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Summary of Work on Coatings and Claddings for Fossil Energy Applications

R. W. Swindeman

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Metals and Ceramics Division

SUMMARY OF WORK ON COATINGS AND CLADDINGS FOR FOSSIL ENERGY APPLICATIONS

R. W. Swindeman

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SUMMARY OF WORK ON COATINGS AND CLADDINGS FOR FOSSIL ENERGY APPLICATIONS*

R. W. Swindeman

ABSTRACT

A summary of efforts to examine coatings and cladding materials for high-strength austenitic steels is provided. Chromized coatings on 17-14CuMo stainless steel and a modified type 316 (HT-UPS) stainless steel were investigated. Claddings included alloy 671, 690, and an iron-aluminide intermetallic alloy. Structural alloys that were clad included type 304 stainless steel, modified type 316 stainless steel, and modified alloy 800H. The capability of producing co-extruded tubing of the experimental alloys was demonstrated.

1. INTRODUCTION

In 1986, a 6-year program was started to evaluate materials for use in the boiler of a conceptual advanced steam cycle coal-fired power plant being studied by the Electric Power Research Institute (EPRI).[1,2] The program included various groups of alloys that were selected for their strength, steam corrosion resistance, or ash corrosion resistance. It was recognized that for some alloys the combustion of high ash or chlorine content coal would require the protection of a coating or cladding.[2-4] Various combinations were examined. These included chromized coatings for strong, lean stainless steels; nickel-chromium alloy cladding on a modified type 316 stainless steel and modified alloy 800H; and iron-aluminide cladding on type 304 stainless steel. This report reviews the work that has been undertaken over the last 6 years.

2. COATINGS

Coatings have been used with great success to protect waterwall tubing from corrosion fatigue and waterwall distress.[5] Carbon steel and low-alloy steels have been coated with

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high-chromium materials for extended life. More recently, chromized 9Cr-1Mo-V steel (Gr-91) has been evaluated as a superheater material for advanced steam cycle plants, and in this condition, it appears that the material has a corrosion resistance equivalent to 300 series stainless steels.[6] Since Gr-91 steel may be heat treated to recover microstructure and strength (assuming minimal decarburization), chromizing appears to be attractive. Indeed, chromized superheater tubes of 9Cr-1Mo-V-Nb steel in the Tennessee Valley Authority Kingston Steam Plant Unit 5 have been in service for more than 10 years.

Good coal ash corrosion resistance has been reported for chromized 17-14CuMo stainless steel,[4] but no information is available on the strength and ductility of composite materials. To examine this issue, specimens of two lean austenitic stainless steels [17-14CuMo stainless steel and modified type 316 stainless steel] were chromized by Babcock & Wilcox (B&W) Research Laboratory and tested at Oak Ridge National Laboratory (ORNL). More details regarding the coating compositions and characterizations are provided elsewhere.[7,8] The microstructures of chromized coatings after creep testing are shown in Figs. 1 and 2 for the two steels in which the coatings were two phase and 100 to 150 μm thick. These photomicrographs show the cracks in the coatings that develop during creep testing at 700°C strains of a few percent. These cracks exposed the base metal to the environment. The 17-14CuMo stainless steel (see Fig. 1) was found to be creep brittle, and intergranular creep cracks initiated in the base metal at locations where the coating cracked. The modified 316 stainless steel was creep ductile, and cracks in the coating were blunted at the coating/base metal interface (see Fig. 2). In addition to the brittle coating, the long time at high temperature required to produce a 100-μm-thick coating degraded the creep strength of the base metal.[9] Although the modified type 316 stainless steel was found to retain more strength than the 17-14CuMo stainless steel, it was concluded that higher chromium content steels would be more desirable for coal ash corrosion resistance under severe service conditions.

3. CLADDINGS

Use of clad tubing in aggressive atmospheres is accepted in the fossil, waste incineration, and petrochemical industries. Typical base metals include carbon steel, 18-8 stainless steels, and alloy 800H. Initially, superheater tubing of alloys with high creep strength were clad. The target in the current research was to produce diameter tubing 50–60 mm with thicknesses of 7 to 12 mm, clad with nickel-chromium alloys at least 2 mm thick. Development of the clad tubing was undertaken by B & W Research Center, [10,11] and

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Fig. 1. Chromized coating on 17-14CuMo stainless steel after creep testing at 700°C.

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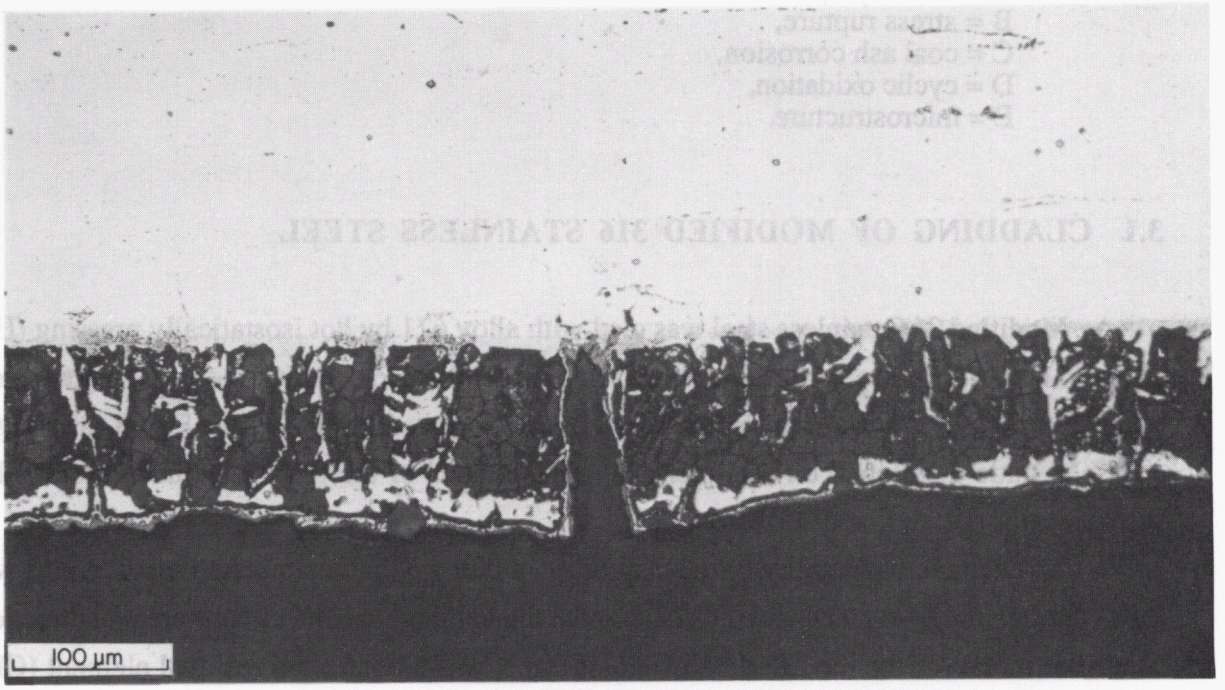


Fig. 2. Chromized coating on modified 316 (HT-UPS) stainless steel after creep testing at 700°C.

combinations of materials are provided in Table 1. Three materials were clad: modified type 316 stainless steel, modified alloy 800H, and type 304 stainless steel. Weld overlay cladding of plates was also performed, but results are discussed elsewhere.

Table 1. Summary of work on claddings

Base material	Cladding	Process*	Source†	Evaluations‡
Mod 316SS tube	alloy 671	HIP/coextrusion	B&W	A, B, C, D, E
Mod 316SS tube	alloy 690	coextrusion	B&W	C, E
Mod 316SS plate	alloy 672	weld overlay	B&W	C, E
Mod 316SS plate	alloy 690	weld overlay	B&W	E
Mod 800 tube	alloy 690	coextrusion	B&W	D, E
Mod 800 plate	alloy 672	weld overlay	B&W	C, E
Mod 800 plate	alloy 690	weld overlay	B&W	E
Alloy 800 tube	alloy 671	coextrusion	INCO	D
TP304SS tube	Fe_3Al	coextrusion	B&W	A, C, D, E

*HIP = hot isostatic pressing.
†B&W = Babcock & Wilcox Company.
‡A = ductility by crush testing,
B = stress rupture,
C = coal ash corrosion,
D = cyclic oxidation,
E = microstructure.

3.1 CLADDING OF MODIFIED 316 STAINLESS STEEL

Modified 316 stainless steel was clad with alloy 671 by hot isostatically pressing (HIP) alloy 671 powder onto a tube blank and subsequently coextruding the composite tube at 1200°C (ref. 11). A sound interfacial bond was produced, as shown in Fig. 3, although a coarse carbide developed on the interface. Evaluations of the tubing included weldability, mechanical properties, and corrosion.[8]

To examine weldability of the clad tubes, a butt weld and simulated repair welds were made through the base metal and the clad in both the longitudinal and circumferential directions. The filler metal for the modified 316 stainless steel was a controlled residual element (CRE) 16-8-2 stainless steel, while alloy 92 was used for the cladding. No problem was encountered

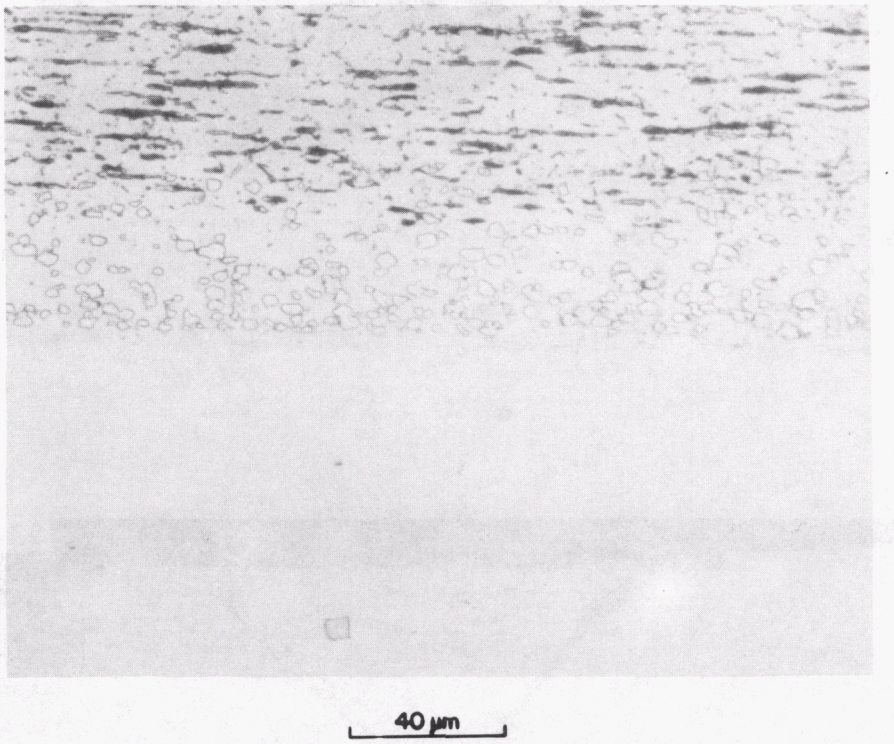
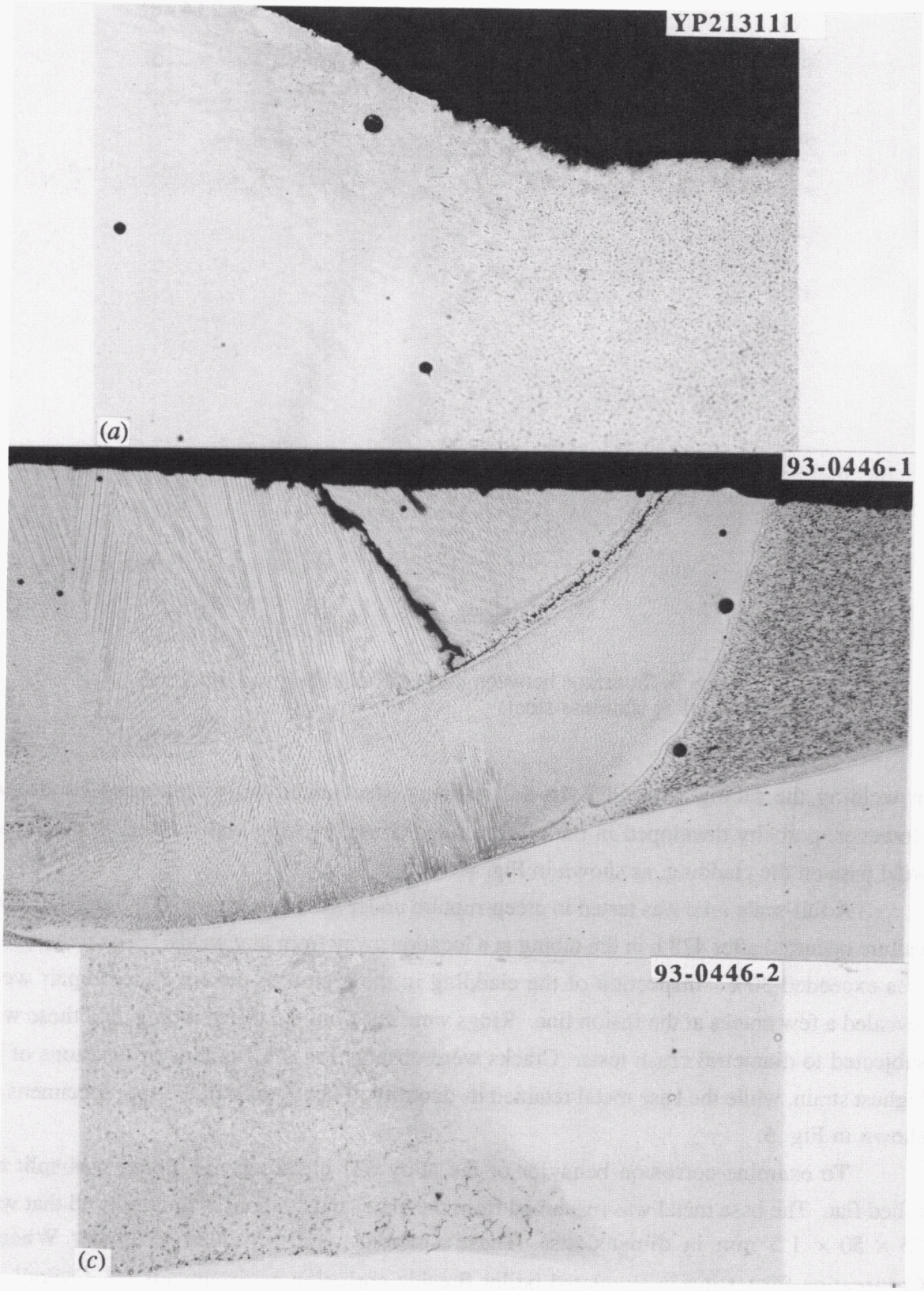


Fig. 3. Interface between alloy 671 cladding and modified 316 (HT-UPS) stainless steel.

in welding the tubing with CRE 16-8-2 stainless steel under fully restrained conditions. However, porosity developed in the cladding and some cracking was noticed in the second weld pass on the cladding, as shown in Fig. 4.

A full-scale tube was tested in creep-rupture under axial loading at 700°C and 217 MPa. Failure occurred after 478 h in the tubing at a location away from any welds.[9] The reduction of area exceeded 30%. Inspection of the cladding in the region of the simulated repair welds revealed a few cracks at the fusion line. Rings were cut from the tested tubing, and these were subjected to diametral crush tests. Cracks were observed in the cladding at locations of the highest strain, while the base metal retained its ductility. Photographs of the ring specimens are shown in Fig. 5.

To examine corrosion behavior of the alloy 671 cladding, the tubing was split and rolled flat. The base metal was machined from the plate, and coupons were produced that were 25 × 50 × 1.5 mm in dimensions. These coupons were provided to Foster Wheeler Corporation for testing in simulated boiler fireside corrosion environments.[7-9] Overall, the 671 cladding was found to have good corrosion resistance compared to alloys with lower chromium contents. A typical comparison of alloys is shown in Fig. 6 and was taken from the work of Van Weele and Blough.[7]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(c)

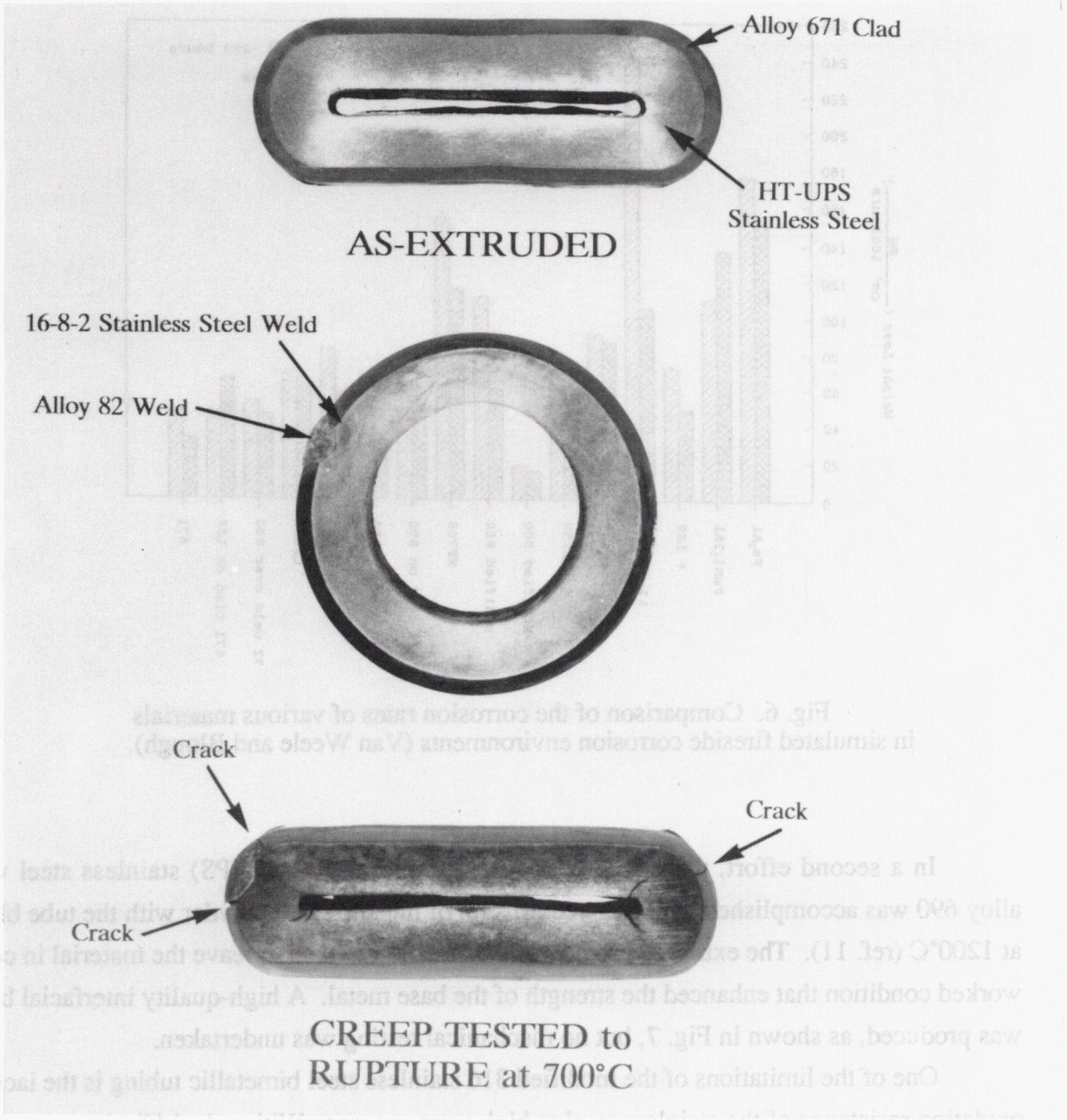

Fig. 5. Effect of creep exposure at 700°C on the ductility of 671 cladding on modified 316 (HT-UPS) stainless steel tube.

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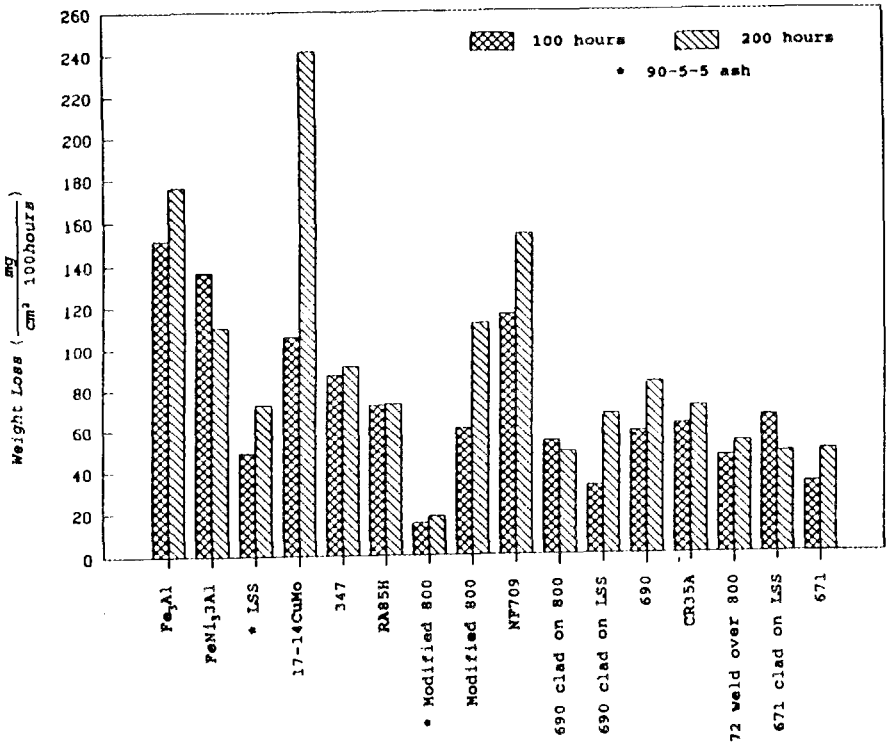


Fig. 6. Comparison of the corrosion rates of various materials in simulated fireside corrosion environments (Van Weele and Blough).

In a second effort, the cladding of the modified 316 (HT-UPS) stainless steel with alloy 690 was accomplished by direct coextrusion of the alloy 690 powder with the tube blank at 1200°C (ref. 11). The extruded product was then cold finished to leave the material in cold-worked condition that enhanced the strength of the base metal. A high-quality interfacial bond was produced, as shown in Fig. 7, but no mechanical testing was undertaken.

One of the limitations of the modified 316 stainless steel bimetallic tubing is the lack of oxidation resistance of the stainless steel at high temperatures. With only 14% chromium, the steel should not be used for steam or air service above 650°C. Some improvement in oxidation resistance was gained by cold-working the modified 316 stainless steel before oxidation testing at 800°C as shown in Fig. 8. Here, a comparison is made between the modified 316 stainless steel (heat AX7) and cold-worked type 316 stainless steel. The annealed modified 316 stainless steel exhibited a high rate of oxidation, as measured by weight gain. The as-received (10% cold-rolled) modified 316 stainless steel started with a high rate of oxidation but

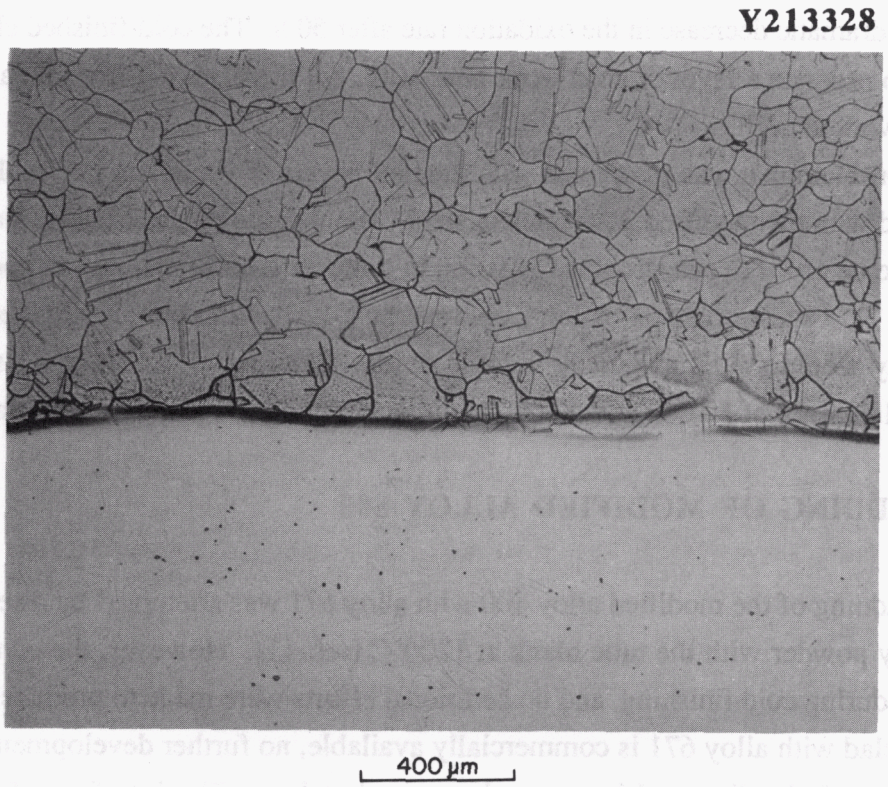


Fig. 7. Interface between alloy 690 cladding and modified 316 stainless steel tube.

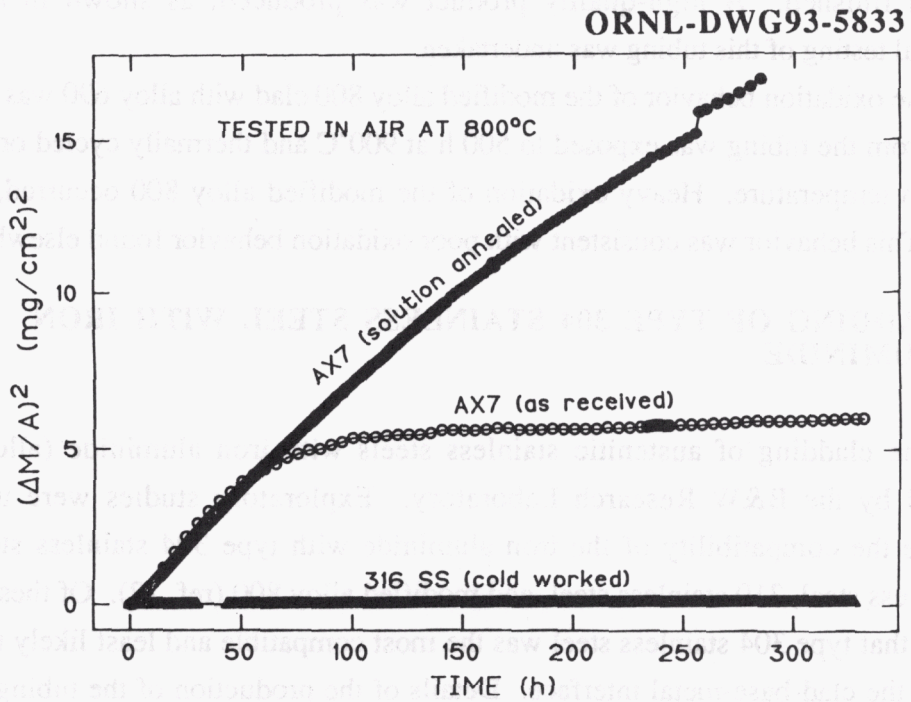


Fig. 8. Oxidation curves for annealed and cold-worked modified 316 stainless steel in comparison to 316 stainless steel at 800°C.

exhibited a dramatic decrease in the oxidation rate after 50 h. The cold-finished clad tubing was designed to produce a level of cold work near 10%, but the cladding must be able to survive 10% cold work as well.

A problem that was associated with the high levels of vanadium and molybdenum was experienced with the modified 316 stainless steel. The volatile oxides of these elements caused the alloys to be prone to catastrophic oxidation in static air environments at temperatures above 650°C (ref. 7). Catastrophic oxidation would not be expected in steam tubing because the high gas velocity would sweep away any volatile oxide. Even in the laboratory testing, samples were tested to times of 50,000 and 60,000 h without experiencing severe oxidation at 700°C.

3.2 CLADDING OF MODIFIED ALLOY 800

Cladding of the modified alloy 800 with alloy 671 was attempted by direct coextrusion of the alloy powder with the tube blank at 1200°C (ref. 11). However, the composite tubing disbonded during cold finishing, and no additional efforts were made to produce tubing. Since alloy 800 clad with alloy 671 is commercially available, no further development work on this combination of cladding and base metal was undertaken. The interface of a commercial alloy 800 tube clad with alloy 671 is shown in Fig. 9.

Cladding of modified alloy 800 with alloy 690 was accomplished by direct coextrusion of the alloy 690 powder with the tube blank at 1200°C (ref. 12). The extruded product was then cold finished. A high-quality product was produced, as shown in Fig. 10. No mechanical testing of this tubing was undertaken.

The oxidation behavior of the modified alloy 800 clad with alloy 690 was examined. A ring cut from the tubing was exposed to 500 h at 900°C and thermally cycled once per day to near room temperature. Heavy oxidation of the modified alloy 800 occurred, as shown in Fig. 11. This behavior was consistent with poor oxidation behavior found elsewhere.[7]

3.3 CLADDING OF TYPE 304 STAINLESS STEEL WITH IRON ALUMINIDE

The cladding of austenitic stainless steels with iron aluminide (alloy FAS) was examined by the B&W Research Laboratory. Exploratory studies were undertaken to determine the compatibility of the iron aluminide with type 304 stainless steel, modified 316 stainless steel, 310 stainless steel, and modified alloy 800 (ref. 12). Of these materials, it appeared that type 304 stainless steel was the most compatible and least likely to form brittle phases at the clad-base-metal interface. Details of the production of the tubing are provided

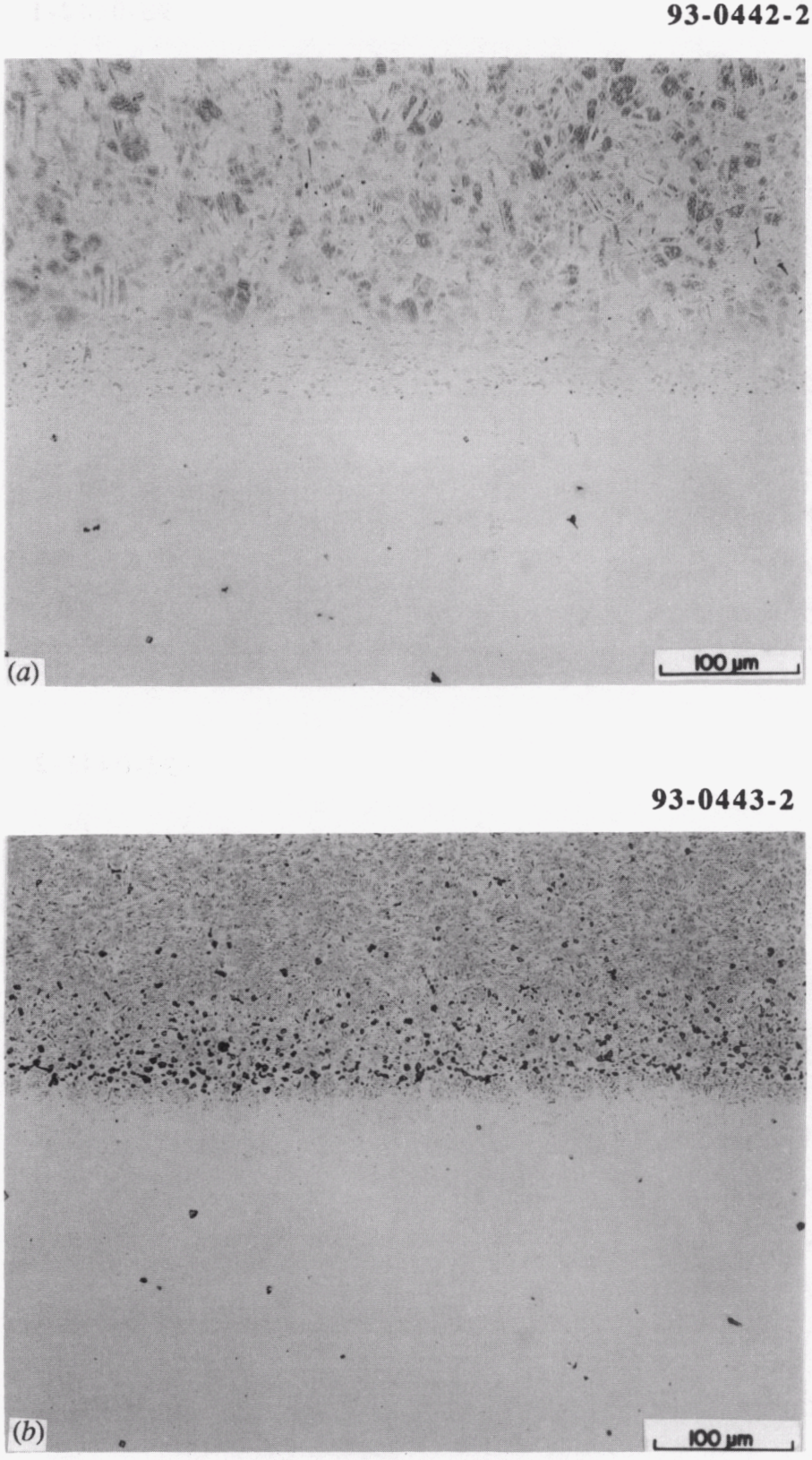
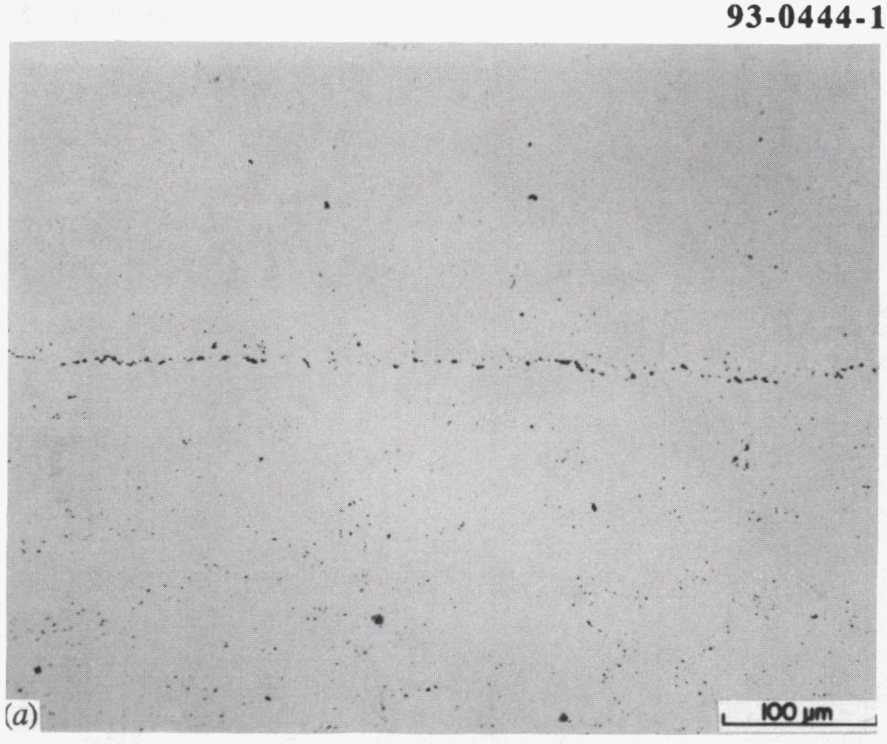


Fig. 9. Interface between alloy 671 cladding and alloy 800 tube: (*a*) as-fabricated and (*b*) after 500 h at 900°C with a cycle to near room temperature each day.



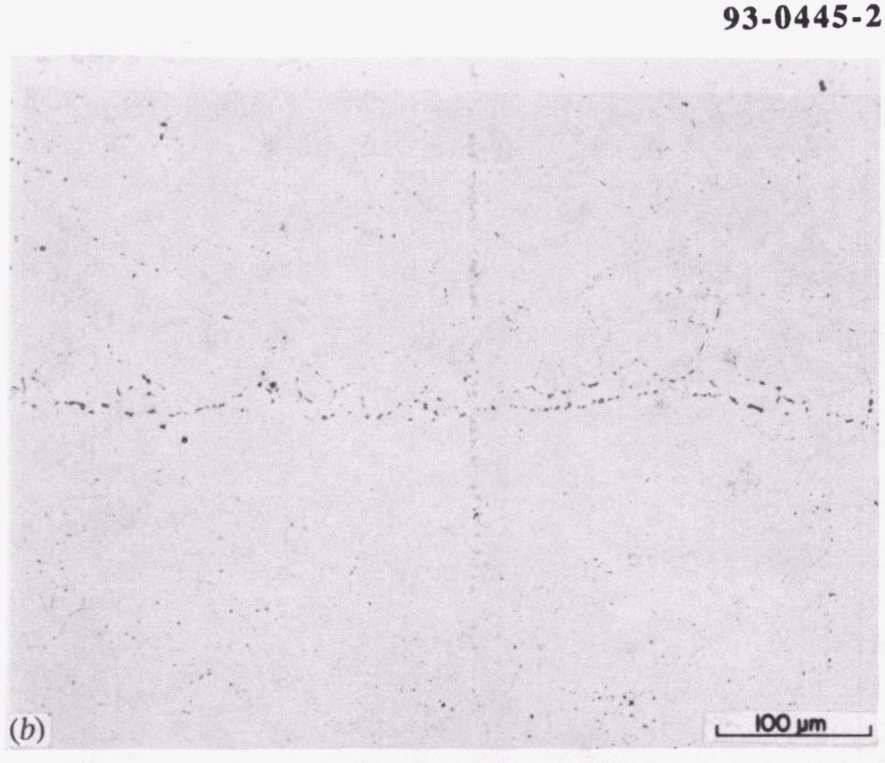


Fig. 10. Interface between alloy 690 and modified alloy 800 tube: (*a*) as-fabricated and (*b*) after 500 h at 900°C with a cycle to near room temperature each day.

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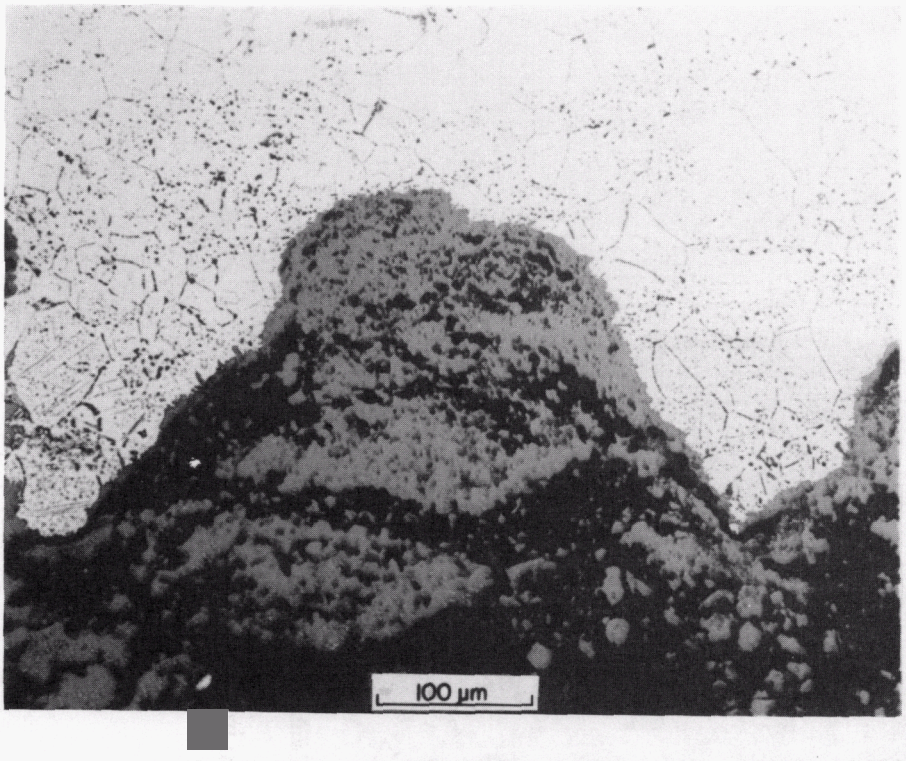

Fig. 11. Oxidation of modified alloy 800 tube after 500 h at 900°C with a cycle to near room temperature each day.

elsewhere.[13] Essentially, iron-aluminide powder was coextruded with a type 304 stainless steel tube blank. Extrusions were made at 1200 and 1100°C. It was found that the extrusion at 1100°C produced a sound product, as shown in Fig. 12.

Mechanical testing consisted of crush tests at several temperatures, and results are shown in Fig. 13. Cracking of the cladding occurred at room temperature, 200, and 400°C, but the severity of the cracking decreased with deformation temperature. Nevertheless, it is apparent that warm-working and bending of the tubing should be performed above 400°C.

Oxidation tests were performed at 760 and 900°C. Ring samples were exposed for approximately 500 h at each temperature with cooling to near room temperature once per day. The cladding-base-metal interface is shown in Fig. 14 and gives no evidence of disbonding.

4. BONDING APPLICATIONS FOR CLADDINGS IN FOSSIL ENERGY APPLICATIONS

Because the cost of clad tubing is high relative to bare (monoblock) tubing, the use of cladding for protection against corrosion at high temperature has been limited in power boiler applications. A few coal-fired boilers in the United States use clad superheater tubing, such as

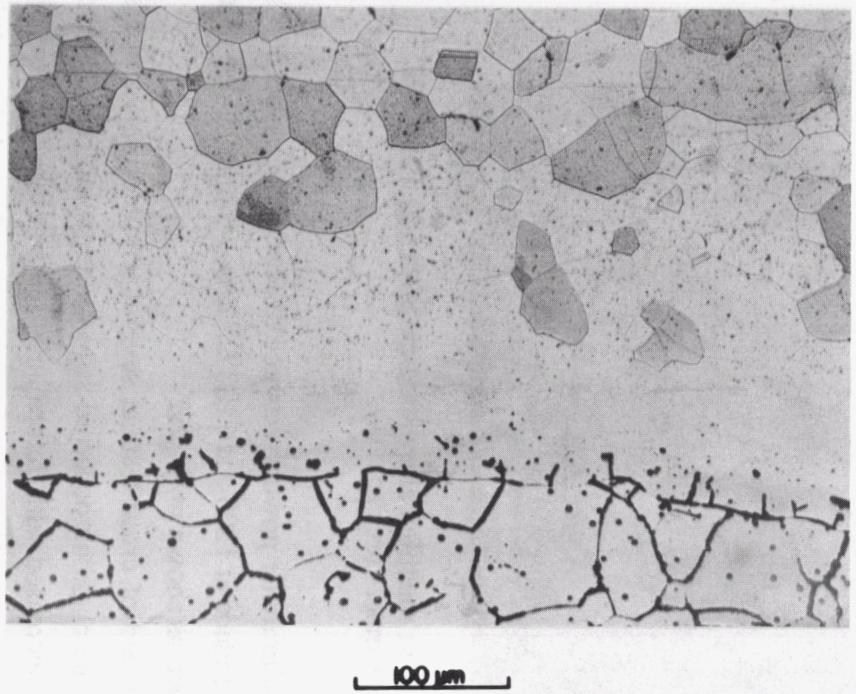

Fig. 12. Interface between iron-aluminide cladding and type 304 stainless steel tube.

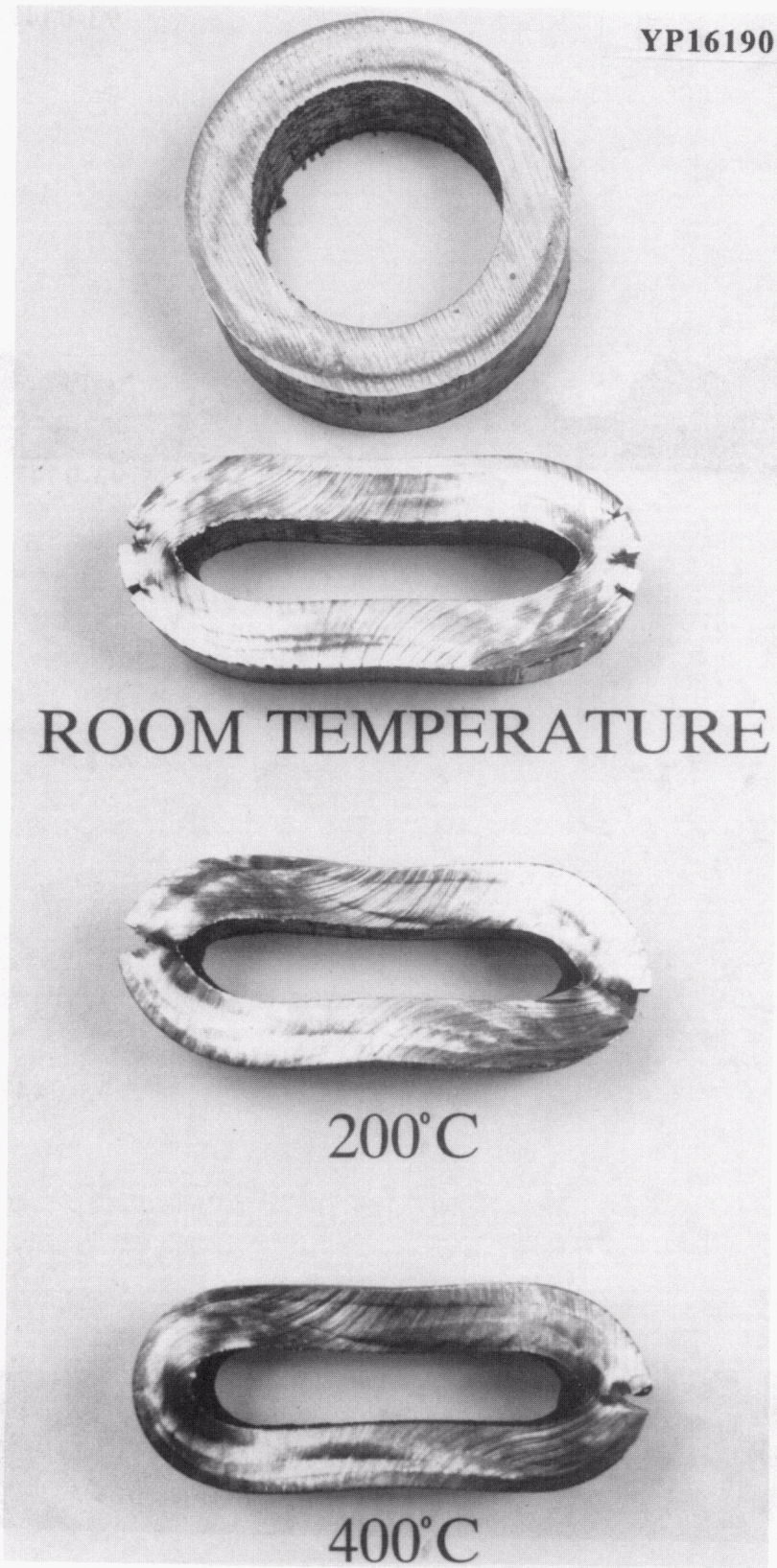

Fig. 13. Effect of temperature on the ductility of coextruded iron-aluminde/304 stainless steel coextruded tube.

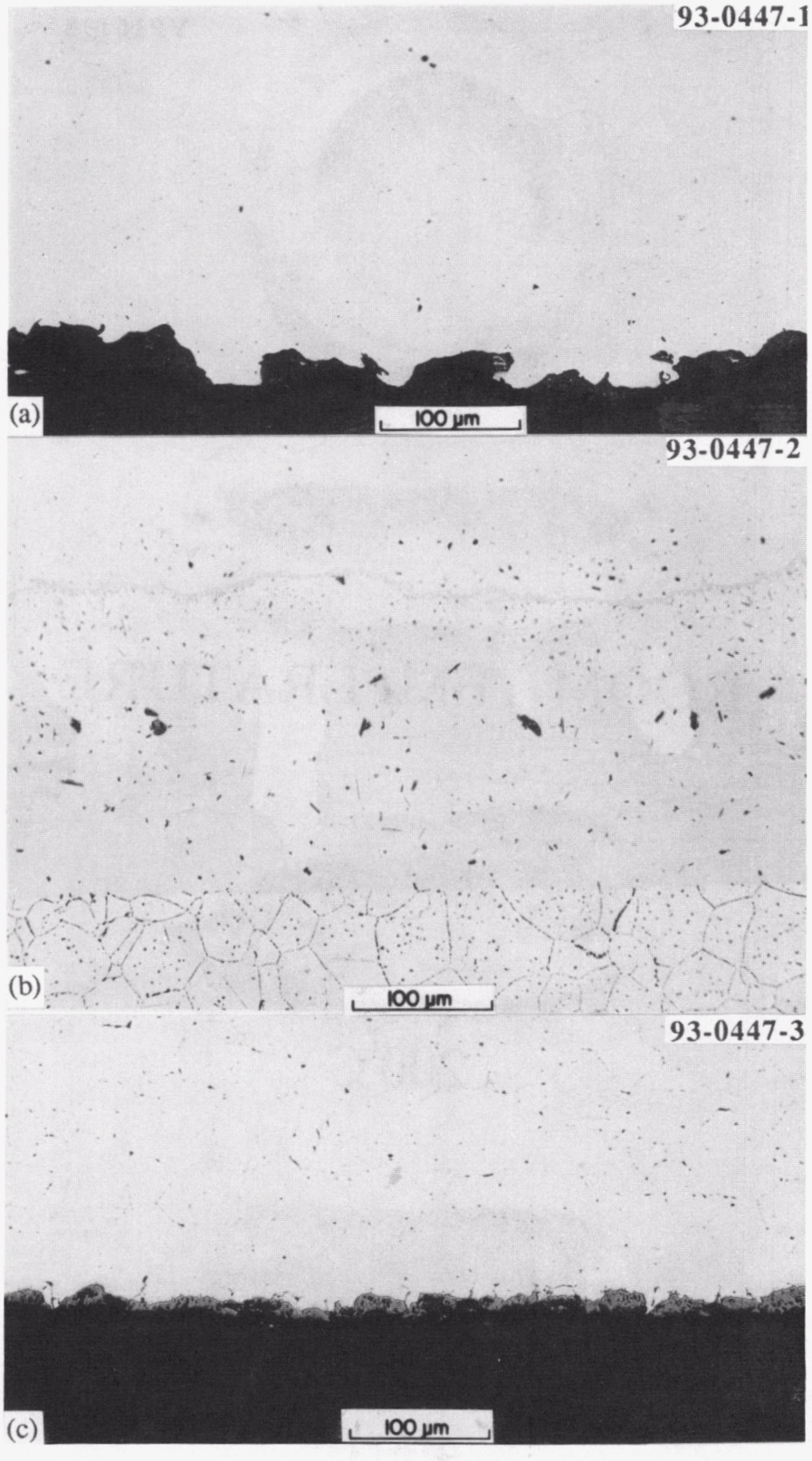

Fig. 14. Effect of exposure on the surface corrosion and interface between iron-aluminide cladding and type 304 stainless steel tube: 500 h at 900°C with a cycle to room temperature each day: (*a*) Fe_3Al surface, (*b*) interface, and (*c*) 304 stainless steel surface.

alloy 671 clad over alloy 800, but the introduction of 310HCbN stainless steel, fine-grained 347 stainless steel, and 20Cr25NiCbN stainless steel may eliminate this requirement since these alloys have relatively good resistance to coal ash corrosion.[6] It is not expected that the use of alloys 690 and 671 will increase in power boiler superheater tubing.

Coal-fired furnaces for the Combustion 2000 project[14] will require tube temperatures in the range of 980 to 1100°C (1800 to 2000°F). Although the eventual goal is to use ceramic heat exchanger tubes, it seems likely that metallic tubing will be needed in the early stages of the developmental work. Materials such as alloy 800H, 253MA stainless steel, and HP-40 could be chosen, but the potential for coal ash corrosion exists, and high-chromium cladding of tubing alloys may be required. Materials such as alloy 671, alloy 690, and CR35A are potential cladding alloys for this application.

For severe sulfidizing conditions, the choices of structural alloys are limited, and metallic components must be cooled to temperatures where sulfidation rates are low. Currently, refractory-insulated carbon steel is used for large-diameter piping and vessels. This practice is likely to continue. To avoid entrainment of refractory particles in the gas stream, exiting cyclones or filters with metallic liners are used. Typically, these are type 310 stainless steel, 253MA, or some similar material when the environment is oxidizing and contains low sulfidizing potential. Studies by DeVan[15] have clearly shown that iron aluminide has outstanding corrosion resistance to gases containing high sulfur. In this respect, iron aluminide has potential as a liner for containment of refractory insulating piping for gasifier or carbonizer gas streams.

5. CONCLUSIONS

Austenitic alloys may be chromized, but the long times and high temperatures required for thick, chromized layers significantly reduce the strength of the base metal. The chromized coatings may be brittle, forming cracks at low strains. These cracks can promote base-metal cracking in creep-brittle stainless steels. The modified stainless steels do not suffer creep embrittlement.

Tubing of modified type 316 stainless steel and modified alloy 800 (HT-UPS) alloys may be clad with either alloy 690 or alloy 671 for improved coal ash corrosion resistance in the temperature range of 650 to 700°C (1200 to 1300°F). Testing at 700°C indicates compatibility of the materials. The 671 cladding exhibits room-temperature embrittlement after exposure at 700°C, but ductility at high temperature is good.

Clad modifed 316 stainless steel tubing should not be used for temperatures above 700°C because of the tendency of base-metal alloys to undergo catastrophic oxidation.

Iron aluminide may be clad onto type 304 stainless steel. The cladding will crack when deformed at low temperatures. Tube bending must be at temperatures above 400°C. Thermal cycling experiments to 760 and 900°C indicate good material compatibility and oxidation resistance on the clad side.

6. ACKNOWLEDGMENTS

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