DEVELOPMENT OF ODS HEAT EXCHANGER TUBING

Quarterly Technical Progress Report

For

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Edison Welding Institute — University of California at San Diego

ABSTRACT
Work continued on four major tasks of this project – increasing the circumferential strength of MA956 tubing, joining of the MA956 alloy, determining the bending limits of MA956 tubing, and determination of the high temperature corrosion limits of the MA956 alloy. With respect to increasing the circumferential strength of a MA956 tube, all of the extrusions plus decanning operations have been completed (total of 180 rods) for Task 2.1.1 (Extrusion Ratio = 20:1, 16:1, 10:1 and Extrusion Temperature = 1000, 1075, 1150, and 1200°C). Also, essentially all of the cold working operations have been completed (0, 10, 20, 30, 40%) with approximately 100 annealing treatments (1000, 1150, 1300°C) remaining. The sample microstructures produced by this processing continue to be analyzed. Creep testing to determine the "stress threshold" curves for this alloy continues. Regarding joining of the MA956 alloy, advances were made using transient liquid phase bonding. And finally, laboratory high temperature corrosion testing of the material continues (both fluid-side and fire-side) with fabrication of the field probes initiated.

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INTRODUCTION

This research is seeking to develop a MA956 heat exchanger tube that will lead to the design and fabrication of a MA956 full-scale tube heat exchanger composed of the referenced alloy. The alloy MA956 is an oxide dispersion strengthened (ODS) material that possesses superior creep strength and corrosion resistance at very high temperatures (e.g. T > 2000°F) compared to traditional wrought or cast alloys. However, the creep properties are unidirectional (typically stronger in the longitudinal direction compared to the transverse direction), fabrication of components made from this alloy is relatively difficult, and the corrosion limits of the alloy MA956 in coal-fired environments are not known. Thus, the technical tasks being executed in this Vision 21 project are:

Task 1: Project Management
Task 2: Improvement of Circumferential Creep Strength of MA956 Tubes
Task 3: Joining
Task 4: Bending of MA956 Tubes
Task 5: High Temperature Corrosion Limits of MA956
Task 6: Generation of Data for Designers
Task 7: Implication of ODS Properties on Heat Exchanger Design
Task 8: Reporting

The members of the team conducting this research are: Huntington Alloys (HA), Foster Wheeler Development Corporation (FWDC), Oak Ridge National Laboratory (ORNL), University of California, San Diego (UCSD), Michigan Technological University (MTU), and the Edison Welding Institute (EWI).

EXPERIMENTAL

Experimental work associated with the tasks identified in the previous section is discussed below.

Task 2: Improvement of Circumferential Creep Strength of MA956 Tubes

The following matrix of tests shown in Table 1 is currently being performed at HA. The execution of this matrix will result in 540 different combinations of extrusion + thermomechanical + annealing parameters. Table 2 shows the work that has been completed thus far.

Table 1
Matrix of Extrusion + Cold Work + Recrystallization Parameters

Extrusion Temp (°C)	Extrusion Ratio	Amount of Cold Work (%)	Recrystallization Temp (°C)	Recrystallization Time (h)
1000	10:1	0	1000	0.5
1075	16:1	5	1150	1
1150	20:1	10	1300	6
1200		15		
		25		

Table 2
Work Completed on Extruded + Cold Work + Recrystallized Samples

Operation	Number Required	Number Complete	% Complete
Extrusion	180	180	100
Decanning	540	540	100
Cold Work	540	535	99
Annealing	540	438	81
Samples Prepared	540	231	43
Microstructure Analysis	540	89	16

A 4 inch piece of tube with dimensions 2.5'' OD x 0.25'' AVWA, was cut in half in the longitudinal direction, and the two halves hot worked into flat pieces of plate. These pieces were sent to ORNL for the purpose of creep testing in the transverse direction of the tube. Specimens are currently being cut and machined from this plate.

Task 3: Joining
Friction Welding: No further friction welds were completed during this quarter.

Transient Liquid Phase Bonding: Additional diffusion bonding trials were completed in the vacuum hot press. These included three additional test runs on the press itself, six exploratory bonding trials using 0.5 inch diameter rod, and initiation of an eight-run parametric study designed to identify the most important process variables in diffusion bonding of the MA956 alloy.

Explosive Welding: No further explosive welds were completed during this quarter.

Magnetic Impulse Welding: The new magnetic impulse welder has arrived at EWI, however no welds have been made with this new machine.

Task 4: Bending of MA956 Tubes
No work was performed on this task this quarter.

Task 5: High Temperature Corrosion Limits of MA956
The lifetime exposure testing in air at 1300°C of has been completed with testing at 1100, 1200, and 1250°C continuing. Also, laboratory fireside corrosion testing has begun using two different simulated flue gases and three different ashes which were selected for being prototypical of what may be experienced in a Vision 21 plant. Regarding field testing of the MA956 alloy, the first utility with the appropriate locations for the air-cooled probes have been determined, the control hardware procured, and the probe design finalized and assembly initiated.

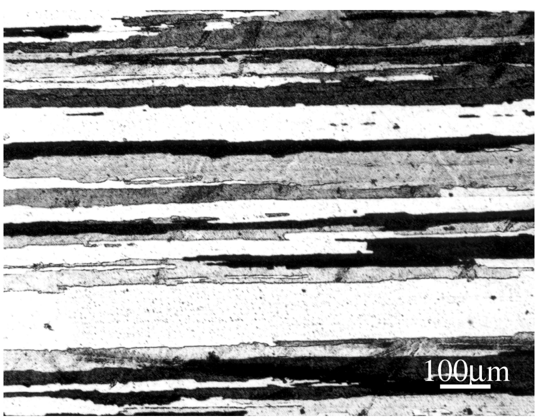
Task 6: Generation of Data for Designers
No experimental work has been accomplished on this task during this reporting period.

Task 7: Implication of ODS Properties on Heat Exchanger Design
No experimental work has been accomplished on this task during this reporting period.

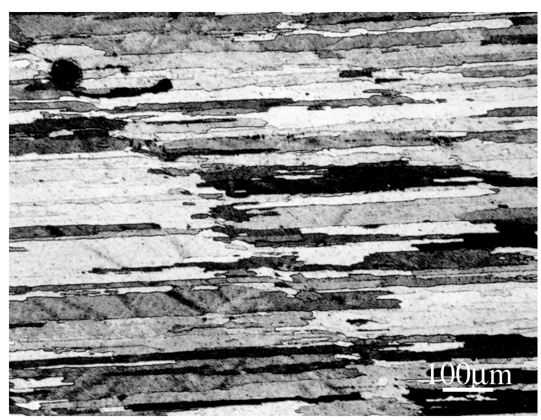
RESULTS AND DISCUSSION

Task 2: Improvement of Circumferential Creep Strength of MA956 Tubes
Microstructural analysis of the 54 MA956 rods that have been extruded + cold worked + annealed has shown a variation in the grain structure and hardness of the samples.

Regarding the effect of recrystallization temperature, and as stated in the last quarterly report, samples annealed at 1000°C did not exhibit any recrystallization, independent of the amount of cold work imposed on the sample. However, samples annealed at 1150°C did show the onset of primary recrystallization, the amount being dependent on the amount cold work. When annealed at 1300°C, all the samples exhibited primary and secondary recrystallization, with the final recrystallized grain morphology being a function of the cold work for a given sample but following a linear relationship. That is, at 10% CW, the mean grain size is of the order of 100 microns, whereas at 30% CW the mean grain size is closer to 50 microns (see Figure 1 below). Thus it would appear that while % CW can initiate recrystallization – it does not guarantee a large processed grain size. It is also important to note that shear bands occur for samples subjected to relatively large amounts of cold work, thereby creating transverse grain boundaries which may restrict secondary grain growth (Fig. 1(b)).



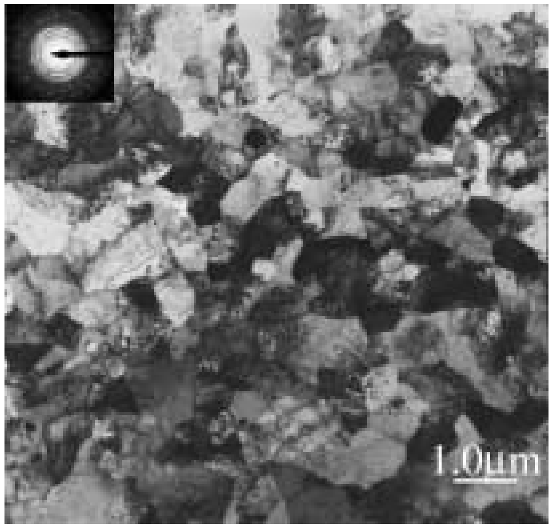
(a) 10% CW



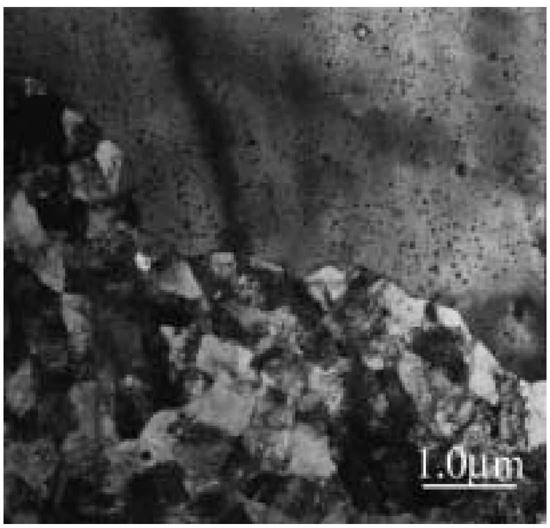
(b) 30% CW

Figure 1. Effect of cold work on grain size for samples extruded at 1000°C using a 20:1 extrusion ratio and annealed at 1300°C for 6 hours.

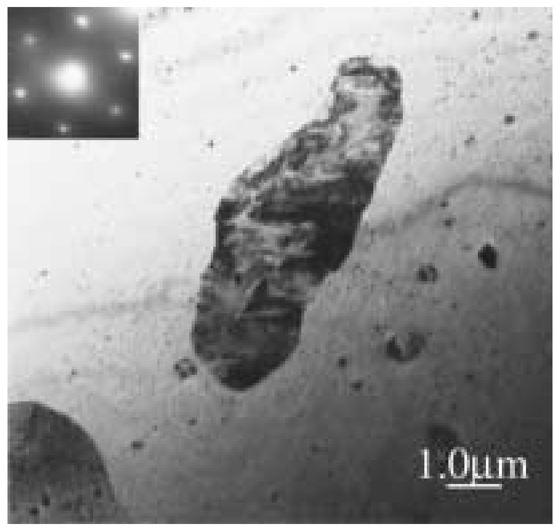
Thus far transmission electron microscopy (TEM) studies have been the most comprehensive for samples extruded at 1075°C using a 20:1 extrusion ratio (A3B series) and annealed at 1150 or 1300°C. The microstructures of these samples appear to be bimodal with regions that are fully recrystallized as well as areas where no recrystallization has occurred. Also, increasing the amount of cold work results in an increase of the volume fraction of recrystallized material, as shown in Figure 2 below.



(a) 0% CW



(b) 10% CW



(c) 20% CW

Figure 2. Effect of cold work on recrystallization for samples extruded at 1075°C using a 20:1 extrusion ratio and annealed at 1150°C for 6 hours.

Creep testing of commercially available MA956 tubing has been completed. In an effort to test MA956 tubing in the transverse direction, pieces of MA956 tubing have been cut in half in the longitudinal direction and the half pieces hot worked into flat pieces of plate (Figure 3). Examination of the microstructure after the hot working operation has shown no noticeable changes.

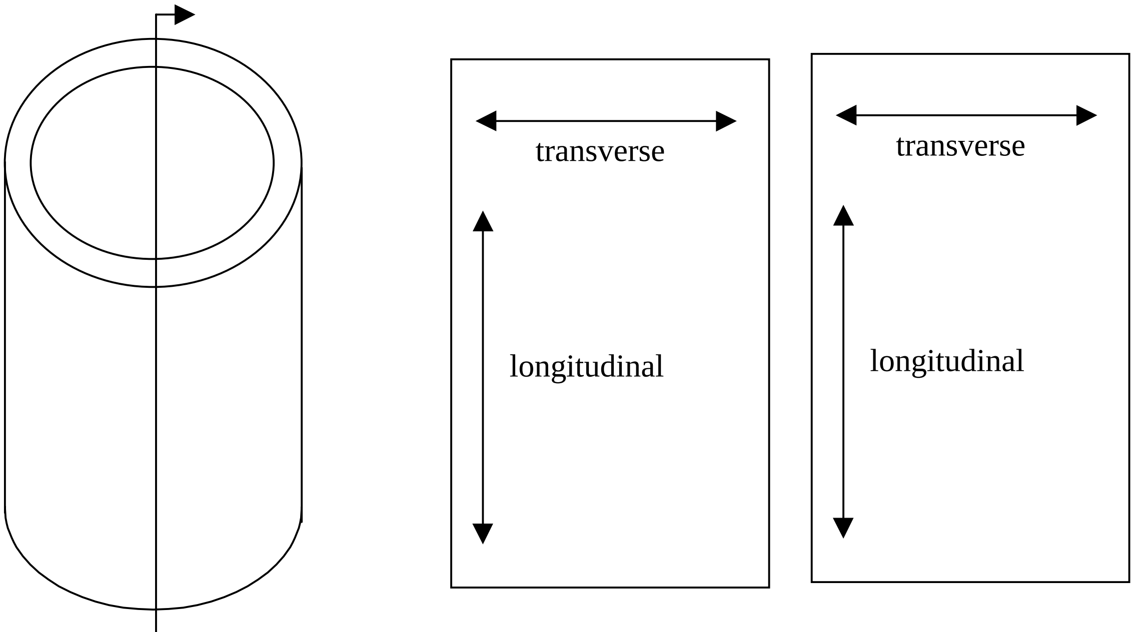
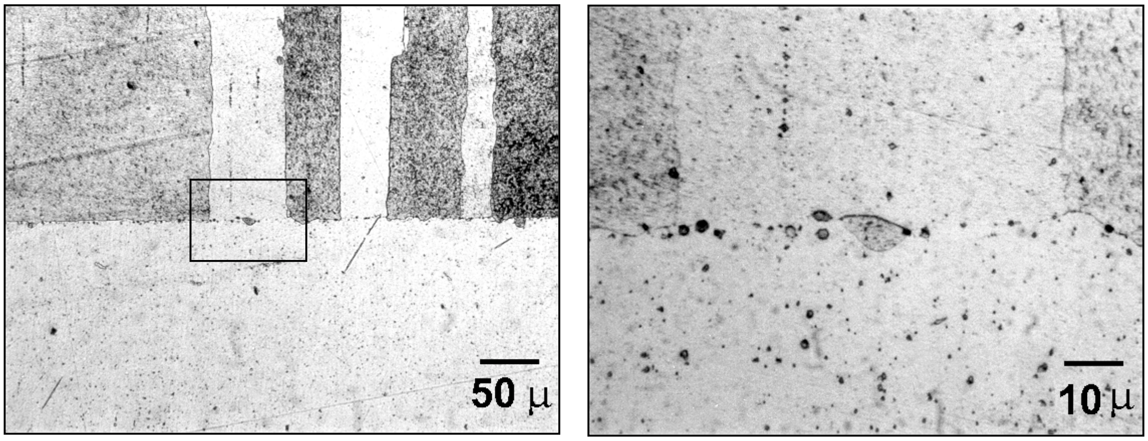


Figure 3. Schematic drawing showing how plate is produced from tube, thus allowing creep samples to be taken in the transverse direction.

Task 3: Joining
Friction welding: During the 4th quarter no additional friction welds were made.

Transient Liquid Phase Bonding: Work continued on the MA956 diffusion bonding trials using the vacuum hot press. This included three additional test runs on the press itself, six exploratory bonding trials on 0.5 inch diameter bar, and initiation of an eight-run parametric study designed to identify the most important process variables in diffusion bonding of the MA 956 alloy.

The six bonding trials included joining borided recrystallized rod to unrecrystallized rod, borided unrecrystallized rod to recrystallized rod, and recrystallized rod to unrecrystallized rod using a thin interlayer of elemental boron. Several of these samples show significantly stronger evidence of grain growth across the prior joint interface than has been observed in prior trials. Figures 4 show the bond line of the fifth bonding trial.

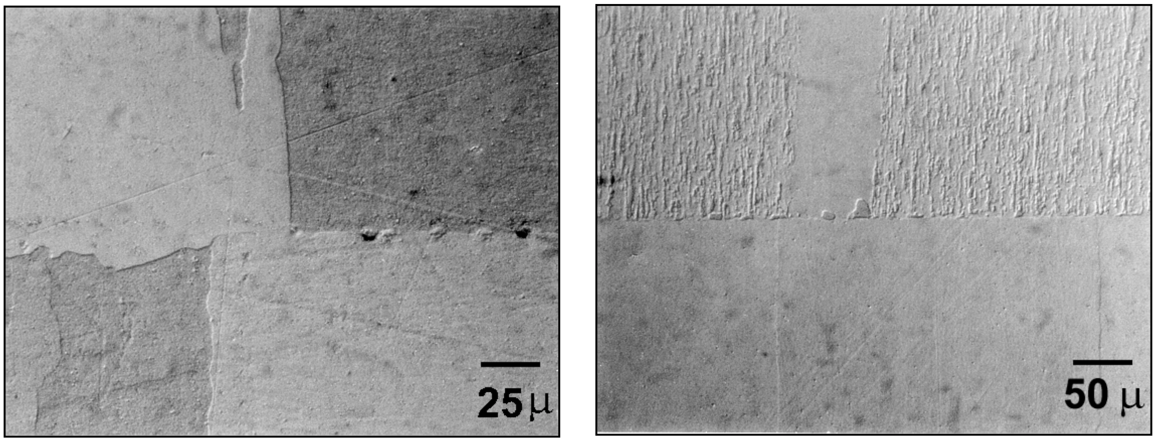


(a) (b)

Figure 4. (a) Micrograph of borided, recrystallized MA956 (top) bonded to non-borided, non-recrystallized MA956. Box in (a) shows approximate region shown in (b). Samples etched with HCl.

The parametric study initiated this quarter is designed to obtain preliminary information on the relative importance of several major diffusion bonding parameters, including final recrystallization temperature, bonding hold time at 1200°C, surface finish, and bonding pressure. The bonded samples will be evaluated by measuring the linear fraction of grains growing across the joint interface. The first five of these runs have been completed and are being prepared for quantitative microscopy. Figures 5 shows the bond line of the second (112001-2) and fifth (112001-5) samples. These two samples have widely varying processing parameters. Sample 112001-2 is a borided/nonborided pair prepared with an 800-grit finish and recrystallized at 1340°C. Sample 112001-5 is boron-free, prepared with a 1200-grit finish and recrystallized at 1260°C. Not surprisingly, the two samples show significantly different behavior. Sample 112001-2 has what appears to be boriding remnants along the bond line, yet still exhibits a fully recrystallized structure on both sides of the joint with some grain growth across the bond line. Sample 112001-5 exhibits a somewhat cleaner interface (presumably because it has no boride remnants), but does not appear to be fully recrystallized and shows little or no grain growth across the bond interface.

Work continues on orientation imaging microscopy (OIM) of diffusion-bonded coupons to verify that grain growth actually does occur across the prior joint interface. The optical microscopy performed to date continues to show evidence of such grain growth, but it is desirable to have independent, crystallographic confirmation and the OIM should provide this information. Since the OIM work is being done using a new microscope here at Michigan Tech, some time has been required to develop appropriate sample geometries and polishing practices. One unanticipated benefit of this work has been development of improved metallographic practices for sample polishing using colloidal silica and vibratory polishing. This polishing approach was initially undertaken to facilitate OIM, but it also appears to be very beneficial for routine optical microscopy.



(a) (b)

Figure 5. Micrograph of (a) borided, recrystallized MA956 (bottom) bonded to non-borided, non-recrystallized MA956, and (b) non-borided, recrystallized MA956 (bottom) bonded to non-borided, non-recrystallized MA956.
Samples prepared using vibratory polish and etched with HCl.

Also, the 2.5 inch OD MA956 tubing required for tubular joints was received from Huntington Alloys shortly before the end of November. Accordingly, the first tubular specimens are to be machined and diffusion bonded shortly after completion of the parametric study.

Explosive Welding: During the 4th quarter no additional friction welds were made.

Magnetic Impulse Welding: A new machine with 4 times the energy of the present machine will be installed and operational in November. This machine will allow for greater energy input in the welding trials.

Task 4: Bending of MA956 Tubes

Due to scheduling conflicts in the fabrication shop at FWDC, the tube bending tests were not performed during the 4th quarter.

Task 5: High Temperature Corrosion Limits of MA956

Laboratory Testing for Working Fluid Side: Work continues on the lifetime prediction of the MA956 alloy in air at very high temperatures. Testing at 1300°C has been completed and five samples (out of a total of seven) of different thickness taken from MA956 bar stock and exposed at 1250°C in air have failed. The observed oxidation-limited lifetimes are shown in Figure 1 with data points for a similar set of samples of the MA956HT alloy included for comparison. Note that the data points with arrows indicate runs that are still in progress, and that the oxidation lifetime will be longer than presently indicated by those points. The lifetimes of MA956 and MA956HT at 1250°C appear to be more than double those at 1300°C. The coincidence of the 1250°C lifetimes for MA956 with the 1300°C data points for MA956HT indicate that the latter alloy has a 50°C advantage at these very high temperatures. Analysis of the kinetic data to generate the data needed for

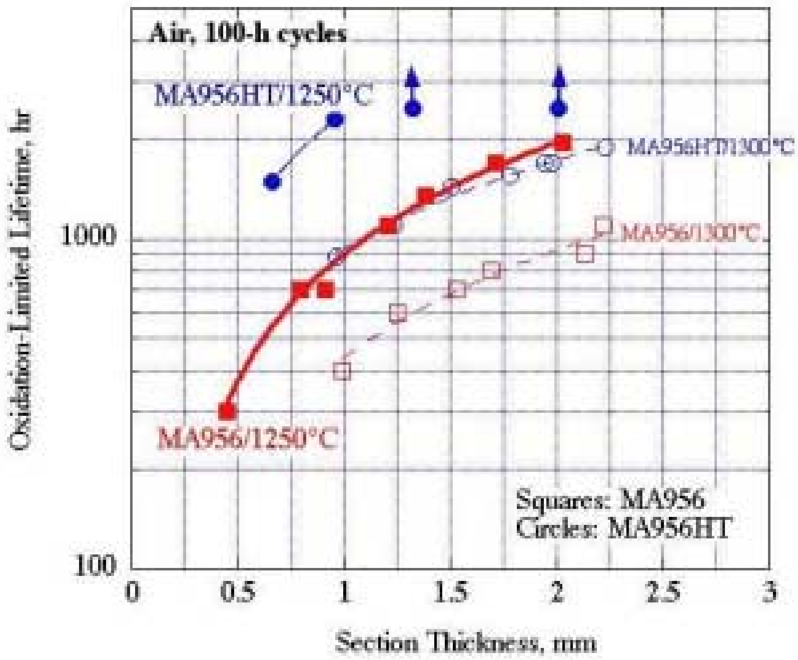


Figure 6. Plot of oxidation lifetimes as a function of sample thickness for the MA956 and MA956HT alloys at 1250°C and 1300°C in air.

testing or modifying the lifetime model has not yet been completed, and will be reported in the next quarter. However, a procedure suggested by Monceau and Pieraggi[1] for deducing the 'true' parabolic rate constant, k_p, from experimental kinetic data has been examined using the oxidation data for MA956 and MA956HT. The 'true' parabolic rate constant is not influenced by any initial, rapid mass gain from transient oxide formation, which often can bias the value usually calculated. Initial results suggest that the use of the values of the true k_p in the life prediction calculations allows an improved fit to the observed lifetime data for MA956 and MA956HT at both 1250 and 1300°C.

And finally, further modification of the lifing model has involved the replacement of the specimen thickness term by a 'shape factor' (volume/surface area). The lifetime data generated on MA956HT in an ORNL in-house program used disc-shaped specimens, whereas the MA956 specimens are parallelepipeds, so that there existed the possibility that the comparison of oxidation behavior was influenced by specimen shape. The range of V/A values of the specimens used so far is 0.03-0.07 cm (discs) and 0.02-0.08 cm (parallelepipeds). Preliminary calculations using the revised model indicate a reasonable fit to the experimental data at 1300°C, without the use of any 'adjusting' parameters, i.e., assuming strictly parabolic (n=0.5) and linear (n=1) segments to the kinetic curves

Lifetime exposure tests at 1250, 1200, and 1100°C are continuing.

Laboratory Testing for Fireside Environment: The laboratory testing using two different flue gases and three different deposits (see Table 3 and 4 below) at 2000°F continues. The exposure of the samples is terminated every 100 hours for deposit replenishment and at 500 hours one set of samples was removed for metallurgical examination. To date the test has completed 600 hours of the 1000-hour exposure and metallurgical examination of the 500-hour samples has been initiated

Table 3
Flue Gas Compositions to be Used in Laboratory Fireside Testing

Species	Amount (vol %)	
	Gas Mixture 1	**Gas Mixture 2**
O_2	4	2
CO_2	15	15
H_2O	10	5
SO_2	0.25	1.0
N_2	Bal	Bal

Table 5
Deposit Compositions to be Used in Laboratory Fireside Testing

Species	Amount (wt%)		
	Ash 1	**Ash 2**	**Ash 3**
Si Dioxide	14.6	11.6	7.6
Al Dioxide	6.0	6.0	6.0
Ti Dioxide	0.3	0.3	0.3
Fe Oxide	1.3	1.3	1.3
Ca Oxide	3.3	3.3	3.3
Mg Oxide	0.3	0.3	0.3
Na Oxide	0.4	1.4	2.4
K Oxide	0.3	1.3	2.3
S Trioxide	1.2	2.2	3.2
P Pentoxide	0.3	0.3	0.3
KCl			1.0
Carbon	72.1	72.1	72.1

Field Exposure Testing: The first utility with the appropriate locations for the air-cooled probes have been determined, the control hardware procured, and the probe design finalized and assembly initiated.

CONCLUSIONS

No technical conclusions are available at this time, however the change in grain morphology as a function of the extrusion + TMP parameters for the MA956 rods does show promise in being able to control the grain size as a function of % CW and recrystallization temperature. Also, recrystallization across the joint interface during the transient liquid phase bonding process is encouraging. Work will continue under Tasks 2, 3, 4, and 5.

REFERENCES

1. D. Monseau and B. Perragi, Oxid. of Met., vol. 50, no. 5-6, pp. 477-493, Dec. 1998.