Preprint
UCRL-JC-137727

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This article was submitted to
The Minerals-Metals-Materials Society Conference
St. Louis, MO
October 8-12, 2000

U.S. Department of Energy

Lawrence
Livermore
National
Laboratory

June 15, 2000

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INFLUENCE OF THERMAL AGING ON THE MECHANICAL AND CORROSION PROPERTIES OF C-22 ALLOY WELDS

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Abstract

The phase stability of C-22 alloy (UNS #N06022) gas tungsten arc welds was studied by aging samples at 427, 482, 538, 593, 649, 704, and 760°C for times up to 40,000 hours. The tensile properties and the Charpy impact toughness of these samples were measured in the as-welded condition as well as after aging. The corrosion resistance was measured using standard immersion tests in acidic ferric sulfate (ASTM G 28 A) and 2.5% hydrochloric acid solutions at the boiling point. The microstructures of weld samples were examined using scanning electron microscopy (SEM). One weld sample (aged 40,000 hours at 427°C) was examined using transmission electron microscopy (TEM).

The structure of the unaged welds was dendritic with tetrahedrally close-packed (TCP) phase particles in the interdendritic regions. Long-range order was seen in the weld aged at 427°C for 40,000 hours and was assumed to also occur in other welds aged below approximately 600°C. At temperatures above about 600°C, TCP phase nucleation and growth of existing particles occurred. This precipitation occurred near the original particles presumably in regions of the highest molybdenum (Mo) segregation. Lower temperatures had little or no effect on the morphology of TCP phases. The C-22 weld samples were approximately 25% stronger but 30-40% less ductile than the base metal. Strengthening of the weld during aging occurred significantly only at 593°C for the aging times investigated. Because strengthening was not seen at higher temperatures, it was assumed to be due to ordering which has been seen in C-22 base metal at this temperature. A small amount of strengthening was seen at 427°C after 40,000 hours where ordering was just beginning. The Charpy impact toughness was reduced dramatically with aging. The time at which this reduction occurred decreased as aging temperature increased suggesting that the reduced ductility is due to the presence and growth of the brittle TCP phases. The corrosion rate of weld samples tested in the standard ASTM G 28 A solution and in a 2.5% HCl solution was higher than was seen with C-22 base metal. After aging, however, the corrosion rate of weld and base metal samples became comparable.

Introduction

The current design for nuclear waste containers in the potential repository at Yucca Mountain calls for a dual-metal container with 316 NG stainless steel on the inside mainly for structural integrity and C-22, or an equivalent Ni-Cr-Mo alloy, on the outside to provide corrosion resistance. Each container would be constructed by bending or rolling a plate into a cylinder and closing the seam with a longitudinal weld. Two of these cylinders would then be welded together with a circumferential weld. After welding on the bottom lid, the entire container would be solution annealed to eliminate any residual stresses in the C-22. A similarly produced 316 NG stainless steel container would be fit inside the C-22. The waste would be put in the container, and the stainless steel and C-22 lids would be welded onto the container. These closure welds cannot be heat treated as the other welds because the waste cannot be taken to the temperatures required to solution anneal the C-22. Because stress corrosion cracking is now considered one of the most likely failure mechanisms for the waste package, it is currently planned to locally induction anneal the C-22 closure weld and/or laser peen the weld to put the surface residual stresses into compression. The containers are required to maintain integrity without substantial leakage for greater than 10,000 years. This long lifetime combined with a somewhat elevated temperature (less than approximately 260°C) causes phase stability of the C-22 welds as well as the base metal to be of concern.

Phase stability of C-22 and similar alloys has been studied in some detail. At temperatures above approximately 600°C up to at least 760°C, Tetrahedrally Close-Packed or TCP phases [1] (primarily the Mo-rich μ and P phases) form [2-9]. Because Mo provides the Ni-Cr-Mo alloys with their resistance to localized corrosion, segregation of the Mo to the TCP phases can cause a depletion of Mo in the matrix and lead to localized corrosion [2-4,6]. Below approximately 600°C, $Ni_2(Cr,Mo)$, which has an ordered Pt_2Mo-type structure, forms [4,6,7-9]. This long-range ordering has been linked to an increased susceptibility to stress corrosion cracking and hydrogen embrittlement [4]. While there have been many studies of C-22 base metal phase stability, relatively little is known about the stability of C-22 weld structures.

Cieslak et al. [10] and Ogborn et al. [11] investigated the microstructures of C-22 and other similar alloy welds. They found segregation of primarily Mo but also to some extent W in the interdendritic regions of the weld. This enrichment of Mo and W causes TCP phases to form during welding of C-22; μ, P, and σ phases were seen in C-22 welds. This segregated structure tends to increase the corrosion rate somewhat over the base metal [12, 13] and reduce the ductility [14].

In order to predict long-term behavior of the welds, it is important to know whether these precipitates present in the as-welded condition are thermodynamically stable at the low repository temperatures and, if so, how fast they grow and what effect they have on the properties of the weld. Some limited testing of C-4 welds was done by Matthews [14] who found that weld metal was less ductile than base metal and both showed decreased ductility after aging 8000 hours at 649°C. Rebak and Koon [12] found that C-22 welds had a higher corrosion rate than base metal when tested using the ASTM G 28 B procedure but that the corrosion rate decreased after aging between 10,000 and 40,000 hours at 427°C.

Experimental

Mechanical property samples were made from 0.5-inch thick HASTELLOY® C-22® plate. Corrosion samples were prepared from 0.125, 0.25, or 0.5-inch plate. Welds made for tension testing in the as-welded condition and after aging at 427°C were double V groove Gas Tungsten Arc Welding (GTAW) welds produced under 100% Ar with six passes. All other welds were 9-pass single V groove GTAW welds also formed under 100% Ar. Base metal and welded samples were aged at 427, 482, 538, 593, 649, 704, and 760°C for times up to 40,000 hours. The aging was done in air, and the temperature was maintained to within ±6°C. Upon removal, samples were rapidly air cooled (allowed to cool at room temperature above a fan). The heats used for sample preparation are listed in Table I and the sample chemical compositions are given in Table II. Specimens in the as-welded and aged conditions were tension tested at room temperature according to ASTM Specification E 8 using standard round bar specimens with 0.25-inch diameter in the gage section. Specimens were oriented perpendicular to the welds with the welds centered in the gage section. The strain was measured using an extensometer over 1 inch of the gage section. Charpy impact testing was done at room temperature according to ASTM Specification E 23 using full-size standard V-notch specimens with the notch centered on the weld and running through the thickness of the plate. Changes in the corrosion resistance were measured using the standard ASTM G 28 A (boiling solution of 50% H_2SO_4 and 42 g/l of $Fe_2(SO_4)_3$) 24-hour immersion test. Immersion tests were also done in a boiling 2.5% HCl solution for 96 hours (changing the solution every 24 hours) in accordance with ASTM G 31. Prior to corrosion testing, samples were cleaned using a high-pressure water spray containing a very fine Al_2O_3 powder. Samples were prepared for metallographic examination using standard polishing techniques and an electrochemical etch in a solution of 5 g oxalic acid in 95 cc of 37% HCl solution at 6 V for only a few seconds. The weld aged for 40,000 hours at 427°C was examined in TEM. Samples from this weld were mechanically thinned to 175-200 μm followed by jet polishing in a 5% perchloric - acetic acid solution at room temperature and 40 - 60 V. A JEOL JEM-200CX TEM operated at 200 kV was used to examine the TEM foils. Although base metal samples have been examined previously in TEM [7-9], no other weld samples have been examined to date.

Table I. C-22 Heats Used in Base Metal and Weld Sample Aging Studies

Base Metal	Weld Metal	Aging Conditions	Properties Measured
2277-3-3223	–	Mill annealed* (MA) and aged 593 to 760°C	Mechanical
2277-0-3195	–	MA + aged 593 to 760°C (2000 and 16,000 hours only)	Mechanical
2277-7-3173	–	Aged 427°C	Mechanical and Corrosion
2277-6-3181	–	Aged 482 to 760°C	Corrosion
2277-9-3201	2277-8-3281	As-welded + aged 593 to 704°C	Mechanical
2277-9-3201	2277-8-3277	Aged 760°C	Mechanical
2277-6-3171	2277-7-3181	As-welded	Mechanical
2277-7-3173	2277-3-7281	Aged 427°C	Mechanical
2277-9-3237	2277-8-3277	Aged 482 to 760°C	Corrosion
2277-6-3181	2277-7-3173	Aged 427°C	Corrosion

*The mill anneal is done at 1020-1135°C for 20-30 minutes depending on plate thickness.

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Table II. Chemical Composition (wt. %) of C-22 Heats used in Aging Study

Heat*	Al	C	Co	Cr	Fe	Mg	Mn	Mo	N	Ni	Si	V	W
3-3223	.25	.002	1.56	21.60	4.3	.017	.24	13.50	.04	55.33	.037	.15	3.00
0-3195	.29	.003	1.74	21.10	4.7	.010	.21	13.50	.02	55.67	.023	.12	2.90
6-3171	.31	.002	0.70	21.97	4.42	.036	.23	13.31	.03	56.2	.032	.15	2.86
7-3173	.26	.003	1.13	21.64	3.77	.020	.24	13.46	.04	55.78	.027	.14	3.01
9-3201	.36	.003	0.65	21.07	3.67	.025	.25	13.76	.04	55.20	.025	.16	2.90
6-3181	.32	.004	1.11	21.59	3.90	.023	.28	13.64	.03	55.93	.024	.17	3.03
9-3237	.34	.004	0.90	21.26	3.97	.036	.25	13.15	.02	55.97	.027	.21	2.90
8-3281	.32	.002	1.47	21.58	3.97	.031	.32	13.49	.04	55.33	.025	.14	2.96
8-3277	.33	.006	1.10	21.58	4.17	.023	.25	13.29	.03	55.5	.022	.18	3.18
7-3181	.29	.003	1.47	21.32	4.29	.023	.25	13.25	.03	55.24	.027	.15	3.03
3-7281	.21	.003	0.21	21.49	3.13	–	.18	13.38	.04	57.97	.060	.15	3.00

*All heats were C-22 alloy (designated as 2277 in heat number). See Table I for a list of which heats were used for base metal and which for weld metal.

Results

The properties of aged base metal have been presented elsewhere [7-9]. The mechanical properties of the weld are displayed in Figures 1-4. All data points in these figures represent at least two measurements. The welds are approximately 25% stronger than the base metal initially. After aging, significant strengthening occurs only at 593°C in about 1000 hours. This increase in strength is accompanied by a decrease in ductility as shown in Figures 2 and 3. There is a slight increase in strength and decrease in elongation in welds aged at 427°C. However, all samples aged at 427°C broke in the base metal rather than in the weld. Some ductility is also lost in aging at 760°C, but the tensile elongation remains fairly constant with aging at 649 and 704°C. The tensile reduction in area (Figure 3) and Charpy impact toughness (Figure 4) decrease with aging time at all temperatures above 593°C. The Charpy impact toughness of samples aged at lower temperatures was not tested.

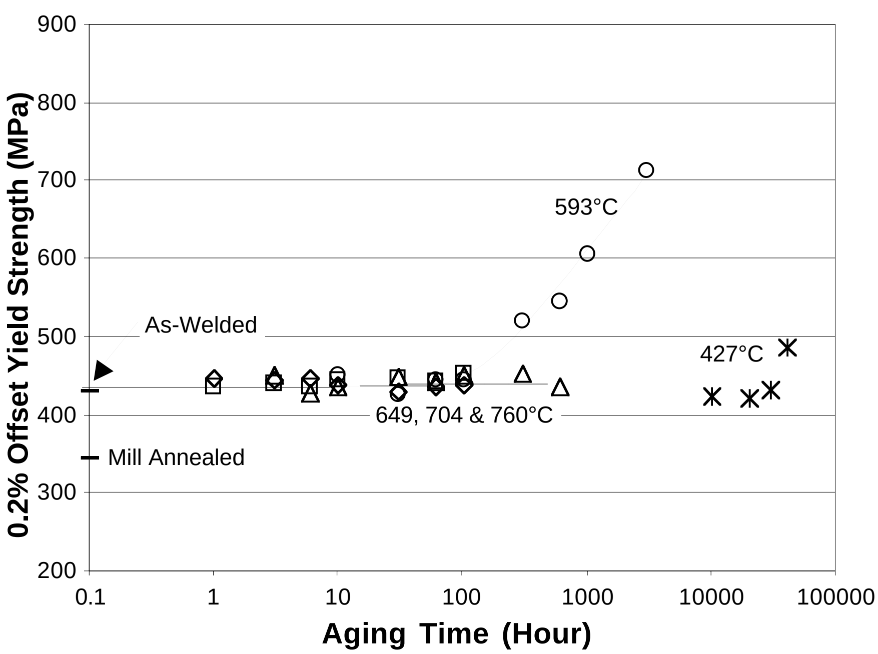

Figure 1: Room temperature yield strength of aged C-22 welds.

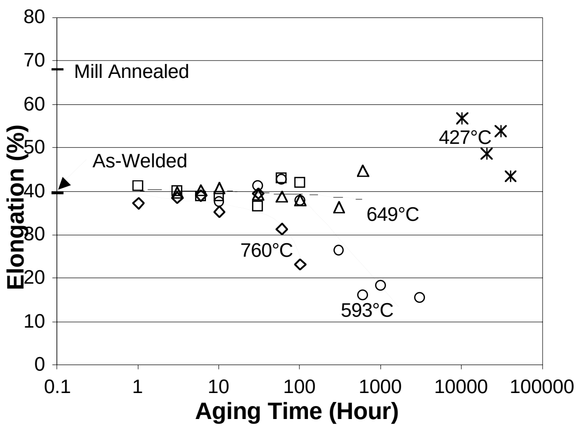

Figure 2: Tensile elongation of aged C-22 welds.

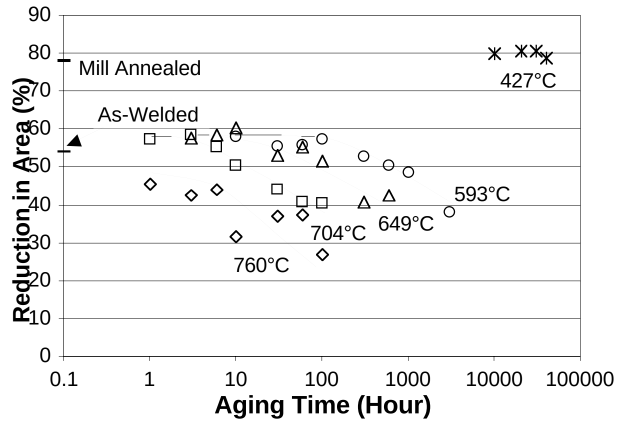

Figure 3: Tensile reduction in area of aged C-22 welds.

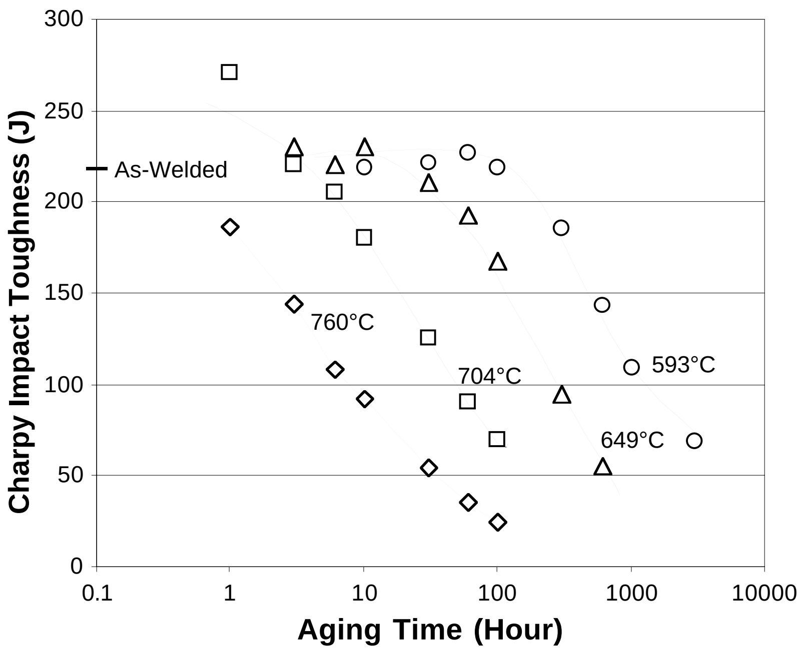

Figure 4: Room temperature Charpy impact toughness of aged C-22 welds.

The corrosion rate data for the aged C-22 welds is shown in Figures 5 and 6. Again, all data points represent at least two measurements. For both types of corrosion testing, the corrosion rate increases dramatically with aging time at the higher aging temperatures above approximately 500-600°C. At the lower temperatures, the corrosion rate remained essentially unchanged or decreased after aging.

The microstructure of an unaged C-22 weld is shown in Figure 7. A dendritic structure is evident, and TCP phases can be seen along the interdendritic regions. After aging at temperatures near and above 600°C, these TCP phase particles tend to grow as shown in Figure 8. Nucleation of new particles occurs after some time at the higher temperatures, but this nucleation tends to occur near the original particles so the particle clusters remain rather widely spaced. A film of precipitation was also observed to form possibly along grain boundaries in some areas of these samples. After aging at lower temperatures (Figure 9), there are no significant changes in the structure that can be seen in the SEM. That is, the size and distribution of TCP phase particles, dendrite spacing, etc. have not changed significantly. In TEM, long-range ordering was seen in the weld sample aged for 40,000 hours at 427°C. This ordering was in the very early stages of forming. The size and distribution of domains in this weld sample was comparable to that seen after aging C-22 base metal under the same conditions [7].

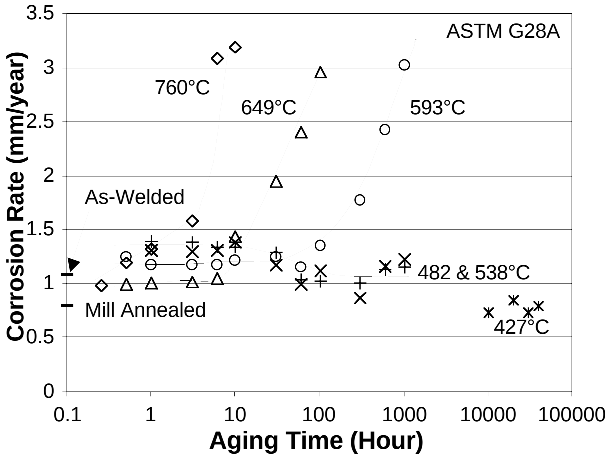

Figure 5: ASTM G28 A corrosion rates for aged C-22 welds.

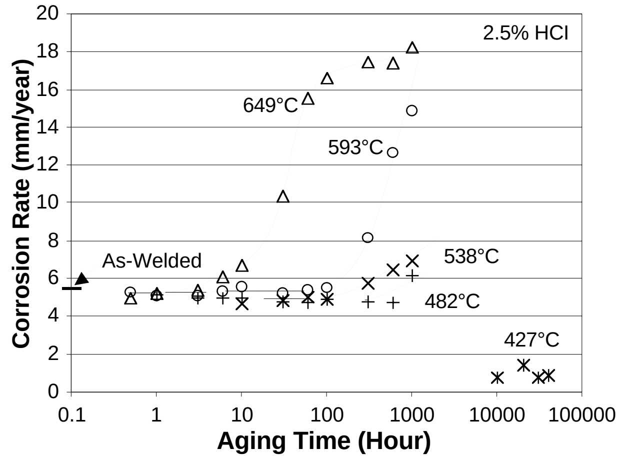

Figure 6: Corrosion rates for aged C-22 welds in 2.5% HCl.

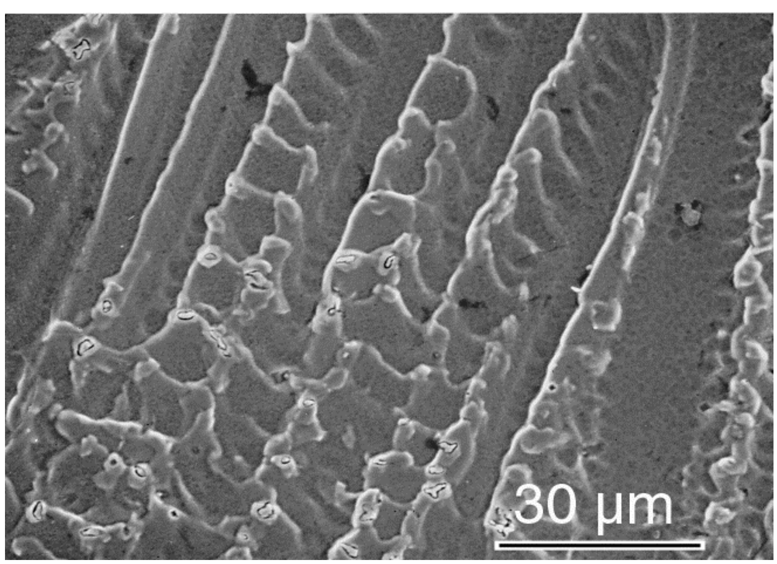

Figure 7: The microstructure of an unaged C-22 GTAW weld.

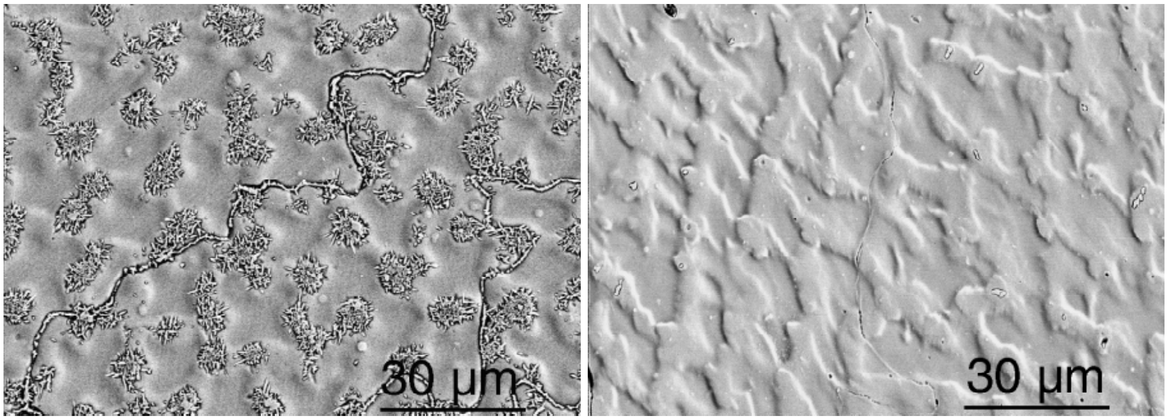

Figure 8: C-22 GTAW welds after aging 100 hours at 760°C (left) and 593°C (right).

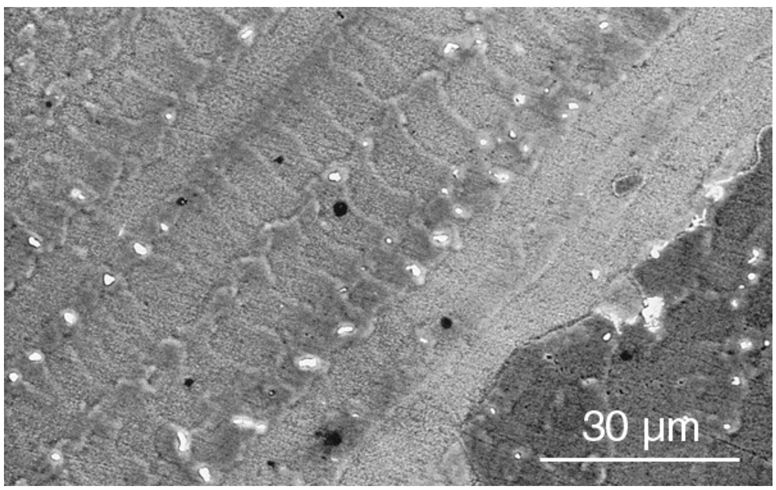

Figure 9: C-22 GTAW weld after aging 40,000 hours at 427°C.

Discussion

Figure 10 compares the strength of aged C-22 welds to that of aged C-22 base metal. The welds are initially approximately 25% stronger than mill annealed C-22 base metal. This strengthening is most likely due to the relatively hard TCP phases that form in the interdendritic regions of C-22 welds during welding. It is not clear at this time why significant strengthening occurs with aging only in the weld samples aged at 593°C. Strengthening of base metal occurs at all temperatures above 593°C investigated but after much longer times. This strengthening is also not as significant, becoming comparable to the as-welded samples only after aging for 16,000 hours. In the base metal, long-range ordering occurs sometime before 1000 hours at 593°C [8]. The very early stages of ordering have been observed in both the weld and base metal aged for 40,000 hours at 427°C [7]. As can be seen in Figure 10, some strengthening which might be attributable to ordering is seen in these samples. It is possible that the strengthening seen at 593°C is due to ordering which occurs with a very fine distribution of precipitates. Long-range ordering does not occur in C-22 above about 600°C [7] which would explain why strengthening was not observed at the shorter times to any great extent at the higher temperatures. Apparently, the TCP phases which form in the interdendritic regions are too widely spaced to cause further strengthening of the welds as they coarsen during aging. It is possible that strengthening might occur after longer times at the higher temperatures as more of the TCP phases nucleate. It is not known at this time why the strengthening observed occurs much sooner in the weld metal than in the base metal. It is possible that the chemical segregation present in the welds affects the ordering kinetics.

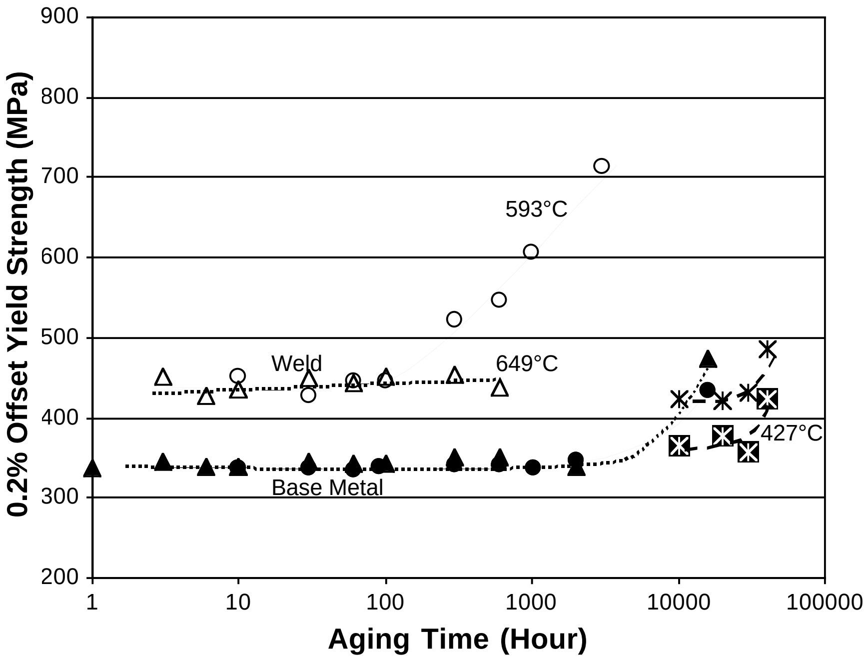

Figure 10: Comparison of aged C-22 base metal and weld strengths.

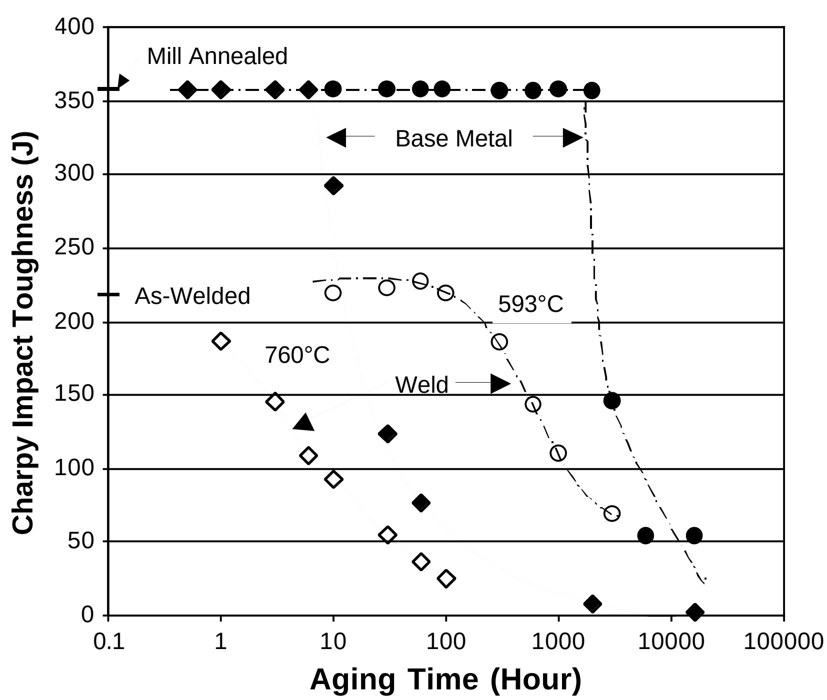

Figure 11: Comparison of aged C-22 base metal and weld toughness.

In Figure 11, the change in impact toughness in response to aging of C-22 welds is compared to that of the base metal. It has been concluded previously that the loss of toughness of C-22 base metal during aging at temperatures of approximately 593°C and above is due to the formation of TCP phases particularly since they form along grain boundaries [7]. These brittle TCP phases are present even before aging in C-22 welds, and as-welded C-22 has much lower ductility and toughness than base metal in the mill annealed condition (about 40% of the mill annealed condition when measured as % elongation or Charpy impact toughness). As with base metal, C-22 weld ductility decreases after aging at temperatures between 593 and 760°C. This decrease in ductility occurs sooner in the welds than in the base metal probably because the TCP phases are present prior to aging.

The corrosion rate of C-22 welds in boiling acidic ferric sulfate and boiling hydrochloric acid solutions increases after aging at temperatures at or above approximately 593°C as shown in Figures 5 and 6. The corrosion rate abruptly increases at times which decrease with increasing aging temperature. Because TCP phase growth kinetics increase with temperature, it appears likely that they are responsible for the increased general corrosion rate after aging. In the weld structure, the TCP phase distribution appears to be too coarse to affect strength with aging, but depletion of Mo still occurs to a sufficient extent to affect corrosion properties. The corrosion rate of aged welds is compared to that of aged base metal in Figure 12. The corrosion rate of the welds is initially more than 30% greater than that of the base metal. After aging at the higher temperatures, however, the corrosion rates eventually become comparable. These samples are approximately 2/3 base metal and 1/3 weld metal. Whether the corrosion rates become comparable because of structural changes occurring with aging or because the relatively rapid corrosion of the base metal overwhelms the corrosion occurring in the weld is currently under investigation. After aging at the lower temperatures, the weld and base metal corrosion rates are essentially the same. As shown in Figure 9, the TCP phases do not dissolve at 427°C, but they do not grow significantly either. It is possible, at 427°C for such long periods of time, that the chemical segregation in the weld relaxes somewhat. Thus, after aging at all temperatures investigated, the welds appear to be no worse than the base metal as far as the effect of phase stability on the corrosion rate in these environments is concerned.

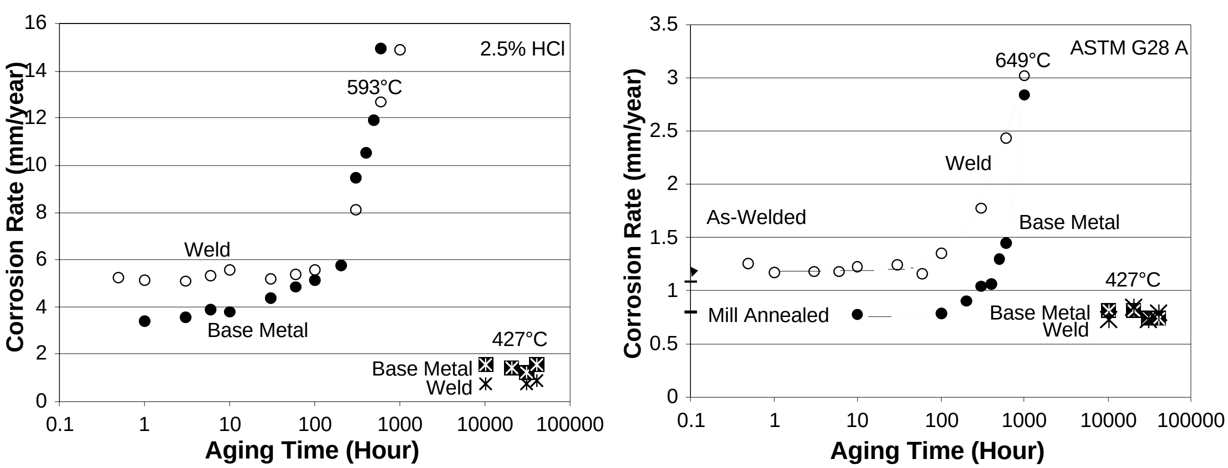

Figure 12: Comparison of aged C-22 base metal and weld corrosion resistance.

Conclusions

Multipass GTAW C-22 welds have a segregated, dendritic structure with TCP phase precipitation in the as-welded condition. Aging at temperatures above approximately 593°C, causes growth of these TCP phase particles as well as nucleation of particles beginning near the original particles. A film of precipitation that appeared to be forming along some sort of boundary was also seen in these samples. At the lower aging temperatures, no significant changes in structure that can be seen with SEM occur. In TEM, long-range ordering was seen in a weld aged for 40,000 hours at 427°C.

In the as-welded condition, C-22 welds (when tested perpendicular to the weld) are approximately 25% stronger but 30-40% less ductile than base metal. Significant strengthening occurred in the weld only after aging at 593°C. Some strengthening is apparent in the sample aged at 427°C for 40,000 hours as well. The cause of this strengthening is likely due to ordering. Unlike the strength, the ductility and toughness decreased with aging at all temperatures investigated above 593°C. This decrease in ductility is most likely due to the formation and growth of the brittle TCP phases.

Using standard immersion testing, the effect of aging on C-22 weld corrosion properties does not appear to be any worse than the effect on the properties of base metal. In boiling acidic ferric sulfate (oxidizing) and hydrochloric acid (reducing) solutions, the corrosion rate of weld samples was more than 30% greater than that of the base metal samples. After aging for a few hundred hours at temperatures near 600°C, however, the rates become comparable. After aging at lower temperatures, weld corrosion properties were essentially the same as those of the base metal. The reason for the decrease in corrosion rate after aging at the lower temperatures is not known at this time.

ACKNOWLEDGMENTS

The authors appreciate the efforts of E. Sedillo and J. Ferreira in metallography and SEM characterization, R. Gross in TEM sample preparation, and M. Wall for TEM microscopy at Lawrence Livermore National Laboratory. The work of Bill Rubush in mechanical testing and Jeff Dillman in corrosion testing at Haynes International is also appreciated. Part of this work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48. This part of the work is supported by the Yucca Mountain Site Characterization Project, LLNL.

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