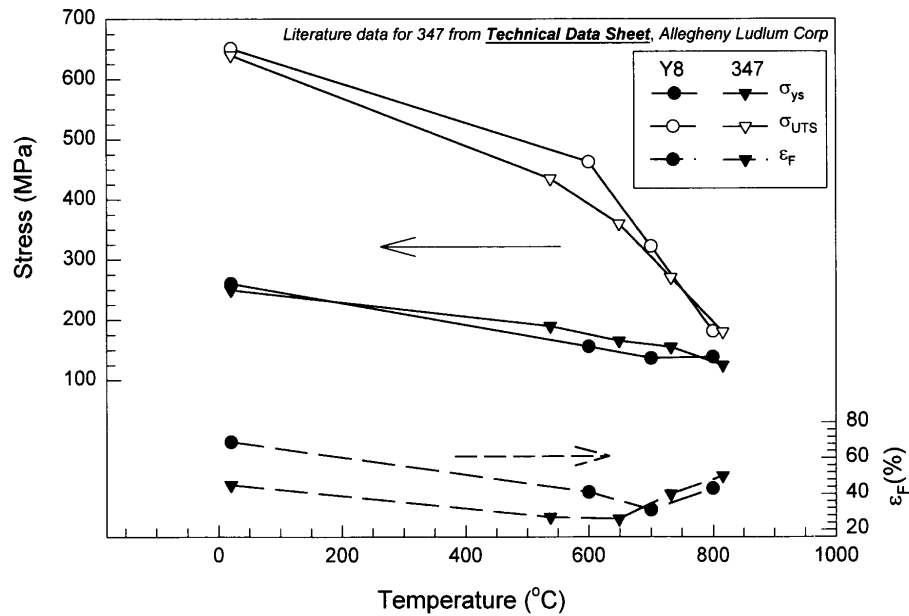


Figure 9. Comparison between the properties of alloy Y8 (Fe-16Cr-16Ni-2Mn-1Mo-3Si-0.3Ti-0.1Nb-0.4V-0.08C) and literature data (ref. 6) for type-347 stainless steel (Fe-18Cr-11Ni-2Mn-0.75Si-0.8(Nb+Ta)-0.08C).

Joining

Vari-strain welding tests are being performed to establish joining procedures for these alloys. During vari-strain testing, specimens are deformed to various strains simultaneously during welding, as shown in Figure 10. The purpose of the deformation is to mimic residual stresses that can develop during joining of fixed structures. Figure 11a shows die penetrate testing of the weld beads on alloy Y8 deformed to 0, 1, 4, and 6% strain from the initial vari-strain test. Red spots indicate where the die has penetrated into the weld, indicating weld defects. Figure 11b shows a higher magnification of the weld bead on alloy Y8 deformed to 6% strain, the maximum deformation of the test. These initial results indicate that once the welding parameters (e.g., energy input, pre-heating, post-heating, etc.) are optimized, these alloys should be readily joined.

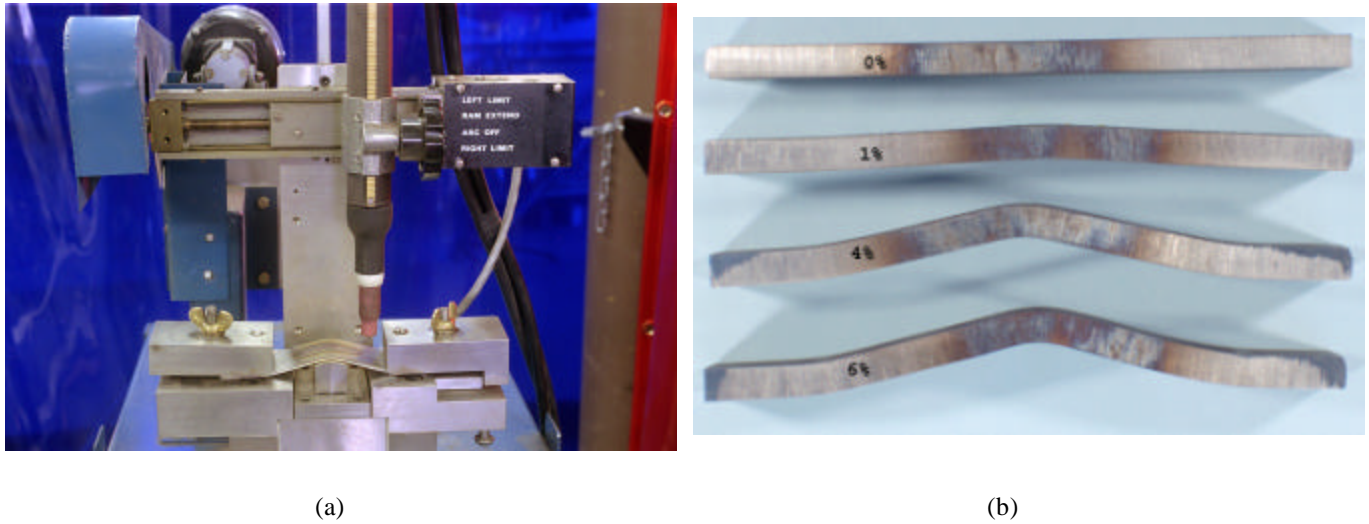


Figure 10. Vari-strain welding test: (a) apparatus; (b) macro-photographs of specimens after testing.

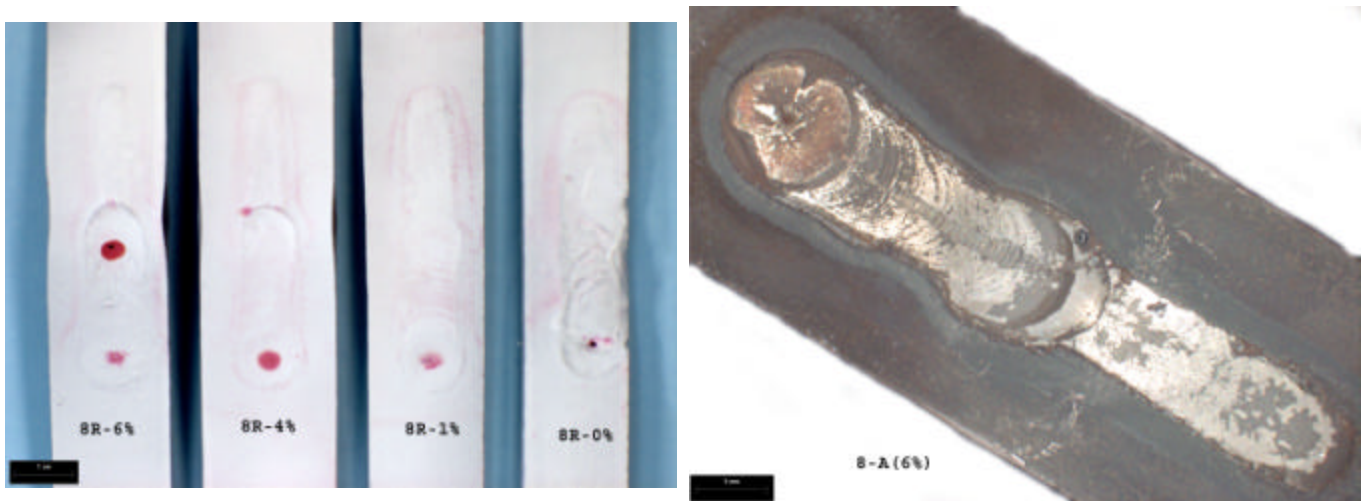


Figure 11. Initial vari-strain testing on alloy Y8: (a) die penetrate testing on weld beads, red indicates where die penetrate into weld; (b) high magnification view of a weld bead subjected to 6% strain.

Summary

- Oxidation characteristics of Fe-16Cr-16Ni-2Mn-1Mo alloys modified with minor Si additions are excellent at 700 and 800°C, superior to type-304 stainless steel.
- Alloys pre-oxidized at 800°C, show no weight gain during subsequent 1000 hour oxidation tests at 700°C. This has the potential for producing in-situ protective coatings.
- SEM and ESCA studies suggest that the effect of minor Si addition on oxidation resistance at 800°C may be associated with grain boundary networks of SiO₂.
- Preliminary exposure testing (1% H₂S at 700°C for 360 hrs) indicates these alloys also have superior sulfidation resistance compared to type-304 stainless steel.
- Elevated temperature tensile results indicate that carbide-strengthened, Si-modified Fe-16Cr-16Ni-2Mn-1Mo alloys have comparable strengths to literature values for type-347 stainless steel.
- Initial vari-strain tests indicate these alloys are joinable.

Current and Future Research

- Fully understand oxidation mechanism.
- Quantify sulfidation resistance.
- Establish a reliable joining procedure.
- Evaluate mechanical properties, including creep resistance.
- Determine corrosion resistance in coal combustion environments.
- Apply alloying approach (minor alloying to improve environmental resistance) to other alloy compositions.

References

1. L.A. Ruth and N. Birks, "Material Needs for High Efficiency Coal Fired Power Plants."
2. R. Viswanathan, R.W. Swindeman, I.G. Wright, R. Purgert, "Materials for Ultra Supercritical Coal-Fired Power-Plants," Proc. 27th International Conference on Coal Utilization and Fuel Systems, Coal Technology Association, Gaithersburg, MD, 2002, p. 257.
3. J.S. Dunning, D.E. Alman, and J.C. Rawers, "Influence of Silicon and Aluminum on the Oxidation Resistance of a Lean-Chromium Steel," Oxidation of Metals, vol. 57, Nos. 5/6, 2002, p. 409.
4. J.S. Dunning, D.E. Alman and J.C. Rawers, "The Effect of Silicon and Aluminum Additions on the Oxidation Resistance of Lean Chromium Stainless Steels" Proc. 15th Annual Fossil Energy Materials Conference," available at www.ornl.gov/fossil.
5. J.S. Dunning and D.E. Alman, "Improvements in High Temperature (>700°C) Performance of Stainless Steels for Power Plant Efficiency," Proc. 27th International Conference on Coal Utilization and Fuel Systems, Coal Technology Association, Gaithersburg, MD, 2002, p. 1131.
6. Allegheny Ludlum, "Technical Data Blue Sheet – Stainless Steel Type 321, 347 and 348." available at www.allegeny-ludlum.com.