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THE USE OF NEW GENERATION STAINLESS STEELS IN COMBUSTION SYSTEMS

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ABSTRACT

Control of emissions in fossil fuel fired power generation plants has brought about significant changes in combustion systems. These changes have increased the demands placed on alloys used in constructing boilers and fluidized bed units. Several new generation stainless steels have been developed to meet these challenges. These include UNS S30815 (RA253MA®), S30415 (RA153MA®), S30615 (RA85H®). Property comparisons with conventional stainless steels UNS 30900 (AISI T309) and S31000 (AISI T310) are given and a review of field applications is provided.

Keywords: alloying, carburization, combustion/coal, erosion, flue gas, RA85H, T309, T310, RA253MA, RA153MA, oxidation, silicon, sulfidation, heat resisting steel

INTRODUCTION

The need to control emissions from fossil fuel fired boiler systems is a major challenge facing industry today. Early solutions to this problem involved primarily after-the-fact systems like precipitators and scrubbers. However, the need to control NOX

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emissions created problems not readily resolved by add-on-systems. NOX emissions are best controlled in the combustion process which brought about changes in how the fuel is burned. Burner nozzles, such as the C.E. design shown in Figure 1, are used to facilitate the controlled burning rates that are required to meet new emission standards.

A second major change had been the development of fluidized bed technology for the generation of power. In this process, which industrially dates back to the 1920's, pulverized coal is combined with a sulfur getter such as crushed limestone and burned in a bed suspended by rapidly upward flowing combustion air. During this process the sulfur reacts with the calcium removing it from the combustion gas stream. It is also important to note that the temperature of combustion must be closely controlled to eliminate NOX from the combustion gas stream.

These innovations have changed the temperature of the combustion systems and increased exposure to sulfur containing compounds. This has shortened the life experience of alloys that have been commonly used for structural members and tube supports. This paper compares the properties and performance of several alloys currently used to address these changing conditions.

REVIEW OF ALLOY SYSTEMS

Table 1 provides the nominal composition of several combustion service alloys that are discussed in this paper. S30908 and S31008 are stainless steels with a long history of service in combustion environments. These grades have reasonable high temperature strength and resistance to the environments involved. In the early 70's the Swedish Company, Avesta, began work with micro-alloying of stainless steels. Micro-alloying is the use of small additions of rare earth elements to significantly change the characteristics of the original alloy (1). In this case the base composition is similar to S30908 and the micro-alloying element is cerium. To further enhance the high temperature strength, silicon was increased and nitrogen added to stabilize the austenite. The result is an alloy with significent improvements in strength and oxidation resistance.

More recently, another alloy, S30415, utilizing similar micro-alloying technology has been introduced (2). While the base chemistry is similar to S30400 (T304), the new alloy with additions of silicon, nitrogen and cerium is much stronger and more oxidation resistant.

The final alloy considered in this discussion is S30615. This stainless steel is a departure from current alloy systems. Carbon, silicon and aluminum additions are balanced to produce a controlled amount of ferrite in this nominally austenitic alloy. As a result welding problems normally associated with high silicon alloys have been eliminated. Also, as will be discussed later, resistance to hot corrosion in fossil fuel environments is excellent.

An important characteristic required of alloys that will be exposed to high temperature is the ability to resist deformation in service. For purposes of comparison, Table 2 lists typical stress to produce 1% strain in 10,000 hours for each of the alloys discussed.

Probably the most broadly recognized and commonly used heat resisting stainless steel is S30908. This grade has reasonable creep strength and is commonly specified for service up to 1900°F. Typically for more severe conditions or increased temperature the choice is to use S31008. For further increases in strength, the choices have been to use heat resistant alloy castings or much more highly alloyed wrought grades.

The benefits of the use of silicon to improve creep strength is clearly seen from Table 2. S30415 is a lean composition, but is much stronger than either S30908 or S31008 at temperatures up to 1600°F. When we compare the properties of S30815 and S30908, the benefits of the use of silicon and micro-alloying in boosting creep strength is very clear. Finally, S30615 which contains 3.5% silicon demonstrates a further increase in creep strength at the higher temperatures.

Another important material property for fossil fuel combustion service is the ability of the alloy to resist the combined effects of carbon and sulfur. High nickel alloys are noted for resistance to carburization, but generally are poor in sulfidation. High chromium levels are beneficial. S31008, while it contains 20% nickel also has 25% chromium and is a good choice for sulfidation risk service particularly under oxidizing conditions. Similarly, S30615 has proven effective in environments where both carburization and sulfidation potential are found. The results of some on going studies are given in Table 3. The samples were packed in powdered coal and heated in the absence of air to 950°C (1742°F) and held for 30 day exposure. In this test S30615 has twice as much resistance to hot corrosion damage as S30908. It was further noted that S30908 failed a simple bend test in a brittle manner after the 90 day exposure while the S30615 accepted a 90 degree bend with only minor surface cracking. These results are illustrated in Figure 2.

FIELD OBSERVATIONS

CONVENTIONAL BOILERS: Materials used in conventional coal fired boilers deteriorate from a combination of factors. These include distortion, erosion, hot corrosion and metallurgical changes brought about by the temperature and atmospheres involved. Erosion tends to wear away the surfaces, which reduces the effectiveness of the protective oxide that is necessary in controlling surface reactions with various contaminants that are present in the fuel stream. These contaminants can include sulfur, chlorides, fluorides, carbon, heavy metals and various alkali compounds. To further complicate the situation the local environment may vary from highly oxidizing to reducing. As a result, the combination of carburization and hot corrosion are major concerns. These reactions are also influenced by the metal temperature involved at the contact interface. Changes in the burner and nozzle design to reduce the formation of NOX has increased actual burner tip temperatures. This increase is brought about by the closer proximity of the flame front to the nozzle tip and the generally higher radiant energy of the flame.

A common alloy choice for nozzles in the past has been S30908. With good aspiration cooling this grade had adequate strength and environmental resistance to get the job done. However, as nozzle temperatures have increased, distortion has been a problem. Changes in nozzle shape affects combustion efficiency which is a major factor in the emissions control equation. To help overcome this loss of efficiency, a stronger alloy is required. One choice has been to use S30815, which provides the improved creep strength that is required to control the undesirable distortion. In addition, the micro-alloying with cerium promotes improved oxidation performance.

Hangers and tube supports can be high maintenance items in boilers. Figure 2 shows photo of a recent installation where S30908 was used. The conditions encountered vary widely with location in the boiler and alloy selection plays a major role in extending the time between replacement. Erosion, hot corrosion, oxidation, contaminants present and metal temperatures are all factors to be considered. In more severe areas of temperature and sulfur attack, S30615 is showing encouraging performance.

In areas of the boilers where the tubes are in a horizontal position, tube shields are commonly employed to protect the tube from erosion and corrosive deposits. A common alloy choice for this service is S30908. The improved oxidation resistance available with S30415 is a consideration for extending the life of tube shields.

<u>FLUIDIZED BED SYSTEMS</u>: Fluidized bed units have two broad areas where heat resisting stainless steels are required. These are the combustion section and the cyclones. In the combustion zone, conditions and alloy requirements vary quite broadly with location. In general, the various structural members, baffles, tube supports, etc., are directly exposed to combustion gases, high sulfur alkali compounds, ash and high temperatures. Conditions vary within and above the bed and alloy choices must take these varying conditions into account. While the actual temperature in these units are not extremely high, the units are designed to control both NOX and sulfur emissions through the combustion process. Sulfur is removed by injection of limestone or dolomite into the fuel stream prior to burning. As a result, the alkali char that forms is very high in sulfur and can be a very aggressive corroding agent. A recent DOE report (3) pointed out that the sulfur captured by the limestone will initiate sulfidation at temperatures above 650°C (1220°F). The article also noted that the use of rare earth containing alloys has proven beneficial in controlling some internal sulfidation reactions.

Testing has been ongoing for S30615 in these fluidized bed units and results support the earlier data regarding the excellent hot corrosion resistance exhibited by this alloy.

In the cyclone section of these systems, erosion and oxidation are major concerns. Some early units were designed with the down-comer or vortex finder tube made with S31600 (T316). Rapid oxidation resulting in short tube life was observed (4). Even though the temperatures are not extreme, erosion is a contributing factor by constantly exposing new surfaces. S30815 resists erosion and oxidation and is being used with good results.

SUMMARY

The need to control emissions from fossil fuel burning power plants has changed the design of conventional boiler systems. It has also resulted in the development of various fluidized bed systems to control the combustion process. This paper reviews some important properties and field performance of both conventional and enhanced grades of stainless steels.

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TABLE 1
TYPICAL COMPOSITION OF SEVERAL COMBUSTION SYSTEM ALLOYS

UNS	CR	NI	SI	C	FE	OTHER
S30908	23.0	13.0	0.8	0.05	62	
S31008	25.0	20.0	0.5	0.05	52	
S30415	18.5	9.5	1.3	0.05	70	0.15N; 0.04CE
S30815	21.0	11.0	1.7	0.08	65	0.17N; 0.04CE
S30615	18.5	14.5	3.5	0.25	61	1.0AL

TABLE 2
STRESS (MPa) TO PRODUCE 1% STRAIN IN 10,000 HOURS

	ALLOY UNS				
TEMP DEG F	S30908	S31008	S30415	S30815	S30615
1400	2970	2870	3500	4000	3780
1500	1690	1720	1850	2680	2500
1600	960	1030	1000	1730	1680
1700	550	620	550	1004	1100
1800	310	370	300	450	750

TABLE 3
COMPARISON OF HOT CORROSION DAMAGE ON EXPOSURE
TO POWDERED COAL AT 950°C (1742°F)

ALLOY	DEPTH OF DAMAGE (INCHES)* 30 DAYS	90 DAYS
S30908	.047	.077
S30615	.024	.038

*TOTAL SULFIDATION PLUS CARBURIZATION ZONE

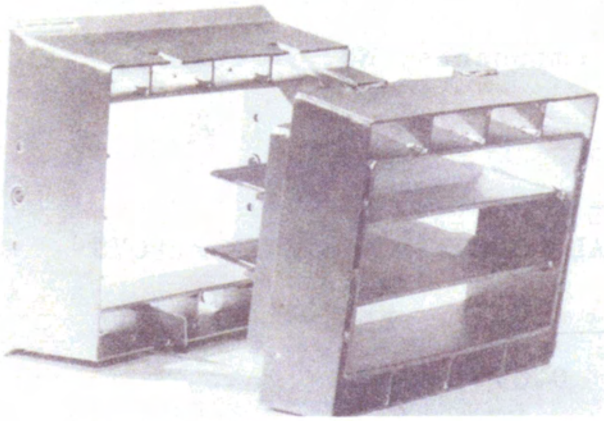

FIGURE 1 - Burner Nozzle
Fabricated with S30815

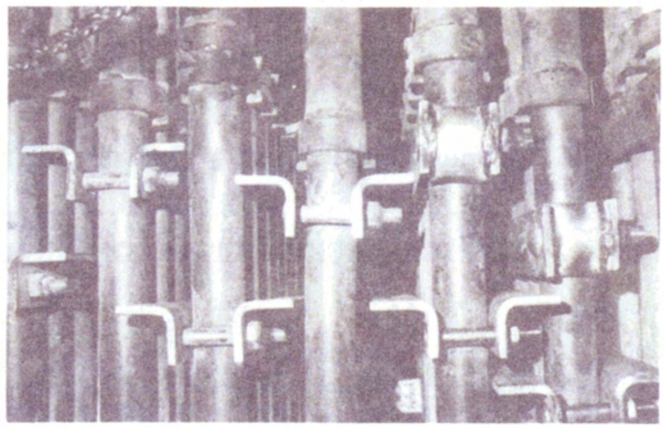

FIGURE 3 - S30908
Fabricated Tube Supports

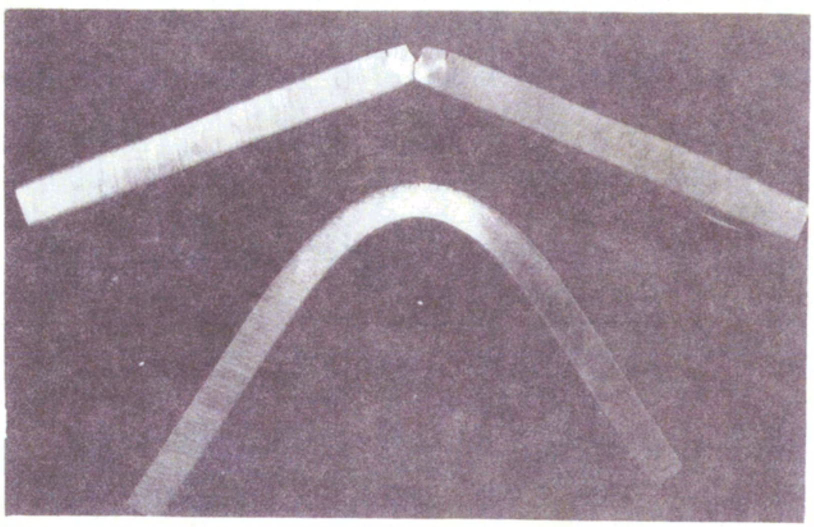

FIGURE 2 - Ductility loss from 90 day exposure at 950°C
in powdered coal - S30908 (Top) and S30615 (Bottom)