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Delta-Ferrite Transformations in a Type 316 Weld Metal

Heat treating at 800 to 850 C for 10 hours results in less distortion than heat treatment at 1050 C, and welds are more ductile

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ABSTRACT. The effects of stress relief heat treatments on the microstructure of a Type 316 stainless steel weld metal are described for temperatures in the range 538 to 800 C (1000 to 1472 F). In the as-welded condition, the weld deposit contains delta-ferrite and austenite and, during stress relief, the delta-ferrite transforms predominantly to carbides and austenite at 538 to 650 C (1000 to 1202 F) and to chi-phase at 800 C (1472 F).

These observations are related to creep crack growth data at 538 and 600 C (1000 and 1112 F) and provide an explanation for the significantly improved ductility caused by heat treating at 800 C (1472 F). Weld metal heat treated at 800 C (1472 F) for 10 h appears to be stabilized against any likely microstructural causes of embrittlement in long term service at up to 650 C (1202 F) and may be treated for design purposes in the same way as base metal steels.

Introduction

Some outline designs for advanced reactor systems contain large section welds in AISI Type 316 stainless steel. While it is most unlikely that austenitic welds will be as creep brittle as some other systems (e.g., ½%Cr-Mo-V and 2¼%Cr-Mo weldments), they do pose other problems. These arise from poor inspectability by ultrasonic techniques of as-welded metal containing delta-ferrite within columnar austenite grains[1] coupled with decreased resistance to macroscopic creep crack growth compared with base metals at 538 C (1000 F) for a weld metal containing 0.03% carbon[2] and at 600 and 700 C (1112 and 1292 F) for a weld metal containing 0.06% carbon.[3]

The compositions of Type 316 stainless steel weld metals are designed to give between 2 and 10% delta-ferrite in the austenitic matrix to avoid hot tearing during solidification.[4] ASME Code case 1592[5] specifies 3 to 9%. The delta-ferrite is surrounded by austenite locally enriched by alloying elements; the brittle crack growth observed by Haigh,[2] however, was closely associated with the delta-ferrite, itself.

There are two possible heat treatments to alleviate the problem: solution heat treatment at about 1050 C (1922 F) to give a completely austenitic structure like the base metal, or stress relief heat treatment at about 800 C (1472 F). An examination of the microstructure after the latter heat treatment shows the continued existence of a second phase in the same lamellar form as the delta-ferrite. However, magnetic measurements indicate that the delta-ferrite has been transformed.[6] Both treatments are likely to give adequate stress relief. Moreover, the 800 C (1472 F) heat treatment (for 10 h) has also been shown to give greater resistance to creep crack growth than the as-welded deposit[7] and hence again to improve confidence in long term behavior.

Work performed so far has not been subjected to thorough metallurgical examination. For this reason, the metallography described here was carried out to provide an understanding of the processes described above and to assess the behavior at extended times in service.

Experimental Procedure

Materials and Heat Treatments

A proprietary weld metal—Babcock and Wilcox "S" type—was deposited by manual metal arc welding in weld pads approximately 90 × 100 × 130 mm on a 25 mm (1 in.) thick base plate. Magnetic measurements showed that these deposits contained between 2 and 4% delta-ferrite. The compositions of two typical pads are given in Table 1, along with the composition of the weld metal used by Okane and Osumi.[3] Weld metals typically contain very low carbon levels, as in the present (8W) pads.

Small samples were heat treated for periods of 1 to 1000 hours (h) in the range 600 to 860 C (1112 and 1562 F) and up to 7700 h at 538 C (1000 F). Thomas et al[6] used these samples to estimate the rate of transformation of the delta-ferrite as a function of

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Table 1—Compositions of Weld Metal, Wt-%

Pad no.	C	Cr	Mn	Mo	Ni	P	Si	S	Ti
BW2	0.03	17.9	0.82	2.5	10.9	0.009	0.30	0.008	<0.1
BW3	0.03	17.9	0.87	2.5	10.9	0.009	0.30	0.008	<0.1
Okane & Osumi's[3]	0.06	20.0	1.69	2.42	11.8	0.002	0.39	0.011	—

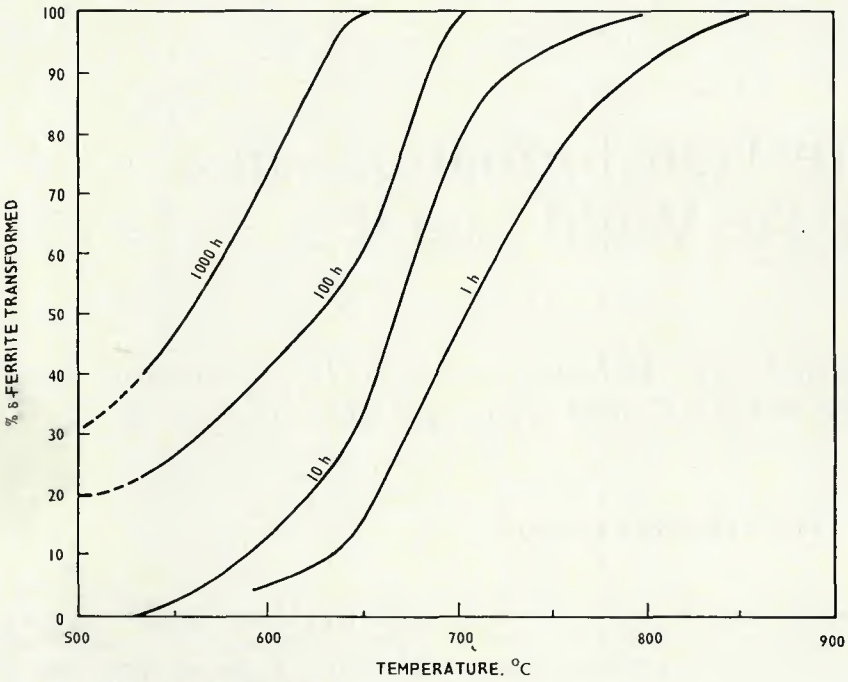

Fig. 1—Rate of transformation of δ-Ferrite[6]

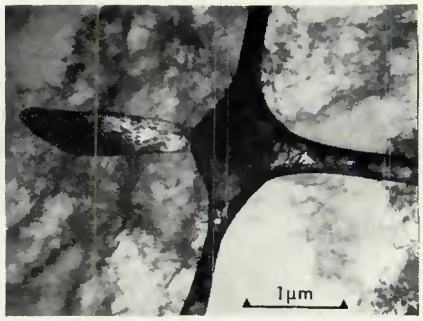

Fig. 2—Delta-ferrite (reduced 38% on reproduction)

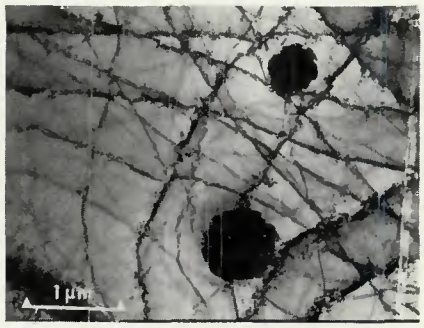

Fig. 3—Slag particles (reduced 38% on reproduction)

temperature and time—Fig. 1. Samples heat treated at 538, 600, 650, 750 and 800 C (1000, 1112, 1202, 1382 and 1472 F) were chosen for metallographic study, and in these the delta-ferrite was transformed between 40 to 100%—Fig. 1.

Metallographic Techniques

Transmission electron microscopy was performed on the JEOL 200 microscope operating at 200 kV. Thin foils were prepared by using the "Tenupol" apparatus with an electrolyte of 5% perchloric acid—95% glacial acetic acid.

For X-ray diffraction studies, samples were dissolved electrolytically in a 10% HCl-90% methanol solution at about 2 volts. The residue was analyzed by standard X-ray powder diffraction techniques using CrK_α radiation.

The polished and etched surfaces of some specimens were also examined by scanning electron microscopy. The compositions of the ferrite and various particles were analyzed by energy dispersive X-ray spectrometry using the "Cambridge Stereoscan" electron microscope with an "E.D.A.X." attachment.

Results

As-Welded Condition

Figure 2 shows the appearance of delta-ferrite in the as-welded condition. Some slag particles were also present (Fig. 3), but attempts to obtain electron diffraction patterns from these slag particles were unsuccessful. X-ray diffraction also failed to detect these particles.

Electron probe microanalysis (EPMA) showed that the particles contain Si, Mn, Cr, Mo and some Ti. It seems likely that these slag particles have amorphous glass-like structures. EPMA also showed that there was considerable segregation of Cr and Mo to the delta-ferrite and surrounding area.

Transformation at 538 to 650 C

X-ray diffraction showed that the predominant new phase formed after 7700 h at 538 C (1000 F) was $M_{23}C_6$ carbide. Only a trace of sigma phase was detected. At 600 and 650 C (1112 and 1202 F) magnetic measurements (Fig. 1) showed that the delta-ferrite was partially (~ 50%) transformed after 100 h at these temperatures. X-ray diffraction again indicated that $M_{23}C_6$ was the predominant new phase in these specimens. Electron microscopy showed that these carbide particles nucleated and grew within the ferrite phase—Fig. 4.

A new precipitate, R-phase, was found by electron diffraction in specimens heat treated for 100 h at 600 and 650 C (1112 and 1202 F)—Figs. 5 and 6. R-phase has not previously been reported in Type 316 stainless steel; it is an intermetallic phase similar to sigma and chi (see below).

In the specimen heat treated at 650 C (1202 F) for 100 h sigma particles had formed at the delta-ferrite/austenite interface—Fig. 7. No sigma-phase was detectable by X-ray and electron diffraction studies in the specimen heat treated at 600 C (1112 F) for 100 h. Both sigma and R-phase appeared to have nucleated at the delta-ferrite/austenite interface.

Since there was only 0.03 wt-% carbon in the weld metal, the maximum weight fraction of $M_{23}C_6$ carbides that can form is only 0.6%. This represents only one third to one sixth of the available delta-ferrite. Since the amount of other phases was small, the remaining delta-ferrite had transformed to austenite.

Transformations at 750 and 800 C

X-ray diffraction on bulk extracted residues showed that chi was the predominant precipitate in all specimens heat treated at 800 C (1472 F).

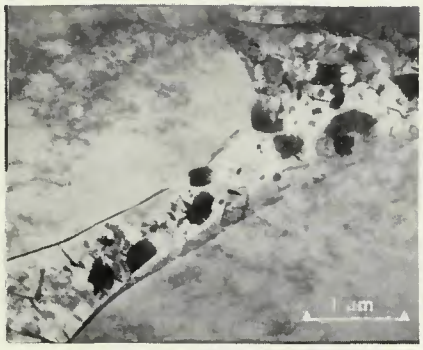

Fig. 4—Carbides in ferrite (reduced 38% on reproduction)

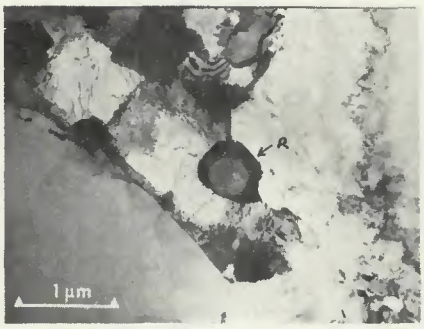

Fig. 5—An R-phase particle—indicated by arrow (reduced 38% on reproduction)

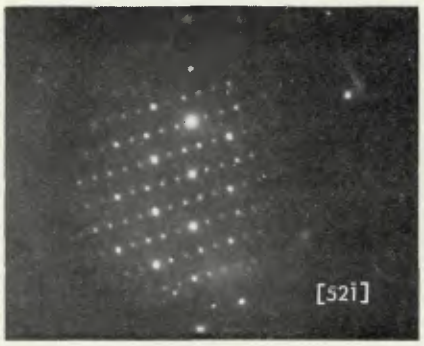

Fig. 6—Selected area diffraction of R-phase (reduced 38% on reproduction)

However, at 750 C (1382 F) the amount of sigma exceeded the amount of chi after 100 h. Magnetic measurements showed that transformation of delta-ferrite was complete after 10 h at these temperatures—Fig. 1.

In the partially transformed specimens, many chi-phase particles were observed nucleating at the delta-ferrite/austenite interface—Fig. 8. Some chi particles appeared to grow preferentially along the delta-ferrite/austenite interface and to coalesce with other similar particles—Fig. 9. The observed particle size of the chi-phase was smaller than that of the delta-ferrite in the as-welded condition, indicating some transformation of delta-ferrite to austenite.

$M_{23}C_6$ carbides were also present in all samples heat treated at these temperatures. However, at 800 C (1472 F) the amount of $M_{23}C_6$ carbides decreased with increasing time of heat treatment. In the 800 C-100 h specimen, evidence of a chi particle growing from a $M_{23}C_6$ particle was obtained—Fig. 10.

The very few sigma particles which were detected appeared to have formed discontinuously within the austenite rather than by transformation of the delta-ferrite—Fig. 11.

In summary, delta-ferrite in the Type 316 stainless steel weld metal transformed readily during heat treatments at temperatures between 600 and 800 C (1112 and 1472 F). At 750 and 800 C

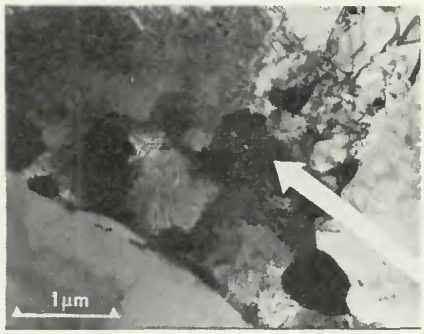

Fig. 7—A sigma particle—indicated by arrow (reduced 38% on reproduction)

(1382 and 1472 F) it mainly transformed into chi-phase, whereas at 600 and 650 C (1112 and 1202 F) it mainly transformed into $M_{23}C_6$ carbide and austenite. Sigma-phase was present only in small quantities in most specimens. At 600 and 650 C (1112 and 1202 F) small quantities of R-phase also formed from the delta-ferrite.

Discussion: Precipitated Phases

The transformation of delta-ferrite in Type 316 stainless steel weld metal during heat treatment is clearly a very complex phenomenon. We found that the transformed products consisted of a variety of inter-metallic phases and the $M_{23}C_6$ carbide. Table 2 lists the phases identified in this work.

Delta-Ferrite

Under equilibrium conditions, Type 316 stainless steel should be fully austenitic on cooling to room temperature. Delta-ferrite in weld metals forms as dendrites prior to solidification of austenite at the peritectic temperature ~ 1450 C (2642 F) and is retained during rapid cooling. The ferrite formed is enriched in (ferrite-forming) elements such as Cr and Mo, and impoverished in Ni which is an austenite former.

The segregation of these elements was confirmed by EPMA in the present investigation. The rapid precipitation of carbides and intermetallic phases in the delta-ferrite can be attributed partly to the segregation of Cr and Mo and partly to the high diffusivities of elements such as Cr and C in ferrite compared with austenite.

Delta-ferrite is known to have a deleterious effect on the creep rupture strength of Type 316 stainless steel. During creep, microcracks can develop readily at the delta-ferrite/austenite interphase boundaries,[8] linking into macroscopic cracks when sufficient delta-ferrite is present.[2]

$M_{23}C_6$ Carbides

This carbide is commonly observed in heat-treated stainless steels, and extensive data are available on its precipitation behavior.[9] In Type 316 stainless steel this carbide is usually

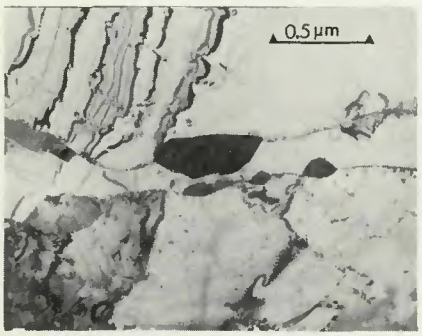

Fig. 8—Chi particles nucleating at delta/austenite interface (reduced 38% on reproduction)

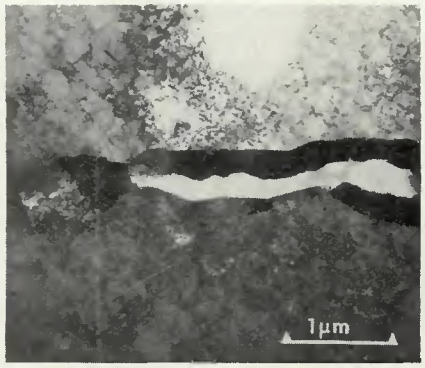

Fig. 9—Chi particles growing along delta/austenite interface (reduced 32% on reproduction)

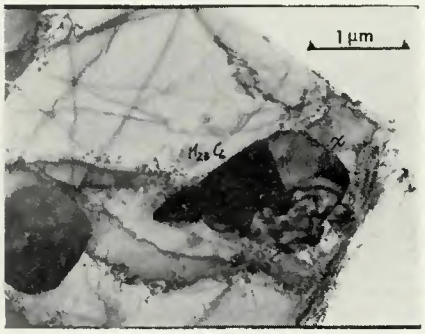

Fig. 10—Carbide transforming into chi-phase (reduced 38% on reproduction)

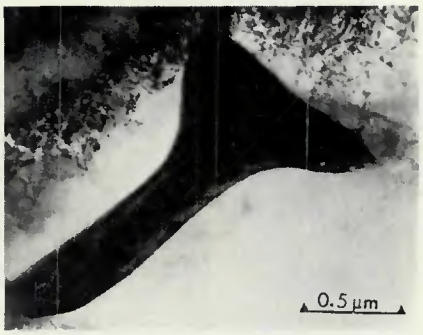

Fig. 11—A large sigma particle (reduced 38% on reproduction)

Table 2—Secondary Phases in Austenite Matrices

Phase	Crystal structure	Lattice parameter	Major constituent elements
$M_{23}C_6$	Face centered cubic	a_o = 10.621	Fe, Cr, Mo, C
Chi	Body centered cubic	a_o = 8.920	Fe, Cr, Mo
Sigma	Tetragonal	a_o = 8.8, c_o = 4.544	Fe, Cr, Mo
R	Hexagonal	a_o = 10.903 c_o = 19.342	Fe, Cr, Mo
Delta-ferrite	Body centered cubic	a_o = 2.866	Fe, Cr, Mo

formed before the intermetallic phases, presumably due to the fast diffusion of carbon atoms.[10]

Many $M_{23}C_6$ carbides were observed within the ferrite matrix in specimens heat treated at 538 to 650 C (1000 to 1202 F)—Fig. 4. This implies either that these carbides were nucleated within the ferrite matrix or that they were nucleated at the delta/austenite interphase boundaries and grew directly into the ferrite matrix. Unlike the chi-phase they did not grow along the interphase boundaries—Figs. 4 and 9.

Few precipitates of $M_{23}C_6$ were observed in the austenite at 600 and 650 C (1112 and 1202 F). This suggests that the degree of supersaturation of carbon in ferrite was greater than that in the austenite at these temperatures. As temperature is increased, the solubilities of carbon in both ferrite and austenite increase. At 750 and 800 C (1382 and 1472 F) the degree of supersaturation of carbon was small, but the concentrations of Cr and Mo in the delta-ferrite were still high. Consequently, the intermetallic chi-phase was formed in preference to the carbide at these temperatures.

As the chi-phase formed, the amounts of Cr and Mo in solid solution decreased. This decrease in Cr and Mo increased the solubility of carbon even further.[11] After 100 h at 800 C (1472 F) the small amount of carbides initially formed redissolved; the carbon went back into solution and chi particles were formed from the Cr and Mo provided by the redissolved carbides—Fig. 10.

Chi-Phase

The chi-phase was first shown to be present in Type 316 stainless steel by Andrews.[12] However, its importance was only realized recently, largely as a result of the publication of Weiss and Stickler's paper on the phase instabilities of Type 316 stainless steel.[10]

The chi-phase is a stable intermetallic compound containing Fe, Cr and Mo. However, it is believed that chi can be a carbon dissolving compound of the type $M_{18}C$. The composition of chi can apparently vary appreciably with a high tolerance for metal interchange. Upon addition of carbon, the metal-atom proportion within chi is shifted towards Mo at the cost of Fe and Cr, i.e., towards the strongest carbide former.[13]

Indeed, EPMA during the present investigation showed that the Mo content of many chi particles in the weld metal was lower than that observed in the ordinary Type 316 stainless steels with higher carbon contents. This variation in Mo content rendered it impossible to distinguish between chi and sigma by the "E.D.A.X." method suggested by Weiss, Hughes, and Stickler.[14]

Little is known about the effect of chi-phase on the mechanical properties of Type 316 stainless steel. Weiss and Stickler[10] measured the impact strength of Type 316 stainless steel at liquid nitrogen temperature as a function of aging temperature and time. They found that the presence of $M_{23}C_6$ led to a sharp decrease in the impact strength, but the presence of chi-phase did not lead to a further significant drop. The creep crack growth work of Haigh and Laidler[7] on weld metal heat treated for 10 h at 800 C (~ 100% transformed) combined with the present work indicates good resistance to brittle (i.e., low displacement) microcracking by the chi-phase and its interfaces.

Sigma-Phase

This is the best known intermetallic phase in heat resisting steels. Its occurrence, crystal structure, composition and effects on physical and mechanical properties have been reviewed by Hall and Algie.[15]

In some casts of Type 316 stainless steel the interface between sigma-phase and austenite is weak. Here the presence of sigma may lead to drastic reductions in long term creep ductility. However, in the present investigation only small amounts of sigma were detected in most specimens, and it is unlikely that it would have a significant effect on the mechanical properties.

R-Phase

This phase had not previously been reported in heat treated Type 316 stainless steel. It is an Fe-Cr-Mo intermetallic phase similar to sigma and chi. It has a hexagonal structure with unusually large lattice spacings—Table 2.

This phase had previously been found in a 12% Cr-6% Mo-10% Co-0.1% C ferritic steel by Dyson and Keown.[16] These authors considered the atomic movements in ferrite to accommodate the R-phase structure based on the experimentally determined crystal structure of R-phase and its orientation relationships with ferrite. They showed that only small atom movements and lattice strains were required for R-phase to form from ferrite. They suggested that it is theoretically more favorable for R-phase rather than sigma to precipitate from ferrite provided that suitable alloying elements are present.

Practical Applications

The present work is aimed at assessing the long term structural stability of Type 316 stainless steel weld metal under creep conditions—and, in particular, to assess the probability for the nucleation and growth of cracks. In this way, it is intended to examine possible design procedures for weld metals, particularly in the present shortage of long term data for these materials. ASME Case 1592, for instance, treats weld metals and wrought steel in the same way when specifying high temperature mechanical properties and it is necessary to examine the validity of this approach. To do this an understanding of the long-term metallurgical behavior is required—first, to justify design rules for the weld metal and, second, for extrapolating short term data.

Crack growth behavior at 538 C (1000 F) can be related to the results at 600 to 650 C (1112 and 1202 F), which provide a useful (accelerated) guide. Both temperatures can give the same brittle (low displacement) microcracks associated with the delta-ferrite (538

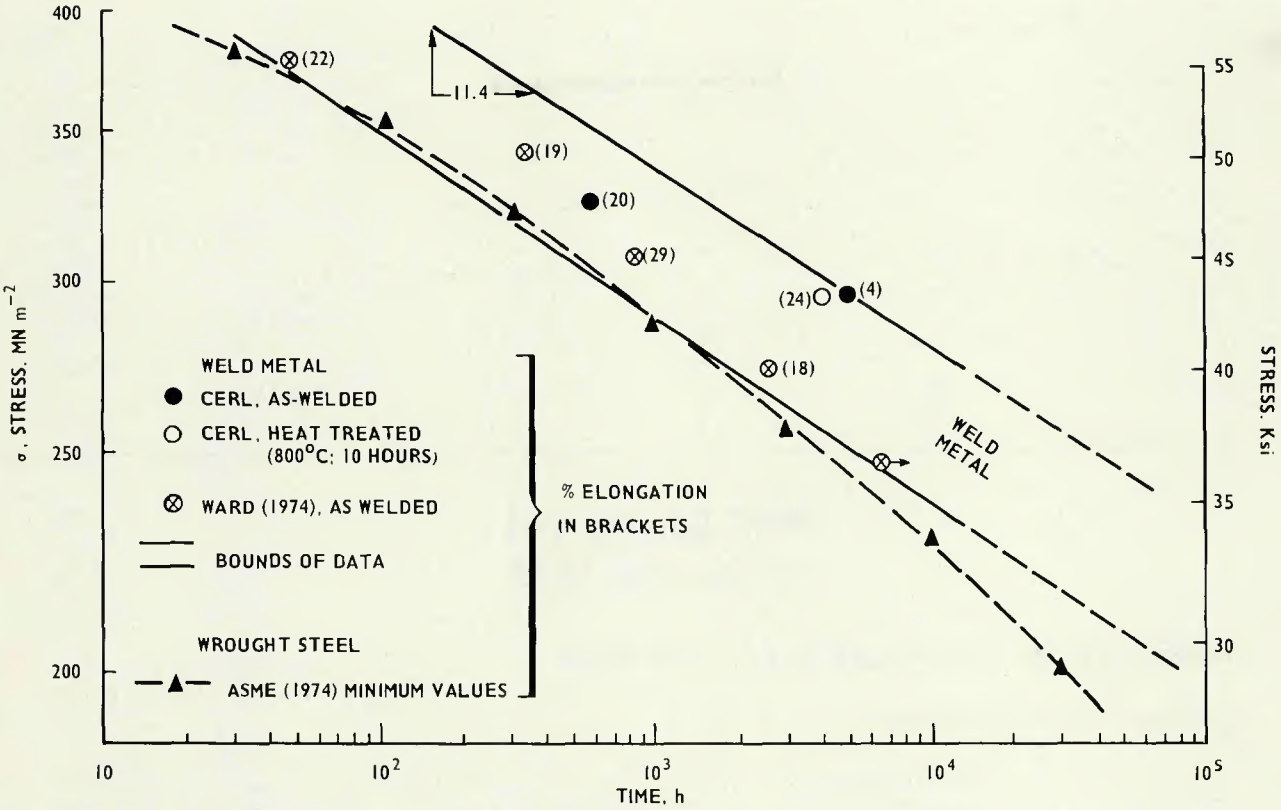

Fig. 12—Creep rupture data for Type 316 stainless steels, 538 C (1000 F)

C;[2] 600 and 700 C[3]). At 538 C (1000 F) there was an incubation period prior to microcracking, suggesting a transformation process as part of the crack initiating and growth mechanism.

The above work indicates that the formation of carbides around and within the delta-ferrite is the embrittling mechanism. Heat treatment at 800 C (1472 F) for 10 h avoids the carbide formation in delta-ferrite by preferential growth of the more stable chi-phase. Subsequent embrittlement at long times at 538 C (1000 F) is most unlikely since the chi-phase possesses long term stability.

Sigma-phase embrittlement, itself, is also no more probable in weld metal than in wrought Type 316 stainless steels. This is because the above work shows that chi-phase is preferred as a transformation product from delta-ferrite in heat treatments at 800 C (1472 F) and that any sigma-phase forms at other sites, as in wrought materials. Thus, at long times the heat-treated weld metal and base metal steels should behave quite similarly. This is not necessarily true of the as-deposited weld metal and is, therefore, a strong argument in favor of stress relief heat treatment at about 800 C (1472 F).

Figure 12 shows the creep rupture and design data for Type 316 stainless steel weld metal and the wrought steel at 538 C (1000 F).[5,7,17] The limited amount of weld metal data available at this temperature indicate that the ASME minimum values for the wrought steel can be applied equally well to the weld metal. Thus, solution treatment of weld metal at 1050 C (1922 F) to give a recrystallized austenite structure will not influence the design stress based on a creep rupture criterion. Furthermore, owing to the high thermal expansion coefficient and low thermal conductivity of Type 316 stainless steel, such high temperature treatment may cause severe distortion in complex components. Therefore, it is recommended that the 1050 C (1922 F) heat treatment of Type 316 stainless steel welds should be replaced by one in the temperature range 800–850 C (1472–1562 F) for about 10 h.

Conclusions

1. Heat treatment of an as-welded Type 316 stainless steel weld metal at 538, 600 or 650 C (1000, 1112 or 1202 F) converts delta-ferrite mainly to austenite and $M_{23}C_6$ carbides which precipitate within and at the boundary of the ferrite. Brittle crack growth in such material at 538 to 600 C (1000 to 1112 F) is attributed to this transformation.

2. Heat treatment of the as-welded material at 800 C (1472 F) converts delta-ferrite mainly to chi-phase by continuous transformation from the delta/austenite interface. Formation of chi-phase explains earlier observations in creep crack growth tests of more ductile behavior of the weld metal after an 800 C (1472 F) heat treatment.

3. The material heat treated at 800 C (1472 F) should have creep resistance and ductility close to those of Type 316 stainless steel base metals.

Acknowledgments

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