**PULSED ION BEAM SURFACE TREATMENT FOR PREPARING RAPIDLY
SOLIDIFIED CORROSION RESISTANT STEEL AND ALUMINUM SURFACES**

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Abstract

Intense, pulsed ion beams were used to melt and rapidly resolidify Types 316F, 316L and sensitized 304 stainless steel surfaces to eliminate the negative effects of microstructural heterogeneity on localized corrosion resistance. Anodic polarization curves determined for 316F and 316L showed that passive current densities were reduced and pitting potentials were increased due to ion beam treatment. Type 304 samples sensitized at 600° C for 100 h showed no evidence of grain boundary attack when surfaces were ion beam treated. Equivalent ion beam treatments were conducted with a 6061-T6 aluminum alloy. Electrochemical impedance experiments conducted with this alloy exposed to an aerated chloride solution showed that the onset of pitting was delayed compared to untreated control samples.

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Introduction

Rapid solidification of liquid metals can produce solid phases with non-equilibrium compositions and structures that exhibit unusual and often highly desirable properties (1,2). In other cases, rapid solidification does not produce non-equilibrium structures, but does eliminate microstructural heterogeneity with significant effects on many properties including enhanced corrosion resistance (e.g. stainless steels and aluminum alloys) (3-8). The generic scheme for rapid solidification of surfaces on bulk metals and alloys involves surface layer melting using an energetic beam followed by rapid solidification ($>10^7$ K/s) due to thermal conduction into the underlying substrate. Laser, electron and ion beams have been successfully used to induce rapid melting and resolidification (RMR). There are certain inherent advantages that can be gained by using ions rather than photons or electrons to deposit energy in surfaces. These inherent advantages, along with recent advances in pulsed power (9), and ion beam technology (10) have been combined to provide a relatively new RMR surface treatment technology that may be more efficient and less expensive to implement than existing energetic beam surface treatment technologies.

The main inherent advantage gained by using ions to deposit energy at surfaces is the ability to treat in depth without ablation while retaining a high quench rate. Figure 1 shows temperature profiles in steel subjected to laser and proton beam pulses with energy fluxes of 1.25 and 4.0 J/cm² respectively. Surface melting using photons relies on thermal diffusion to melt in depth since photons must deposit their energy in the near-surface. Surface temperatures sufficient to induce ablation may be required to generate a thermal profile capable of melting in depth. Under these conditions quench rates may be reduced to $<10^4$ K/s (5). In contrast, ions deposit energy over a range of depth determined by ion energy and stopping cross sections for the incident ion-target material couple. The resulting thermal profile enables melting in depth reducing the risk for surface ablation. The second main advantage is that ions deposit energy with great efficiency. Over 98% of the incident energy is given up as heat to the surface. By comparison, less than 2% of incident photon energy is deposited as heat into a solid metal surface.

Figure 1. Temperature profiles in steel due to laser (squares), and ion beam (circles) heating each after 80 ns.

to determine if pulsed ion beams could eliminate the deleterious effects of microstructural heterogeneity on localized corrosion phenomena common to austenitic stainless steels and wrought aluminum alloys. Studies have focused on improving pitting resistance by eliminating

The treatment method described here is distinct from traditional ion implantation since impinging ions are used to deposit energy and not to modify composition. For example, typical ion doses for RMR treatment are on the order of 10^{13} ions/cm²/pulse which cause only a 0.01% change in composition. Pulsed ion beam RMR can be accomplished using pulse durations of 50 to 500 ns using 0.5 to 1.0 MeV ions over a treatment area as large as 100 cm² and as deep as 10 μm. The capacity now exists to generate these beams at 120 Hz, delivering 150 to 300 kW average power at 15% electrical efficiency from wall plug to energy delivered to the treated surface using hardware capable of 10^9 total lifetime pulses. Pulse widths are intentionally narrow to minimize effects of thermal conduction beyond the ion range that would slow quench rates. To this point in our studies, mixed carbon-proton-oxygen beams have been used, although the capacity to produce beams from any element that can be produced in gaseous form has recently become available.

This paper describes results from studies intended

pit-initiating second phase particles, and on eliminating preferential grain boundary attack in sensitized stainless steels by eliminating chromium-depleted regions at grain margins.

Experimental Procedures

For the austenitic stainless steels, pitting susceptibility studies were conducted on Type 316L and its free machining grade variant, Type 316F. Sensitization studies were conducted using Type 304. The composition of the steels used is given in Table I.

Sample coupons used in this study measured 2.5 cm x 5.0 cm x 0.5 cm. Control samples were polished to mirror finish and degreased prior to testing. Samples for RMR were polished, degreased, beam treated, and degreased a second time prior to electrochemical testing. The 316L and 316F samples were used in the as-received condition. All the 304 samples were solutionized for 24 h at 1100° C and quenched in water. Selected samples were then sensitized by isothermal treatment for 100 h at 600° C.

Table I. Composition limits for the stainless steels used in this study.

Alloy	Fe	Cr	Ni	Mo	Si	Mn	C	S	P
316L	bal.	16-18	10-14	2-3	1.0	2.0	0.03	0.045	0.03
316F	bal.	16-18	10-14	1.75 -2.50	1.0	2.0	0.08	0.1	0.2
304	bal.	16-18	8-10.5	—	1.0	2.0	0.08	0.03	0.045

Aluminum alloy 6061-T6 (Al-1.0Mg-0.6Si) coupon surfaces for testing and RMR treatment were prepared in a manner similar to that described above for stainless steels, except that samples were polished to a 600 grit finish instead of a mirror finish.

RMR treatment was conducted using the Anaconda accelerator located at Los Alamos National Laboratory. Surfaces were treated using a single pulse mixed species ion beam comprised of approximately 50% C ions, 30% H ions, and 20% O ions and other trace species. Pulse voltage varied from 150 to 350 kV over a time interval of 400 ns. The energy flux to the surface was estimated to be 3 to 4 J/cm² for stainless steels and 1 to 3 J/cm² for 6061-T6.

Stainless steel pitting studies, conducted with the two sets of 316 samples, were performed by determining anodic polarization curves potentiodynamically in air sparged pH 2 H₂SO₄ solutions at 22° C with various amounts of Cl⁻ (added as NaCl). Chloride ion concentrations used ranged from 0.5 ppm to 50,000 ppm. Ion beam treated samples were polarized at -1.0 V_{sce} for 2 minutes prior to collection of the polarization curve to reduce any thermal oxide present. Anodic polarization curves were acquired at a scan rate of 1.667 mV/s (6 V/hr) starting 50 mV negative of the steady state open circuit potential and continued until pitting or oxygen evolution was detected. Return scans were acquired to determine a repassivation potential which was defined as the potential where the return scan crossed the forward scan. Measurements were made using a Princeton Applied Research Model 173 Potentiostat/Galvanostat with a Model 276 Interface controlled by a software package installed on a personal computer (11). All potentials were measured versus the saturated calomel scale (sce).

Grain boundary sensitization studies were conducted using a potentiokinetic reactivation method. Tests were performed with 304 samples exposed to 0.5 M H₂SO₄ plus 0.01 M KSCN held at 30° C. The degree of sensitization was determined by first passivating samples at +0.600 V for 2 minutes. The potential was then scanned in the negative direction starting at +0.600 V at a rate of 1.667 mV/s until the open circuit potential was detected. Sample current after reactivation was measured and integrated over time as a measure of charge passed by sensitized regions of the sample. Standard stereological methods were used to measure grain

boundary areas for the different samples so that normalized values could be obtained for comparison among samples and with values reported in the literature.

Aluminum alloy pitting studies were conducted using electrochemical impedance spectroscopy (EIS) on samples exposed to air-sparged 0.1 M NaCl solution under free corrosion conditions. Spectra were collected at regular intervals for approximately 20 hours. Individual spectra were collected from 65 kHz to 5 mHz using a 10 mV sinusoidal voltage perturbation. Measurements were made using a PAR Model 273 potentiostat and a Solartron model 1255 frequency response analyzer. Total specimen capacitance was determined from the slope of the line $Y''(\omega)$ versus ω plot of the data. Total specimen resistance was determined using a partial Kramers-Kronig transformation method (12).

Results and Discussion

Pulsed Ion Beam Processed Surfaces

Stainless steel sample surfaces were originally prepared with mirror finishes. Samples returned from ion beam treatment exhibited a matte surface finish from small hillocks that were resolvable by low power optical microscopy (Figure 2). Hillocks were superimposed on a grain and twin boundary structure. Analysis of grain sizes showed that the grain size in the RMR treated region was comparable to that of the substrate. Mean grain diameters for the base material and treated layer were 95.4 μm and 88.7 μm respectively. Grazing angle x-ray diffraction of treated 316 surfaces yielded diffraction patterns consistent with an austenitic stainless steel, and showed no evidence for amorphous material. This result is not surprising since without deliberate metalloid additions, development of amorphous or fine grained structures in rapidly solidified stainless steels is not expected (13).

In previous studies, it was observed that 50 μm thick surface layers of laser surface melted 304 were crystalline with grains apparently exhibiting an epitaxial relationship with grains in the underlying substrate (4). Metallographic cross sections examined using optical microscopy showed a distinct boundary between the treated layer and untreated underlying region. Thus far, similar examinations of ion beam treated samples have not revealed such a boundary, and determination of treated layer thickness has not been possible by direct examination.

Aluminum 6061-T6 samples also exhibited a matte surface finish after RMR treatment. Grazing incidence angle x-ray diffraction detected no amorphous or nanocrystalline material in RMR surfaces. Figure 3 shows scanning electron micrographs of untreated and RMR treated 6061-T6 surfaces. Second phase particles and scratches from surface preparation are clearly visible on the untreated surface. RMR treatment eliminates the particles in the near surface region and reduces surface roughness. Such surfaces should exhibit enhanced resistance to localized corrosion since the number of pit initiation sites is markedly reduced.

Corrosion Studies

Pitting in Type 316 Stainless Steels. Type 316F has an elevated sulfur content to stimulate formation of sulfide particles. Particles aid in machinability and in mechanical surface finishing, but can reduce resistance to localized corrosion. Particle densities were not quantified in this study, but the number of sulfide particle stringers was notably reduced in RMR treated 316F surfaces. Figure 4 shows anodic polarization curves for RMR and control 316F samples in pH 2 H_2SO_4 plus 5000 ppm NaCl and demonstrates the effect of ion beam RMR on corrosion resistance. Compared to the control specimen, the RMR specimen exhibited reduced current density in the passive region and a pitting potential that was shifted in the positive direction signifying increased resistance to pit initiation. These results are consistent with prior work on laser surface melted 304 (4,5), laser surface melted ferritic Fe-Cr-Mo alloys (5), and rapidly solidified and consolidated stainless steel ribbons (14) which showed increased pitting potentials that were attributed to elimination or dispersion of second phase sulfide and carbide particles.

Repassivation potentials, defined by the intersection of the reverse scan with the forward scan through the passive region, were similar for control and RMR samples. The similarity in repassivation potentials indicates that the treated layer is no more resistant to pit propagation than the untreated substrate, or that the treated layer is thin enough to be penetrated during testing. For thin RMR layers, the gains in corrosion resistance arise from resistance to pit initiation due to elimination of pit initiation sites, and not from resistance to pit propagation.

100 μm

Figure 2. Optical micrograph of an RMR 304 surface.

10 μm

Figure 3. SEM images of 6061-T6, untreated (upper) and RMR treated (lower) showing surface smoothing and dissolution of second phase particles

Figure 5 summarizes pitting and repassivation potential data for RMR and control 316F samples determined as a function of chloride ion concentration. No pitting was observed prior to the onset of oxygen evolution (at $+0.800 V_{\text{sce}}$) at 0.5 and 50 ppm chloride for the control sample surfaces, or at 0.5, 50 or 500 ppm chloride for the RMR 316F surfaces. Reverse scans showed no hysteresis confirming that pitting had not occurred. At 5000 ppm chloride, the forward scan or the RMR surface indicated a pitting potential at or positive to the oxygen evolution potential. The reverse scan (Fig. 4) confirmed that pitting had occurred. When pitting was observed on both types of surfaces, the pitting potentials were equal to or more positive for the RMR surfaces.

Figure 6 shows passive current densities for control and RMR 316F samples as a function of chloride ion concentration. At all but the highest concentrations, RMR surfaces showed significantly lower passive current densities. In prior studies of laser surface melted 304, auger surface analysis showed that Cr and Ni were present in the same concentrations as in the substrate material, hence no improvements in corrosion resistance were ascribed to a redistribution of beneficial alloying elements (4). Surface analysis of the treated layer has not yet been conducted on these samples, but in view of the prior results, there is no reason to expect enrichment or redistribution of Cr, Ni or Mo in ion beam RMR treated layers. Based on these prior results, lower passive current densities for RMR treated surfaces are more likely due to the fact that current passed at second phase particle passive film defects is lower because the

number of defects in smaller, and not because more Cr is available to form a passive film with better barrier properties.

Figure 4. Anodic polarization curves for control (dark) and RMR (light) 316F surfaces in pH 2 H_2SO_4 plus 5000 ppm NaCl.

Figure 5. Pitting (closed data) and repassivation potentials (open data) as a function of $[\text{Cl}^-]$ for control (dark) and RMR (light) 316F in pH 2 H_2SO_4 .

Figure 6. Passive current density at +0.300 V as a function of $[\text{Cl}^-]$ for control (dark) and RMR (light) 316F in pH 2 H_2SO_4 .

Figure 7. Pitting (closed data) and repassivation potentials (open data) as a function of $[\text{Cl}^-]$ for control (dark) and RMR (light) 316L in pH 2 H_2SO_4 .

Type 316L samples contain fewer sulfide and carbide particle stringers, but RMR treatment still results in increased pitting potentials and reduced passive current densities. Figure 7 shows pitting and repassivation potentials for untreated and RMR treated 316L surfaces. No pitting is observed on either type of sample in 5, 50 and 500 ppm chloride solutions, and pitting potentials

remain more positive for the RMR treated surfaces in more aggressive solutions. Figure 8 shows that passive current densities were scattered for the RMR treated surfaces, but were consistently lower than those for the control samples.

Corrosion of Sensitized Type 304 Stainless Steels. Figure 9 is an optical micrograph of a sensitized 304 sample after a reactivation experiment. Due to the severe sensitization treatment used, nearly all of the exposed grain boundaries were attacked. Pitting adjacent to intragranular carbides is also observed. Figure 10 shows the complementary situation of an identically sensitized sample subsequently subjected to RMR treatment. In this case, grain boundary attack is fully eliminated although some pitting has occurred.

The details of the thermal history of RMR surfaces due to ion beam treatment have not been thoroughly modeled or measured, but the results shown in Figures 9 and 10 yield an important minimum bound on the capacity of RMR treatment for eliminating microstructural heterogeneity. The generally accepted width of the chromium depleted zone in fully sensitized stainless steels is on the order of 3 to 5 μm (11). This feature is fully dispersed using a single pulse that delivers an energy flux of 3 to 4 J/cm^2 .

Potentiokinetic reactivation experiments were conducted to quantify the degree of sensitization for RMR treated and untreated control surfaces. The sample treatment regimen, integrated charge per unit area, and charge per unit grain boundary area measured during reactivation are presented in Table II.

The charge passed during reactivation is reported as Q (Coulombs/unit area exposed), and as P_a (Coulombs/unit grain boundary area) which presumes attack at grain boundaries only. As expected, the trends in Q and P_a are identical among the four treatment regimens. Type 304 samples that were solutionized only yielded small Q and P_a values since Cr-depleted regions are largely absent. Q and P_a values for the solutionized and RMR surfaces are scattered, but relatively low indicating that Cr-depleted zones are not formed by RMR. Type 304 samples subjected to sensitization heat treatment exhibited large Q and P_a values as expected due to attack of Cr-depleted zones. The last set of Q and P_a data reported in Table II show that RMR of a sensitized samples can return the surface to a condition similar to that exhibited by a solutionized sample.

Table II. Summary of integrated charge per unit area, Q , and normalized charge per unit area P_a .

Sample Treatment	Q^* (mC/cm^2)	$P_a^\dagger$ (mC/cm^2)
Solutionized	0.94	60
	0.62	40
Solutionized and RMR Treated	4.20	240
	~ 0.01	~ 0.6
Solutionized and Sensitized	330	20,000
	190	11,000
Solutionized, Sensitized and RMR Treated	0.65	37
	1.10	63

* Q refers to charge per unit total area.

$\dagger P_a$ refers to charge per unit grain boundary area. Grain boundary area was computed as total grain boundary length multiplied by grain boundary width which was assumed to be 3 - 5 μm (15).

Figure 8. Passive current density at +0.300 V as a function of [Cl⁻] for control (dark) and RMR (light) 316L in pH 2 H₂SO₄.

Figure 9. Optical micrograph of 304 sensitized for 10 h at 600°C after potentiokinetic reactivation.

50 μm

Figure 10. Optical micrograph of 304 sensitized for 100 h at 600°C subjected to ion beam RMR then tested by potentiokinetic reactivation.

Pitting in Aluminum 6061-T6. Figures 11 and 12 show total specimen charge transfer resistance (R_{tot}), and total specimen capacitance (C_{tot}) plotted as a function of exposure time to aerated 0.1 M NaCl solution for RMR treated and untreated 6061-T6. These plots indicate modest improvements in resistance to localized corrosion due to RMR treatment. In Figure 11, total resistance for the RMR surface is greater than that of the control sample indicating a lower overall corrosion rate. Total capacitance is a sensitive discriminator for the localized corrosion on oxide forming metals and can be used to detect the onset of pitting in aluminum alloys. In Figure 12, C_{tot} for the RMR sample is very small (~ 60 nF/cm²) due to the presence of a protective oxide film on the surface. Once the oxide film is breached and pitting initiates, C_{tot} increases sharply. This increase occurs after 300 minutes of exposure to solution. By comparison C_{tot} is large (8.5 μF/cm²) for the control sample by the time the first measurement is taken (30 minutes exposure to solution) indicating that pitting had already occurred. These results are consistent with the elimination of pit initiating second phase particles by RMR.

Summary

Pulsed ion beams can be used to induce melting and rapid resolidification of stainless steel and aluminum alloy surfaces. Thermal conduction into the underlying substrate after the pulse can enable solidification at rates sufficient to suppress second phase particle formation resulting in chemically homogeneous surfaces. Resolidification rates do not appear to be sufficiently fast to promote formation of amorphous or nanocrystalline structures for these materials however. Nevertheless, these surfaces exhibit enhanced resistance to localized corrosion. In the case of stainless steels, gains in corrosion resistance were due to resistance to pit initiation and not due to resistance of pit propagation since the treated layers examined in this study were relatively thin. Grain boundary attack in sensitized 304 was completely suppressed by ion beam RMR treatment. This result establishes that single ion beam pulse delivering 3 to 4 J/cm² can disperse a microstructural feature with dimensions whose width is similar to that of a Cr-depleted zone in a fully sensitized stainless steel. For aluminum alloy 6061-T6, gains in corrosion resistance were modest though RMR clearly delayed the onset of pitting during exposure to aerated chloride solution. As with the stainless steels, the measured improvement in corrosion resistance was consistent with elimination of second phase particles.

Figure 11. R_{tot} versus time for control (dark) and RMR treated (light) 6061-T6 exposed to air-sparged 0.1 M NaCl.

Figure 12. C_{tot} versus time for control (dark) and RMR treated (light) 6061-T6 exposed to air-sparged 0.1 M NaCl.

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