Prevention of Chi and Sigma Phases Formation in Aged 16-8-2 Weld Metal

Adjusting Mo content eliminates the chi phase, and adjusting the carbon + nitrogen content can prevent the δ-ferrite-σ phase transformation

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ABSTRACT. Type 16-8-2 weld filler metal (16 wt-% Cr, 8 wt-% Ni, 2 wt-% Mo, nominally) is commonly used to weld Type 316 stainless steel base metal, and is formulated to contain a small amount of δ-ferrite to prevent hot cracking during welding. The δ-ferrite is known from previous work to transform to sigma phase on aging (e.g., 10,000 hours at 650°C or 1202°F), and chi phase is also observed to form in this material.

It is shown that suitable control of composition can prevent formation of these two embrittling phases. The chi phase can be eliminated by adjusting the molybdenum content. The δ-ferrite-σ phase transformation can be prevented by suitably adjusting the carbon-plus-nitrogen content. The mechanism of this behavior is discussed.

Introduction

Type 16-8-2 (16 wt-% Cr, 8 wt-% Ni, 2 wt-% Mo, nominally) weld filler metal is commonly used to weld Type 316 stainless steel base metal. Ferrite levels in austenitic welds are usually controlled to ~4 to 8% through control of composition. According to Lundin et al (Ref. 1), this level of ferrite is estimated to be sufficient to avoid cracking or fissuring in austenitic stainless steel welds.

In many conventional austenitic welds the ferrite transforms to sigma during high temperature (~650°C or 1202°F) service. As a result of this transformation the weld is embrittled; internal cracks develop at the austenite-sigma phase boundaries which result in the observed low ductility. Stiegler et al (Ref. 2) have shown, for example, in Type 308 stainless steel weld metal, containing 5 to 8% ferrite initially, that internal cracking of the welds during creep is associated with sigma-austenite boundaries. Cracking was not found where transformation of the ferrite to sigma had not occurred.

Sigma formation also appears to reduce low temperature impact resistance. Canonico (Ref. 3) has observed marked reductions (~50%) in Charpy-V-notch energy measurements at 0°C (32°F) on Type 308 stainless steel weld specimens which had been aged in the sigma-forming temperature range of 650°C (1202°F), 1000 hours (s). Thus, prevention of sigma phase formation would seem to be advantageous.

Hull (Ref. 4) investigated the effect of chemical composition on embrittlement of numerous alloys. Hull's specimens were cast prior to aging 1000 h at 815°C (1499°F). He used an impact test and measured the bend angle at fracture; he used this angle as a measure of embrittlement. (A small angle indicates embrittlement.) Hull defined the "chromium equivalent" as:

$$\text{Cr. Eq.} = \text{Cr} + 0.31\ \text{Mn} + 1.76\ \text{Mo} + 0.97\ \text{W} + 2.02\ \text{V} + 1.58\ \text{Si} + 2.44\ \text{Ti} + 1.70\ \text{Nb} + 1.22\ \text{Ta} - 0.226\ \text{Ni} - 0.177\ \text{Co}$$

He found that the "chromium equivalent" was a vital factor in indicating the degree of brittleness of an alloy. Thus, the principle of controlling composition to control embrittlement of cast samples was established, even though carbon and nitrogen are not considered. Hull also saw a qualitative relationship between brittleness and amounts of chi and sigma phases present in the alloys.

In the present work we examine the microstructural change in simulated (cast) welds of 16-8-2 weld filler metal after aging at 649 and 732°C (1200 and 1350°F) for times up to 10,000 h. We show that the intermetallic phases that occur are functions of composition, as might be expected. We also show that the transformation of ferrite to sigma phase can be prevented when ferrite is present at ~4 vol-% and we show a mechanism by which this can be done.

We have not investigated the relationship of mechanical properties to the intermetallic phases in 16-8-2 welds, although this is an area which needs investigation. Properties of 16-8-2 welds have been studied recently by Brinkman et al (Ref. 5). A great deal of scatter was seen in the properties, and an explanation would clearly be helpful.

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Experimental Procedures

Rather complete details of the experimental procedures used in this work are

Table 1—Compositions of Two 16-8-2 Weld Filler Metal Heats Used in this Study

Element	Content in each heat, wt-% 2367R	D1309T
N[a]	0.0475	0.0394
C	0.040[b]	0.073[c]
Mn	1.19	1.44
Si	0.33	0.42
S	0.013	0.011
P	0.026	0.019
Cr	16.36[d]	15.16[e]
Ni	8.72[f]	8.42[g]
Mo	1.64	1.28
Al		0.20

(a) Analyzed on cast sample at ORNL.
(b) Vendor 0.028; ORNL 0.0395 wt-% on cast sample.
(c) Vendor 0.07; outside Laboratory 0.051 wt-%; ORNL 0.0730 on cast sample.
(d) Vendor 16.36, ORNL 16.4 wt-%
(e) Vendor 15.16, ORNL 15.3, outside Laboratory 15.18, 14.85 wt-%.
(f) Vendor 8.72, ORNL 8.61 wt-%.
(g) Vendor 8.43, ORNL 8.42, outside Laboratory 8.25, 8.27 wt-%. We selected the ORNL carbon values to use in Table 1 because ORNL researchers made strenuous efforts to ascertain the precision of these values. In other cases the vendors' values were accepted, the ORNL value merely serving to justify the result.

In these welds we measured the ferrite content by two techniques, a Magne-Gage and line intercept measure-indicated FN values of 2.1 and 2.4 for as-cast specimen of Heats D1309T and 2367R, respectively. Optical metallography revealed 3.70 ± 0.81 and 4.54 ± 0.40 vol-% δ ferrite, respectively. The difference in the values is related to the magnetic response of the particular δ ferrite.

Table 2—Extraction Results for Weld Samples Aged at 649 and 732°C (1200 and 1350°F)

Specimen sample	Aging conditions: Temperature, °C	Aging conditions: Time h	Precipitate content, wt-%	X-ray results: Phase	Spacing	Value, nm	Intensity: Line	I
				Heat D1309T				
As-cast			0.153	Ferrite[a]	a_o	0.2882		
				Unknown[b]	d	0.2186		
DE-26	649	500	0.787	$M_{23}C_6$	a_o	1.0664 ± 0.0003		
DE-28	649	1,000	0.813	$M_{23}C_6$	a_o	1.0657 ± 0.0005		
				Unknown[b]	d	0.2669		
DE-29	649	5,000	1.046	$M_{23}C_6$	a_o	1.0655 ± 0.0003		
DE-30	732	500	0.997	$M_{23}C_6$	a_o	1.0675 ± 0.0003		
				Unknown[b]	d	0.2448 ± 0.2002		
DE-31	732	1,000	1.081	$M_{23}C_6$	a_o	1.0675 ± 0.0005		
DE-32	732	10,000	1.913	$M_{23}C_6$	a_o	1.0679 ± 0.0005		
				Heat 2367R				
DE-10	649	500	0.92					
DE-11	649	1,000	1.0					
DE-12	649	5,000	1.31	$M_{23}C_6$	a_o	1.0678 ± 0.0005	(333)	73
				Chi	a_o	0.8879 ± 0.001	(330)	5
DE-15	732	1,000	1.22	$M_{23}C_6$	a_o	1.0692 ± 0.003	(333)	110
				Chi	a_o	0.8862 ± 0.001	(330)	25
DE-16	732	10,000	2.63	$M_{23}C_6$	a_o	1.0715 ± 0.0005	(333)	50
				Chi	a_o	0.8901 ± 0.0005	(330)	125

(a) This ferrite was an unusual occurrence. Only in one or two cases have we identified any ferrite in the extracted precipitate from a weld. Usually it is dissolved.
(b) Line of weak intensity is probably a poorly crystallized slag inclusion, since it does not fit any other known phase of the system.

recorded elsewhere (Ref. 6); a brief account is given here. Materials from two commercial weld filler metal heats were used—Table 1. In order to avoid contamination from base metal, welds were simulated by manually casting weld wires from each of the heats into several cylindrical buttons. An argon gas tungsten-arc torch was used, and the filler metal was melted into a copper mold. Specimens cut from these buttons were encapsulated in vacuum in Inconel cans by electron beam welding and aged in air furnaces at one of several temperatures and times reported in Table 2.

After aging, samples were examined by a number of techniques. These included chemical analysis, optical metallography, transmission electron microscopy (TEM), scanning transmission electron microscopy with accompanying analytical x-ray spectroscopy, electrolytical extraction, and x-ray examination of the extracted precipitate.

Results and Discussion

Data from extractions are reported in Table 2. The x-ray data indicate that Heat D1309T contains only $M_{23}C_6$ (a_o = 1.066 nm) in the precipitate with some occasional impurity lines. The other heat—heat 2367R—contained two phases in the extracted precipitate: $M_{23}C_6$ (a_o = 1.069 nm) and chi (a_o = 0.888 nm). A plot of the data in Fig. 1 reveals more clearly the continuing reaction at 649°C (1200°F), even after 5000 h—that is, the 732°C (1350°F) aging of heat 1309T produced 1.93 wt-% precipitate after 10,000 h, and aging at the lower temperature would be expected to produce, eventually, virtually the same amount.

A significant point to note is the absence of any phase other than $M_{23}C_6$ in the extracted residue of heat D1309T. (Ferrite is almost always dissolved in the electrolytic process.) The chi phase formed only in heat 2367R. If chi phase had formed in heat D1309T, it would have been detected. The rate of formation was slower than that of $M_{23}C_6$ initially but became more rapid than that for

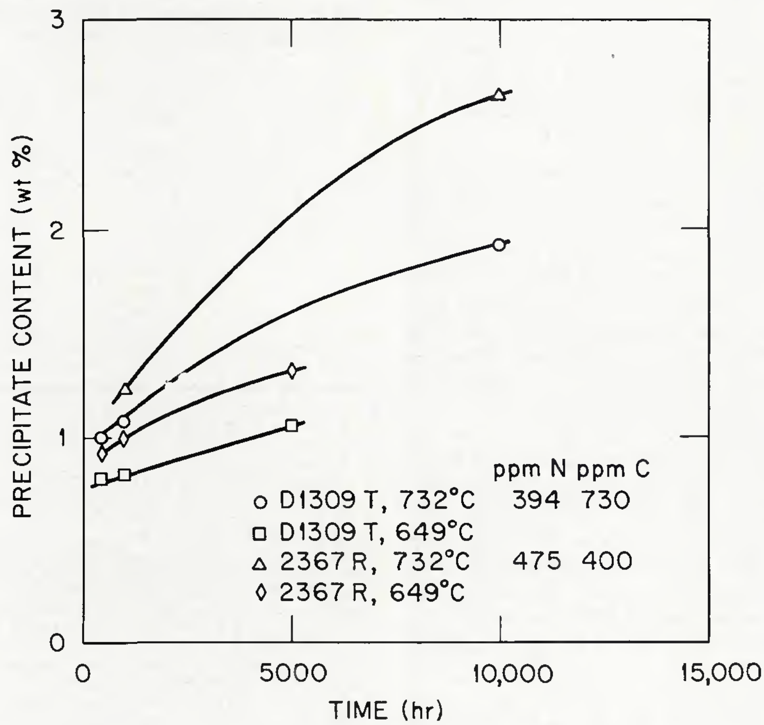

Fig. 1—Plot of weight data from samples aged at 732 and 649°C (1349 and 1200°F)

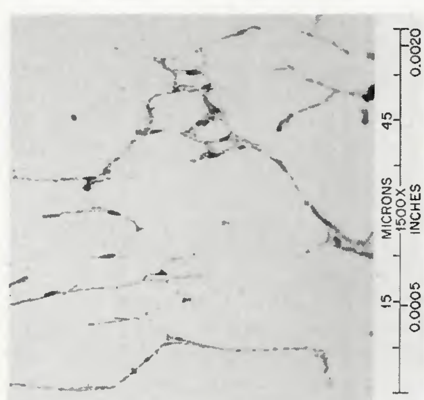

Fig. 2—Optical micrograph of heat 2367R aged 10,000 h at 732°C (1349°F)

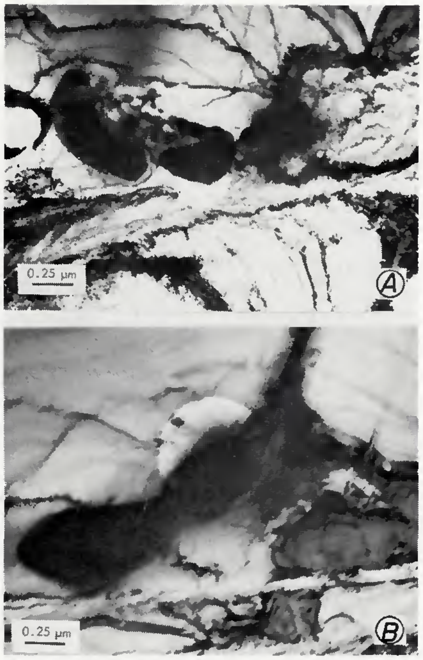

Fig. 3 — Transmission electron micrograph of heat 2367R: A — example of chi phase; B — second example

the carbide later in the aging process — Table 2.

Figure 2 shows an optical micrograph of heat 2367R; note that chi phase precipitates cannot be identified by this technique. The chi phase was seen in heat 2367R by TEM but not, as expected from the x-ray results, in heat D1309T. Examples are shown in Fig. 3.

Compositions of the two heats differed significantly in several respects. As seen in Table 1, heat 2367R has a higher molybdenum content, a slightly higher chromium content, but less carbon plus nitrogen. The formation of chi phase is influenced strongly by the molybdenum content. Weiss and Stickler (Ref. 7), for example, show the composition of chi phase in Type 316 stainless steel as 22 wt-% Mo, 21 wt-% Cr, 52 wt-% Fe, and 5 wt-% Ni. In heat 2367R molybdenum and chromium are not removed from solution by carbon and nitrogen to an extent sufficient to prevent the formation of chi phase. Heat D1309T, on the other hand, did not form the chi phase. One may presume the absence of this intermetallic phase is related to the composition: a lower molybdenum and chromium content plus a higher nitrogen plus carbon content.

The absence of chi phase in one of the alloys deserves additional comment. The presence of chi phase appears to be controlled by the molybdenum. If molybdenum is not present, chi does not form. Type 304 stainless steel, which contains no molybdenum, is an example of a steel that does not form chi phase; Type 316 stainless steel, which contains molybdenum, does form chi phase.

The presence of molybdenum is not a sufficient criterion for the formation of chi; the molybdenum activity must be sufficiently high. The activity is related, of course, to the molybdenum concentration, but also related to the presence of other elements. Chi phase does not form in any of the binary systems, Fe-Cr, Fe-Mo, or Cr-Mo (Ref. 8). It does, however, form in the Fe-Cr-Mo ternary (Ref. 9). The absence of the chi phase at the lower molybdenum concentrations in heat D1309T is in accord with the expectation that there is some molybdenum concentration below which it will not form. These experiments set limits on the concentration of Mo which is allowed in these alloys.

Despite a diligent examination no sigma phase was found in either alloy. Figure 4 gives a typical example of what was seen: a region of ferrite surrounded by carbide precipitate and austenitic matrix. The specimen is from heat D1309T, aged 10,000 h at 732°C (1350°F). An explanation for the lack of transformation by the δ-ferrite to sigma phase is provided from an analysis of the phases shown in Fig. 5.

Figure 5 shows two δ-ferrite regions in an as-cast specimen. Figure 5 (left) is the usual situation for δ-ferrite in an as-cast structure. Figure 5 (right) was an illustration of a case in which carbides had formed around the δ-ferrite very early in the aging cycle (actually during the cooling of the original sample). For this specimen, elemental analyses were performed using an energy-dispersive x-ray detector interfaced to the electron microscope (Ref. 10). These data are reported in Table 3.

In Table 3, one sees that the ferrite with no $M_{23}C_6$ around it (area D) has a high Cr/Fe intensity ratio relative to the matrix. On the other hand, ferrite which is surrounded by $M_{23}C_6$ (area A), has a lower Cr/Fe ratio. The $M_{23}C_6$ is strongly enriched in Cr and to a lesser extent in Mo. A reasonable explanation for (a) the depletion of Cr (and Mo, to a lesser extent) in the ferrite in Fig. 5 (left) and (b) the lack of the tendency for this particular alloy to form sigma from δ-ferrite is that carbide formation at the α-γ interface reduces the Cr concentration in the δ ferrite.

The chromium diffuses from the δ ferrite to the interface rather than from the austenite because the diffusivity of chromium is about two orders of magnitude faster in the ferrite than in the austenite (Ref. 11). One can set qualitative limits on compositions required to prevent the sigma formation by this mechanism. First, for a given level of ferrite one must have enough carbon plus nitrogen to reduce the chromium content to the appropriate level. Second, the δ ferrite must be narrow enough so that the chromium can diffuse to the interface before sigma phase formation begins.

Experimentally, both heats studied are sufficiently "protected" against sigma formation. The limits of this protection can be approximated. The composition of the δ ferrite observed corresponds to ~24 wt-% Cr. We have observed that, if the Cr content is reduced to ~16 wt-%, sigma phase does not form (Ref. 12). If there is ~4% δ ferrite (Table 1) in which the chromium content must be reduced from ~24 wt-% to ~16 wt-%, then one must provide at least the following to form enough $Cr_{23}C_6$:

$$4 \times (0.24\text{-}0.16)\,\frac{12}{52} \times \frac{6}{23} \text{ wt-\% carbon}$$

If one recognizes that the formula is more nearly $Cr_{16}Fe_5Mo_2(C,N)_6$ (Ref. 7), then the amount of carbon (or carbon plus nitrogen) must be increased by the factor 23/16. This would mean that about 0.028 wt-% carbon or 2.3×10^{-3} mol carbon plus nitrogen per 0.1 kg of alloy would be adequate — if all the reaction reduced the chromium in δ ferrite to the desired level. However, some additional amount would be necessary to take into account the possibility that not all would react as desired.

The argument that sigma phase can be prevented in weld metal containing δ ferrite is on a sound thermodynamic basis and is conclusive — that is, from phase diagram considerations if the chromium

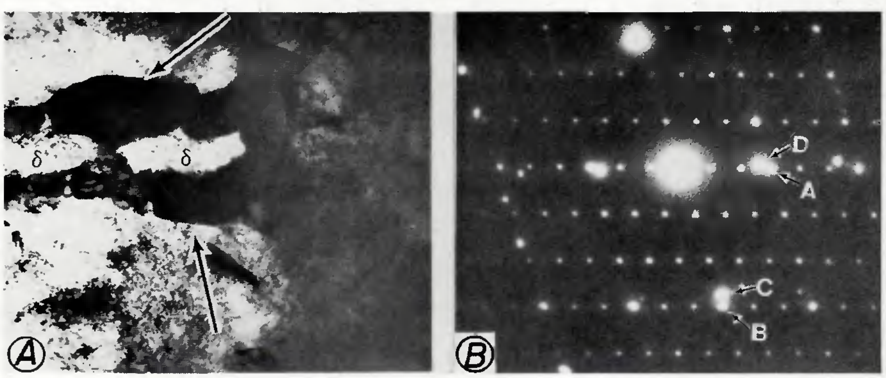

Fig. 4 — Delta ferrite region heat D1309T aged 10,000 h at 732°C (1349°F): A — arrows point to $M_{23}C_6$, which surround ferrite (δ), and matrix is austenite (γ); B — selected-area diffraction pattern. Arrows in Fig. 4B point to: A, $(200)_\gamma$; B, $(1\bar{3}1)_\gamma$; C, $(12\bar{1})_\gamma$; and D, $(\bar{1}10)_\alpha$. Poles are $(013)_\gamma$ and $(113)_\alpha$

Table 3—Intensity Ratios of Ferrite Regions in As-Cast 16-8-2 Welds[a]

Region[b]	Intensity ratio (~ atom ratio) Cr/Fe	Ni/Fe	Mo/Fe	Si/Fe
Ferrite A	0.232	0.034	0.015	0.016
$M_{23}C_6$ at B	0.551	0.075	0.035	0.010
Matrix near ferrite at C	0.248	0.10	0.010	0.019
Ferrite 2, center at D[c]	0.322	0.045	0.017	0.012
Ferrite 2, edge	0.305	0.049	0.018	0.019
Matrix near ferrite 2, at E	0.209	0.10	0.008	0.012
Matrix further from ferrite 2, at F	0.213	0.11	0.006	0.009
Bulk composition[d]	0.223	0.11	0.010	0.011

(a) Data were corrected for "in-hole" measurements (Ref. 10).
(b) Areas labelled in Fig. 5, except F which is out of the field of view.
(c) Other analyses were performed on similar areas and consistent results were obtained.
(d) Bulk composition values are given in atomic ratios.

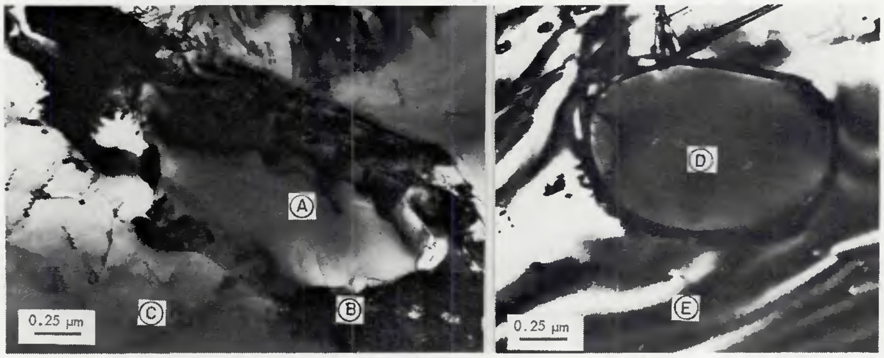

Fig. 5—Examples of δ ferrite in austenite matrix of as-cast heat D1309T. Labeled areas are: A, δ-ferrite; B, $M_{23}C_6$; C, austenitic matrix; D, center of δ-ferrite; E, austenitic matrix

content of the δ ferrite could be reduced enough then sigma phase *cannot* form. The significant point of the observation is that the assemblage can be arranged in such a way that this reduction of chromium is achieved.

In the cases examined the desired result of sigma prevention was achieved. However, in a general case one may need to pay more attention to the δ-ferrite morphology and the factors controlling it. In a real weld this may not be accomplished as readily as in our simulated welds. The amount of carbon plus nitrogen must be rather closely controlled. The limits of control attainable under present welding conditions have not been investigated extensively but there is some work which indicates suitable control may be possible (Ref. 13).

Control of the chi phase appears easier. We observe that chi phase does not form at 1.28 wt-% Mo but does at 1.64 wt-% Mo. In order to allow a margin of error, one should perhaps lower the Mo to ~1 to 1.2 wt-% in the 16-8-2 filler metal. Since the specification for 160802 filler metal is now 1.0 to 2.0 wt-%, special alloys would have to be made up to take advantage of this proposal.

It may not be out of place to comment briefly on Hull's chromium equivalent equation. He was trying to describe an embrittling tendency with a straightforward equation—which fits his data reasonably well. Within a given alloy system the error in his equation is much smaller than for the wide range of alloys covered in Hull's paper, as Hull himself recognized (Ref. 14). The reason is seen to be that different but related factors control the formation of sigma and chi phases. Thus, chromium is necessary to form both chi and sigma in such alloys as we are discussing. But the nature of the requirement differs and one equation might not be expected to cover requirements of both phases, at least over wide ranges.

Conclusions

1. The embrittling chi phase can be eliminated in 16-8-2 chill-cast structures, which have been aged up to 10,000 h at 732°C (1350°F), by reducing the molybdenum level to ~1 to 1.2 wt-%.

2. Transformation of δ ferrite to sigma phase on aging at high temperatures can be prevented by control of the carbon-plus-nitrogen content. The mechanism responsible is the removal of chromium from the δ ferrite by formation of $M_{23}C_6$ at the γ-α interface. Obviously, the amount of carbon-plus-nitrogen needed will depend not only on the amount of total chromium present but also on the distribution.

3. Control of welding parameters will be necessary to secure the necessary conditions for sigma phase prevention in actual welds. The extent of control needed is not yet known.

Acknowledgments

James Bentley provided assistance with operation of the electron microscope, particularly in securing those data in Table 3 and Fig. 5. D. P. Edmonds had aged the weld specimens prior to our examination. G. A. Potter and W. H. Smith thinned the TEM specimens. R. H. Shannon provided assistance with electrolytic extractions. S. P. Buhl typed the manuscript.

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12. The exact value of Cr is not critical to this discussion. The general problem has been investigated by many people; see, for example, J. M. Leitnaker and J. Bentley, "Precipitate Phases in Type 321 Stainless Steel after Aging 17 Years at ~600°C," *Met. Trans. 8A,* 1605 (1977).

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