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Surface Treatments for Improved Performance of Spinel-coated AISI 441 Ferritic Stainless Steel

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Abstract

Ferritic stainless steels are promising candidates for IT-SOFC interconnect applications due to their low cost and resistance to oxidation at SOFC operating temperatures. However, steel candidates face several challenges, including long term oxidation under interconnect exposure conditions, which can lead to increased electrical resistance, surface instability, and poisoning of cathodes due to volatilization of Cr. To potentially extend interconnect lifetime and improve performance, a variety of surface treatments were performed on AISI 441 ferritic stainless steel coupons prior to application of a protective spinel coating. The coated coupons were then subjected to oxidation testing at 800 and 850°C in air, and electrical testing at 800°C in air. While all of the surface-treatments resulted in improved surface stability (i.e., increased spallation resistance) compared to untreated AISI 441, the greatest degree of improvement (through 20,000 hours of testing at 800°C and 14,000 hours of testing at 850°C) was achieved by surface blasting.

Introduction

In recent years, progress in materials and fabrication techniques has allowed for a reduction in SOFC operating temperatures to a range in which oxidation-resistant alloys, such as ferritic stainless steels, can be considered as replacement materials for the traditional ceramic interconnect materials used in high temperature SOFC stacks. One candidate steel, which offers appropriate CTE, good oxidation resistance, an electrically conductive oxide scale, and relatively low cost is AISI 441.[1] To reduce Cr volatility and improve oxidation resistance, protective coatings, such as Ce-modified $(Mn,Co)_3O_4$ (Ce-MC) spinel, have been developed for application to the cathode side of the interconnect.[2] Long-term testing of AISI 441 coated with Ce-MC spinel indicated stable, low area-specific electrical resistance (ASR) for over 20,000 hours at 800ºC in air. However, it was observed that, while thermal cycling of oxidized spinel-coated AISI 441 coupons did not result in spallation or de-bonding at the interface between the coating and the oxide scale that grew over time beneath that coating, thermal cycling did sometimes result in spallation of the oxide scale from the underlying AISI 441 substrate. In an SOFC stack, this scale spallation could lead to a substantial increase in ASR and release of volatilized Cr. In response to these observations, a long-term study was initiated in which a number of surface treatments for AISI 441 are being evaluated in order to determine whether or not they can result in improved oxidation/spallation resistance. A report (PNNL-20177) discussing preliminary results of the study was issued in February 2011. This report summarizes results of the on-going study through December 2012.

Surface Treatments

Four different alloy surface-modification treatments – de-siliconization, surface blasting, surface grinding, and temper rolling – are being evaluated as methods to modify surface morphology. The surface treatments were performed by ATI Allegheny Ludlum on 0.5 mm thick AISI 441 sheet stock. The de-siliconization treatment is intended to selectively remove silicon from the material surface. Removal of silicon may minimize the formation of silica beneath the chromium oxide scale, thereby decreasing electrical resistance across the interconnect. Surface blasting and surface grinding alter the near-surface grain structure, while temper rolling (50% thickness reduction through cold rolling) alters the through-thickness grain structure. After surface treatment, multiple (16, in most cases) coupons (0.5" x 0.5") for each surface treatment were coated with Ce-MC spinel. Untreated acid pickled ("mill reference") coupons, which were hand polished with 1200 grit abrasive paper prior to application of the spinel coating, were also included in the study as a baseline material.

Oxidation testing for scale spallation/de-bonding

Coupons of the surface-treated steel coated with Ce-MC spinel were subjected to oxidation testing in air in a box furnace at 800ºC or 850ºC. At 2,000 hour intervals, the coupons were cooled down to room temperature and examined. In many cases, one coupon from each surface treatment was removed from the study for SEM evaluation, while the rest of the coupons were reheated for continued oxidation testing.

<u>800ºC</u>

Results of the 800ºC tests through December 2012 are summarized in Table I. The five surface conditions under study are listed in the primary columns of the table. Under each primary column, two sub-columns are listed. The first sub-column, labeled "Macroscopic Spallation," contains the results of a visual examination of the cooled coupons. If any coupons for a given surface condition exhibited clear signs of scale spallation to the naked eye, an X was entered into the appropriate cell of the table. The second sub-column, "Microscopic De-bonding," contains results from cross-section SEM examination of the scale/alloy interface of coupons removed from the study for microscopic analysis. If de-bonding along that interface was observed over the entire length of the sample, a "C" was entered into the appropriate cell; if regions of localized de-bonding (~10 microns or more in length) were observed, an "L" was entered. It is clear from the table that all of the surface treatments resulted in improved scale adhesion compared to the mill reference material, as none of the mill reference coupons survived beyond 10,000 hours, while at least some of the coupons from the various surface treatments were still intact after 20,000 hours. The most impressive results came from the surface blasted coupons, none of which exhibited either macroscopic spallation or localized de-bonding after 20,000 hours.

Representative cross-section microstructures taken from SEM analysis of coupons removed from the study after 20,000 hours of oxidation are shown in Figure 1. In these images, the oxide scale that developed during the oxidation test appears as a dark gray layer between the lighter gray spinel coating (top) and steel substrate (bottom). It is evident that the surface ground and surface blasted samples exhibited much higher surface roughness than the other surface conditions, leading to very irregular scale/alloy interfaces. Figure 2 shows a higher magnification SEM image of the surface blasted sample; results of the indicated EDS area analyses are listed in Table II. It is evident that, over the course of time, some transport of Cr into the protective spinel coating occurred. However, it is also clear that the Cr activity at the surface of the coating (~5 at%) is much lower than would be the case for an unprotected steel surface with an exposed chromia-based scale (~40 at%); this lower Cr activity would be expected to result in a substantial reduction in Cr volatility from the interconnect surface.

850ºC

Results of the 850ºC oxidation tests are shown in Table III, which uses the same format as Table I. While the 850ºC tests have not been operating as long as the 800ºC tests, it is again apparent that the surface treatments (especially surface grinding and surface blasting) resulted in improved scale adhesion compared to the mill reference material.

Representative cross-section microstructures taken from SEM analysis of coupons removed from the study after 14,000 hours of oxidation are shown in Figure 3. (Due to the limited number of surface blast coupons available for the 850ºC study, a surface blast coupon was not removed for SEM analysis after 14,000 hours). Figure 4 shows a higher magnification SEM image of the surface ground sample; results of the EDS analyses are listed in Table IV. As was the case for the 800ºC sample (Figure 2), some transport of Cr into the protective spinel coating occurred, but (also similar to the 800ºC sample), the Cr activity at the surface of the coating (~4 at%) was much lower than would be the case for an unprotected steel surface with an exposed chromia-based scale.

Scale growth kinetics

Average scale thickness for the coupons removed at 2,000 hour intervals is shown in Figures 5 and 6 for 800 and 850ºC, respectively. Each data point represents the average scale thickness as calculated from ~100 SEM measurements along the length of each coupon, although it should be noted that only one coupon for each temperature and time interval was available for analysis. In comparing Figure 5 with Table I, and Figure 6 with Table III, it will be noted that the tendency for scale spallation to occur does not correlate directly with scale thickness, as would be expected to be the case if spallation behavior was dominated primarily by buildup of residual stresses during thermal cycling due to thermal expansion mismatch between the scale and the steel. It is likely that other factors, such as the surface roughness of the surface ground and surface blasted samples, play a significant role in determining scale adhesion. Studies to improve our understanding of the mechanisms responsible for the observed scale adhesion/spallation behavior are in progress.

Electrical resistance testing

Several surface-treated, spinel-coated AISI 441 coupons are being subjected to area-specific resistance (ASR) testing at 800°C to determine the effect, if any, of the surface treatments on electrical resistance. Details of the test methodology, and previous test results for mill reference AISI 441 can be found in Reference 3. Results of the ASR tests (which are still in progress) are presented in Figure 7. The disruptions in the plots correspond to unscheduled facility power outages which resulted in a rapid cool-down when the furnace lost power. Despite some jumps in resistance associated with those occasional thermal cycles, the ASR for all three samples remained relatively low after ~15,000 hours of testing, with the surface blasted sample exhibiting the lowest ASR (~24 mOhm-cm^2).

Conclusions/Benefit Statement

Oxidation studies indicate that modifications to the surface of AISI 441 ferritic stainless steel prior to application of a protective spinel coating can significantly increase the adhesion at the oxide scale/steel interface, thereby improving spallation resistance of the scale and coating. Based on the results obtained to date, surface blasting appears to be the most promising surface modification. While it must be recognized that this study was based on testing of small steel coupons, and that other parameters such as thickness, local temperature variations, and compressive load could also have a significant impact on scale adhesion/spallation, coupons subjected to surface blasting prior to coating application have thus far exhibited ≥2.5X increase in lifetime at 800°C compared to unmodified coupons. Results from further testing (including longer oxidation times, evaluation of surface blast parameters, and testing of larger samples) will be reported as they become available.

Acknowledgements

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2. Z.G. Yang, G.G. Xia, Z. Nie, J.D. Templeton, and J.W. Stevenson, Electrochem. Solid-State Lett., 11, B140 (2008).
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Table I. Effect of surface condition on spallation behavior of spinel-coated AISI 441: 800ºC

Time (h)	Mill Reference (1200 grit)		Temper Rolled		De-siliconized		Surface Grind		Surface Blast	
	Macroscopic Spallation	Microscopic De-bonding	Macroscopic Spallation	Microscopic De-bonding	Macroscopic Spallation	Microscopic De-bonding	Macroscopic Spallation	Microscopic De-bonding	Macroscopic Spallation	Microscopic De-bonding
2000										
4000	X									
6000	X			C	X					
8000	X			C						
10000	XX			C						
12000	XX						X	L		
14000	XX					L				
16000	XX									
18000	XX									
20000	XX					L	X			

X - spallation on at least one coupon
XX - no unspalled coupons left in study
C - complete de-bonding of scale of SEM/EDS sample
L - localized de-bonding of scale of SEM/EDS sample

Table II. Results of EDS analyses on the indicated regions of Figure 2; concentrations are in atomic%.

Spectrum	Si	Ti	Cr	Mn	Fe	Co	Ce
1	0.27	0.27	35.38		0.17		
2		0.27	13.42	11.65	1.90	11.59	
3	0.30	0.43	7.72	15.94	2.78	12.22	0.28
4		0.50	5.52	18.42	2.99	13.15	
5	0.60	0.51	5.25	19.30	3.09	13.28	0.29
6	0.68	0.44	5.07	18.84	2.81	12.78	0.48
7	0.75	0.48	5.28	19.79	2.87	13.21	0.56
8	0.41	0.49	5.37	19.59	2.96	13.53	0.36
9	0.42	0.43	4.61	17.30	2.67	12.50	0.24

Table III. Effect of surface condition on spallation behavior of spinel-coated AISI 441: 850ºC

Time (h)	Mill Reference (1200 grit)		Temper Rolled		De-siliconized		Surface Grind		Surface Blast	
	Macroscopic Spallation	Microscopic De-bonding	Macroscopic Spallation	Microscopic De-bonding	Macroscopic Spallation	Microscopic De-bonding	Macroscopic Spallation	Microscopic De-bonding	Macroscopic Spallation	Microscopic De-bonding
2000										
4000										
6000		C								
8000		C				C				
10000	X		X			C				
12000	X		X		X					#
14000	X		X		X	L				#
16000	XX	#		#		#		#		#

X - spallation on at least one coupon
XX - no unspalled coupons left in study
C - complete de-bonding of scale of SEM/EDS sample
L - localized de-bonding of scale of SEM/EDS sample
- coupon not removed for analysis due to limited number of coupons remaining

Table IV. Results of EDS analyses on the indicated regions of Figure 4; concentrations are in atomic%.

Spectrum	Si	Ti	Cr	Mn	Fe	Co	Ce
1		0.41	34.41		0.15		
2		0.42	9.46	15.25	0.42	13.18	
3		0.47	4.21	19.31	0.45	14.12	0.19
4	0.22	0.49	2.93	20.83	0.52	13.78	0.24
5	0.21	0.48	2.73	21.24	0.50	13.91	0.28
6		0.47	3.09	20.33	0.45	14.19	0.23
7		0.46	3.56	20.02	0.51	14.78	0.31
8	0.24	0.42	3.71	20.93	0.48	15.00	0.45

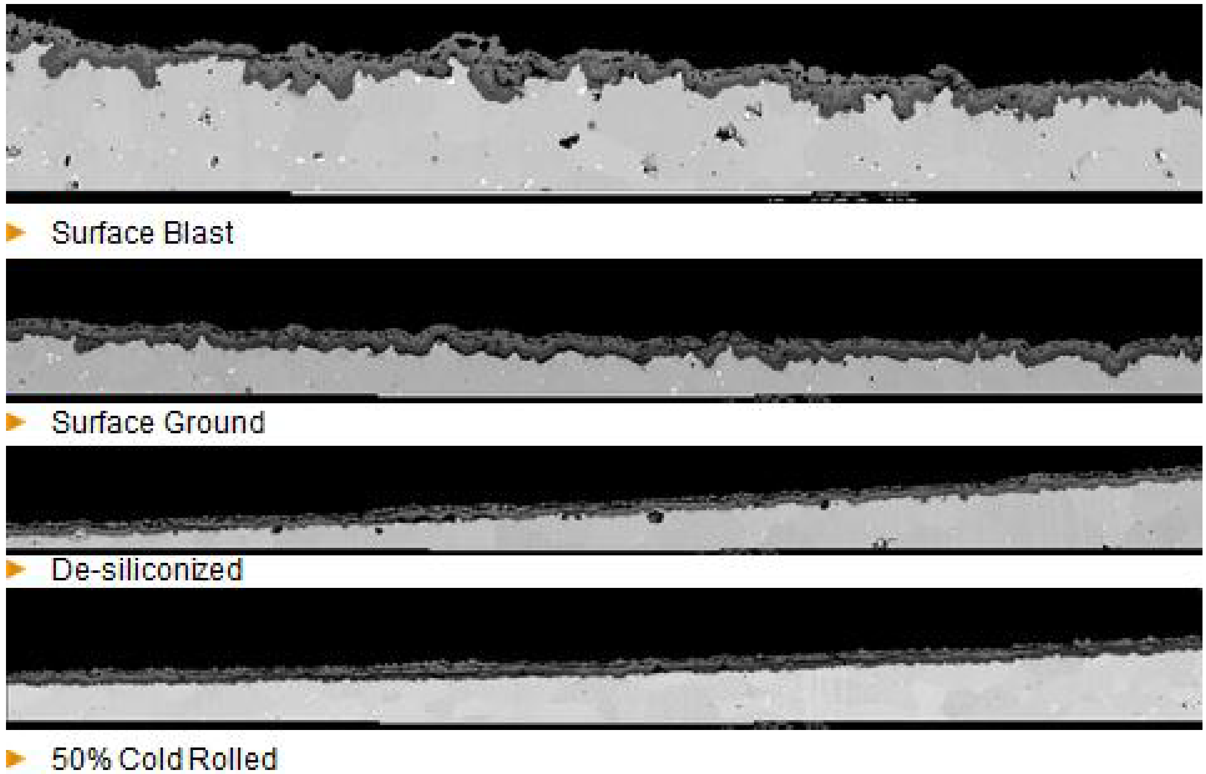

Figure 1. SEM images of spinel-coated AISI 441 subjected to the indicated surface treatments prior to coating application. Samples were heated in air for 20,000 hours at 800ºC.

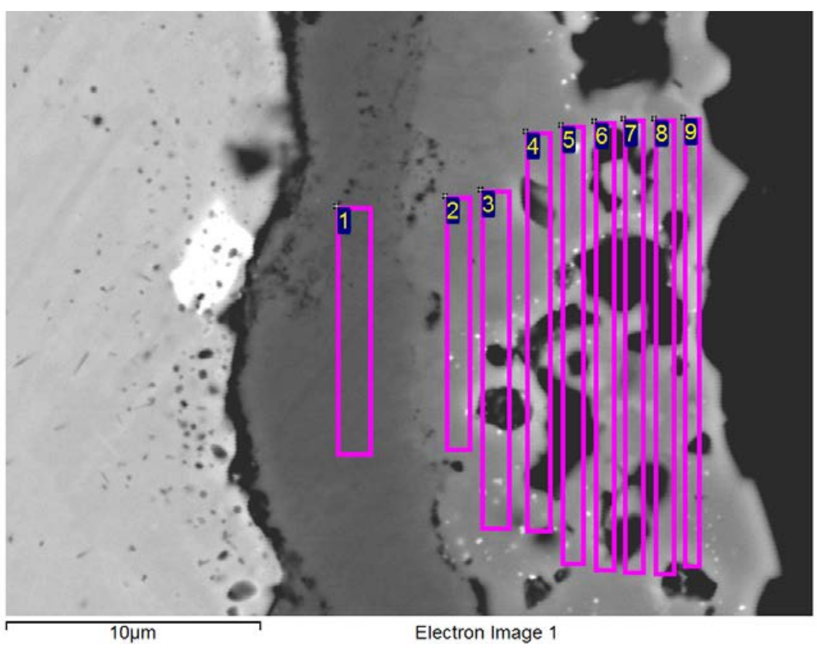

Figure 2. SEM image of surface-blasted, spinel-coated AISI 441 after 20,000 hours at 800ºC in air. EDS results for the indicated regions are listed in Table II.

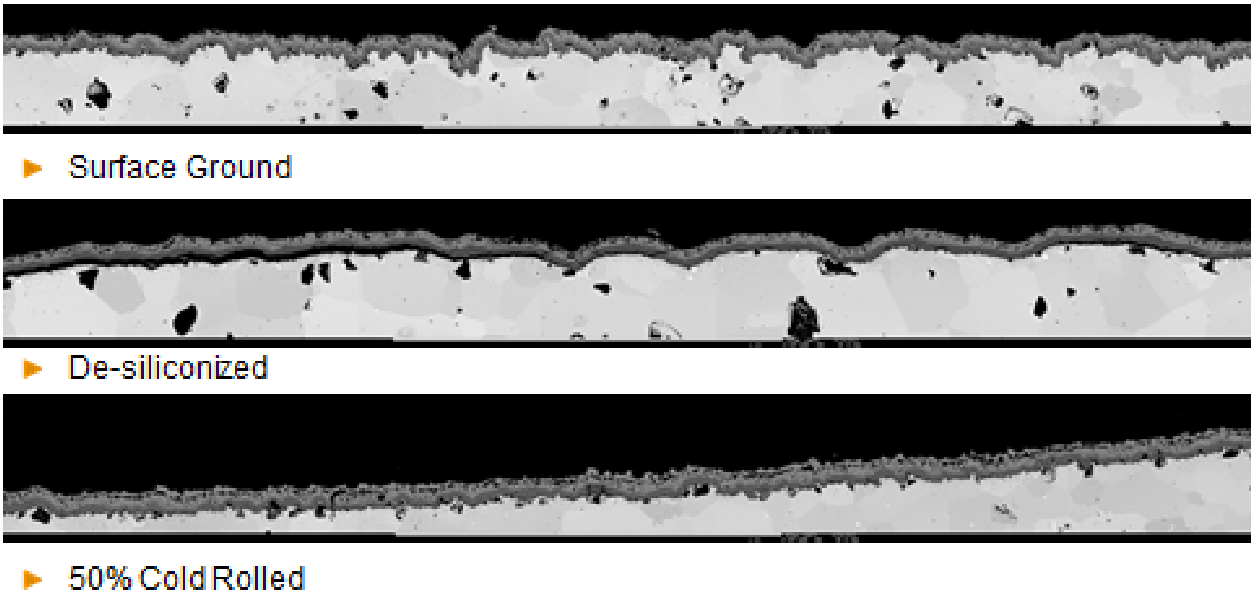

Figure 3. SEM images of spinel-coated AISI 441 subjected to the indicated surface treatments prior to coating application. Samples were heated in air for 14,000 hours at 850ºC.

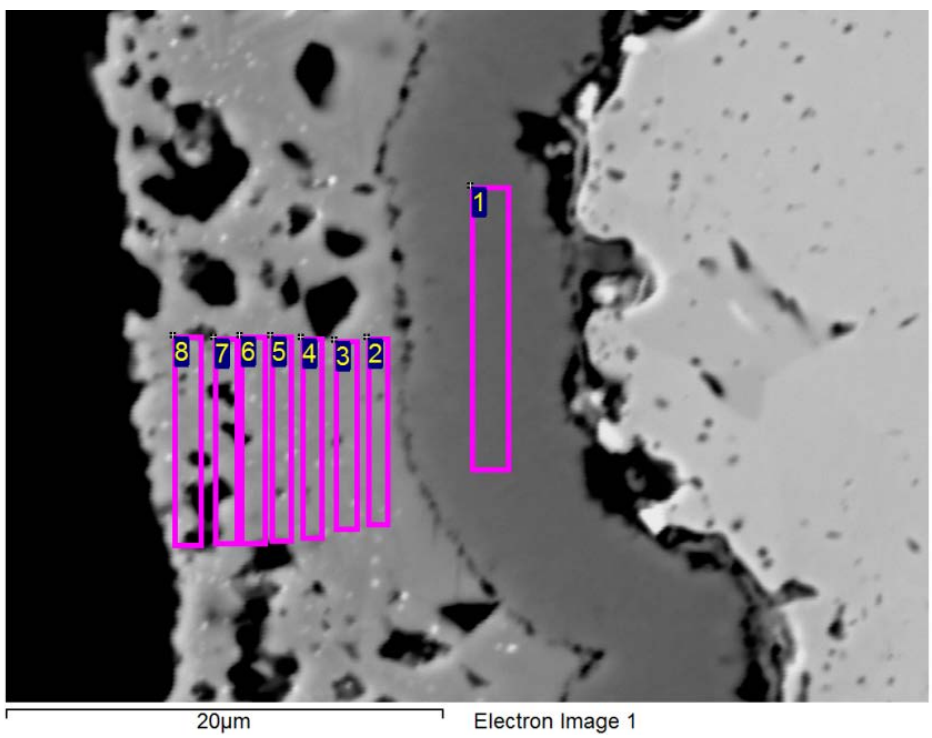

Figure 4. SEM image of surface-ground, spinel-coated AISI 441 after 14,000 hours at 850ºC in air. EDS results for the indicated regions are listed in Table IV.

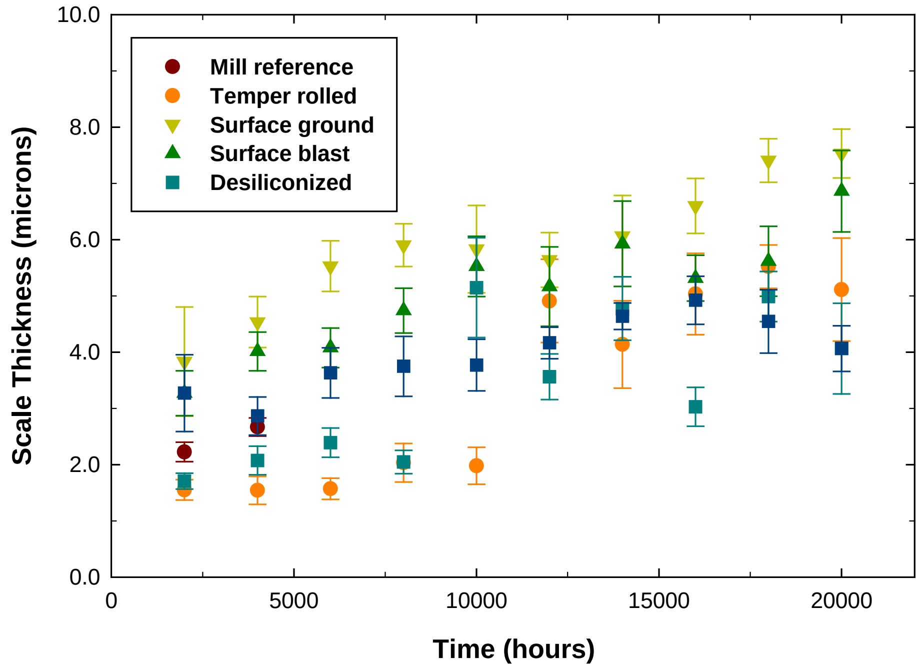

Figure 5. Oxide scale thickness as a function of time at 800ºC in air for spinel-coated AISI 441 with the indicated surface conditions.

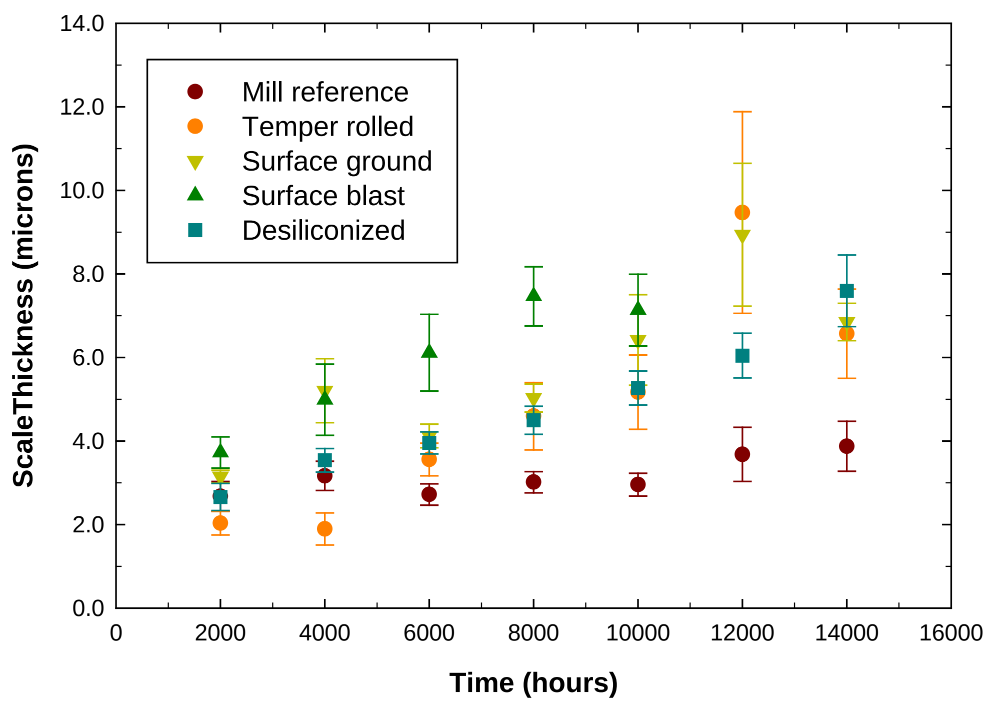

Figure 6. Oxide scale thickness as a function of time at 850ºC in air for spinel-coated AISI 441 with the indicated surface conditions.

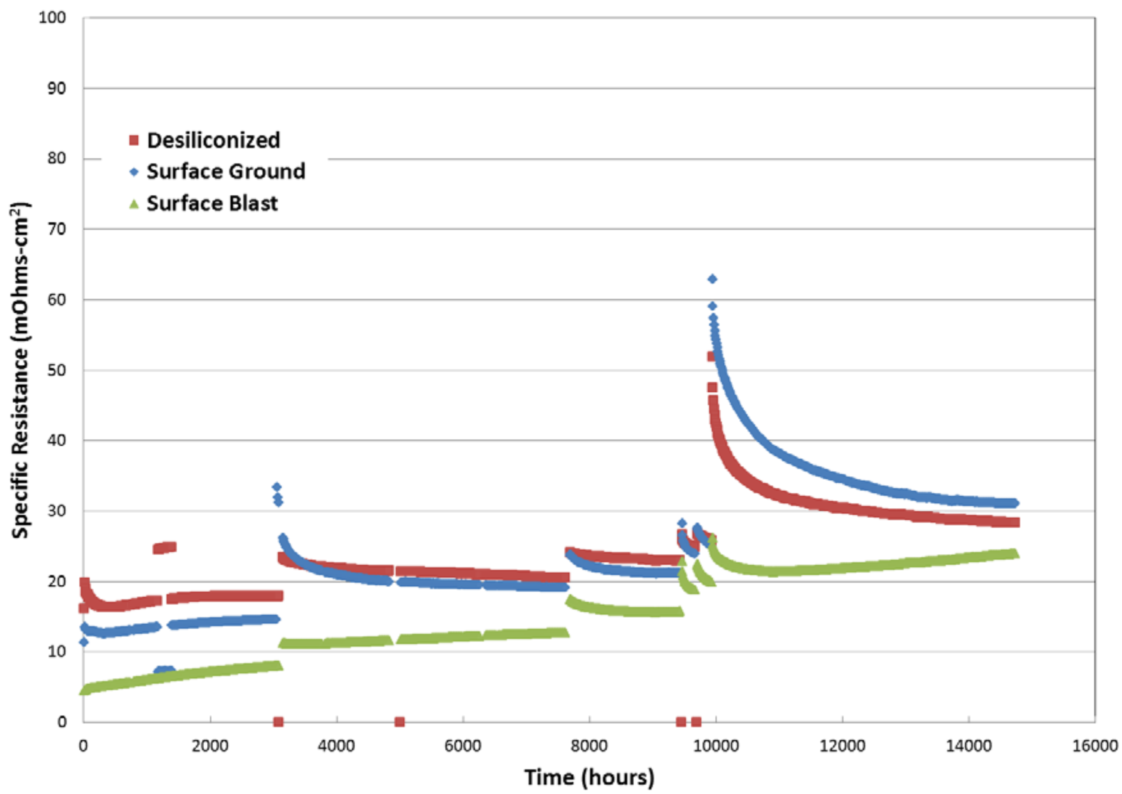

Figure 7. ASR test results at 800ºC in air for spinel-coated AISI 441 with the indicated surface conditions.