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The Potential of Modified Type 310 Stainless Steel for Advanced Fossil Energy Applications

R. W. Swindeman

Fossil
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THE POTENTIAL OF MODIFIED TYPE 310 STAINLESS STEEL FOR ADVANCED FOSSIL ENERGY APPLICATIONS

R. W. Swindeman

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THE POTENTIAL OF MODIFIED TYPE 310 STAINLESS STEEL FOR ADVANCED FOSSIL ENERGY APPLICATIONS*

R. W. Swindeman

ABSTRACT

An evaluation was undertaken to determine the potential of modified type 310 stainless steel for fossil energy applications. First, alloy performance criteria for components in several emerging technologies were identified. Then, a brief review of existing alloy technology was undertaken relative to performance criteria. Key issues were the tendency for type 310 stainless steel to embrittle due to the formation of intermetallic phases, the poor resistance of type 310 stainless steel to highly sulfidizing environments, the need to examine the strength and ductility of weldments, and the lack of a long-time data base and criteria for setting allowable stress at temperatures in excess of 800°C. An activity was outlined that would address several of the key issues.

1. INTRODUCTION

In the last ten years, several competing advanced energy technologies have been developed to improve thermal efficiency and reduce emissions resulting from the combustion and conversion of coal.[1-3] As these technologies move toward the construction of demonstration plants, the selection of the structural materials becomes of paramount importance.[4] The temperatures, pressures, and environments under which the structural materials will operate vary considerably from one concept to another, so one can expect a large range of materials to be utilized. Materials will range from steels, nickel-base alloys, cobalt-base alloys, and titanium alloys, to ceramics. Important considerations in materials selection have always been the cost, availability, and depth of experience. The U.S. Department of Energy (DOE), Office of Fossil Energy, Advanced Research and Development (AR&TD) Materials Program addresses the materials needs of each technology and attempts, where possible, to develop or identify materials that could serve as many applications as possible.

Earlier, research was undertaken to examine alloys for the advanced steam cycle. Here, emphasis was on materials for superheater tubing. Alloy design and evaluation criteria were identified, and work was begun to examine four groups of alloys.[5] These included lean

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stainless steel (containing less than 20% chromium); higher chromium iron-base alloys; nickel-base alloys; and aluminum-bearing, high-temperature alloys. Most of the work on lean stainless steel and higher chromium iron-base alloys has been completed.[6,7] During the six years of the activity, technological interests shifted from the pulverized-coal (PC) advanced steam cycle to combined cycles. Operational requirements changed accordingly, and higher operating temperature became of interest. Of the materials included in the research on advanced steam-cycle tubing, a modified alloy (800H); a modified type 310 stainless steel; and some aluminum-bearing, high-temperature alloys could be extended to the higher temperatures of interest. Type 310 stainless steel, which is relatively cheap, has been an alloy of preference in many high-temperature systems and, if properly modified, is judged to have potential as a structural material in several advanced energy systems. Experience has shown that some improvements to the steel could be of benefit in improving component life, and this report addresses research needs to accomplish this goal.

2. ALLOY PERFORMANCE CRITERIA

Alloy performance criteria are closely linked to applications, and Table 1 provides information regarding temperatures, pressures, and environments for several fossil energy technologies.[8] These technologies cover a broad range, from life extension of existing fossil power plants to the second-generation, combined-cycle (CC) concepts.

Table 1. Operating conditions for structural materials in various fossil energy applications where modified type 310 stainless steel is of interest

Application	Component	Temperature	Pressure	Environment
Conventional PC plant	superheater/ reheater	540 to 650°C 1000 to 1200°F	10 to 25 MPa 1.5 to 3.5 ksi	steam, coal ash
Advanced PC plant	superheater/ reheater	600 to 700°C 1100 to 1300°F	25 to 30 MPa 3.5 to 4.5 ksi	steam, coal ash
PFBC[a] CC	cyclones, ducts, tubes, heat exchangers, hot-gas cleanup	800 to 900°C 1475 to 1650°F	1 to 3 MPa 0.15 to 0.4 ksi	oxidizing, dry ash, steam
IGCC[b]	heat exchangers, internals, hot-gas cleanup	800 to 980°C 1475 to 1800°F	2 to 10 MPa 0.3 to 1.5 ksi	sulfidizing, steam, ash
Fuel cells	current collector	650°C 1200°F	atmospheric pressure	carbonate

[a] Pressurized fluidized bed combustor.
[b] Integrated gasification combined cycle.

In existing plants the burning of more corrosive coals in fossil plants has increased corrosion in superheater/reheater tubing. In the replacement of boilers, corrosion resistance and cost are the major considerations in the selection of the tubing. In at least one instance, a modified type 310 stainless steel was selected in preference to type 347 stainless steel or alloy 800H as replacement tubing in the reheater.[9]

In the near term, the Electric Power Research Institute (EPRI) is sponsoring a project focused on a "state-of-the-art" power plant (SOAPP).[10] These advanced PC plants are being designed to produce steam at temperatures approaching 600°C (1112°F) and are constructed of high-performance materials and components, as sketched in Fig. 1. With cogeneration or topping cycles, these plants could operate at efficiencies nearing 50% (ref. 11). In the selection of materials for the superheater, strength and corrosion resistance are more significant than cost. Depending on the ash and chlorine content of the coal, either clad or bare tubing is being considered. Because of its excellent coal ash corrosion resistance, modified type 310 stainless steel has emerged as a strong candidate for the superheater/reheater tubing.[9,12]

The atmospheric fluidized bed combustor (AFBC) and PFBC require materials that can resist erosion/corrosion under conditions of oxidation where sulfur-bearing particulates are present. A schematic drawing of one of these second-generation PFBC units is shown in Fig. 2 (ref. 2). Here, corrosion-resistant alloys will be needed in the bed and freeboard regions of the combustor, filter units, and heat-recovery steam generator. Although pressures are low compared to PC boilers, temperatures are much higher, and structural materials in the gas stream are usually protected by refractory liners. Heat exchanger tubing cannot be insulated, however, and the structural materials in the hot-gas cleanup systems must operate at gas temperatures that may be in the range of 800 to 900°C. Type 310 stainless steel and modified type 310 stainless steel have been found to be two of the better alloys for use in these systems in regard to corrosion resistance.[13] The low-creep strength and tendency toward embrittlement in type 310 stainless steel are issues of concern; hence, modification of the steel to improve strength and ductility is of interest.

Operating conditions in gasifiers are severe. High temperatures and sulfidizing environments have made it difficult to find a suitable material for vessel internals. The advanced IGCC concept, sketched in Fig. 3, will be no exception.[2] To date, the best metallic materials for gasifier internals appear to be cobalt-base alloys, but cyclones, heat exchangers, and hot-gas cleanup components could operate at lower temperatures, or less corrosion-resistant alloys could be protected by sulfidation-resistant claddings such as iron aluminide.[14]

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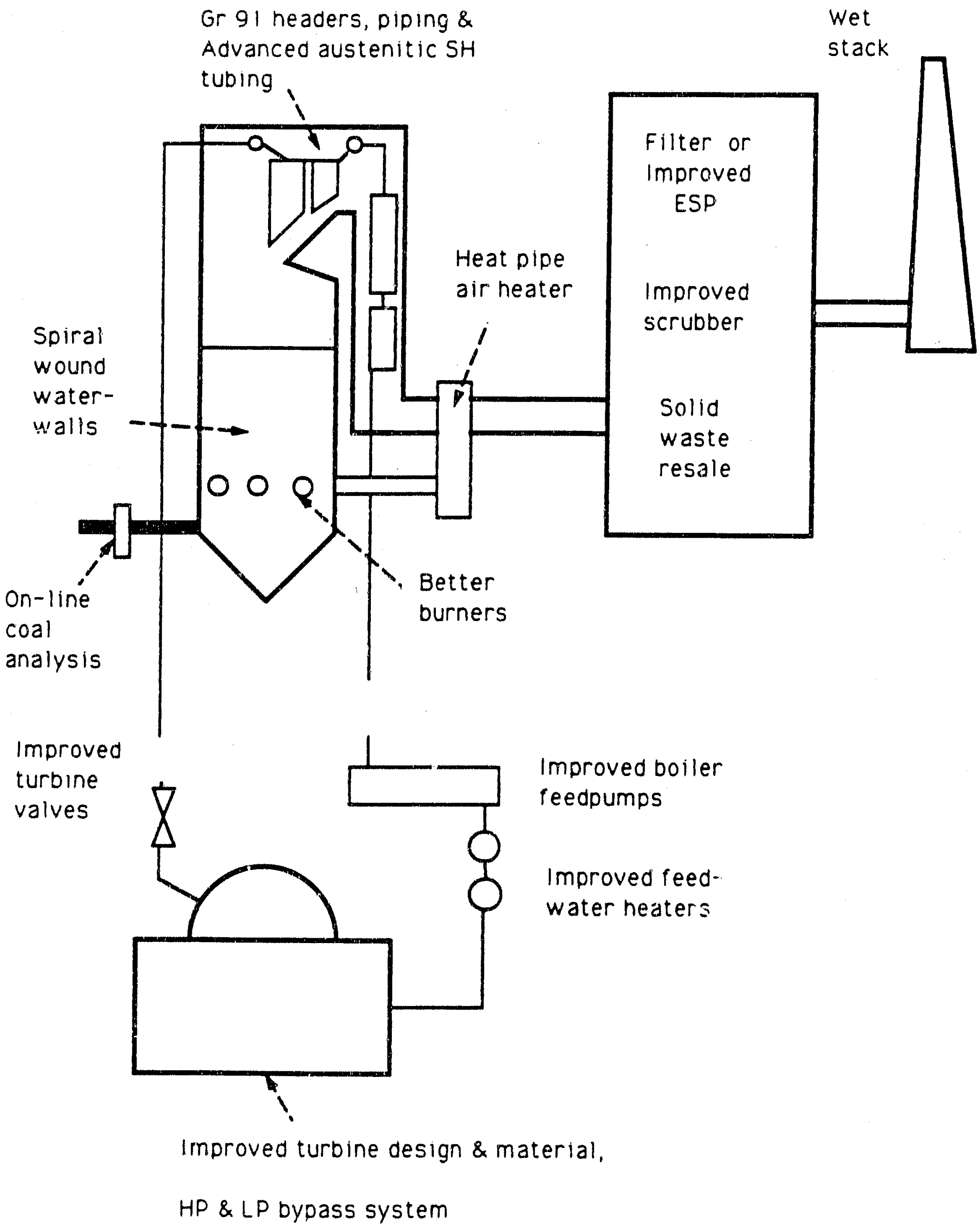

Fig. 1. Schematic drawing of the EPRI SOAPP. (Applications for modified type 310 stainless steel could be in the superheater/reheater tubing.)

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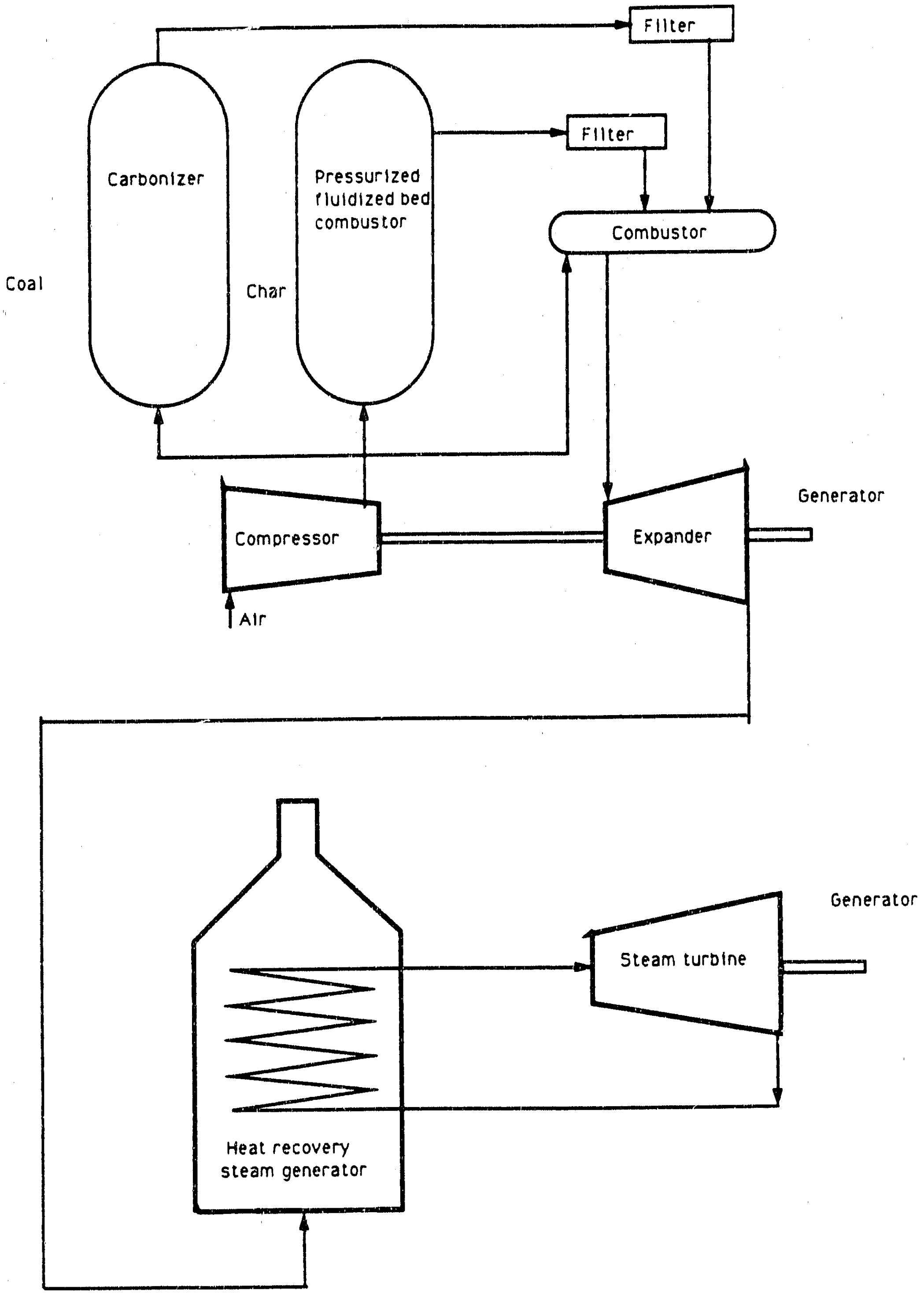

Fig. 2. Schematic drawing of a second-generation PFBC plant. (Applications for modified type 310 stainless steel could be for filter structural support and heat-recovery steam generator tubing.)[2]

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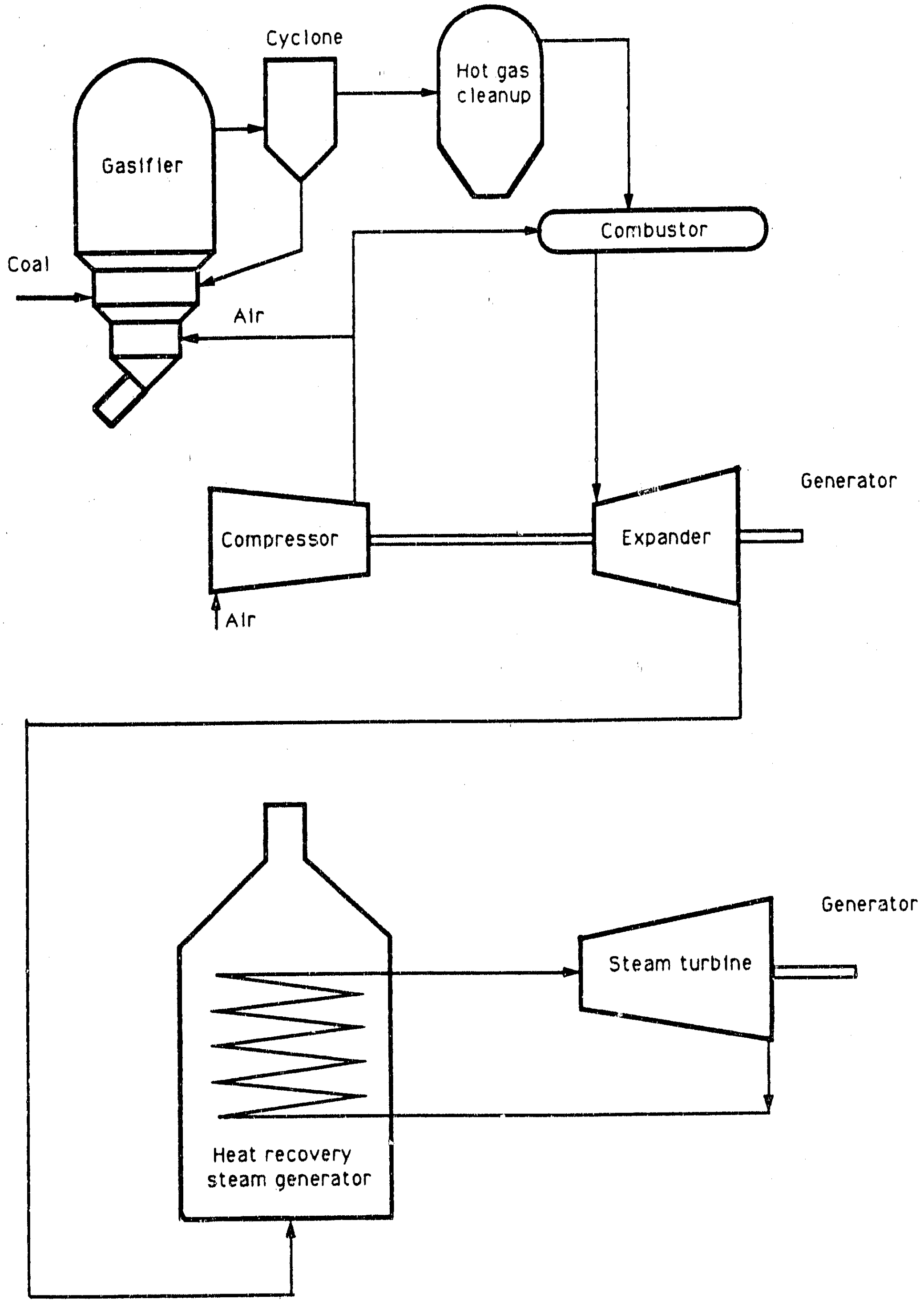

Fig. 3. Schematic drawing of an advanced IGCC plant. (Applications for modified type 310 stainless steel could be for cyclones, hot-gas cleanup internals, and heat-recovery steam generator tubing.)[2]

Type 310 stainless steel has been found to be superior to many other high-temperature alloys as a heat exchanger material, and modifications to the steel have improved its corrosion resistance.[15,16] Hence, it seems likely that this steel could see service in IGCCs.

Finally, corrosion is a problem in fuel cell technology. Molten alkali carbonates attack structural materials, and the extent of attack is related to both the carbonate composition and the gas composition. Modified type 310 stainless steel has been considered in this application.[17]

Alloy performance criteria for modified type 310 stainless steel cannot be as specific as those identified for superheater tubing in the advanced steam cycle application.[5] However, there are a number of generic criteria that could be useful in guiding a design and evaluation program. These may be grouped into four categories: Metallurgical Stability, Fabrication and Joining, Mechanical Behavior, and Corrosion Behavior. Briefly, the following guidelines should apply:

1. Metallurgical stability. The steel shall be austenitic. Composition shall be adjusted to limit the precipitation of carbides, nitrides, and intermetallic compounds to levels that ensure reasonable ductility and toughness in the temperature range of interest. A target room-temperature elongation in the tensile test after aging or simulated service exposure shall be 10% (or greater), and the Charpy V toughness shall be set at 15 J (or greater).

2. Fabrication and joining. The steel shall be capable of being fabricated as sheet, plate, tubing, and bar products by good steelmaking practice. Thicknesses up to 25 mm (1 in.) shall be required. The capability of co-extruding tubing with commercial ferritic and austenitic alloy shall be demonstrated. The steel shall be weldable, either autogenously or by means of a commercially available filler metal.

3. Mechanical behavior. Useful strength levels shall be required at temperatures in the range of 760 to 900°C (1400 to 1650°F). A target rupture strength shall be set at 10 MPa (1.4 ksi) for 100,000 h at 900°C (1650°F).

4. Corrosion behavior The corrosion resistance of the steel shall be equivalent to, or better than, type 310 stainless steel for the service conditions outlined in Table 1.

3. DESCRIPTION OF CURRENT MATERIALS TECHNOLOGY

Type 310 stainless steel is a high-chromium, high-nickel steel that has been in service for decades. There are several modifications currently available, and typical chemistries are provided in Table 2. Wrought alloys include types 310, 310S, 314, 310Cb, and a new steel, type 310HCbN stainless steel, developed by Sumitomo under the name HR3C (ref. 18). The standard-grade, type 310 stainless steel is quite simple in regard to its chemistry and allows the highest level of carbon (0.15% for tubing) of any 300 series stainless steel. Type 310S stainless steel is similar to type 310 stainless steel, except that the maximum carbon is set at 0.08%. Type 314 stainless steel includes a higher level of silicon (1.5 to 3%). Type 310Cb stainless steel has a maximum limit of 0.08% on carbon and a 1.1% limit on niobium. The type 310HCbN stainless steel contains niobium and nitrogen with some restrictions on residual element chemistry.[18] More details of the chemical specifications can be found in the American Society for Testing and Materials (ASTM) standards for the applicable product.

Table 2. Typical chemistries for 25Cr-20Ni stainless steels

Element*	Type 310	Type 310S	Type 310Cb	Type 310HCbN	Type 314
C	0.13	0.03	0.06	0.06	0.14
Mn	1.4	1.1	1.2	1.2	0.5
Si	0.6	0.4	0.5	0.4	2.2
P	0.03	0.03	0.03	0.01	0.02
S	0.02	0.02	0.02	< 0.01	0.01
Cr	25.0	25.0	25.0	25.0	25.0
Ni	20.0	20.0	20.0	20.0	20.0
Nb	--	--	10 x C	0.4	
N				0.2	

*Nb is niobium in the element column, but the ASTM and the American Society of Mechancial Engineers (ASME) use the symbol Cb. Mo is permitted to a level of 0.75% in type 310Cb and type 310S. The Nb value for type 310Cb is 10 x C but cannot exceed 1.1%. The N content of the type 310 steels is generally not reported but is typically around 0.02%. The S and P contents of recently melted steels are often well below 0.03%.

3.1 METALLURGICAL CONSIDERATIONS

Type 310 stainless steel solidifies as austenite and remains austenitic at usual working temperatures, say at 1100°C (2000°F), as shown in the ternary diagram in Fig. 4(*a*) [refs. 19,20]. The steel enters the austenite plus sigma phase field somewhere below 980°C (1000°F), as shown in Fig. 4(*b*) for 650°C (1200°F). The amount of sigma phase formed and the kinetics of the sigma phase precipitation process, however, are influenced by various element additions. The development of sigma phase in type 310, type 314, and type 310Cb stainless steels was examined by Menard in 1952 (ref. 21), and more recently Barcik examined sigma phase in type 310, type 314, and type 310S stainless steels.[22] Figure 5 shows the time-temperature-precipitation (TTP) diagrams constructed for the three steels by Barcik. In type 310 stainless steel, sigma phase developed at 950°C (1750°F) in less than 200 h and reached 5% after 10,000 h. The nose of the TTP curves was near 800°C (1500°F) where sigma phase started in less than 10 h and reached 5% in approximately 100 h. At 600°C (1100°F) sigma appeared in less than 1000 h. Type 314 stainless steel exhibited a TTP diagram that was similar to type 310 stainless steel. Near 800°C (1500°F) approximately 5% sigma precipitated within 100 h at 950°C. In type 310S stainless steel, sigma phase formed more slowly and less precipitated. For example, less than 0.2% formed after 1000 h at 800°C (1500°F). Menard found that the addition of niobium in type 316Cb stainless steel shortened the time to precipitate sigma phase.[21]

The precipitation of the $M_{23}C_6$ carbide is also important to the development of sigma phase. Carbide precipitation was found to promote the formation of sigma, since it depletes the matrix of carbon that helps to stabilize austenite relative to sigma phase.[21,23] The TTP diagram for the $M_{23}C_6$ carbide in type 310 stainless steel was constructed by Binder, Brown, and Franks[23] from intergranular corrosion sensitization data, and their diagram is provided in Fig. 6. For a steel with 0.028% carbon, the nose of the curve occurs around 750°C in less than 0.1 h. The appearance of the carbide also results in embrittlement of the type 310 stainless steel.

Bungart and coworkers[19] examined the influence of nitrogen on the stability of steels whose compositions bracketed type 310 stainless steel, as shown in Fig 7. They found that the solubility of nitrogen diminished with increasing nickel content and decreasing temperature. The sigma phase was observed in alloys aged at 750°C and lower, regardless of the nitrogen level, but the amount of sigma phase, relative to $M_{23}C_6$, decreased with increasing temperature. Sigma phase was not observed at 850°C and higher, regardless of the

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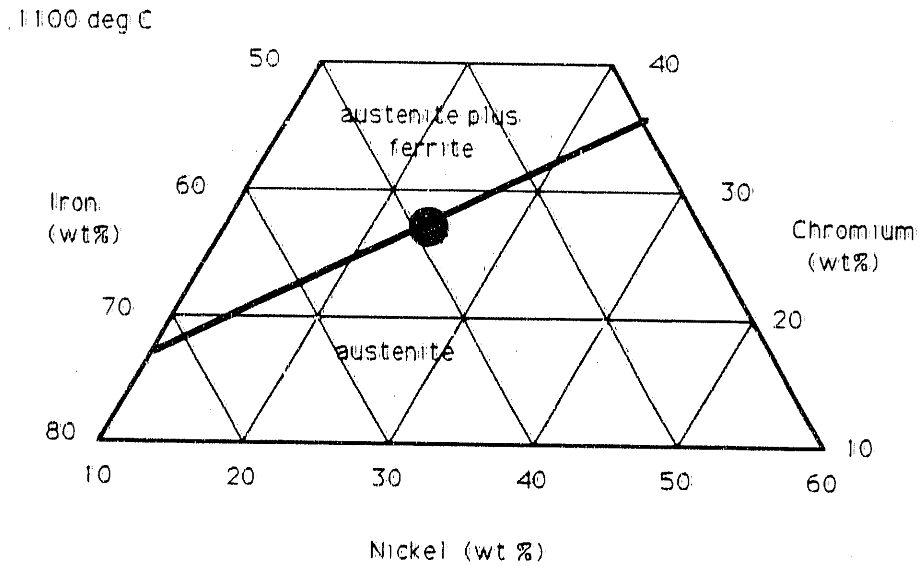

(*a*)

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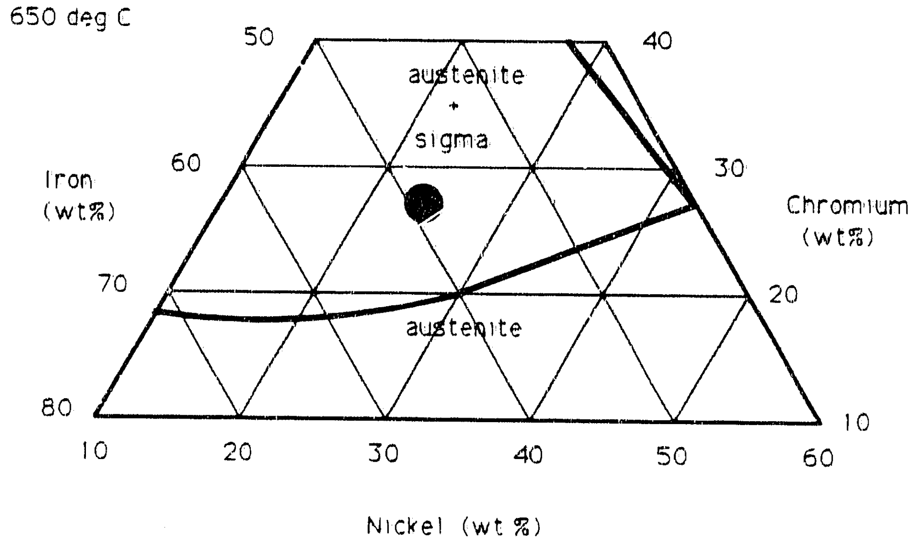

(*b*)

Fig. 4. Location of various stainless steels in the iron chromium nickel equilibrium diagram at: (*a*) 1100°C and (*b*) 650°C (ref. 20).

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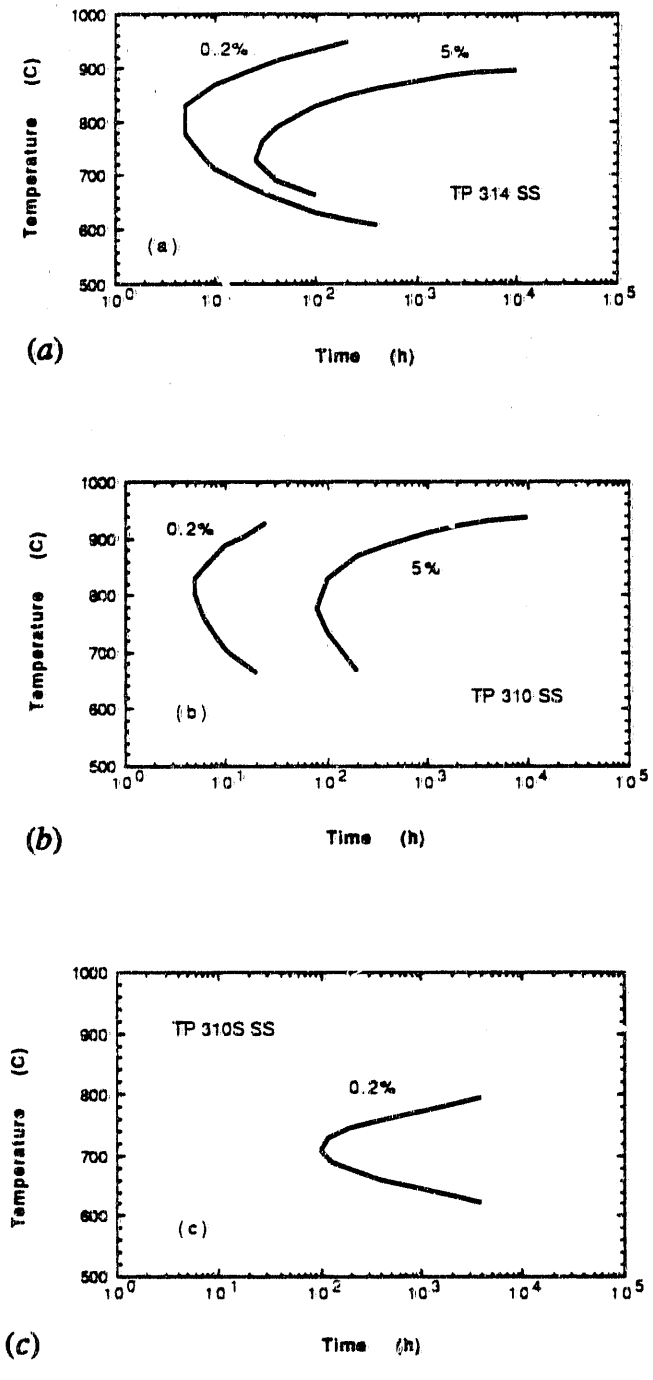

Fig. 5. TTP curves for sigma phase in three 25Cr-20Ni stainless steels: (*a*) type 314 stainless steel, (*b*) type 310 stainless steel, and (*c*) type 310 stainless steel.[22]

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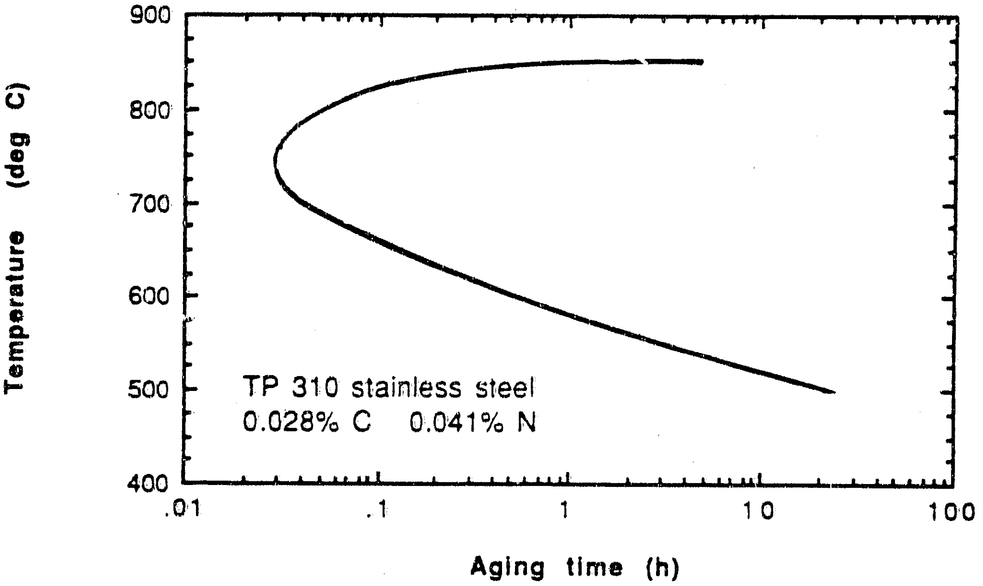

Fig. 6. TTP curves for $M_{23}C_6$ in type 310 stainless steel based on corrosion tests.[23]

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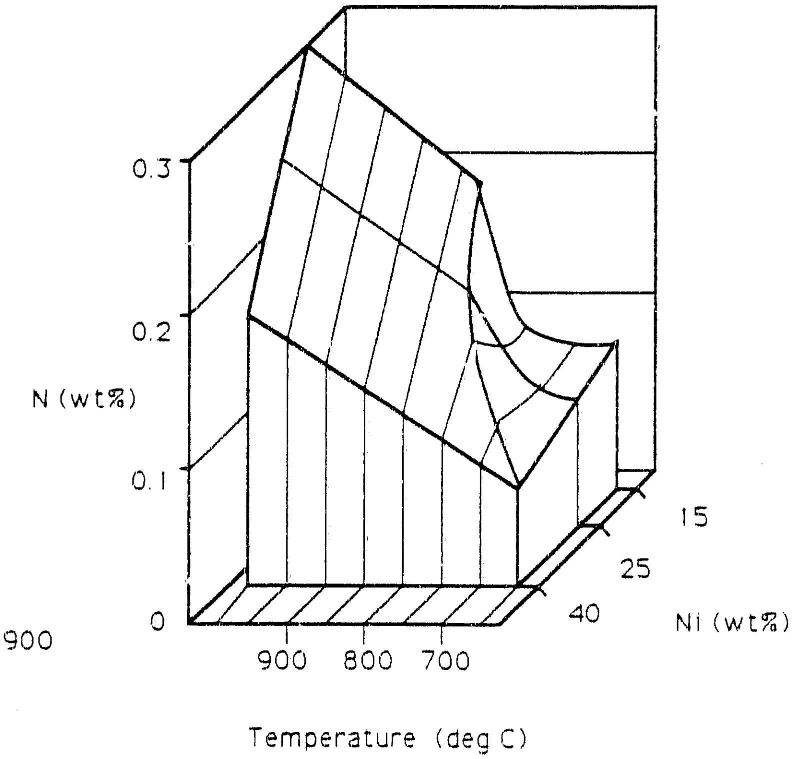

Fig. 7. Influence of chromium, nickel, and temperature on the solubility of nitrogen in 25 Cr stainless steels.[19]

nitrogen content (either 0.02 or 0.2%). A nitride phase (Cr_2N) was observed in alloys containing 0.2% nitrogen, and there was some evidence that the amount of sigma phase was less at 800°C in the steels with 0.2% nitrogen.

Yoshikawa and coworkers[18] examined the stability of type 310HCbN stainless steel at temperatures in the range of 600 to 800°C for times to 10,000 h. They observed $M_{23}C_6$ and NbCrN precipitation. Precipitates increased with increasing time and temperature, but most nitrogen remained in solid solution. They observed that sigma formed when the steel contained less than 20% nickel and less than 0.2% nitrogen. They observed the precipitation of Cr_2N phase when the steel contained more than 22% nickel and 0.25% nitrogen. The appearance of either phase produced lower toughness. Hence, the composition range of type 310HCbN was selected to minimize the quantity of sigma and Cr_2N phases.

Ductility and toughness vary significantly in the 25Cr-20Ni stainless steels. Generally, the formation of sigma phase reduces room-temperature ductility with modest increases in hardness and strength, while the precipitation of carbides and nitrides may increase strength significantly with a corresponding decrease in ductility and toughness. Data are available in the literature that reveal the effect of high-temperature exposure on the ductility and toughness of type 310 stainless steel.[21, 24-26] The effect of time-temperature exposure on the Charpy keyhole impact toughness of type 310 stainless steel has been summarized by the diagram shown in Fig. 8. Here, it may be seen that very low toughness values are likely at temperatures of interest in advanced energy system components after 10,000-h exposures. The Charpy V toughness values were around 7 J (5 ft-lbs) for aging 10,000 h at temperatures in the range of 649 to 732°C (1200 to 1350°F) [ref. 27]. Cold work prior to aging produced values as low as 4 J (ref. 25). Similarly, type 310Cb and type 314 stainless steels suffer degradation, as shown in Fig. 9 (ref. 21). Both of these steels embrittled more rapidly than type 310 stainless steel, and type 314 produced the lowest toughness at 10,000 h. Charpy keyhole toughness numbers were roughly half those observed for type 310 stainless steel. In contrast, the type 310HCbN stainless steel exhibited good toughness after long-time exposures to 750°C, as indicated in Fig. 10 (ref. 18). Here, Charpy V toughness values exceeded 40 J (~ 30 ft-lbs) for times to 10,000 h and aging temperatures in the range of 600 to 800°C. It would appear, therefore, that a range of chemistries can be found for which modified 25Cr-20Ni stainless steel can maintain acceptable toughness values.

Room-temperature tensile ductilities diminished in a pattern similar to impact energy values. The type 310 stainless steel exhibited elongation values less than 10% for some combinations of aging temperatures and times,[25,27] while type 310HCbN stainless steel retained at least 30% tensile ductility for times to 10,000 h at temperatures to 800°C. (See Fig. 11.)

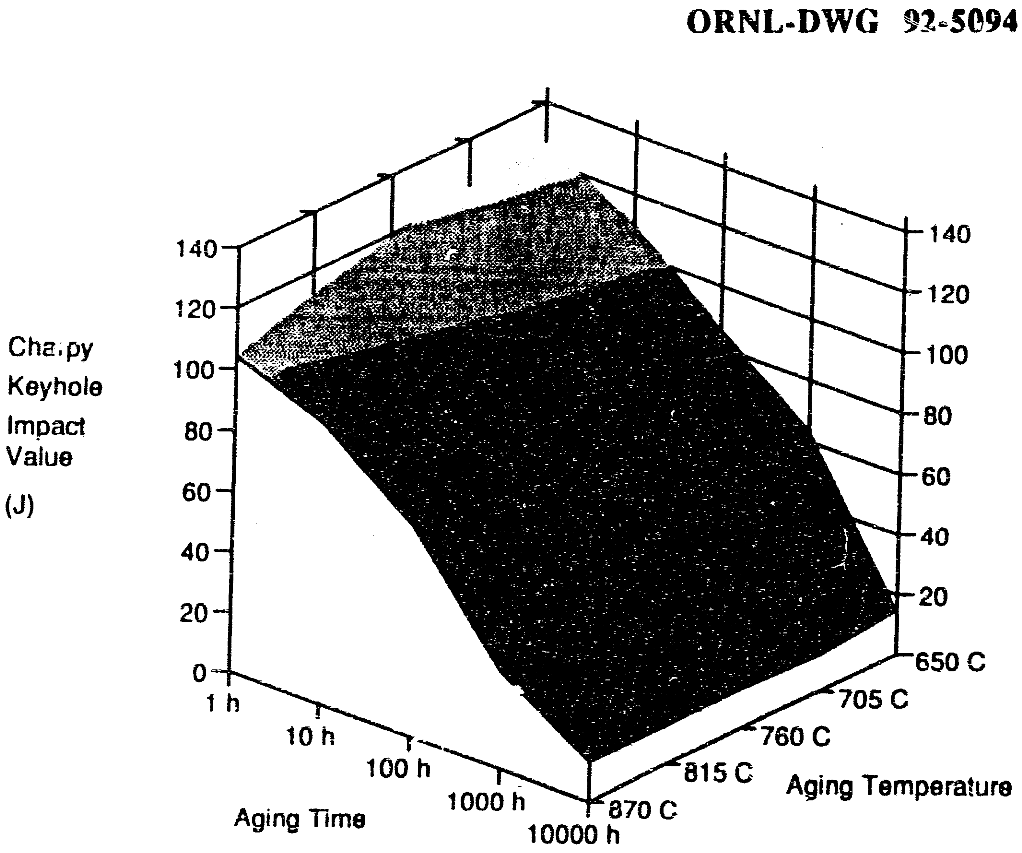

Fig. 8. Effect of temperature and time on the room-temperature impact energy of type 310 stainless steel.27

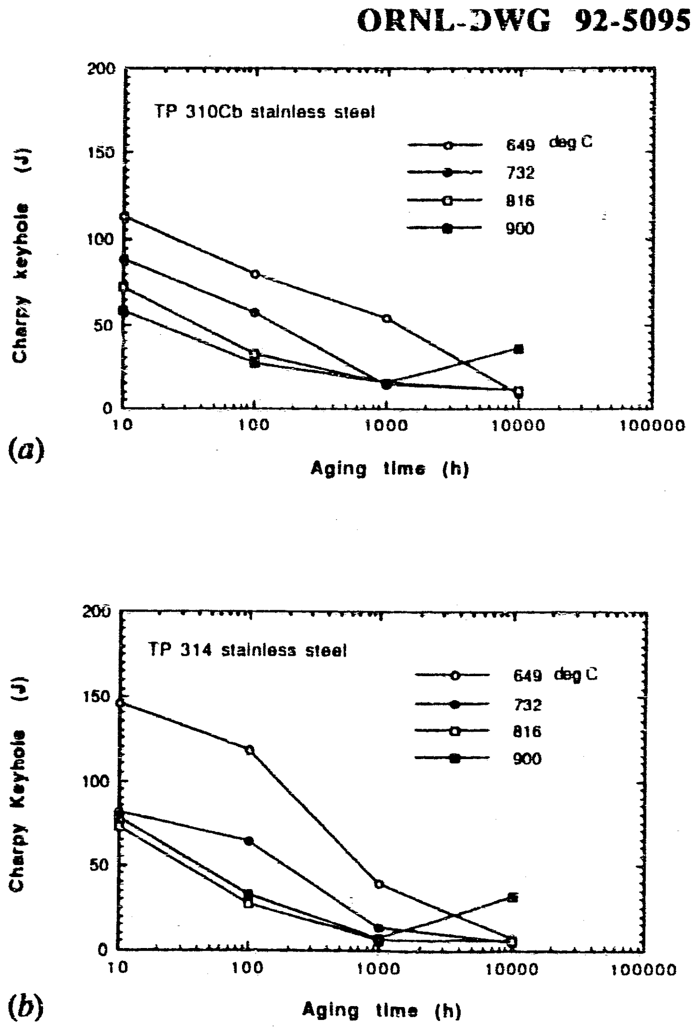

Fig. 9. Effect of temperature and time on the room-temperature impact energy of: (*a*) type 310Cb stainless steel and (*b*) type 314 stainless steel.21

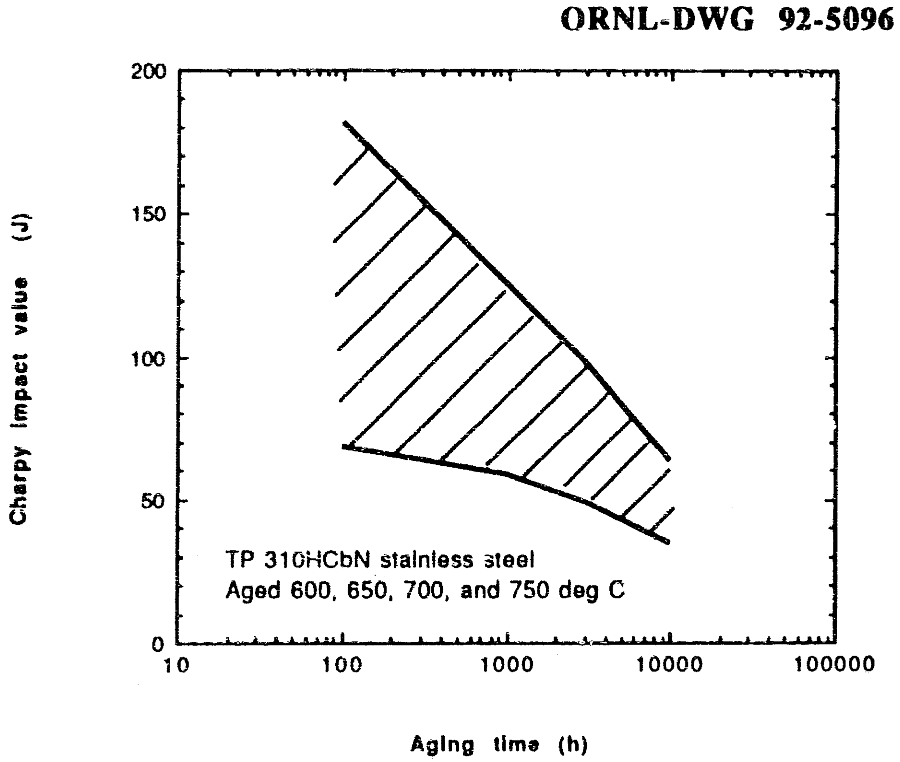

Fig. 10. Effect of temperature and time on the room-temperature impact energy of type 310HCbN stainless steel.[18]

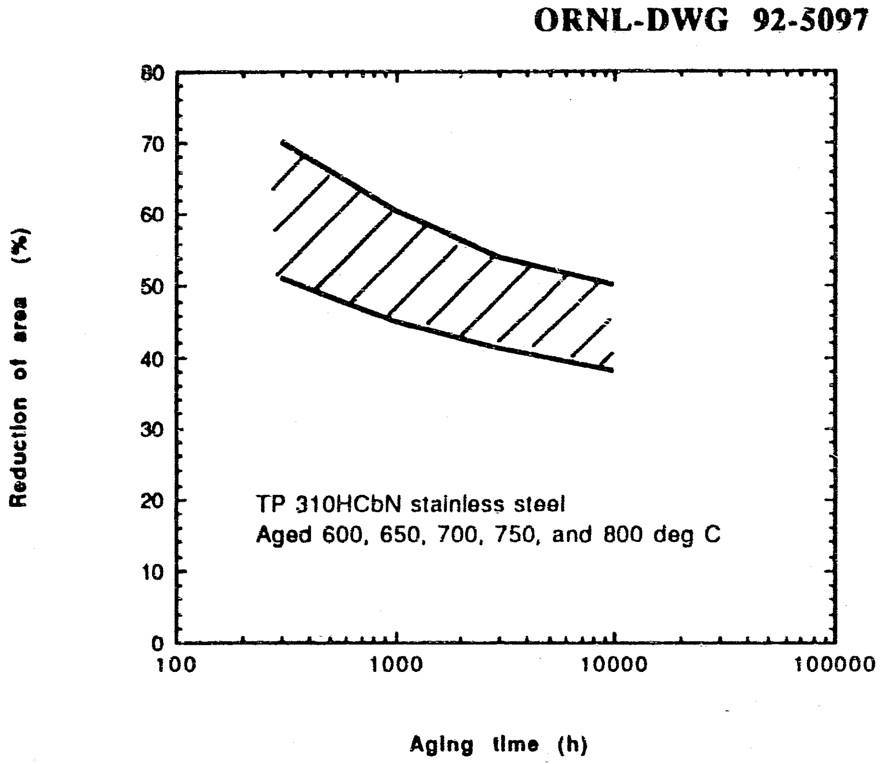

Fig. 11. Effect of temperature and time on the room-temperature tensile ductility of type 310HCbN stainless steel.[39]

A more complete understanding of the metallurgical factors that contribute to strengthening and embrittlement of modified type 310 stainless steel is judged to be a worthy research undertaking.

3.2 FABRICATION AND JOINING

As mentioned above, type 310 stainless steel solidifies as austenite, and the absence of delta ferrite may cause cracking during the breakdown and hot working of ingots. The steel behaves like a high-strength nickel-base alloy, not an iron-base alloy that is at least partly ferritic, and for best fabricability requires special attention in regard to melting practice.[28] A fairly detailed evaluation of the chemistry, melting, and working considerations of high-nickel-equivalent steels was undertaken by Domian and LeBeau,[29] and their findings were summarized in previous reports.[6,7] Essentially, a clean steelmaking process is necessary to minimize the content of embrittling elements such as lead, bismuth, tin, antimony, and arsenic. Following such practice, a high-quality type 310HCbN stainless steel has been produced, and it seems likely that other modified type 310 stainless steels could be produced without great difficulty.

In the United Kingdom, both type 310 and type 310Cb stainless steels have been used as cladding materials over carbon steels and lean austenitic stainless steels.[30] Boiler tubes were produced by co-extrusion, and the overall experience has been satisfactory. Kubo et al.[31] also examined type 310 stainless steel as a corrosion-resistant, co-extruded cladding on a strong but lean austenitic stainless steel. Thus, current technology can produce co-extruded duplex tubing of type 310 stainless steel (or modified type 310 stainless steel) on ferritic or austenitic alloys. A more challenging technology is the production of an iron-aluminide cladding on type 310 stainless steel. Here, a highly sulfidation-resistant cladding could protect an oxidation-resistant pressure envelop material that could be exposed to temperatures exceeding 760°C (1400°F). **Hence, the cladding of a 25Cr-20Ni stainless steel with iron aluminide is judged to be a worthy research objective.**

Welding of 25Cr-20Ni stainless steels could involve the resolution of major technological problems. As with castings, the steel solidifies from the weld pool with little or no ferrite and is susceptible to hot cracking, as illustrated in the diagram (Fig. 12) constructed by Kujanpää and coworkers.[32] Many types of weldability tests have been developed to assess and quantify hot-cracking tendencies in stainless steels, and these are too numerous to be covered here. Many of these weldability evaluation methods have been reviewed by Lundin

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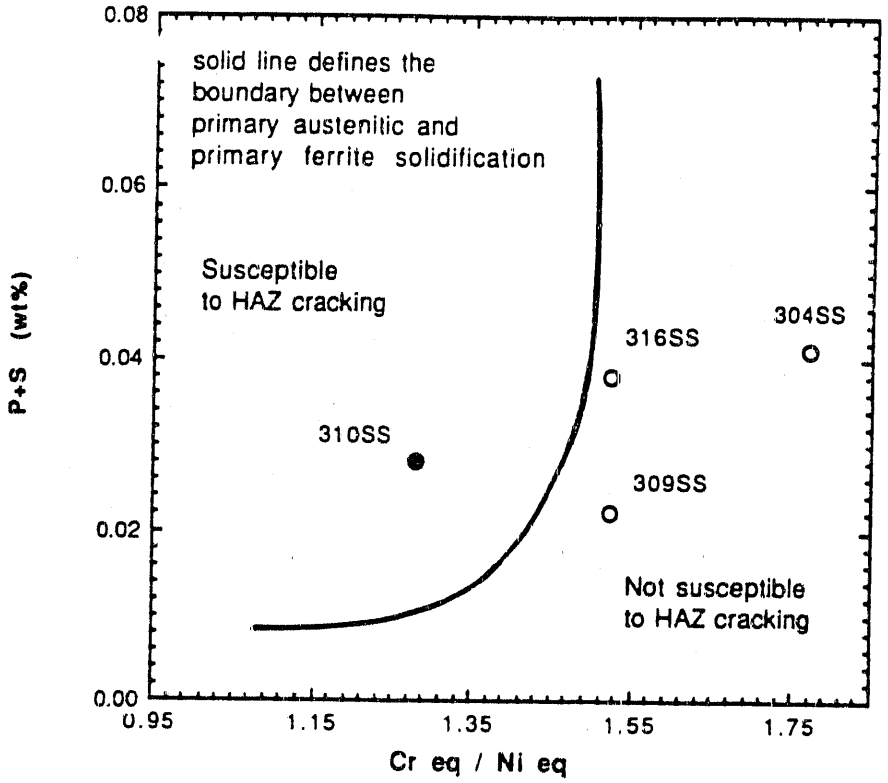

Fig. 12. Effect of nickel, chromium, phosphorous, and sulfur on the HAZ cracking tendency of stainless steels. (The solid line defines the boundary between primary austenitic and primary ferritic solidification.)[32]

and coworkers in connection with the development of advanced austenitic stainless steel filler metals.[33] Depending upon such factors as base and filler metal chemistry, welding process, weld configuration, and weld restraint, these weldability evaluation methods can reveal tendencies toward weld metal cracking, weld metal heat-affected zone (HAZ) cracking in multiple-pass welds, liquation cracking in the base metal HAZ, or base metal HAZ cracking due to hot shortness. In many of these weldability tests, cracking has been observed in type 310 and type 310HCbN stainless steels. Yoshikawa et al. found slightly less cracking in type 310HCbN stainless steel than type 347 stainless steel[18] but did not recommend autogenous welding of the steel. Filler metals that they successfully used included alloys 625 and 82. These are nickel-base alloys and tend to have poor sulfidation resistance. The development of a suitable filler metal for joining a modified 25Cr-20Ni stainless steel that may be clad with an iron aluminide is considered to be a very important research objective.

3.3 MECHANICAL BEHAVIOR

Type 310 stainless steel is a relatively high-stacking fault energy stainless steel[34] and does not develop the creep strength of steels containing lower chromium contents. Figure 13 compares the strength of type 310 stainless steel to strengths for several other high-temperature alloys used in the temperature range of 600 to 815°C (1112 to 1500°F). Leaner (less chromium) stainless steels, such as type 347, type 316, and specialty steels, such as 253MA® stainless steel and RA85H® stainless steel, are stronger at temperatures around 800°C (1472°F) but may not be suitable for those advanced energy system components that require higher chromium content for corrosion resistance. A further problem is the limitation on service temperatures for all these stainless steels. Type 310, 310S, 347, and 316 stainless steels are approved for use to 815°C (1500°F) in the ASME Boiler and Pressure Vessel (BPV) Code, Sect. I. Type 310HCbN stainless steel is currently approved for use to only 730°C (1350°F), and RA85H has yet to be approved. Only 253MA has stress levels for temperatures above 815°C (1500°F) in the ASME BPV Code.

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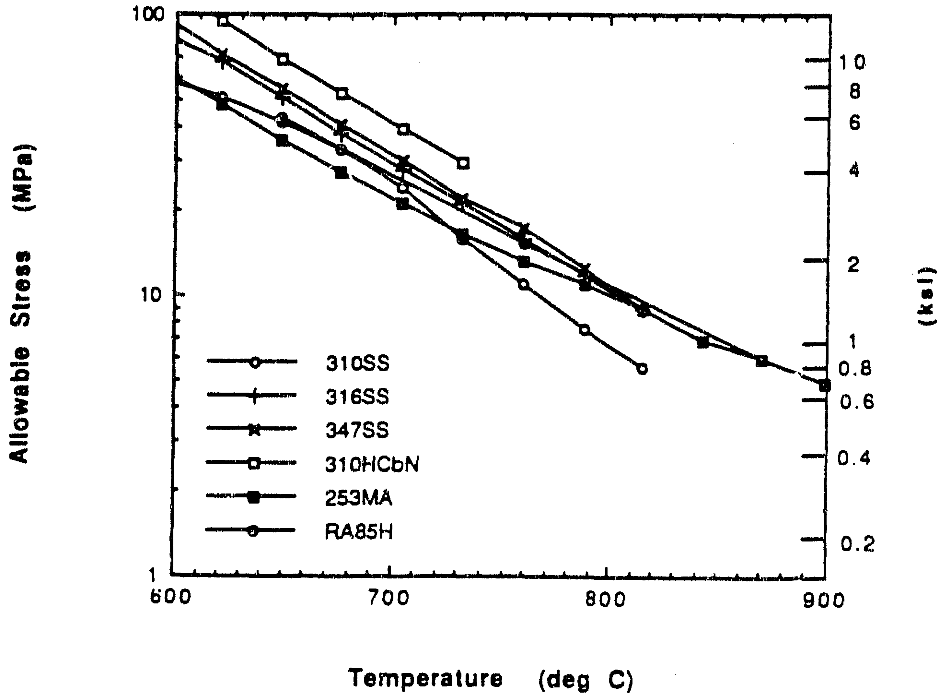

Fig. 13. Comparison of stress allowables as a function of temperature for several stainless steels. (Data are based on ASME Boiler and Pressure Vessel Code, Sect. II, except for RA85H stainless steel.)

Potential applications for the steels in advanced fossil energy applications may require temperatures as high as 900°C (1650°F). Above 815°C (1500°F) the data base for all of the stainless steel is quite limited in terms of number of heats and duration of testing. Some supplementary testing of type 310 stainless steel was recently undertaken to aid in the re-examination of the allowable stresses in the ASME (BPV) Code. Additional data to 870°C (1600°) were produced.[35] Existing strength data for type 310 stainless steel at temperatures above 815°C (1500°F) indicate a high degree of variability, and some data indicate that the alloy is quite weak relative to heat-resisting steels such as 253MA and RA85H stainless steels. A comparison of the rupture strength for 10,000 h versus temperature is shown in Fig. 14 for several steels. These data were obtained from the compilation of Simmons and Van Echo,[36] vendors,[37-39] and the literature.[40] Included is an extrapolation of data for type 310HCbN stainless steel that was based on a stress versus Larson-Miller parameter constructed by Sumitomo Steel.[39] The strength of type 310HCbN stainless steel appears to be better than the other steels to 870°C, and the steel may be slightly stronger than 253MA at 900°C. More data are needed to establish the improved strength and ductility of modified 25Cr-20Ni steels for long times at the higher temperatures. **The evaluation of the strength of modified type 310 stainless steel, type 310HCbN, and MA253 for service in the range of 800 to 900°C (1472 to 1650°F) is judged to be a worthy research objective.**

3.4 CORROSION BEHAVIOR

A major effort has gone into a search for alloys that will resist corrosion in the hostile environments expected in advanced fossil energy systems.[8] For fluidized bed combustion alone, over 30 alloys have been examined by Natesan and Podolski.[13] Similarly, a large number of alloys have been examined for use in PC combustion by Blough and Bakker[41] and Van Weele[42] and for use in gasification applications by Natesan and coworkers.[43]

As temperatures increase in a coal ash environment, increasing chromium is needed for corrosion protection. The trend observed by Van Weele[42] is indicated in Fig. 15, which shows the thickness loss rate versus alloy chromium content for alloys ranging from nil to 48% chromium. Two levels of sulfate ash were examined along with two levels of sulfur dioxide introduced in the combustion gas. Generally, the corrosion rate diminished rapidly with increasing chromium, but near 25% the rate tended to level off. Thus, an alloy near 25% chromium could be optimum.

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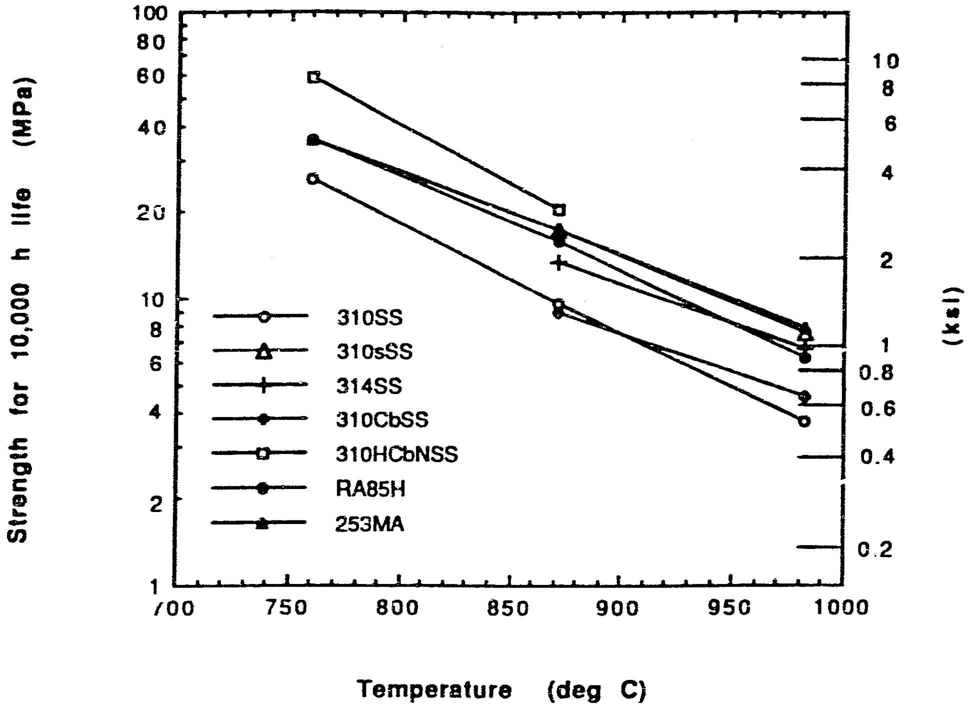

Fig. 14. Comparison of typical strengths for 10,000-h life for several stainless steels in the temperature range of 760 to 900°C.

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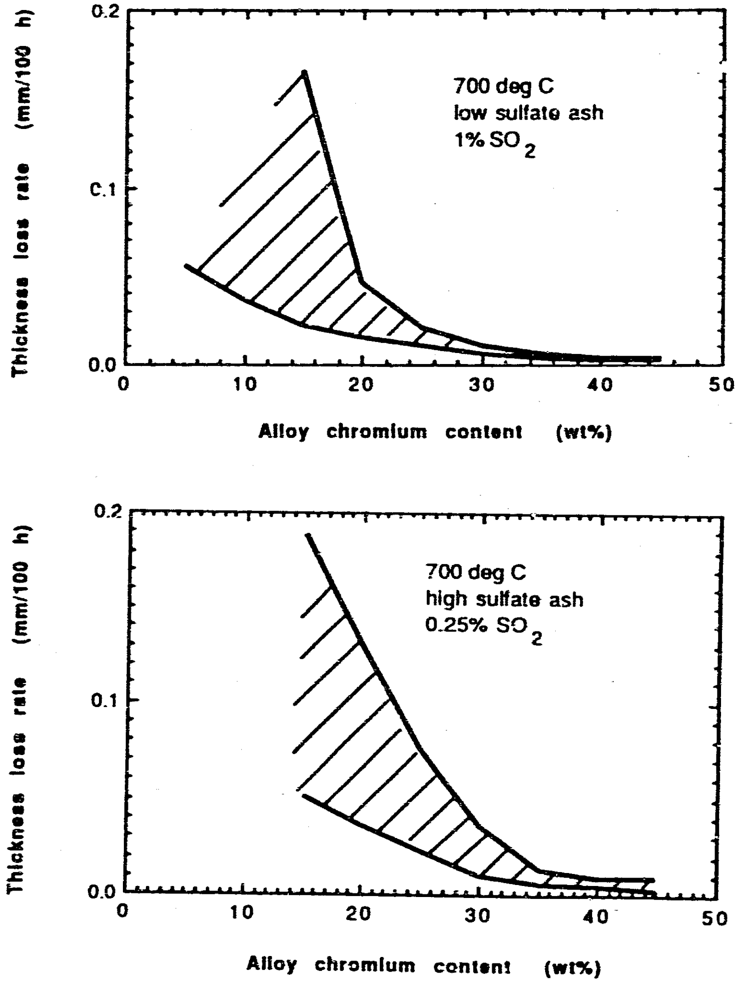

Fig. 15. Effect of alloy chromium content and %SO_2 on laboratory-simulated ash corrosion at 650 and 700°C (ref. 42).

In sulfidizing atmospheres with no ash, the cobalt-bearing alloys tend to be superior, and high-nickel alloys perform poorly. Typical results produced by Haynes are provided in Fig. 16 (ref. 44). Here, the attack (mils/year) is shown on the abscissa for a number of alloys. Alloys at the bottom contain cobalt, while those at the top are high in nickel. Type 310 stainless steel falls in the middle. Some additional corrosion resistance in type 310 stainless steel can be produced by the addition of zirconium or niobium,[42] and further studies would be of interest. **The examination of bare and clad modified type 310 stainless steel in sulfidizing atmospheres is judged to be a worthy research undertaking.**

4. OUTLINE OF AN EVALUATION PLAN

The plan below is designed to address several of the issues that must be favorably resolved in developing advanced fossil energy concepts for commercialization in the early 21st century. The alloy performance criteria indicated in Sect. 2 of this report will be addressed by the evaluation plan. Focus is narrow in regard to the material selection since it only concerns modified type 310 stainless steel, but this narrow focus will permit a better control of cost and time schedule. The plan consists of thrusts in the categories indicated above, namely fabrication and joining, microstructural optimization, mechanical behavior, and corrosion behavior. However, additional activities involving codes and standards development must be added later to ensure that the material can be commercially available when needed.

4.1 FABRICATION AND JOINING

The first activity to be undertaken will be the procurement of materials. It is expected that quantities of type 310 and type 310HCbN stainless steels will be obtained from commercial sources. While these materials are being procured, several laboratory heats of modified type 310 stainless steel will be produced. At least two types of elemental additions will be considered in the laboratory heats: one element (a high-melting-point element) to produce solid solution hardening at temperatures above 760°C (1400°F) and one element (a rare earth) to improve cyclic oxidation resistance. The fabricability will be examined in small laboratory heats to establish the hot- and cold-rolling characteristics. Thermal-mechanical processing studies will identify the schedules needed to produce optimum grain size for strength and corrosion resistance.

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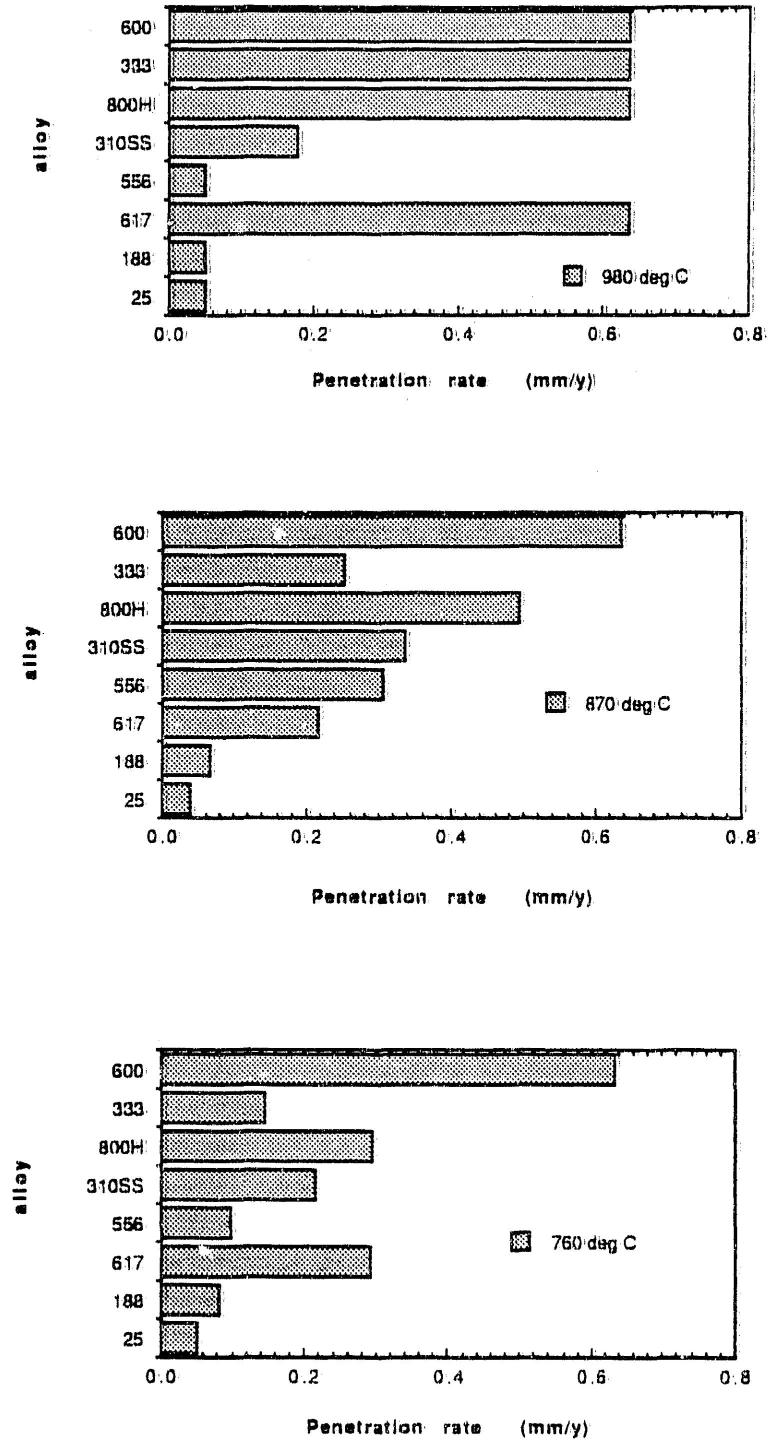

Fig. 16. Sulfidation resistance of several cobalt, nickel, and iron-base alloys exposed 215 h in laboratory-simulated sulfidizing gas.[44]

All materials will be rolled in sheets and provided to a university subcontractor to examine the weldability by means of the varestraint test. Tendencies toward hot cracking in the weld and HAZ will be established for both commercial and developmental steels.

Butt welds will be made in restrained tubes or plates using commercially available filler metals. Working with industrial contractors, welding consumables will be obtained to more closely match base metal performance criteria.

Type 310 stainless steel and promising modified type 310 stainless steels will be overlay clad with iron aluminide by an industrial subcontractor. If the cladding of type 310 stainless steel is successful, techniques for butt welding composite tubes and plates will be examined under a university subcontract.

Flare tests, side bend tests, tube bend tests, and other techniques for evaluating the integrity of weldments and cladding/base metal interface will be undertaken by university and industrial subcontractors.

Depending on the results of the research, a decision will be made as to the potential of the developmental alloys relative to commercially available type 310HCbN stainless steel. If the developmental alloys are sufficiently attractive, larger heats will be procured, working in collaboration with industrial sponsors, and further development will be undertaken.

4.2 METALLURGICAL STABILITY

Specimens of the candidate alloys and their weldments will be aged at temperatures in the range of 650 to 900°C for times to 10,000 h. Microstructural analysis, hardness, tensile, and Charpy V impact testing of the coupons will be performed to examine the influence of phase instability on ductility. A university will be subcontracted to perform detailed characterization of microstructures, and TTP diagrams will be constructed for both commercial and developmental steels.

Aging studies will be performed to examine the interface between the cladding and the base metal for diffusion interactions and compatibility resulting from long times at high temperatures.

4.3 CORROSION

Coupons of commercial and developmental steels will be exposed to the various environments of interest in advanced fossil energy components. These will include, but not be limited to, PC combustion, PFBC, and gasification. Some of these exposures will be laboratory simulations and will be undertaken by participants currently involved in the

AR&TD Materials Program. Other exposures will be in operating systems such as the Tidd PFBC hot-gas cleanup vessel and the Tennessee Valley Authority Gallatin PC-fired boiler. Industrial collaboration will be sought for some of this testing. Other work will be undertaken through subcontracts.

Clad and unclad specimens will be evaluated for times up to 10,000 h and at temperatures that encompass the anticipated service temperatures for the advanced energy systems identified in Table 1. Corrosion rates will be determined from weight loss (or gain), thickness loss, and metallographic measurements of the penetration of oxides and sulfides. The influence of stress on corrosion rates will be examined in laboratory tests. The influence of environment on creep and fatigue-crack growth will be examined.

4.4 MECHANICAL BEHAVIOR

Tensile and creep testing of commercially available type 310HCbN steel will be extended to 950°C (1740°F). Similar testing will be undertaken if a promising developmental steel is found. Mechanical testing will include an examination of strain-rate effects, cyclic effects, fatigue, creep fatigue, thermal fatigue, and dimensional stability under varying temperatures. Times will extend to beyond 10,000 h.

Compatibility of cladding and base metal will be examined under mechanical loadings, such as those produced by fatigue, thermal cycling, and restrained thermal cycling.

Weldment strength will be determined in tensile, stress-rupture, and fatigue loadings. Included will be stress-rupture testing of full-size tubing and longitudinally welded plates. Notched-bar tensile tests and creep-crack growth testing of weldments will be included. Charpy V impact tests will be performed.

Working with industry and consultants, the principles of a design methodology will be outlined for components operating in the temperature range of 760 to 900°C (1400 to 1650°C). The materials data requirements will be specified. Requirements for the development of an ASME code case permitting the use of a candidate material will be identified. Included here will be the need for any structures or basic component testing. The high-temperature extension of ASME Code Case N-47 will form a basis for the development of rules for design.[45]

Working with industry, the collection of engineering design data for a candidate steel will begin. If a new steel is selected, an ASTM specification will be obtained.

5. SUMMARY

This report briefly reviews the fabricability, weldability, metallurgical stability, high-temperature strength, and corrosion resistance of type 310 stainless steel and modifications of type 310 stainless steel. A nitrogen-niobium modified steel, namely type 310HCbN stainless steel, shows potential for use in advanced energy system components that may operate in the temperature range of 760 to 900°C. However, a number of issues need to be resolved before such a steel can be used for pressure containment. An experimental program is outlined that would address these issues.

6. ACKNOWLEDGMENTS

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