APPLICATIONS FOR DISPERSION-STRENGTHENED ALLOYS IN THERMAL POWER SYSTEMS

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ABSTRACT

Dispersing small quantities of ceramic particles along the grain boundaries of an alloy can substantially increase its resistance to creep at high temperatures. This creep resistance, if matched with corrosion resistance, makes these alloys particularly suited for the highest-temperature applications within thermal power systems. The University of North Dakota Energy & Environmental Research Center (EERC) is working with Oak Ridge National Laboratory to determine corrosion resistance and methods of joining oxide dispersion-strengthened (ODS) alloys in laboratory, pilot-scale, and commercial-scale tests. The EERC has previously demonstrated a very high-temperature heat exchanger (HTHX) that could be used to produce pressurized air at up to 1090°C for an indirectly fired combined-cycle (IFCC) power plant. An IFCC using this type of heat exchanger has the potential to reach efficiencies of 45% when firing coal and over 50% when a natural gas-fired duct burner is used to additionally heat the gas entering the turbine, efficiencies similar to those of an integrated gasification combined cycle, but with operation almost identical to those of current pulverized coal-fired boilers. IFCCs have the added benefit of minimizing water usage by dramatically reducing the amount of cooling and makeup water as compared to a typical pulverized coal (pc) plant because only half as much steam is produced. Because of its high efficiency, an IFCC system is the most appropriate power concept for employing oxygen-enriched combustion in order to make carbon dioxide removal more economical. After water condensation, only carbon dioxide is left in the gas stream, which can then be used industrially or sequestered, leaving near-zero emissions. If the system is cofired with coal and biomass, sequestration of the carbon dioxide would create a net reduction of its concentration in the atmosphere.

In addition to their use in IFCC systems, heat exchangers made of corrosion-resistant dispersion-strengthened alloys can be used in many types of thermal power systems. In advanced gasification systems they can be used to preheat steam to high temperatures for steam gasification of coal in order to produce the highest possible hydrogen concentration in the syngas. This is especially important in a FutureGen scenario where the hydrogen is to be separated from the syngas for use as a transportation fuel. In addition to power generation systems, there are many scenarios for the use of HTHXs to increase the efficiency of many industrial thermal systems. One such case is the recuperation of heat from the flue gas of an aluminum melter. In 2006 and 2007, rings of MA754, MA956, HR160, and 304 stainless were exposed in an aluminum melter at the Superior Aluminum Alloys plant in New Haven, Indiana. Analyses showed that the MA956 or other alumina scale-forming dispersion-strengthened alloys may be suitable for use in heat exchangers in these systems at up to approximately 1100°C.

THE NEED FOR HIGHER TEMPERATURES IN POWER GENERATION

The electricity generating capacity in the United States is projected to grow by 250,000 MW by 2030.[1] Initially, the greatest growth will occur in natural gas-fired power systems, but will then shift back to coal-fired systems so that one-half of the net growth will be in coal-fired systems by 2020, and all of the net growth will be coal-fired from 2020 to 2030. To fuel these plants, coal production is expected to grow from 1125 million tons in 2004 to 1355 million tons in 2020, and 1703 million tons in 2030, 96% of which will be for electric power generation. Yet this growth occurs at a time of increased public concern over the emission of greenhouse gases, particularly CO_2. Since coal utilization creates more CO_2 per unit of power produced than any other form of fuel, the growth in coal firing will be accompanied by increased pressure from the public, boardrooms, and lawmakers to convert the coal as efficiently as possible.

In thermal power systems, the need for greater efficiency will require the use of higher-temperature materials for construction because the quality of the heat produced is more important than quantity in determining efficiency. That is, the heat in a small volume of gas at a high temperature is more efficiently converted to kinetic energy in a turbine than if the same amount of energy were present in a larger volume of gas at a lower temperature. This means that the heat exchangers used to contain the working fluid, the turbine blades against which the fluid pushes, and the materials from which they are made will ultimately limit the efficiency of a power system. Without employing higher-temperature materials than at present, the efficiencies of the energy conversion systems cannot grow substantially.

COAL COMBUSTION SYSTEMS

The greatest research efforts in advanced coal combustion technologies are currently pursuing ultrasupercritical steam technology. By pushing toward 760°C steam and 35 MPa pressure, energy conversion efficiencies over 45% can be reached. Up to 675°C high-chromium austenitic steels appear workable, but above that temperature nickel-based alloys are suggested,[2] although some new austenitic alumina scale-forming dispersion-strengthened steels are under development that may also reach 750°C with both creep and oxidation resistance.[3]

To reach even higher efficiencies, a different type of energy cycle is required than just the standard Rankine steam cycle. One such type of coal combustion system was researched extensively in the 1990s and early 2000s by the U.S. Department of Energy (DOE). The indirectly fired combined cycle (IFCC) power plant was developed under the High Performance Power System, or HiPPS Program. An indirectly fired combined-cycle plant uses, essentially, a coal-fired boiler where a fraction of the boiling water heat exchanger pipes near the hottest part of the flame are replaced with pipes carrying 1 MPa air being heated to as much as 1100°C. This hot air is sent to a gas turbine where it offsets over two-thirds of the natural gas normally burned in the turbine. Figure 1 is a schematic of such a system which is, essentially, a natural gas-fired combined-cycle power plant in which much of the heating of the gas turbine comes through the combustion of coal. The waste heat from the turbine and the coal combustion system is used to produce steam, perhaps ultrasupercritical, to turn a steam turbine. The Brayton (gas turbine) cycle which make one-half of the electricity in the IFCC is inherently more efficient than a Rankine (steam) cycle because there is no loss of the heat of vaporization of the water in the Brayton cycle. Therefore, an IFCC system will always be more efficient than a system based solely on the Rankine cycle.[4,5]

IFCCs have the added benefit of minimizing water usage by dramatically reducing the amount of cooling and makeup water, since only half as much steam is produced as in a typical steam plant. The high efficiency of an IFCC system also makes it suitable for oxygen-blown combustion in order to make carbon sequestration more economical. In that case, flue gas is recirculated and pure oxygen added to the stream to burn the coal, leaving a gas stream comprising mostly CO_2 and steam. After water condensation, only carbon dioxide is left in the gas stream, which can then be used industrially or sequestered, leaving near-zero emissions. If the system is cofired with coal and biomass, sequestration of the carbon dioxide would create a net reduction of its concentration in the atmosphere. Oxygen firing also prevents the formation of thermal NO_x. In addition, by staging combustion of the coal, the volume of flue gas would be dramatically reduced, shrinking the overall size and capital cost of the system.

Although IFCC systems have many potential benefits, materials requirements for the high-temperature air heater and turbines are stringent. Pressures for the air heaters are much lower than those for ultrasupercritical systems, so the need for creep resistance is much reduced and austenitic steels are not automatically required. However, temperatures of as much as 1200°C require materials exceptionally resistant to oxidation or corrosion by the products of coal combustion. Ferritic oxide

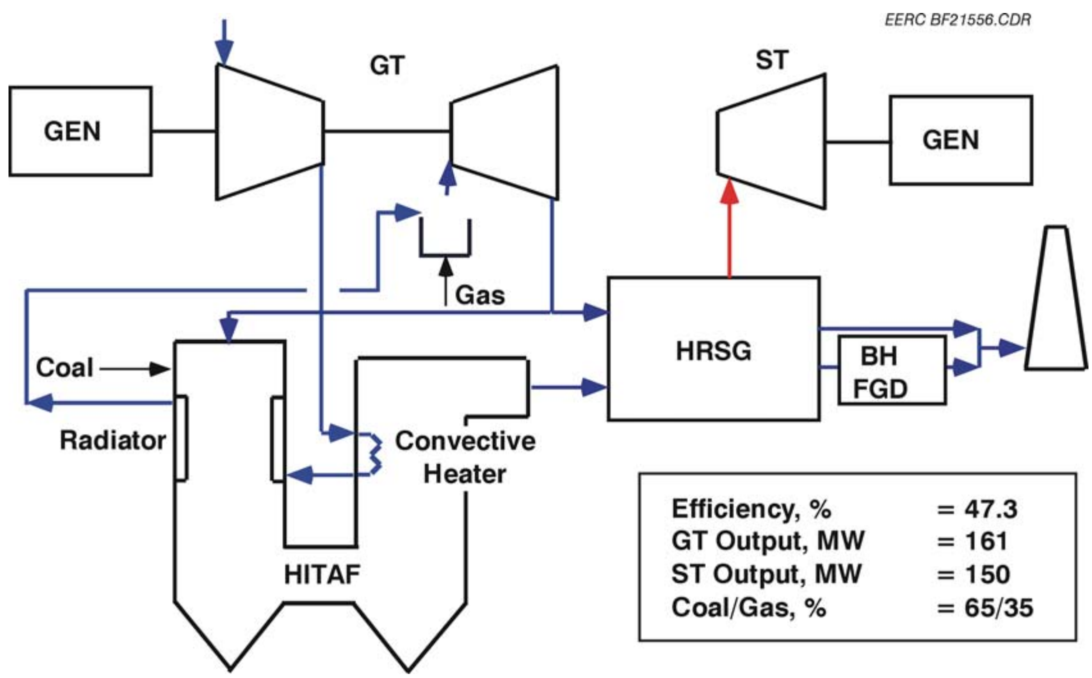

Figure 1. The United Technologies Research Center High-Performance Power System concept.

dispersion-strengthened (ODS) alloys are excellent candidates for this type of environment.[6–9] The presence of small stable oxides (often yttria [Y_2O_3]) helps to prevent dislocation motion and preserve the high-temperature strength of these materials. Grain boundary sliding and Herring–Nabarro diffusional creep are both retarded by the elongated grain structure typical of ODS alloys. Iron-based ODS alloys such as MA956 have excellent corrosion resistance at high temperatures if they contain approximately 4.5% aluminum or more. The aluminum forms a protective oxide layer that can resist even direct contact with flowing slag, as long as the surface is cooled below the solidus temperature of the slag.[7]

COAL GASIFICATION SYSTEMS

Research on the IFCC concept was largely stopped in the early 2000s when DOE decided to focus instead on the FutureGen power system concept.[10] Based on coal gasification, FutureGen plants can reach similar efficiencies as IFCCs, but have the added benefit of being able to separate hydrogen from the syngas during offpeak hours for use in the transportation sector. As shown in Figure 2, taken from Sondreal et al.,[11] the hydrogen concentration in the syngas produced in atmospheric-pressure oxygen-blown coal gasifiers is increased at lower temperatures. However, in order to fire the syngas in a turbine, it has to be produced at high pressures. The figure shows that in high-pressure gasification, temperatures of over 900°C are required to produce the highest hydrogen

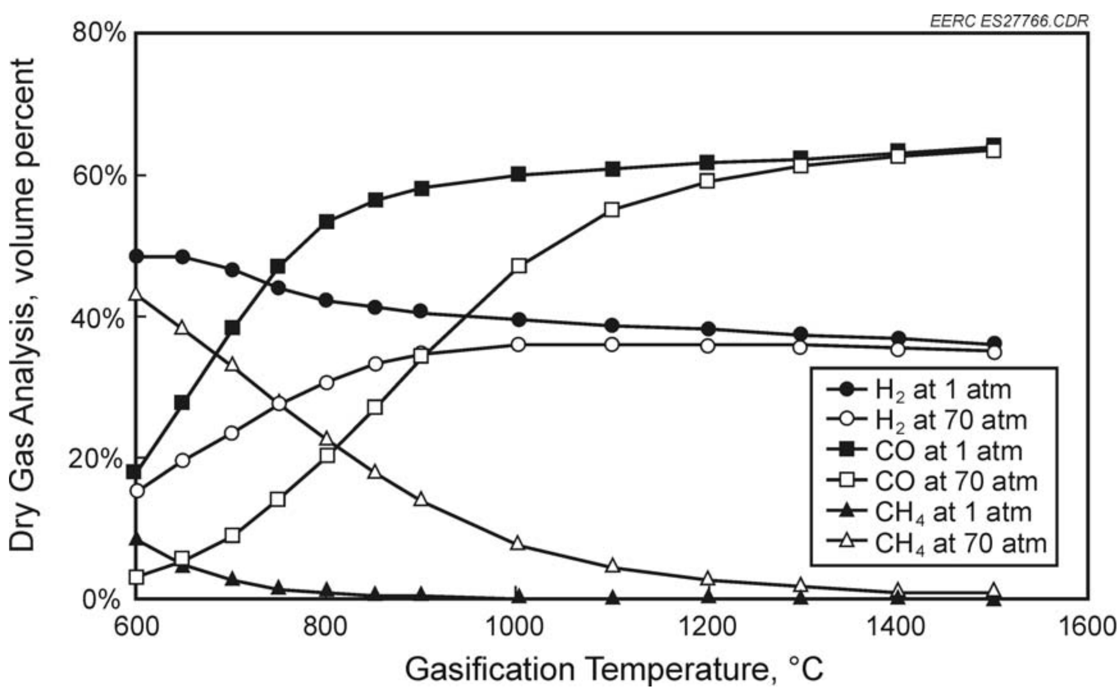

Figure 2. The effects of temperature and pressure on syngas compositions produced from oxygen-blown coal gasification.

concentrations. To increase them even further, the steam gasification reaction must be emphasized in the gasifier:

$$H_2O + C \rightarrow CO + H_2 \qquad \text{[Eq. 1]}$$

However, the steam gasification reaction is endothermic, requiring 56,490 Btu per mole of carbon consumed. To produce the heat required, more carbon can be burned in the gasifier by firing with higher oxygen concentrations, but then more carbon dioxide is produced rather than the preferred carbon monoxide. Another option is to inject superheated steam into the system. In this case, a very high temperature heat exchanger (HTHX) carrying the steam can be placed within the combustion zone of the gasifier to heat the steam and then inject it into the reducing zone where the steam and other endothermic reactions take place, reducing the need for added oxygen combustion and increasing the overall hydrogen content of the syngas. The HTHX would most likely be made from alumina-forming ODS alloys.

EXPOSURE IN AN ALUMINUM REMELTER

In addition to power generation systems, there are many scenarios for the use of HTHXs to increase the efficiency of many industrial thermal systems. One such case is the recuperation of heat from the flue gas of an aluminum melter such as that shown in Figure 3. In 2006 and 2007, rings of MA754, MA956, HR160, and 304 stainless were exposed in an aluminum melter at the Superior Aluminum Alloys plant in New Haven, Indiana. The rings were placed at the flue gas exit from the aluminum bath as shown in Figure 4a. Figure 4b shows a close-up of the rings composed of three identical sets of four. From the left to the right, the four rings in each set are 304 stainless, MA754 (NiCr ODS), MA956 (FeCrAl ODS), and HR150 (NiCoCr nonODS). They are supported on alumina rods carried on mullite refractory blocks. The gases to which the samples were exposed were the products of natural gas combustion with 1% excess air and vapors of the aluminum fluxes containing Na, K, Cl, F, and O, as well as alloying agents Cu, Mn, Mg, Zn, Si, and S. They were exposed for 5 ½ months at temperatures which were 85% of the time between 1200° and 1290°C, the rest of the time below that range.

At the end of the exposure, the samples were found in a rubble pile formed when the supports and additional refractory from above had collapsed onto the samples. The stainless steel was completely disintegrated (unrecoverable), and the HR160 was badly warped and corroded. Figure 5 shows a cross section of an MA956 ring showing suspected catastrophic corrosion through the formation of a liquid phase. The rings lost up to 25% of their mass during the exposure. Initial scanning electron

Figure 3. A typical aluminum melter.

Figure 4. The placement of the samples in the melter: a) from the position of the aluminum bath looking out into the flue section, b) close-up of the samples showing three identical sets of four metal types.

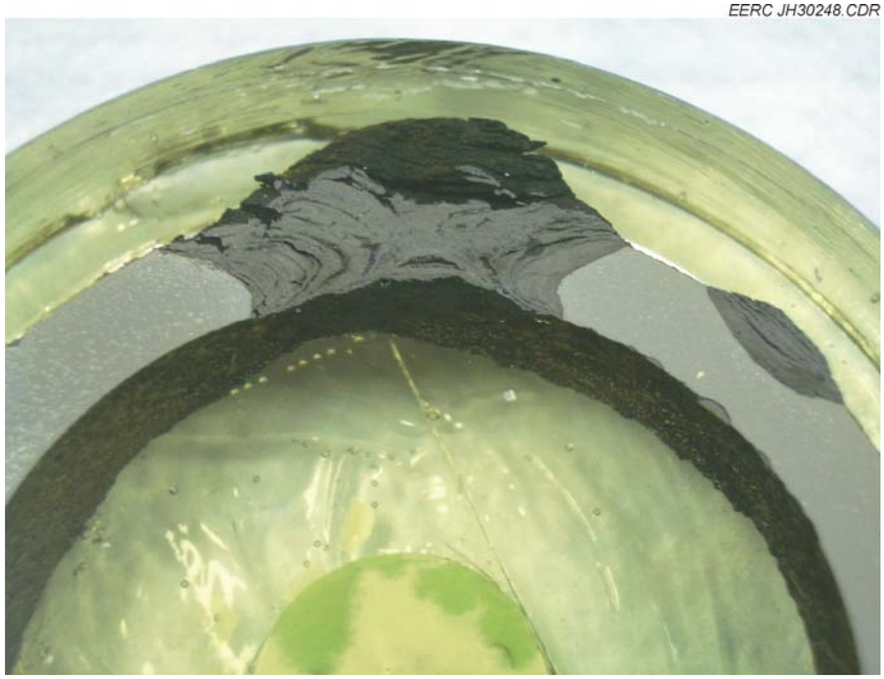

Figure 5. Polished cross section of an MA956 ring showing probable catastrophic corrosion.

microscopy (SEM) analyses howed no unusual concentrations of fluxing elements in the corroded areas, but did show substantial increases in aluminum near the heavily corroded regions, indicating that they were possibly splashed with liquid aluminum that may have dissolved the oxide scale leading to rapid catastrophic corrosion. However, further SEM analyses will be performed to determine the specific cause of the heavy corrosion.

Figure 6 shows a cross section of an MA754 ring. In contrast to the MA956, there was no catastrophic corrosion, but the samples were badly oxidized with a 15% loss of weight, mostly through vaporization of the chromia scale. Initial SEM analyses showed substantial void space development through 20% of the metal thickness. In general, it appears that neither the MA956 or MA754 formed any adverse reaction products with the aluminum fluxing agents. However, they may have been splashed with aluminum metal, and otherwise were simply exposed to temperatures that exceeded the ability of their oxide scales to protect them, so that there was substantial oxidation and vaporization of the oxides produced. However, more detailed SEM analyses are planned to better determine the loss mechanisms and whether they could be used in such systems, but at somewhat lower temperatures.

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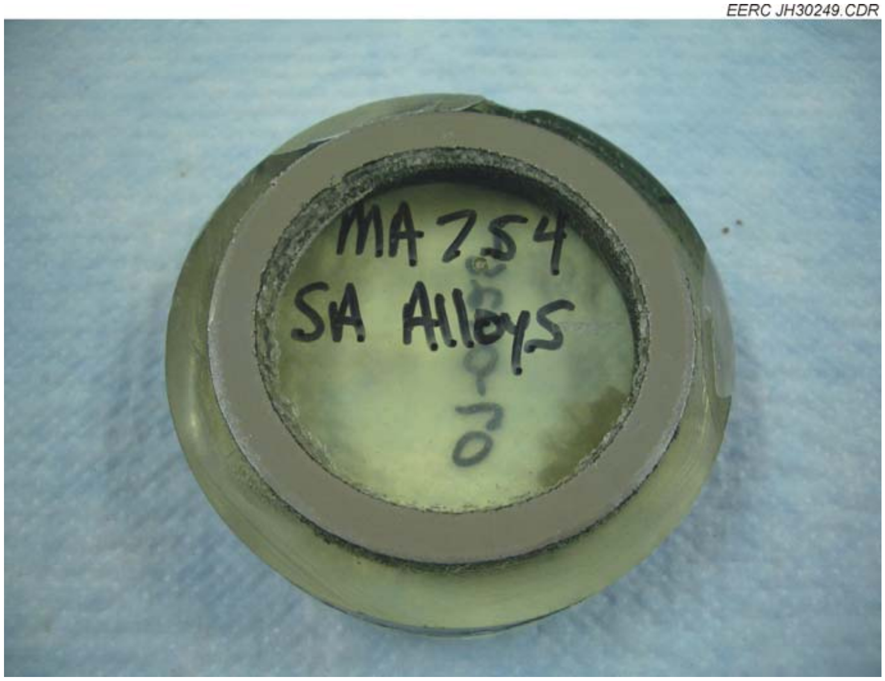

Figure 6. Polished cross section of an MA754 ring.

SUMMARY

In order to increase the efficiencies of advanced thermal energy systems, whether combustion or gasification for electric power generation or industrial systems such as aluminum melters, higher-working fluid temperatures must be reached. To reach the highest temperatures, especially over 1000°C, EERC experience shows that creep and corrosion-resistant dispersion-strengthened alloys are usually the best suited for these applications. However, careful testing in both simulated and actual systems for long durations is necessary in order to best define the temperature windows in which these materials are best used.

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