INVESTIGATION OF ADVANCED ALLOYS FOR HEAT RECOVERY SYSTEMS

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INTRODUCTION

The objective of the research on advanced alloys is to provide databases and design criteria that will assist contractors in selecting optimum alloys for construction of components needed to contain process streams in advanced heat recovery systems. Typical components include steam line piping and superheater tubing for ultracritical steam cycles (600 to 815°C), heat exchanger tubing for advanced steam systems (650 to 870°C), foil materials for recuperators on advanced turbine systems (700 to 750°C), heat exchanger tubing for pulsed combustors (650 to 950°C), and tubesheets, plenums, and liners for hot gas cleanup systems (850 to 1000°C). The near term objective is to gather data that will permit the consideration of advanced steels for applications to 900°C in oxidizing environments or to 870°C slightly sulfidizing environments. Studies include the collection of data that will permit the consideration of third-generation advanced ferritic steels for service to 650°C, Ni-Co-Cr-Al alloys for service to 950°C, and oxide dispersion strengthened (ODS) alloys in aggressive environments to 1000°C.

Background

In the United States, new power generation needs are being met by the use of co-generation and the installation of medium-size gas turbines. Research in the fossil power industry is largely focused on condition assessment and life extension of aging components. Research related to inspection, damage assessment, and repair is actively supported by fossil power and petrochemical industries (1). In both industries, replacement of components with “new” and “advanced” materials is sometimes required, and research on the performance of the advanced materials for such components is in progress. Development of advanced materials for the fossil power industry has largely performed in Japan under sponsorship of the Electric Power Research Institute (2,3). Alloys such as tungsten-vanadium-modified 2 ¼%Cr (T23), 9%Cr (T92), and 12%Cr (T122) steels have reached ASME Code status and are being used to replace T11, T22, and austenitic stainless steels such as 304H and 321H. These advanced ferritic steels are candidates for the construction of piping systems, headers, and tubing for steam service to 600°C and higher, but more research is needed before the complex metallurgical constitution of the alloys is fully understood and their reliability for long-time service can be guaranteed. Advanced austenitic stainless steels for service above 600°C include niobium-modified 310 stainless steel (HR3C), a titanium-modified 20Cr-25Ni-Nb stainless steel (NF709), and copper-modified stainless steel (super 304 and SAVES 25).

Of these steels, HR3C has attained Code status as 310HCbN and a copper-modified stainless steel is in the Code- approval process. The steels are intended for superheater tubing, and the code-approved allowable stresses are generally limited to 732°C. The database for some of these stainless steels (NF 709, SAVES 25, and 310TAN) extends to 900°C but the poor oxidation resistance of the stainless steels limits their use. Similar to the advanced ferritic steels, there is much to be learned about the behavior of the complex austenitic steels in high-temperature environments. For service above 732°C, alloys containing over 30% nickel, such as HR 120 and alloy 230, have been developed. Also, there is renewed interest in cobalt-containing alloys, such as alloy 617 and Inconel 740.

Advanced Martensitic Steels

Issues have arisen in regard to the usage of the advanced ferritic steels in high-temperature service. Recently, concerns were raised about the welding procedures for the advanced martensitic steels. To avoid hydrogen cracking, a pre-heat of 204°C or higher is required for these alloys. Pre-heat temperatures may be close to the martensite finish temperature for steels such as Grade 91, hence some of the austenite produced in the welding heat cycle could remain untransformed. It would save energy if fabricators could proceed to the post weld heat treatment (PWHT) without cooling below 204°C, but there is concern that austenite retained in the weldment at 204°C would produce fresh martensite after the PWHT. Further, filler metals used for welding Gr91 are permitted to contain up to 1% Nickel. Nickel and manganese are known to lower the critical temperature where martensite or tempered martensite begins to transform to austenite (Ac1 temperature) on heating. If the PWHT is above this temperature, some of the austenite during PWHT could produce fresh martensite or softer ferrite upon cooling slowly. The influence of untempered martensite on the high-temperature performance Gr91 is unknown. To assist in the resolution of the issue, weldments of Grade 91 are being examined (4). Collaboration with industrial includes the Babcock and Wilcox Company and the Stoody Company. The (Ni+Mn) compositions being investigated are provided in Table 1 and include a range of (Ni+Mn) from 0.43 to 1.89. The Ac1 at 0.43% (Ni+Mn) is estimated to be around 830°C which is well above the typical PWHT range of 760 to 780°C. The Ac1 at 1.89 (Ni+Mn), however, is estimated to be 740°C. This temperature below the typical PWHT and near the minimum PWHT permitted for Gr91, namely 732°C. Hence, fresh martensite could form by virtue of retained austenite at the pre-heat temperature or from austenite that formed as a result to the PWHT above the Ac1.

Creep rupture testing was started on samples of a submerged arc weldment (SAW) containing high (Ni+Mn). Temperatures were at 550, 600, and 650°C with emphasis on 600°C. Samples were tested after

Table 1. (Ni+Mn) content of Grade 91 materials under investigation

Material	Wt % (Ni+Mn)	Estimated Ac1 (°C)
Base 2	0.55	830
Base 3	0.53	830
SA weld	1.41	775
FCA weld 1	1.42	775
FCA weld 2	1.38	775
FCA weld 3	0.43	830
FCA weld 4	1.89	740

SA = submerged arc weld in 50-mm plate;
FCA= flux core arc weld in 25-mm plate.

exposure to PHWT temperatures of 740 and 780°C. These temperatures represent the extremes for the PWHT temperature. Testing to 10,000 hours indicated that specimens containing fresh martensite (hold pre-heat at 204°C) had lower creep rates and lower rupture ductilities than specimens with fully tempered martensite (drop pre-heat to room temperature). In all cases, weld metal was stronger than base metal.

Flux core arc welds (FCAW) were produced. One had low (Ni+Mn) and the other high (Ni+Mn). The low (Ni+Mn) weld had a martensite finish temperature at or above the preheat temperature (204°C). The initial creep rupture testing indicated that holding or dropping preheat made no difference in creep after a PWHT of 4 hours at 760°C. The high (Ni+Mn) weld metal had a martensite finish temperature below the preheat temperature. Here, the specimens from the hold pre-heat had lower creep rates than the specimens from the drop pre-heat weld after a PWHT of 4 hours at 760°C. These results are being considered by the Electric Power Research Institute in developing industry guidelines for joining advanced martensitic steels.

Efforts continued to examine the long time stability of martensitic steels (5,6). Working with the Babcock & Wilcox Company, Gr91 specimens exposed to service conditions were evaluated in comparison to samples from laboratory aging exposures. Exposure times in service ranged to 155,000 hours, while the laboratory exposures ranged to 75,000 hours. Also, some specimens were removed from creep testing after times as long as 100,000 hours. Generally, it was observed that service exposures produced metallurgical conditions similar to thermal aging and low-stress creep. The coarsening of the substructure resulting in softening. Generally, the rupture life decreased and creep rate increased for a given post exposure condition. However, the ability to accelerate the damage rate and relate the properties observed in short-time test to long time performance has not yet been demonstrated.

New martensitic steels are being developed for advanced steam cycle applications. High nitrogen 12%Cr show exceptional strength (7), and studies of their creep resistance are just beginning. Sheet and bar products have been produced of a cobalt bearing 12%Cr steel have 0.16% nitrogen. This steel will be

subjected to a variety of heat treatments including austempering to bring our stable vanadium nitride particles.

Advanced Austenitic Stainless Steels

Creep testing was started on Inconel 740 supplied by Special Metals. Material that was solution annealed at 1050°C was found to be weak relative to expectations. Re-annealed at 1200°C was performed and testing resumed.

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