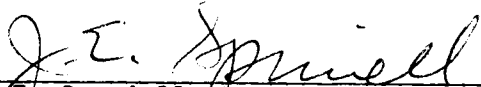


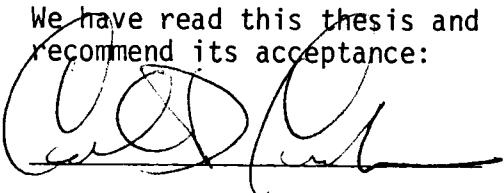
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I am submitting herewith a thesis written by Thomas Malcolm Andress, Jr., entitled "Some Aspects of the Thermal Stability of 316L Weld Metal." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Metallurgical Engineering.



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SOME ASPECTS OF THE THERMAL STABILITY OF 316L WELD METAL

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Thomas Malcolm Andress, Jr.

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DEDICATION

This thesis is dedicated to the author's parents, Mr. and Mrs. Thomas M. Andress, and to the technicians of the Chemical, Metallurgical, and Polymer Engineering Department of The University of Tennessee, Knoxville, and Oak Ridge National Laboratory, without whose advice and encouragement this work could not have been completed.

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ABSTRACT

This investigation has been concerned with some aspects of the thermal stability of the austenitic stainless steels and in particular that of 316L weld metal. Thermal stability might be considered as the ability of a material to maintain its properties after exposure to elevated temperatures. Poor thermal stability of the austenitic steels is generally linked to precipitation reactions and most often to formation of the brittle, intermetallic compound sigma phase. The thermal stability of welds is often found to be lower than that of the base metal. This effect is most often linked to the presence of ferrite in the weld deposit which greatly increases the rate of sigma formation. The presence of certain residual elements in the weld deposit is found to have major effects on the thermal stability.

This investigation was directed toward characterizing the effect of ferrite content upon the structural stability of 316L weld metal. Standard argon shielded 316L gas tungsten arc deposits contained about 5% ferrite. The addition of one volume percent nitrogen to the shielding atmosphere effectively prevented ferrite presence in the weld deposit. These two types of deposits when aged at 650°C had significantly different responses. The argon shielded-high ferrite deposit formed sigma phase, carbides, and probably austenite. The argon-nitrogen shielded deposit formed carbides with only trace amounts of sigma phase.

The effect of stress on structural stability was studied. An eight station stress-rupture laboratory was set up for stressed aging experiments. Results of this investigation indicated that stress had

no effect upon the structural changes of the standard deposits but appeared to retard carbide formation in the argon-nitrogen shielded deposits.

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CHAPTER I

INTRODUCTION

Metals Handbook (1) has noted that the most difficult material selections are for applications such as elevated temperature service in which material behavior can change with time. This problem is clearly illustrated by the stress-rupture behavior of the nickel alloy U700 (1). The 10,000 hour rupture stress for this alloy at 815°C based upon extrapolation of data for rupture times up to 1000 hours was 262 MPa (38,000 psi) whereas the actual 10,000 hour rupture stress was 145 MPa (21,000 psi)—nearly half that predicted. This reduced behavior was linked to precipitation of the brittle, intermetallic compound sigma phase. Behavior of this nature illustrates the need for determining the structural stability of a material proposed for elevated temperature service.

Structural stability falls within the province of thermal stability which might be considered as the resistance of a material to changes in mechanical properties as a result of elevated temperature exposure. Poor thermal stability in general can result in softening or embrittlement (2).

Assessment of thermal stability involves separating those conditions of service environment, operating parameters, and material treatments where adequate properties are maintained from those where properties are adversely affected. This determination is complicated by the interdependence of the variables influencing thermal stability and the large variations in service conditions and design life.

Determination of thermal stability should begin with the realization that changes in material behavior are in response to the material's tendency to come to equilibrium with the environment. Furthermore, since many of the processes by which equilibrium is attained are diffusion controlled, any effect that tends to increase atomic mobility would be expected to decrease the time for equilibrium. Some of the more important variables in this regard are temperature and gradients in composition and stress. Other variables such as grain size, segregation pattern, and dislocation density might also have important effects by offering easier nucleation sites or shorter diffusion paths and thereby change the manner or time for equilibrium. Also since the significance of any change is dependent upon the initial state, consideration must also be made of the response of various product forms such as wrought material, castings, and weld deposits.

This investigation has been concerned with some of the aspects affecting the thermal stability of the austenitic stainless steels. These alloys are often specified for use in applications such as power plants where temperatures exceed 500°C and service life is apt to be at least 25 years. Furthermore, anticipated increases in operating temperature and pressure to improve the efficiency of future plants require appreciation for the limits imposed by thermal stability. Softening in these alloys, since the only significant hardening mode is cold working, can be controlled by limiting the amount of cold work. Embrittlement which is concerned with the ability of a material to withstand shock loading is generally linked to precipitation reactions in the austenitic stainless steels (2). Embrittlement can lead to

changes in crack propagation, fracture mode, and ductility of the material. If these change significantly, unexpected failure might occur.

The following subject areas seem vital in assessing the thermal stability of the austenitic stainless steels.

1. The structural changes apt to occur—not only the final structure, but also any intermediate steps along with the mechanisms of these changes.
2. The effect of changes in service conditions or operating environment upon properties and structure.
3. A comparison of the behavior of the different product forms.
4. How the mechanical properties are affected by structural changes.
5. The effect of the thermal-mechanical history of the material.
6. The effect of compositional changes on each of the previous five areas.

Complete understanding of each of these areas should enable an accurate prediction of thermal stability.

Since welding plays a major role in the fabrication of the austenitic stainless steels, this investigation was concerned with some aspects of the thermal stability of welds. This decision is supported by the results of King et al. (3) who have indicated that weldments can be either stronger or weaker or more or less ductile than wrought material. They further noted that design practice in nuclear power plants was developed to guard against weld failure through safety factors on stress and strain and by requiring weld location in areas of

relatively low stress. This practice was attributed at least in part to lack of design information on weld behavior. A further support for selection of this area is the ASME Boiler Code (4) which allows design to be made assuming the same strength for welds and wrought material but welds are assumed to have only half the ductility of wrought material. Such arbitrary procedures indicate a definite lack of data in the area of weld metal properties and behavior.

This limited investigation was directed toward determination of the thermal stability of 316L weld deposits since this alloy is currently favored for power plant applications. Preliminary determinations of the effects of composition and service conditions on structural stability were made on welds furnished by Oak Ridge National Laboratory. Using the automatic gas tungsten arc process, two sets of welds were made. One set of welds was made using an argon shielding atmosphere and the other by shielding with an atmosphere of 1% nitrogen in argon. This procedure allowed some assessment of the effect of nitrogen content upon structural stability. The effect of service environment was investigated by comparing the structural changes due to aging under load to those occurring after aging in the absence of load. Constant load stress-rupture testing equipment was constructed for this determination.

CHAPTER II

LITERATURE REVIEW

I. THERMAL STABILITY IN THE AUSTENITIC STAINLESS STEELS

The purpose of this section is to illustrate that exposure of the austenitic stainless steels to elevated temperatures can cause reductions in their mechanical properties. This survey is not meant to be comprehensive but rather to highlight some of the more significant effects.

As pointed out in the introduction, the detrimental effects of thermal instability in the austenitic stainless steels are softening and embrittlement (2). However, since softening can be controlled by limiting the amount of cold working, the major concern is the embrittling effect of thermal instability. The importance of preventing embrittlement is in maintaining the material's ability to relieve localized stress concentrations through plastic flow rather than by crack propagation. Even the sophisticated techniques of fracture mechanics which relate load condition, material toughness, and flaw size become severely limited if material behavior changes with time. Common techniques used to assess embrittling tendency are elongation at rupture, tensile and impact tests after service exposure, and notched rupture tests (2).

One of the clearest demonstrations of the adverse effects of elevated temperature exposure on the properties of an austenitic stainless steel was reported by Joy and Nutting (5). A wrought specimen having the composition 17% Cr, 13% Ni, 2.2% Mo, 2.5% Cu, 1.0% Ti, 0.1% C, and the

balance iron after an initial treatment (half an hour at 1150°C, air cooled, three hours at 850°C, and air cooled) had a room temperature izod impact energy of 88 J (65 ft-lbs) and a room temperature tensile reduction in area of 58%. Another sample after undergoing the same initial treatment and subsequently aged four years at 700°C, however, had a room temperature izod impact energy of only 11 J (8 ft-lbs) and a room temperature tensile reduction in area of only 18%. In effect, exposing this alloy for four years at 700°C caused an 88% reduction in the energy necessary to fracture the material in the izod impact test and reduced the tensile ductility by nearly 70%—both clear indications of embrittlement. The ultimate tensile and 0.2% offset proof strengths on the other hand showed only slight increases.

Kirkly and Morley (6) investigated shearing and bending problems in 12.7 mm (0.5 in) plate of composition 0.07% C, 0.80% Si, 0.63% Mn, 18.0% Cr, 8.52% Ni, 3.22% Mo, 0.67% Ti, and the balance iron. They found that when large sections of this material were solution treated and allowed to air cool, the material had rather low ductility and fractured fairly readily with a rather laminated fracture appearance. However, laboratory size samples undergoing the same treatment had adequate ductility and ductile fracture appearances. The bulk samples after air cooling from 1050°C showed a bend ductility of only five degrees whereas the laboratory sample quenched from 1050°C had a bend ductility of 170 degrees.

In an effort to explain this phenomena, laboratory size samples were quenched from 1050°C and aged for one hour at temperatures from 500 to 1000°C. This investigation demonstrated that aging for one hour

in the temperature range from 650 to 950°C caused reductions in bend ductility with the largest effect occurring at about 800°C. After one hour at 800°C, the bend ductility was reduced from over 170 degrees to near 50 degrees. Therefore the bulk heat treatment was suggested to allow enough time in some critical temperature range for thermal instability to occur.

Hills and Harries (7) reported thermal instability in wrought 347. A solution treated sample underwent an 18% reduction in tensile elongation, a 23% reduction in tensile reduction in area, and a 72% reduction in room temperature charpy vee notch impact energy after exposure to 650°C for 7.5 years.

Lena (8) has reported thermal instability in wrought 310 stainless steel. He noted that exposing this material at 760°C for 1000 hours reduced the impact strength by 88%, reduced the tensile elongation by nearly 36%, but had essentially no effect on tensile strength. Lena (8) further reported that an 18% Cr, 8% Ni, 3% Mo, 1% Ti wrought alloy underwent a severe decrease in bend ductility and impact strength after aging at 760°C.

In an effort to determine the effect of composition on thermal instability in wrought alloys, Foley and Krivobok (9) aged a series of alloys having compositions from 30 to 35% Ni, 25 to 35% Cr, 0.05% C 1.9% Mn, 0.07% Si, and the balance iron at from 649 to 899°C. The amount of reduction in room temperature toughness was found to depend upon the composition of the specimen. Generally, those specimens with the highest nickel contents and the lowest chromium contents showed the least amount of reduction in toughness. Furthermore, the amount of

reduction in toughness for a given composition was found to depend upon the aging temperature with an intermediate temperature showing the largest effect. A comparison of changes in toughness after aging 100 hours to those after aging 3000 hours showed that the increase in aging time caused a more severe decrease in toughness and also broadened the composition range where severe embrittlement occurred.

Thermal instability of a cast austenitic stainless steel was reported by Blower and Cox (10). As-cast specimens of composition 0.024% C, 2.13% Si, 1.72% Mn, 0.01% S, 0.008% P, 25.7% Cr, and 22.8% Ni, 0.016% N, and the balance iron had unnotched room temperature impact energies from 20 to 43 J (15 to 32 ft-lbs). However, after aging samples of this material for 4000 hours at 800°C, the impact energies were reduced to between 3.4 and 4.1 J (2.5 and 3 ft-lbs).

Thermal instability of weld deposits was reported by Creamer et al. (11). They found that 347 shielded metal arc deposits in the as-welded condition had charpy impact energies of 67.8 J (50 ft-lbs) below -18°C, but that a three-month exposure at 727°C required a testing temperature of 538°C for the charpy impact energy to exceed 27 J (20 ft-lbs). In effect, the transition temperature was shifted some 550 degrees.

Further examples of weld thermal instability were reported by Willingham and Gooch (12). They collated work on the effect of aging 308, 309, 310, 316, 321, and 347 weld metal at various temperatures for various times on impact behavior. Plots of aging temperature for a reduction in impact energy of 50 and 80% versus aging time for each of these alloys took the form of C curves with the most rapid effect at

some intermediate temperature. Also of note was that the time and temperature for the most significant effect were dependent upon the composition of the material. For example, type 321 weld metal was most rapidly embrittled at 650°C with a 50% reduction in impact energy at from 200 to 800 hours whereas type 316 weld metal showed most rapid embrittlement at 850°C in two to seven hours.

The effect of thermal instability on creep behavior is seen in the work of Cullen and Davis (13). Creep test curves of wrought 316 stainless steel containing 0.070 and 0.099% nitrogen at 649 and 704°C showed distinct breaks in plots of stress versus logarithm of rupture time. Similar results for wrought 304 were reported by Wilson (14). This type of behavior is similar to that of U700 discussed in the introduction.

The role of composition in stress-rupture behavior is illustrated by the work of Okane and Osumi (15). In stress-rupture testing of transverse sections of weldments in 304 and 316, they found that the two materials had similar properties at 600°C but that the 316 samples were significantly weaker than the 304 samples at 700°C.

Another example of the effect of thermal instability on creep behavior in weld deposits is seen in the work of King et al. (16). The general result of creep testing of 308 weld deposits was that the longer the rupture life, the lower the rupture ductility. This is contrary to the expected phenomena where longer rupture times would allow more plastic deformation by allowing more time for diffusional processes.

In summary, exposure of the austenitic stainless steels to elevated temperatures can lead to significant changes in mechanical

properties. These effects have been seen in wrought materials, castings, and weld deposits. The most severely affected property is toughness with smaller reductions seen in tensile reduction in area and elongation. Bend ductility can also be affected. Generally, yield and tensile strengths are found to be only slightly increased. Rupture ductility in stress-rupture testing can become severely reduced in long term tests. The magnitude of each of these effects is found to depend upon composition, exposure temperature, and time of exposure.

II. EXPLANATIONS FOR REDUCED BEHAVIOR

Changes in mechanical behavior of the austenitic stainless steels after exposure to elevated temperatures have often been linked to precipitation reactions and in particular to formation of the brittle, intermetallic compound sigma phase (2). In fact, all of the results given in the previous discussion were linked to precipitation reactions. Some reductions were attributed to carbide precipitation but these effects are generally much less severe than those caused by sigma formation.

Sigma phase formation appears to have its largest effect upon notch toughness and ductility (8). Although sigma is very hard (Rockwell C 68), its presence does not greatly increase the hardness of the material (8). Tensile proof stress and ultimate tensile strengths are most often unaffected or only slightly increased by sigma precipitation (8).

Several investigations have indicated that the largest amount of embrittlement occurred when the largest amount of sigma was present

(5,6,9,17). This result is normally found in cases where impact energy is measured against aging time or aging temperature. For example, Creamer et al. (11) found that a 347 weld deposit when exposed for three months at 593°C formed about 5% sigma and gave an impact value of 39.8 J (22 ft-lbs). Other samples aged at 727°C for the same time produced nearly 19% sigma and further reduced impact energies to 2.7 J (2 ft-lbs). Similarly, Joy and Nutting (5) found that after one year at 700°C during which sigma phase had formed at grain boundaries, the izod impact toughness had been reduced from 88 J (65 ft-lbs) to 29.8 J (22 ft-lbs). However, after aging for four years at 700°C during which sigma particles had coarsened, the izod impact energy was further reduced to 10.8 J (8 ft-lbs). Henry et al. (17) also verified the relationship between the amount of sigma phase and the degree of embrittlement. They exposed samples of AISI 310, 321, and 347 austenitic stainless steel at 649, 732, and 843°C for 1500 hours and found that although the temperature at which maximum sigma phase precipitation occurred depended upon the particular alloy, the largest amount of embrittlement occurred when the largest amount of sigma phase was present.

Lena (8), however, pointed out that the effect of sigma phase on mechanical properties is dependent not only upon the amount present but also upon the particle size and distribution. Similarly, Hills and Harries (7) noted that the extent of room temperature embrittlement was related to the amount of sigma along with its distribution which was closely linked to grain size. They reported that sigma phase in fine grained 25% Cr, 20% Ni steel precipitated as massive grain boundary particles. Coarse grained samples of the same material, however,

precipitated sigma phase as a semicontinuous grain boundary film for sigma contents less than 5% and showed a much larger degree of embrittlement than fine grained samples. Foley and Krivolok (9) also pointed out that the large scatter in impact strength versus percent sigma at low sigma contents indicated that location of sigma particles may have an influence additive to the actual amount. Creamer et al. (11) have summarized the effect of sigma phase by noting that the degree of embrittlement is related to both the concentration and distribution with a greater degree of embrittlement when sigma is present as a continuous grain boundary film rather than as random equiaxed particles.

Austenitic stainless steels containing sigma phase have been found to retain some ductility at elevated temperatures (8). Willingham and Gooch (12) have noted that the effect of sigma phase becomes evident at temperatures below 200°C.

Sigma phase can also change the fracture mode. Joy and Nutting (5) found that their material in the unaged condition showed in both tensile and impact room temperature tests a ductile fracture surface with titanium cyanonitride particles acting as dimple nuclei. Upon aging the fracture mode changed to intergranular but was still ductile with sigma particles acting as dimple nuclei and decohesion occurring at austenite-sigma interfaces. When the particles achieved a size greater than about two micrometers in length and 20 micrometers in thickness, the fracture mode changed to brittle fracture through the sigma phase. The initial high izod impact energy of 88 J (65 ft-lbs) was reduced to about 27 J (20 ft-lbs) upon changing to the intergranular mode and to about 6.8 J (5 ft-lbs) when changing to the brittle mode.

Hull (18) has noted that the purpose of limiting sigma formation is to protect equipment against fissuring during repair welding or cracking due to thermal shock or mechanical impact when components are cooled down after elevated temperature exposure. Hills and Harries (7) in this regard have noted that a 26% Cr, 12% Ni alloy containing sigma and carbides could only sustain 161 cycles of rapid heating to 870°C followed by rapid cooling before splitting into several pieces. The same alloy containing only carbides underwent 472 cycles without cracking.

Another important consideration when using the austenitic stainless steels at elevated temperatures is the effect of structural changes upon creep-rupture behavior. Hills and Harries (7) have noted that for low stress states (long rupture times), a decrease in creep strength is associated with the presence of sigma phase. They further reported that initial precipitation of sigma phase in an 18% Cr, 8% Ni stainless steel resulted in an improvement in creep strength but that the subsequent growth of sigma phase had a detrimental effect on rupture behavior. Similar results have been reported by Lena (8).

In an effort to determine the mechanism of fracture and the criteria governing the final fracture stage, Morris (19) performed a number of creep-rupture tests on wrought 316 at 625°C. Failure was found to occur after the formation of triple point wedge cracks by intragranular tearing of the regions between the cracks. For grain sizes less than 25 micrometers, there was a low density of cracks with failure occurring when the work hardening capacity of the ligaments between the cracks was exceeded. In larger grain sizes, a larger number

of wedge cracks was observed with final fracture occurring after a certain amount of crack extension.

Second phase particles could have the following effects upon fracture: to hinder or permit grain boundary sliding, affect crack nucleation, allow easier crack growth, restrict grain deformation and thereby restrict stress relaxation, and to harden grain interiors and thereby force more grain boundary sliding (19). In examining ruptured samples, a very dense distribution of grain boundary particles was observed in all samples, no evidence of grain boundary migration was observed, and no link was seen between the amount of precipitation and crack density. Morris (19) noted that cracking could occur relatively easily at suitably aligned triple points and made the conclusion that crack formation was based mainly upon grain boundary geometry. He suggested that crack growth could occur by particle cracking or particle-interface decohesion for intermetallic particles but noted that such behavior was unlikely for carbide precipitation.

Morris (19) distinguished four effects of second phase particles occurring in different time intervals. During the first time interval (rupture time less than 10 hours), only carbides were observed. The density of intragranular carbides was very low resulting in relatively soft grain interiors so that extensive stress relaxation could occur. This distribution of carbide particles requires high stress intensities to cause failure resulting in large fracture stresses and high ductilities. Crack aspect ratios are relatively low due to the difficulty of crack propagation. In the second stage (rupture lives of from 20 to 30 hours), the greater density of intragranular particles

makes stress relaxation more difficult causing a decrease in the stress required for crack propagation. This results in lower ductility fracture and larger crack aspect ratios. Still longer times (rupture times from 30 to 1000 hours) caused particle coarsening which allowed stress relaxation capability to return. This resulted in greater rupture ductility and lower crack aspect ratios. For the longest rupture times (greater than 1000 hours), intermetallic phases were observed in the grain boundaries. These particles did not appear to affect crack nucleation but crack growth was suggested to be somewhat easier due to matrix-interface decohesion. Morris suggested that the effect of intermetallic phases in making crack growth easier was to decrease the stress concentration necessary for crack propagation thereby resulting in lower ductility failures.

Weaver (20) in creep-rupture testing of Nimonic 80A found that specimens containing large particles of carbide in the grain boundaries had higher elongations and longer rupture lives than samples with intra-granular carbide distributions. He suggested that the presence of large carbide particles in the grain boundaries served to nucleate cavities but also to restrict them to inter-carbide spaces. This in effect blunts cracks and allows more grain boundary sliding prior to the link up of cracks to cause the final fracture. This process by limiting crack propagation increases the time to rupture. This serration of the grain boundaries by the semicoherent nature of carbide precipitation in Nimonic 80A might also be expected in the austenitic stainless steels.

Creep properties of austenitic stainless steel weld deposits are complicated by the presence of intergranular delta ferrite which

decomposes at least in part to sigma phase during the course of the test. Fractographic analysis of creep-rupture specimens of 308 shielded metal arc deposits has revealed extensive cracking at austenitic-sigma interfaces with final fracture occurring by ductile tearing between these cracks (21). Stiegler et al. (21) have suggested that when enough cracks are formed, the reduction in cross section increases the stress on the remaining material resulting in a shear failure. Standard 308 weld deposits had rapid sigma formation so that matrix-particle decohesion occurred fairly early resulting in little elongation or reduction in area. Higher as-welded ferrite contents resulted in more nearly continuous sigma distributions which provided longer interphase boundaries and therefore longer crack paths. Loss of ductility was related to the time required to form sigma and the amount and distribution of ferrite in the as-welded deposit.

III. ELEVATED TEMPERATURE PHASE TRANSFORMATIONS

The previous section has demonstrated that structural changes occurring during elevated temperature exposure can lead to degradation of properties. This section is directed toward a more thorough description of these changes and the variables governing their occurrence with special emphasis on the aging response of 316. This survey will describe the phases observed after elevated temperature exposure and the general conditions for their formation.

The phases most commonly observed are intermetallic compounds and carbides. The phases present, their morphologies, the rates of transformation, the reaction sequences, and the transformation

mechanisms are found to depend upon variables such as composition, product form, thermal-mechanical history, and exposure temperature.

A. Sigma Phase

The most frequently discussed intermetallic compound in the austenitic stainless steels is sigma phase. This compound is normally described as having a tetragonal crystal structure with thirty atoms per unit cell and a c over a ratio of 0.52 (22). The atoms in this structure are distributed over five types of sites with coordination numbers ranging from twelve to fifteen (22).

Hall and Algie (22) have reported that binary sigma phase formation tends to occur when one element is from group VA or VIA of the periodic table with the other from either the first, second, or third long period. This criteria was found to hold for all but seven of 53 binary sigma phases. The electron to atom ratios for these compounds were found to vary from 5.6 to 7.6. The atomic radii ratios and the exchange factors (difference in atomic radius divided by the larger atomic radius) showed little consistency other than a maximum exchange factor of 13%. They further suggested that ordering occurred in sigma phase in which the smaller atomic species occupy those sites with the smallest coordination numbers.

These compounds do not have definite stoichiometry but rather show a range of compositions. For example, sigma in the iron-chromium binary system is found from 46 to 52 atomic percent chromium (22).

Ternary sigma phases are suggested to be electron compounds with approximately constant electron to atom ratios (6.2 to 7.2). Hall and Algie (22) reported one quaternary having a composition of 35 weight

percent chromium, 25 weight percent molybdenum, and 15 weight percent nickel.

Weiss and Stickler (23) used energy dispersive x-ray analysis to determine the composition of sigma phase in wrought 316 stainless steel. They reported a composition of 55% iron, 29% chromium, 11% molybdenum, and 5% nickel. A formula for this sigma phase was given as $(\text{Fe,Ni})_x(\text{Cr,Mo})_y$.

Lena (8) has suggested that essentially all the AISI steels with chromium contents greater than 17% are capable of forming sigma phase. Hall and Algie (22) noted that if the iron, chromium, and nickel contents of the AISI stainless steels are plotted on the Fe-Cr-Ni phase diagram, the majority of the austenitic stainless steels fall in the austenite and sigma phase area. Hills and Harries (7) have suggested that variations within the compositional specifications and the presence of normal amounts of steel making inclusions allow sigma formation in the majority of the austenitic stainless steels.

Composition appears to be the prime factor in sigma formation with other variables influencing the kinetics or morphology of precipitation. Creamer et al. (11) have suggested that alloying elements can promote sigma phase formation through their effect on ferrite formation since sigma is found to form more rapidly from ferrite. Those elements which are termed ferrite formers such as chromium, silicon, molybdenum, aluminum, tungsten, vanadium, and niobium promote sigma phase (7). Those elements classed as austenite stabilizers such as carbon, nitrogen, nickel, and manganese generally retard sigma formation (7). Foley and Krivobok (9) have suggested that carbon

and nitrogen retard sigma formation by either stabilizing austenite or by tying up those elements which would normally form sigma phase in carbo-nitrides.

The large number of components, the complicity of phase relationships, and the sluggishness of sigma formation in many instances have prohibited comprehensive phase diagram determinations for the austenitic stainless steels. A number of empirical relations have been developed in an effort to overcome these limitations. Two of the more prominent methods for predicting sigma phase formation are Phacomp (24) and Hull's equivalent chromium method (18).

The Phacomp sigma prediction method is based upon the idea that sigma formation is the result of electron vacancies in the 3d subshell (24). Each atomic species in an alloy is assigned a certain number of electron vacancies based upon its behavior in other systems. An average electron vacancy number is calculated for the alloy by multiplying the electron vacancy number for each atomic species by its mole fraction and summing the products. If the average electron vacancy number exceeds some empirically determined value, then sigma phase is predicted in the alloy.

Bagnall and Shiels (25) have reported the results of applying one form of the Phacomp technique to 304 and 316. This formulation predicted a higher sigma formation tendency in 304 than in 316. However, experimental evidence indicated that the reverse occurred. Bagnall and Shiels (25) suggested this result indicated that incorrect allowances or assumptions were made for these compositions or that important partitioning influences or minor alloying elements such as

silicon should be factored into these calculations. They discounted the possibility that reaction kinetics could explain this result. However, sigma phase, as predicted by Phacomp, was observed in both alloys.

Hull's equivalent chromium method (18) was developed through multiple regression analysis of the impact behavior of aged samples with variations in 15 alloying elements. Embrittlement was suggested to be primarily due to precipitation of the brittle, intermetallic compounds sigma and chi.

Specimens were made from high purity raw materials by levitation melting. After melting and a certain amount of induction stirring, the samples were cast as tapered pins approximately 50.8 mm (2 in) long and 6.4 mm (0.25 in) in diameter.

Impact testing was performed using a pendulum instrument with an energy of two joules (1.5 ft-lbs) on samples with hacksaw cuts half way through the diameter of the sample. The samples were restruck until either fracture occurred or the sample bent 90 degrees. Specimens were tested in the as-cast condition and after aging 17, 100, and 1000 hours at 816°C.

The effects of the various elements were summarized by linear regression analysis of the logarithm of the bend angle versus composition. The ratio of this coefficient for a given element to the coefficient for chromium gave the chromium equivalent for the particular element. A final expression was developed for each aging condition which consisted of the sums of the coefficients times the weight percentage of each of the particular alloying elements. This allowed

conversion of the nominal composition to its effective chromium content. The general result was that the higher the equivalent chromium content, the greater the possibility of embrittlement.

Hull (18) noted that the equivalent chromium content of an alloy provides a semiquantitative relationship between embrittling tendency and composition. He suggested that this method could be used to estimate the expected behavior of an existing material or to balance the composition of a proposed alloy to achieve a desired result.

Sigma formation demonstrates C type reaction kinetics indicating a nucleation and growth transformation mode (6,7,8,11,23). The reaction has been observed at temperatures from 450 to 970°C with the temperature range and temperature for most rapid rate of transformation dependent upon the composition of the particular alloy.

Weiss and Stickler (23) have reported that sigma nucleation always required high energy interfaces in wrought 316 and 316L. They observed sigma precipitation first at grain boundary triple points, next at grain boundaries, then on incoherent twin boundaries, and finally intragranularly with sigma nucleating on oxide particles.

Spruiell et al. (26) noted that even in cold deformed material, sigma phase was observed to nucleate solely at high energy interfaces such as grain boundaries and particularly at grain boundary triple points.

Blenkinsop and Nutting (27) noted that favored sites for sigma precipitation were austenitic grain boundary triple points.

Further support for the heterogeneous nucleation of sigma phase is seen in the work of Duhaj et al. (29). A single crystal of 25% Cr-25% Ni steel did not form sigma phase when aged 6500 hours at 800°C,

whereas another crystal that had been deformed prior to aging formed sigma phase after 2000 hours at 800°C with sigma forming on recrystallized austenite grain boundary triple points and twin boundary-grain boundary intersections.

After long aging times, Weiss and Stickler (23) observed sigma phase present as massive grain boundary particles and as bulky intragranular particles with long needle-like shapes.

Blenkinsop and Nutting (27) observed a general trend for sigma phase to grow along austenite grain boundaries rather than into the grains.

Higher solution treating temperatures prior to aging are found to retard sigma formation. Weiss and Stickler (23) have suggested that this effect is due to larger grain sizes and the associated longer diffusion paths. Hills and Harries (7) have pointed out that the distribution of sigma formed at 800°C in a 25% Cr-20% Ni steel was considerably influenced by prior heat treatment only insofar as its effect on grain size. They reported that after 500 hours at 800°C, coarse grained material had only started to form sigma phase whereas fine grained material had almost the equilibrium sigma content. A sample that had undergone an 1150°C solution treatment prior to aging was found to require 72 hours at 800°C for sigma initiation whereas a sample solution treated at 1050°C only required 24 hours at this temperature for sigma precipitation. Sigma phase in fine grained material was in the form of granular or equiaxed particles on grain boundaries especially at triple points. Coarse grained material, however, had sigma phase present as grain boundary films and as plate-like intragranular Widmanstatten lathes.

Spruiell et al. (26) have suggested that the manner in which a particular grain size was obtained had a more significant effect than just the final grain size. They found that a sample which had been pulse heated prior to aging to form a fine grain size did not form sigma phase during the span of their investigation unless the material had been cold worked prior to aging. Material that had a fine grain size as a result of repeated cold working and annealing treatments, however, formed sigma phase rapidly. Spruiell et al. (26) suggested that the explanation for this difference was due either to the cold working-annealing treatments providing ready sites for sigma nuclei or that sigma nuclei were already present in the material after the treatments prior to aging.

Plastic deformation prior to aging is also found to have a significant effect upon the kinetics of sigma precipitation. Foley and Krivobok (9) have reported that in aging a series of austenitic stainless steels at 649°C, the samples cold worked 23% prior to aging formed about seven times more sigma phase in 3000 hours than those samples that had not been cold worked prior to aging. Furthermore, the compositional range for sigma phase formation was broader in the cold worked material than in the unworked material. However, samples in both conditions aged for 3000 hours at either 801 or 871°C did not show these effects. Hills and Harries (7) also observed that sigma phase formed more rapidly and over a wider compositional range in cold worked than in annealed material. They suggested a recrystallization transformation in which strained austenite of one composition upon recrystallization transforms into sigma phase and austenite of a

different composition. They observed that cold work had little effect on sigma formation unless recrystallization occurred. Weiss and Stickler (23) also observed that the number of sigma particles was increased by prior cold work in 316 and 316L, but only if recrystallization occurred. Similarly, Spruiell et al. (26) noted that cold work accelerated sigma precipitation in wrought 316 with sigma precipitation especially enhanced if recrystallization occurred during aging. They further noted that the first observation of sigma phase occurred at the onset of recrystallization and reported that cold worked material that did not recrystallize did not form sigma phase. A similar observation was made by Singhal and Martin (28) in a 24% Ni-25% Cr alloy. They reported that small amounts of cold work (less than the amount necessary for recrystallization) retarded the nucleation and growth of sigma.

Blenkinsop and Nutting (27) observed that as little as 10% cold work resulted in the formation of hexagonal martensite in wrought 316L. The presence of this phase was found to promote intragranular sigma formation and to retard intergranular precipitation. Increased amounts of cold work promoted more intragranular precipitation and further retarded grain boundary precipitation. However, if recrystallization occurred during aging, the growth of intragranular sigma phase appeared to be arrested as the boundaries of the new austenitic grains provided more favorable sites for sigma formation. Longer times at temperature after recrystallization had started were observed to cause resolution of the intragranular sigma particles with growth of the intergranular particles.

Another important consideration in sigma formation is the relationship between carbide precipitation and sigma formation. Weiss

and Stickler (23) have reported that scanning electron microscopic spectrographic studies of wrought 316 indicated that depending upon the aging temperature, sigma forms either on previous carbide sites or grows on carbide particles that are dissolving. However, at the lower levels of temperature for sigma formation, sigma was found to nucleate on grain boundary triple points without any indication of prior carbide formation. Weiss and Stickler (23) have suggested that lowering of the carbon content of the matrix by carbide precipitation promotes the formation of various intermetallic compounds which deplete the austenite in chromium and molybdenum. Since the carbon solubility of the matrix is increased by lowering its chromium and molybdenum contents, carbides formed earlier tend to go back into solution. However, the greater diffusivity of carbon leaves areas behind which are rich in chromium and molybdenum and which can act as nucleation sites for intermetallic compound formation.

Ivanov and Petrov (30) have suggested that in a duplex (austenite-ferrite) matrix, sigma nuclei form on carbide particles at the same time that the carbides go back into solution. They observed that the quantity of carbide initially increased during aging but later decreased with the simultaneous increase in the amount of sigma phase. They also noted that sigma formed earlier at interfaces that had initially contained carbide and that the alloy content of carbide at the time of sigma formation was approximately the same as that of sigma phase. They suggested that when carbides dissociate, the greater diffusivity of carbon results in conditions favorable for sigma formation due to the enrichment of these areas in elements that promote

sigma formation. This concentrating effect was further suggested to retard sigma formation in other areas. Ivanov and Petrov (30) suggested that the original ferrite upon aging decomposed into carbide and ferrite lower in sigma forming elements. With longer aging the carbides lose carbon and transform to sigma phase. The lower alloyed ferrite was suggested to pickup carbon and form austenite.

Bagnall and Shiels (25) have also reported a relationship between carbide and sigma phase. They observed that in wrought 304, massive sigma particles formed at grain boundary triple points after aging at 732°C and noted that these locations were chromium rich and ferritic once the metastable carbides originally present had decomposed. They observed that carbides nucleated and grew mainly on grain boundaries and that after relatively long times and dependent upon the carbon content the carbides decomposed. Prior to the decomposition, the amount of intragranular carbide precipitation had been rather small but upon decomposition of grain boundary carbides, tended to increase in areas adjacent to the grain boundaries. Bagnall and Shiels (25) suggested that the carbides had acted as chromium collectors at prime nucleation sites for sigma formation and that as a result of this process, sigma formation was promoted by higher carbon contents. They suggested that in 316, molybdenum aids in carbide formation so that higher carbon contents would lead to a more uniform distribution of carbide particles thereby decreasing the concentrating effect of alloying elements at grain boundaries. Although sigma phase was still observed, it was suppressed by higher carbon contents and appeared as smaller more numerous particles than those in 304.

Singhal and Martin (31) observed ferrite as an intermediate product in sigma formation in a 24% Ni, 25% Cr steel. They reported that carbide and chromium oxide particles acted as intergranular nucleation sites for ferrite. However, since no intragranular carbide precipitation was observed but copious amounts of intragranular sigma and ferrite were observed, they suggested that prior precipitation of carbide was not essential for sigma precipitation. They further noted that since precipitation of grain boundary ferrite took nearly 150 hours but intragranular ferrite formation took only 25 hours, carbide precipitation tended to retard ferrite formation. They suggested this was the result of carbide tying up chromium and iron necessary for ferrite and sigma formation. Further aging resulted in ferrite growth which eventually lead to carbide resolution.

In investigating the structural stability of a 21.1% Cr, 24.4% Ni steel, Singhal and Martin (31) observed that grain boundary $M_{23}C_6$ carbides were generally replaced by TiC carbides which later transformed to gamma prime and a hexagonal close packed Ni_3Ti . Sigma phase was observed to form after long aging times as large, irregular shaped particles. They suggested that grain boundary sigma phase could be interpreted in terms of the effect of titanium upon the effective chromium content. Alloys without titanium did not form sigma phase but did form $M_{23}C_6$. An 0.6% titanium alloy formed small amounts of sigma phase associated with the dissolution of $M_{23}C_6$ and precipitation of TiC. In the 1.34% titanium alloy, grain boundary TiC which replaced $M_{23}C_6$ and intragranular gamma prime both increased the proportion of chromium in the matrix thereby promoting sigma formation.

Sigma formation is found to be more rapid in alloys containing ferrite than those consisting solely of austenite (7). This phenomenon appears to be the result of a concentration of those elements that promote sigma formation in the ferrite. Omsen and Eliassom (32) have reported that ferrite contains 110% of the chromium and 142% of the molybdenum that austenite contains in 316L castings. Daemen and Dept (33) have reported that microprobe analysis of 316L weld deposits indicated an enrichment in chromium of 126% and an enrichment in molybdenum of 200% in the ferrite over the nominal composition of the alloy. Gray et al. (34) have reported that microprobe analysis of ferrite particles in wrought 304 plate had 134% higher chromium concentration than the austenitic matrix. Similarly, those elements which retard sigma formation are found in lower concentrations in ferrite than in austenite. Daemen and Dept (33) observed sigma formation from ferrite in 316L welds in from one to two minutes at 850°C. However, Weiss and Stickler (23) did not observe sigma phase until after 10 hours at 850°C in initially fully austenitic wrought 316L.

Kirkby and Morley (6) investigated the aging response of a wrought duplex (ferrite and austenite) steel of composition 0.07% C, 0.8% Si, 0.63% Mn, 18.0% Cr, 8.52% Ni, 3.22% Mo, and 0.67% Ti. The material quenched from 1050°C consisted of equal amounts of ferrite and austenite. Upon aging the material for one hour at temperatures from 600 to 950°C, the ferrite was observed to decompose into sigma and carbide with some retained ferrite. The reaction occurred most rapidly at 850°C—starting within two minutes. Transformation of the ferrite began at ferrite boundaries and then grew into the ferrite.

Kirkby and Morley (6) suggested that the ultimate products of ferrite decomposition were sigma phase and austenite. This conclusion was supported by the observation that after aging, less sigma phase was present than the initial amount of ferrite and that chemical analysis of bulk extractions indicated that sigma had higher chromium, molybdenum, and iron contents than those of ferrite. They further suggested that the austenite formed from ferrite decomposition had a different composition from the original austenite which led to a difference in etching behavior. After long aging times, this effect was no longer present suggesting a smoothing out of the compositional gradients in the austenite. Longer aging times caused spheroidization of the sigma phase.

Gray et al. (34) observed a similar phenomena in wrought 304 containing ferrite stringers. They suggested that the higher chromium content of sigma phase relative to that of ferrite reduced the composition of the remaining ferrite to a level where austenite formed. When aged at temperatures from 593 to 649°C, the transformation was fairly rapid with austenite and sigma phase appearing to form on the same habit plane in the ferrite.

Steigler et al. (21) have reported that after 100 hours at 650°C, 308 shielded metal arc weld deposits which initially contained from 5 to 8% ferrite contained sigma phase. The rate of transformation of ferrite to sigma phase was found to vary greatly from weld to weld and from position to position within any given weld. Sigma formation occurred in patches which initially maintained the ferrite morphology but with longer aging times tended to spheroidize. After 1300 hours at 650°C, only small untransformed regions were observed.

Daemen and Dept (33) also observed a patch-like ferrite to sigma transformation in weld deposits. In investigating compositions of various areas in 316L weld deposits, they found that although the iron and chromium contents of the ferrite particles were fairly uniform, the molybdenum contents showed substantial scatter. Since molybdenum greatly promotes sigma phase, they suggested that the transformation was initiated first in those areas with the highest molybdenum contents.

Scott and Spruiell (35) have investigated the effect of prior plastic deformation on the aging kinetics of 316 and 16-8-2 weld deposits containing ferrite. They observed that cold working prior to aging changed the morphology of intermetallic compound precipitation but not the amount or rate of precipitation. They reported that two intermetallics (sigma and chi) formed and that cold work appeared to suppress chi phase in favor of sigma phase.

Cole et al. (36) reported that weld substructure size affected the response to heat treatment of 308 weld deposits. They noted that finer ferrite substructures were more easily redissolved by solution annealing than coarser substructures and that coarser ferrite structures formed sigma phase sooner and in larger amounts than finer substructures.

Ferrite has been observed as an intermediate phase in sigma formation in wrought 24% Ni, 25% Cr steel (31). Ferrite which precipitated within the grains and at the grain boundaries during the initial stages of aging was eventually transformed into sigma phase.

Intragranular ferrite precipitation began after 25 hours at 750°C and after 500 hours was distributed as a Widmanstätten precipitate.

After 1000 hours at 750°C, intragranular sigma phase was observed growing parallel to the ferrite particles. Upon aging for longer times, the sigma particles thickened preferentially in regions close to the adjacent ferrite particles and eventually consumed them.

Ferrite precipitation on incoherent twin boundaries and grain boundaries was not observed until 150 hours at 750°C. This delay was suggested to be due to precipitation of carbides. With longer aging times, the carbides dissolved and were replaced by ferrite. Sigma phase which eventually replaced the ferrite consisted of large particles of irregular shape.

Singhal and Martin (31) have suggested that since no sigma precipitation was observed on existing dislocations or residual particles and that since sigma initially had similar shapes and growth directions as those of ferrite, that sigma formation occurred by an in situ transformation of ferrite. They have pointed out that no direct evidence of this was seen but that since both ferrite and sigma consist mainly of chromium and iron, once a nucleus was formed, transformation would be very rapid and as a result, the possibility of observing a partially transformed ferrite particle would be slight.

White and LeMay (37) have also observed ferrite formation during aging studies. They reported that wrought 316 aged at 800°C formed ferrite particles on grain boundaries after 70 hours which during longer aging grew at the expense of carbides which had precipitated before the ferrite. After 2000 hours, sigma particles were observed nucleating on ferrite-austenite interfaces. Eventually all the ferrite was consumed.

White and LeMay (37) have suggested that ferrite is not a transition phase in sigma formation because sigma phase was also observed to form directly from austenite in intragranular locations. The rate of sigma phase formation at intragranular sites was much more rapid than at grain boundary locations.

B. Laves Phase

Laves phase in 316 is observed to have a hexagonal crystal structure and is represented by the formula Fe_2Mo (23). Weiss and Stickler (23) reported that a scanning electron microscope x-ray analysis of a Laves particle indicated a molybdenum content of 45%, a chromium content of 11%, an iron content of 38%, and a nickel content of 6%. Wallwork and Croll (38) have reported a general formula for Laves phase as $(\text{Fe},\text{Ni},\text{Cr})_2\text{Mo}$.

Binary Laves phases are found to exist between atoms having elemental radius ratios between 1.10 and 1.46 (38). Laves is not observed if the average electron concentration is equal to or greater than eight. These two considerations appear to dictate whether or not Laves will be present.

Weiss and Stickler (23) observed Laves phase in 316 at temperatures from about 450 to 815°C. The phase formed as intragranular equiaxed particles or as clusters of particles and was only occasionally seen at grain boundary locations.

Spruiell et al. (26) observed Laves phase in 316 as elongated plate-like particles on deformation bands and as globular particles along grain and twin boundaries.

Higher solution treating temperatures were found to cause greater Laves precipitation, but only after longer aging times (23). Higher carbon contents were found to retard Laves formation (23).

Cold work appeared to accelerate Laves precipitation (23). Spruiell et al. (26) observed that larger amounts of Laves were formed in 316 with increased amounts of cold work only if recrystallization did not occur. If the material recrystallized, Laves particles appeared more equiaxed and less plentiful indicating resolution might be taking place at the recrystallizing interfaces.

C. Chi Phase

Chi phase is normally described as having a body centered cubic crystal structure isomorphous with alpha manganese (39). Weiss and Stickler (23) have reported that an energy dispersive x-ray analysis indicated a 22% molybdenum, 21% chromium, 52% iron, and 5% nickel compound. Suggested formulas for chi phase are $(\text{FeNi})_{36}\text{Cr}_{18}\text{Mo}_4$ and $\text{Fe}_{36}\text{Cr}_{12}\text{Mo}_{10}$ (23). Chi phase has also been suggested as being an M_{18}C type carbide (23). Deighton (40) reported that a small amount of chi phase was observed in 316 samples aged at from 900 to 1000°C as the carbon content was increased from 50 to 1000 parts per million.

Seventeen binary chi phases have been reported having the general formula $\text{A}_{10}\text{B}_{48}$ (38). The electron to atom ratios for these compounds were from 6.3 to 7.6 (38).

Six ternary chi phases were given (38). The ternary chi phases appear to occur by the B atomic species being replaced by two atomic species. The electron to atom ratios for these phases varied from 6.3 to 7.6 and the ratios of atomic radii from 1.03 to 1.15 (38).

Weiss and Stickler (23) observed chi phase precipitation at temperatures from 700 to 900°C with the reaction exhibiting C type reaction kinetics and the temperature for most rapid rate of transformation about 850°C. Precipitation occurred first at grain boundaries, next on incoherent twin boundaries, and finally intragranularly.

Koh (39) observed chi phase formation in the temperature range from 760 to 982°C with a maximum rate of transformation at 873°C in 316. He noted that chi phase precipitation tended to occur along preferential atomic planes.

Chi phase has been found to nucleate on grain boundaries independently of carbides but growth of chi phase is often linked to carbide dissolution (23).

The phase morphology of chi phase is found to vary from rod shaped to massive globular shaped particles (23).

Higher solution treating temperatures are found to have little effect upon chi phase nucleation but do appear to reduce the size of chi particles (23).

At temperatures above 900°C, Weiss and Stickler (23) observed that chi and sigma nucleated at grain boundaries as alternating clusters. They suggested that the degree of grain boundary misorientation determined the nucleation sites for the various phases.

Spruiell et al. (26) reported that the amount of chi phase was increased by cold deformation providing recrystallization did not occur.

Weiss and Stickler (23) noted that in solution treated material, the amount of chi phase exceeded the amount of sigma phase whereas the reverse occurred in deformed material. In cold deformed 316, chi phase was frequently observed along planar faults.

Duhaj and Ivan (29) observed that in 316L cold deformed 10 to 20% and then aged at 800°C; chi phase precipitation occurred intragranularly mainly on epsilon martensite plates.

Omsen and Eliasson (32) have reported that chi phase can form by an eutectic reaction in 316L castings.

Lai and Haigh (41) noted that for aging temperatures above 800°C, chi phase was the major precipitating phase in shielded metal arc welds initially containing between 2 and 4% ferrite. Only slight amounts of sigma phase were observed. Lai and Haigh (41) have suggested that chi phase formation leads to much less embrittlement than either carbide or sigma phase precipitation.

D. R Phase

At temperatures from 600 to 650°C, samples of 316 weld metal were observed to precipitate R phase in small amounts at ferrite-austenite boundaries (41). This phase has a hexagonal crystal structure and is composed of iron, chromium, and molybdenum (41).

E. Carbide Phases

The most commonly observed carbide phase in the austenitic stainless steels is $M_{23}C_6$. This phase has a face-centered cubic crystal structure with a lattice parameter slightly less than three times that of austenite (23). Weiss and Stickler (23) have reported that an energy dispersive x-ray analysis indicated that $M_{23}C_6$ carbide particles in 316 were composed of 14% molybdenum, 63% chromium, 18% iron, and 5% nickel.

Bagnall and Shiels (25) reported a formula for this carbide in wrought 304 as $\text{Cr}_{16}\text{Fe}_7\text{C}_6$. Weiss and Stickler (23) gave $\text{Cr}_{16}\text{Fe}_5\text{Mo}_2\text{C}_6$ as the formula for this carbide in wrought 316.

Carbide precipitation was observed by Weiss and Stickler (23) at temperatures from about 490 to 900°C with the most rapid formation near 815°C. Precipitation was observed first at grain boundaries, next on incoherent twins, then at coherent twin boundaries and finally intra-granularly. Spruiell et al. (26) have observed a similar precipitation sequence.

DaCasa et al. (42) have reported the results of aging type 304 stainless steel at 750°C for periods up to 500 hours. They observed that after five minutes exposure, three different grain boundary morphologies were present: small dendritic particles, very small particles grouped in the form of cross grids, and triangular shaped particles. After one hour at temperature, the amounts of each of the three morphologies observed earlier had increased and the presence of a precipitate in the form of thin sheets was observed. Samples aged for five hours revealed precipitation of triangular particles on twin boundaries as well as the presence of all four grain boundary morphologies which had continued to form and grow. After 25 hours, very large dendrites, extensive thin sheets, areas of heavy triangular precipitates, and areas of cross grids composed of triangles or cubes were observed. The 500 hour sample revealed the same general type of precipitation as that after 25 hours but with a general increase in the size and number of particles.

Wilson (43) used scanning electron microscopy of deeply etched samples to determine carbide morphologies in aged samples of an 18% Cr-10% Ni steel. He reported that at temperatures from 600 to 800°C, carbides nucleated at austenite grain boundaries and then grew within the plane of the grain boundary. Coherent twin boundary precipitates were found to be in the form of small triangles and as long needles in the plane of the twin connected by lacy carbide networks. Samples aged at 900°C had carbide particles which grew in the plane of the grain boundary as long unconnected needles which in some cases developed facets within the plane of the grain boundary.

Weiss and Stickler (23) observed that carbides formed in 316 at higher aging temperatures tended to be more bulky and massive than those formed at lower temperatures.

Bagnall and Shiels (25) noted that samples of wrought 304 containing less than 400 parts per million carbon aged for 2000 hours at 549°C had extensive intergranular precipitation composed of almost continuous networks of carbide particles. But samples aged for the same time at 732°C had grain boundary carbides made up of discrete, discontinuous, spheroidal particles. The authors suggested that this was due to a lower supersaturation of carbon at the higher temperature as well as the material's natural tendency to minimize its intrinsic energy state.

Samples of 304 containing carbon contents greater than 500 parts per million contained considerable carbide precipitation after 2000 hours at 549°C, whereas samples of the same material aged for 2000 hours at 732°C had few intragranular precipitates but instead had

carbide precipitation in zones adjacent to the grain boundaries. Bagnall and Shiels (25) have suggested this to be due to intragranular precipitation being more difficult at lower carbon supersaturations and the tendency of grain boundary carbides to dissolve after long aging times thereby setting up an inward carbon influx which collides with an outward chromium flux to the depleted zones adjacent to the grain boundaries.

Weiss and Stickler (23) observed that the increased carbon content of 316 compared to that of 316L led to an increase in carbide stability. X-ray analysis of chemical extractions of precipitated phases after 3000 hours aging time revealed that $M_{23}C_6$ carbides were no longer present in 316L but that the amount of this carbide continued to increase in 316.

DaCasa et al. (42) also aged a high purity sample of 304 which contained less phosphorus, manganese, and nitrogen than the commercial grade. They observed a general retardation of carbide precipitation in the higher purity material along with the absence of dendritic carbide precipitation. They further noted that the carbide composition changed with time—tending to increase the chromium to iron ratio of the carbide. The higher purity material was found to have a higher chromium to iron ratio than the commercial which the authors suggested to be due to the temperature dependence of the equilibrium composition of the carbide. In both cases, no stable carbide composition was observed after aging up to 500 hours; however, all particles appeared to have the same composition in a given sample after a given aging period.

Weiss and Stickler (23) have reported that increased aging times resulted in larger lattice parameters of carbides in 316 and 316L. They suggested this was due to an increase in molybdenum content with aging time.

Higher solution treating temperatures resulted in larger grain sizes, and larger solute segregations (23). These results gave a more uniform distribution of intragranular carbide precipitation than those treated at lower temperatures (23).

Cold work was observed to accelerate carbide precipitation but to decrease the particle size (23). Both the rate of nucleation and growth appeared to increase with cold working. The precipitation sequence of carbides in cold worked material was: first at grain boundaries, then at fault intersections, next on incoherent twins, then at coherent twins, and finally on dislocations and fault planes (23).

Spruiell et al. (26) observed that carbide precipitation occurred on deformation bands almost as readily as at grain boundaries. They further noted that aged annealed samples had cubic shaped carbide particles but that cold worked samples had faceted disc shaped particles. Upon recrystallization, carbide particles appeared more equiaxed and less plentiful suggesting the possibility of partial resolution.

Carbides are normally reported to have parallel orientations with the matrix (23,26). White and LeMay (37) have reported that carbides formed in wrought 316 aged at 800°C for times less than three hours had this orientation but that after three hours, the orientation showed that some twisting about the face diagonal directions had occurred and after very long times, no unique orientation relationship existed.

After 1500 hours at 630°C, Weiss and Stickler (23) observed M_6C carbides in 316L but not in 316. This carbide was observed in 316L at temperatures from 580 to 670°C and its formation appeared to be retarded by cold work. This phase has a face centered cubic crystal structure and is represented by the formula $Fe_3Mo_3C_6$ (23).

IV. THE EFFECTS OF SERVICE CONDITIONS ON STRUCTURAL STABILITY

In attempting to assess the thermal stability of a material in a particular application, the question arises as to the effect of the service conditions upon thermal instability. The most obvious difference between the aging studies discussed previously and actual applications is the stress condition. Several investigations have indicated that the structural stability of a material aged under load is apt to be different from that of a material aged without stress.

Poole (44) reported a difference in structural stability in a 310 weld deposit. In examining a stress-rupture sample that failed after 108 hours at 871°C, he found that the necked gage region contained about 12% sigma phase but that the threaded grip sections contained sigma phase only at the edges where some cold deformation had been introduced during the threading operation.

Cole et al. (36) observed sigma phase in ruptured samples of 308 weld deposits which had been tested for 44 and 576 hours. Similar material aged without stress at the same temperature had formed only slight to moderate amounts of sigma phase after 1000 hours.

Williams et al. (45) in stress-rupture testing of wrought 316 observed that intragranular precipitates were coarser and fewer in

number in the strained gage sections than in the grip sections. They further reported a higher proportion of intergranular precipitation at a stress of 110 MPa (16,000 psi) than at 62 MPa (9000 psi) with the reverse observed for intragranular precipitation.

Biss et al. (46) examined stress-rupture samples of wrought 304 that had failed after over 4900 hours at 690°C. They observed evidence of grain boundary migration and sigma precipitation in the gage section which were absent in the grip section. The sigma particles were about 10 micrometers wide and up to 40 micrometers in length and frequently observed along migrated grain boundaries. In areas of the gage section where grain boundary migration was not observed, the precipitation was similar to that in the grip sections.

Morris and Harries (47) observed massive carbide particles in stress-rupture samples of wrought 316. These particles were not observed in specimens with rupture times less than 24 hours but were seen in tests with rupture lives of from 24 to 2000 hours. These particles consisted of parallel plates of $M_{23}C_6$ carbides emanating from the original austenite grain boundaries. Often these particles were observed to be bounded on one side by a migrating boundary and on the other by a line of small precipitates. The particles were shaped like small discs up to 100 micrometers in diameter often occupying an entire grain boundary facet. No association was observed between particle orientation and the applied stress direction. However, there appeared to be a strong dependence of particle density on stress level. Particles were not observed in unstrained grip sections but the particle density was observed to increase with creep strain. The particle

density appeared to decrease in the necked portion of the samples with this reduction associated with extensive cracking. The amount of cracking was greater than that expected for a random distribution of particles which led to an association of these massive particles with cracks.

Morris and Harries (47) aged specimens containing massive carbide particles for 3000 hours at 625°C and for 1000 hours at 800°C to investigate their effect upon intermetallic compound formation. They found that although these particles decomposed during aging, the size and density of intermetallic precipitates after aging was typical of samples which had not formed these massive carbide particles.

LeMay et al. (48) investigated the changes in structure of wrought 316 and 310 during creep testing. They found that the 316 specimens which contained many carbides prior to testing due to a low finishing temperature formed ferrite particles during the course of creep testing. The amount of ferrite precipitation was greater in the reduced sections of the specimens than in the grip sections indicating a promotion of ferrite formation by stress. Furthermore, specimens aged under higher stresses had more ferrite within the reduced sections than those aged under lower stresses. In all cases, ferrite formed primarily at grain boundary triple points and grew along austenite grain boundaries. The sample of 310 showed no evidence of a relationship between stress and structural stability.

Wilson (14) observed that plots of logarithm of stress versus logarithm of rupture time for annealed 304 had changed in slope during long-term testing but that material that had been in service for long

times had relatively linear stress-rupture time relationships. He pointed out the impracticability of full-term testing and that parametric extrapolation for materials with nonlinear stress-rupture time relationships was hazardous. He attempted to overcome these limitations by developing a technique for simulating long-term service exposure. He attempted to simulate the effect of a 100,000 hour service exposure at 649°C by aging samples for 100 hours at 774°C and by exposing the material to the 699°C, 100,000 hours rupture stress at 718°C until secondary creep occurred. Neither of these simulations produced a microstructure like that of samples which had undergone exposure under the actual service conditions. Wilson (14) suggested that since precipitation reactions were responsible for these changes in slope and that the most rapid rate of transformation appeared to occur at the intended service temperature, higher temperature exposures could not achieve any greater rates of precipitation. Therefore, simulated service treatments were not appropriate for determining long-term properties.

V. WELDS IN THE AUSTENITIC STAINLESS STEELS

Since welding plays a major role in fabrication of the austenitic stainless steels, design of components for long-term elevated temperature applications require consideration of the effect of this service on weld mechanical properties. The importance of this consideration is further emphasized by the finding of several investigations that the thermal stability of welds was lower than that of the base metals (11,17,49,50). Furthermore, as noted by Thomas and Yapp (51), any

installed weld joints are areas of critical importance since they are likely to contain a higher density of defects and that the physical properties of welds can differ significantly from those of wrought material. These results indicate a need for more detailed information concerning the effect of long-term elevated temperature exposure on weld properties and why these properties might be different from those of wrought material. This section will survey the general nature of welds in the austenitic stainless steels with an eye toward understanding the differences between their thermal stabilities and those of the base metals.

Brinkman et al. (52) have pointed out several characteristics of welds in the austenitic stainless steels that make their behavior inherently more difficult to analyze. They noted that welds may have highly anisotropic mechanical properties, that as-deposited weld metal can be heterogeneous due to dilution, segregation, and systematic variations in microstructure arising from solidification shrinkage and thermal expansion stresses, and that welds often contain more complex microstructures than the base metals.

Garland and Davis (53) noted that anisotropy of weld mechanical behavior is due to the way in which welds solidify. They reported that no nucleation event was required for weld pool solidification because the molten pool readily wets the unmelted grains in the base metal leading to epitaxial growth of these grains at the solid-liquid interface. After initiation, subsequent solidification occurs by competitive growth processes which dominate the remainder of weld pool solidification. They noted that in general, the overall solidification

macrostructure of a weld is determined solely by the nature of the competitive growth process.

Solidification usually proceeds along the easy growth direction (a crystallographic direction determined mainly by the crystal structure) most closely aligned with the direction of the maximum thermal gradient. Since the direction of the maximum thermal gradient is perpendicular to the weld pool boundary, the shape of the weld pool has a major effect upon the solidification structure of the weld deposit. A teardrop shaped pool has an almost invariant direction of maximum thermal gradient which allows any grain favorably oriented at the fusion boundary to grow during the entire solidification process. An elliptically shaped pool (formed at lower welding speeds or higher welding currents than teardrop shaped pools), however, has the direction of maximum thermal gradient changing continuously from the fusion boundary to the weld center. Under this condition, no one grain experiences favored growth for any extended period of time which results in many more grains surviving to reach the weld center. Any grain that does survive over any great distance exhibits considerable curvature due to the progressive change in favored growth direction. This curvature is the result of repeated side branching of the solidification structure.

King et al. (16) investigated the anisotropy of 308 welds made in 304 plate. They observed systematic variations in properties through the thickness of the weld due to variations in microstructural features and perhaps local chemical compositional variations. The yield strengths of samples from near the surface were from 34.5 to 103.4 MPa

(5,000 to 15,000 psi) lower than those of samples taken from near the weld center. Tensile strengths, however, showed little variation. Specimens from near the center of the weld had significantly lower uniform and total elongations than those of samples taken from near the surface. The deformation resistance varied with the orientation of the specimen with transverse specimens significantly stronger than longitudinal specimens.

These variations in properties were linked to the nature of weld pool solidification and the complex thermal-mechanical history of metal deposited before the last pass. Solidification and thermal stresses were suggested to contribute to the relatively heavy deformation of the initial passes. Systematic variations in dislocation density and carbide precipitation as a result of the greater number of thermal-mechanical cycles experienced by the initial passes were major factors for these variations in properties.

Garland and Davis (53) have pointed out that macroscopic solidification rates in welds are orders of magnitude greater than those encountered in ingot solidification and that the motion of the molten metal in a weld pool is much greater than that in a casting. These conditions result in welds having different segregation patterns from those of castings. The mode of solidification and the partitioning characteristics of the system are found to control the size and pattern of grain development and the nature of solute segregation in weld deposits. Garland and Davis (53) noted that microsegregation was pronounced in weld beads and that the more dendritic the solidification mode the greater the amount of segregation. Segregation at grain

boundaries is found to be greater than that encountered within the substructure composing the grains. Grain boundary segregation is more pronounced at the weld center where the grains growing from each side impinge and tend to trap the solute rich liquid. This effect is more severe in welds having teardrop shaped pools in which the solidifying grains impinge at a steep angle.

A characteristic segregation pattern in welds is that of solute banding. This pattern, the result of regions of solute enrichment or depletion, is revealed in etched deposits as light and dark lines marking successive positions of the advancing solidifying interface. The most generally accepted explanation for this pattern is the cyclic nature of welding power supplies which cause periodic variations in solidification rate through their effect on arc force and heat input. Less regular segregation effects are seen in welds made with equipment not having periodic power supplies. These are suggested to be due to oscillation of the weld pool surface after removal of the arc pressure.

Welds in the austenitic stainless steels generally contain some amount of delta ferrite. The presence of this phase is found to greatly increase the resistance of the weld to hot cracking.

Hot cracks are supersolidus cracks which occur in welds or castings during solidification (54). Crater cracks, star cracks, root cracks, longitudinal cracks, transverse cracks, and microcracks are all considered manifestations of hot cracking differing only in appearance, location, and orientation (54). All are found to depend upon restraint, weld geometry, and welding variables (55).

A related phenomena known as fissuring can occur in multipass welds (55). This type of cracking occurs during the reheating of

existing weld metal as additional beads are deposited adjacent to or over existing beads. Fissures generally appear as small cracks with preferred orientations perpendicular to the axis of the weld and normal to the direction of maximum residual stress (55). Usually these cracks are confined to the heat-affected-zone in previously deposited beads which have been reheated to temperatures just below the melting point, but these cracks may extend into the bead which caused them (55).

DeLong (55) has pointed out that the presence of these fissures in very notch tough materials such as the austenitic stainless steels should have little effect upon their mechanical properties. He further noted that from a practical standpoint, millions of pounds of 310, 316, and 316L weld metal used in a range of products and applications have never experienced failure due to the presence of fissures. The reason for the tendency to completely remove any possibility of fissuring appears to result from the inability to predict the occurrence and orientation of these cracks.

Linnert (56) has stated that five factors appear to control hot cracking: (1) the microstructure of the weld deposit upon solidification; (2) the composition of the weld metal, especially the levels of certain residual elements; (3) the amount of stress on the weld deposit as it solidifies; (4) the high temperature ductility of the weld deposit; and (5) the presence of notches at the edges of the weld.

Gooch (57) has suggested that cracking behavior is determined mainly by composition, weld pool shape, and overall joint restraint. Each of these factors if found to depend upon the welding process and procedure through their effects upon the amount of dilution and element

transfer and pickup, the amount of control on pool shape and solidification rate, and the amount of restraint.

Two methods have been used to minimize the amount of hot cracking (56). The first results in a wholly austenitic weld deposit. Cracking susceptibility is decreased in this technique by: (1) holding crack promoting elements such as boron, phosphorus, sulfur, selenium, silicon, columbium, and tantalum to as low levels as possible; and (2) by increasing the amounts of elements such as carbon, manganese, and nitrogen which increase crack resistance. The second technique is to adjust the composition of the weld deposit so that a small amount of ferrite is present in the solidified weld deposit. Of these two methods, the one giving a wholly austenitic weld deposit produces a deposit so much more crack sensitive that it is used only in special cases.

The exact manner in which ferrite suppresses hot cracking is unknown (54). Hull (54) has listed five previous explanations. The first is that delta ferrite by having a greater solubility for crack promoting elements which would otherwise be in the austenite grain boundaries removes these elements from places where cracks could develop. A second possible explanation is that since ferrite decreases the amount of austenite boundary intersection, it effectively reduces the area where cracks can form. A third theory was that ferrite refines the austenitic grain size and hence by increasing the grain boundary area dilutes the crack promoting elements. A fourth possible explanation is that structures containing ferrite solidify over a much narrower temperature range and as a result do not allow enough time for segregation to concentrate crack promoting elements. Hull (54) has

pointed out that the fallacy of this theory is the gradual decrease in solidification temperature range as compared to the drastic effect on cracking with a small increase in the amount of ferrite. The fifth possible explanation is that ferrite by having a smaller coefficient of thermal expansion decreases the solidification stresses. Hull (54) has noted that the problem with this theory results from the small percentage of ferrite.

Hull (54) has proposed a theory based on differences in interfacial energies in which the effect of ferrite is to change the shape of the last amount of liquid from a film around the austenitic grains to a globular form. This would allow any cracks which form to be healed since liquid would be able to flow while in the globular form. He further believed that the ferrite could absorb some of the contractual strain during solidification.

Astrom et al. (58) investigated the theory that ferrite increased hot cracking resistance by having a greater solubility for trace impurities such as sulfur and phosphorus thereby preventing the formation of low melting point films. They used scanning transmission electron microscopy to determine segregation patterns in shielded metal arc weld deposits having the nominal composition 18% chromium and 10% nickel. The sulfur and phosphorus contents were increased to twice their normal levels to facilitate segregation analysis.

Some hot cracks were observed in the weld deposit along with a ferrite level of from four to five volume percent. A number of inclusions were observed in the weld deposit containing a number of elements such as manganese, sulfur, and nickel.

Line scans over the cracked regions revealed distinctive sulfur peaks at the cracks with much lower levels in the austenite. Phosphorus was found in the austenite but still higher levels were present in the cracked areas.

Analysis of the ferrite-austenite regions showed that the ferrite contained about five weight percent more chromium and five weight percent less nickel than the austenite. Practically no long range segregation of chromium, nickel, silicon, or manganese was seen in the austenite. A slightly larger amount of manganese was present in the austenite than in the ferrite. Silicon appeared to be evenly distributed in both phases. Phosphorus was found only in the ferrite being more concentrated at the austenite-ferrite boundaries. Nonmetallic inclusions were found to be concentrated in areas near the austenite-ferrite boundaries with those in the austenite mainly silicon based and those in the ferrite containing manganese, chromium, and sulfur.

The authors suggested that when a weld solidifies directly as austenite, sulfur and to a lesser extent phosphorus remain in the liquid ahead of the solidifying front and that manganese by remaining in solution in the austenite is not free to form manganese sulfide or to decrease the wettability of iron sulfide thereby promoting hot cracking.

They suggested that the lower solubility of manganese in ferrite allows more manganese to be free to tie up the sulfur and phosphorus thereby reducing hot cracking susceptibility.

Given that the most effective way to prevent hot cracking is to adjust the composition of the weld deposit to cause some percentage of delta ferrite in the final deposit, the question arises as to the optimum ferrite content.

Hull (54) used the cast pin tear test in which material is allowed to solidify under various amounts of restraint to determine the microstructure least sensitive to hot cracking. He found that a microstructure in which ferrite covered approximately half of the austenitic grain boundaries and cell boundaries and had begun to branch into the interiors of cells to be the most crack resistant. This corresponded to between 5 and 10% ferrite.

Brooks and Lambert (59) investigated the relationship between ferrite and the phosphorus and sulfur content in 309 stainless steel. They found that as the content of these elements was increased, the amount of ferrite necessary to prevent hot cracking had to be increased. They suggested that two methods were available to prevent hot cracking—either to ensure that enough ferrite was produced in the weld deposit to prevent cracking at the maximum anticipated sulfur and phosphorus contents or to reduce the allowable levels of phosphorus and sulfur such that less ferrite is required to maintain the same level of cracking resistance.

However, as noted in the phase transformation section of this review, ferrite accelerates the formation of sigma phase. Hull (54) and Gooch (57) have noted that ferrite levels should be kept as low as possible to prevent this occurrence. To determine the minimum amount of ferrite necessary to prevent cracking, the effects of welding process variables must be investigated.

Lundin et al. (60) in comparing the number of fissures to the ferrite content for shielded metal arc weld pads found that the amount of ferrite necessary to completely suppress hot cracking was dependent

upon the composition of the weld deposit. Electrode E347-16 was found to require about six times more ferrite to prevent fissures than either E316L-16 or E308-16.

Gooch (57) has noted that the welding process and travel speed can cause a variation in the amount of ferrite necessary to prevent hot cracking through their effects on solidification rate.

It is therefore concluded that the amount of ferrite necessary to suppress hot cracking varies with the welding process, joint geometry, and composition of the filler metal. This result indicates that any investigation of thermal stability must include an investigation of the effect of variable ferrite content.

Ferrite content is determined primarily by the composition of the weld deposit (55). Schaeffler (61) used metallographic techniques to determine the amount of ferrite present for a given composition. He presented this data by a diagram on which weighted effects of the austenite formers (Ni,C,Mn) were plotted against weighted effects of ferrite formers (Cr,Mo,Si,Cb). Accuracy for this diagram was stated to be plus or minus four volume percent ferrite. DeLong (55) modified this diagram by using magnetically determined ferrite values and taking into account the effect of nitrogen on ferrite formation. This diagram claimed plus or minus three volume percent ferrite accuracy.

Dilution of the weld deposit by the base metal can significantly affect the ferrite content (55). Depending on the composition of the base metal, ferrite levels can be increased or decreased. DeLong (55) has noted that dilution can be as much as 65% in submerged arc and gas metal arc weldments. Joint geometry also plays an important role.

Wrought materials generally lower ferrite levels and cast materials tend to increase ferrite levels.

DeLong (55) has reported the results of the ASME Joint Task Group on Stainless Steel as finding that heat input over rather broad ranges has little effect on ferrite content. Heat input, however, did affect the size, shape, and distribution of ferrite.

The high solidification rate of weld deposits results in a very fine ferritic-austenitic structure with ferrite occurring in a lacy, interlocked dendritic form. DeLong (55) has suggested that ferrite levels in the range of four to seven volume percent are continuous.

Goodwin et al. (62) investigated the effect of welding parameters on ferrite morphology. They used three nominal compositions of filler material and four welding processes to join one inch thick pieces of 304. Ferrite was found in all cases to be located in the substructure boundaries. These boundaries are the last to solidify in a single phase alloy.

Welds made with 308 and 308L using submerged arc, gas tungsten arc, and gas metal arc processes showed that the coarseness of the ferrite distribution was dependent upon the substructure size. Substructure size is a function of composition, solidification growth rate, and the thermal gradient in the liquid at the solid-liquid interface. With similar compositions of filler material and joint geometry, the major variation in ferrite morphology is due to energy

input—a process variable. Higher energy inputs result in coarser substructures and hence coarser ferrite morphologies.

Goodwin et al. (62) pointed out that due to the inherent heterogeneity of the weld solidification process, large variations in local ferrite content occur. DeLong (55) has noted a similar finding. It was further noted by Goodwin et al. (62) that this large variation cannot be detected by bulk nondestructive techniques. Metallographic investigations have revealed substantial variations in ferrite content from weld to weld produced under identical conditions, from location to location along the centerline of a particular deposit, and from point to point within a particular transverse weld cross section.

Berggren et al. (63) have reported ferrite morphologies in 308 shielded metal arc weld deposits of variable ferrite contents. They noted that increasing ferrite contents become more nearly continuous. Ferrite at low levels was present as widely separated patches. Ferrite contents near 12% were present as almost continuous networks. Transmission electron microscopy of these weld deposits revealed the dislocation densities of austenite were an order of magnitude greater than those in the ferrite. The dislocations in the low ferrite containing austenite were arranged in a cellular structure with some dislocations within the cells. The austenitic dislocation density was higher in the lower ferrite level deposits. The tendency for dislocations to form cellular networks appeared to decrease with increasing ferrite levels.

Gugelev (64) investigated the effect of ferrite content on the 650°C tensile properties of weld deposits. He found that for strain

rates greater than 10% per hour, increased amounts of ferrite increased the strength and decreased the ductility of weld deposits. However, at strain rates of about 1% per hour, deformation became localized at ferrite-austenite interfaces causing discontinuities to form and grow leading to decreased strength and ductility with increased amounts of ferrite. He reported that the overall effect of ferrite was to decrease ductility—at high strain rates ferrite particles acted as obstacles to slip and at low strain rates, deformation became localized to austenite-ferrite boundaries leading to less overall deformation. He concluded that the strength of weld metal increased with increased ferrite contents only at high strain rates and low temperatures, but at low strain rates, the weld strength was reduced by increased ferrite levels.

Berggren et al. (63) have noted that efforts to relate ferrite content to elevated temperature mechanical properties are confounded by the need to vary either chemical composition or welding variables to vary ferrite contents. They further noted that if creep ductility could be related even empirically to ferrite content for even a limited range of compositions and process variables, the properties of welds might be improved by controlling ferrite levels to produce acceptable weldability and properties for specific applications.

Results of elevated temperature tensile and creep tests of 308 weld metal containing ferrite contents from 0 to 15% indicated that lower ferrite levels resulted in better properties. This observation was somewhat clouded by the zero ferrite content deposit containing a higher carbon content than those at other ferrite levels.

Observations of the fracture surfaces of the zero ferrite deposits regardless of rupture time, revealed that the fracture surfaces

were composed mainly of ductile dimples with only isolated areas of interphase fracture indicating that the fractures were mainly shear in nature. The zero ferrite level deposits developed isolated cracks during testing but these cracks were blunted during deformation and did not appear to link up to form the final fracture.

The high ferrite content deposits had fracture surfaces similar to those of the low ferrite deposits after short time tests. As the rupture time increased, the fractures were found to be markedly affected by substructural separations. The amount of sigma phase formed from ferrite decomposition increased with testing time. In long-term tests, high ferrite deposits showed large amounts of sigma phase and the final fracture appeared to result from linking up of cracks formed at austenite-sigma boundaries. Fractured specimens in this case showed little reduction in area or necking. The authors drew the conclusion that ferrite content and morphology had a profound influence on creep ductility.

VI. RESIDUAL ELEMENTS IN THE AUSTENITIC STAINLESS STEELS

Linnert (56) has noted that residual elements are of considerable importance in welding since their presence has been shown to have profound effects on cracking, porosity, slag formation, corrosion susceptibility, and embrittlement.

Residual elements are those elements present in an alloy in small quantities which were not intentionally added (65). Heger (65) has listed over thirty common residual elements in stainless steel. He further noted that these elements can affect the melting temperature,

change the nature or morphology of phase transformations, and can have general effects on mechanical properties.

Arsenic, boron, copper, phosphorus, sulfur, and antimony are found to cause drastic reductions in melting temperature (65).

Boron has been found to decrease the solubility of carbon in stainless steel and to segregate to grain boundaries causing a lower carbon diffusivity and thereby stabilizing the carbide size (65). There is also the possibility that boron retards carbide precipitation and also renders the resolution of carbides more difficult (65).

Linnert (66) pointed out that the effect of a given residual element was dependent upon the overall alloy composition, microstructure, and condition of the steel. He further noted that a number of residual elements can have multiple effects which can improve some properties while decreasing others. Linnert (66) has reported that boron and phosphorus promote hot cracking, however Binkley et al. (67) have found that welds containing higher phosphorus and boron contents have improved creep-rupture properties.

Binkley et al. (67) investigated the effects of variations in carbon, boron, silicon, phosphorus, and sulfur on the creep strength and rupture ductility of 308 weld deposits. All of the variations were confined to the limits imposed by specifications for the composition of 308 weld metal. They found that increases in carbon content increased creep strength at the expense of rupture ductility. Increased boron contents were found to increase both the creep strength and rupture ductility. Reductions in silicon level appeared to increase rupture ductility without significantly reducing creep strength. Increased phosphorus contents were found to increase both creep strength and

rupture ductility. Sulfur content was found to have little effect on either strength or ductility.

Standard 308 weld metal stress-rupture tested at 649°C for long times had low ductility fractures frequently initiating at the original austenite-ferrite boundaries with the final fracture attributed to a link up of cracks formed at those boundaries (21). The 308 weld deposits, containing 0.04% P, 0.007% B, and 0.06% Ti known as CRE welds, had predominately shear stress-rupture fractures with little evidence of fracture initiated by internal cracks and much greater rupture ductilities (21).

Steigler et al. (21) concluded that the reason CRE welds exhibited greater ductilities was that small chemical modifications retarded or prevented the formation of internal cracks at austenite-sigma boundaries. These chemical modifications appeared to retard the formation of sigma phase thereby suppressing interfacial cracking.

Williams et al. (45) observed that the creep-rupture strengths and ductilities of wrought 316 specimens were increased by increased boron contents. Samples with boron contents less than 30 parts per million tested at 700°C under a stress of 62 MPa (9,000 psi) had fracture surfaces which revealed extensive grain boundary cracking with the main fracture occurring in an intergranular manner. Samples containing 50 parts per million boron tested under the same conditions failed in a transgranular manner with extensive grain elongation. The authors suggested that the effect of increased boron was to inhibit failure along grain boundaries.

In an effort to determine the effect of boron on structural stability, Williams and Talks (68) aged samples of wrought 316 stainless steel

containing boron levels of 0.001 and 0.006 weight percent at carbon levels of 0.06 and 0.12 weight percent. They found that the higher boron containing samples showed a reduced tendency toward sigma formation with the effect more pronounced at lower carbon levels. In fact, sigma phase formation was completely suppressed in the low carbon-high boron samples. He suggested that the effectiveness of boron in improving elevated temperature properties was related to the boron to carbon ratio in the steel and that the effect of boron was to stabilize carbides by forming carbo-borides thereby postponing or preventing sigma formation.

VII. NITROGEN IN THE AUSTENITIC STAINLESS STEELS

Janzon (69) has reported that commercial 18% Cr-8% Ni alloys may contain nitrogen at levels ranging from 0.02 to 0.2 weight percent with the lower level set by commercial practices and the upper by the solubility of nitrogen. DeLong (55) has noted that the nominal nitrogen content in SMAW and GTAW austenitic stainless deposits was 0.06 weight percent but was 0.08 weight percent for GMAW deposits. Since many residual elements have significant effects upon the properties of the austenitic stainless steels and the nitrogen content is apt to be variable, the effect of this variation should be assessed.

Cox and Eckel (70) have pointed out that substitution of nitrogen for the more costly nickel while maintaining austenitic structures may be economically attractive.

Neigebaur and Yaskevich (71) have determined the effect of nitrogen relative to that of nickel on austenite formation. A series of alloys with variations in carbon, chromium, nickel, manganese,

silicon, and nitrogen were cast into ingots and the amounts of ferrite in each of these castings was determined magnetically. Using the relations developed by Shaeffler (61), they plotted nickel equivalent versus chromium equivalent for each of these alloys. Variations in these results as compared to those predicted by the Shaeffler diagram allowed assessment of the effect of nitrogen. They reported that nitrogen was 25.8 times more potent than nickel in promoting austenite. DeLong and Long (72) determined that nitrogen was 30 times more effective than nickel in promoting austenite in weld deposits.

Cox and Eckel (70) investigated the solubility of nitrogen in 384, 304, and 308 AISI stainless steels at temperatures from 538 to 1010°C excluding the temperatures associated with sensitization. They reported that the solid solubility exhibited a linear dependence with the reciprocal of absolute temperature in each of these alloys. Values near 0.3 weight percent nitrogen were determined at 1010°C and values of near 0.12 weight percent nitrogen at 538°C. Differences in the solubility among the three alloys were linked to variations in chromium content since the primary nitrides forming in the austenitic stainless steels are those of chromium. They suggested that the chromium content significantly influenced the solid solubility of nitrogen with increasing chromium contents decreasing nitrogen solubility.

Omsen and Eliasson (32) have investigated the structures of 316L castings with variable nitrogen contents. They observed that at nitrogen contents from 0.05 to 0.07 weight percent, the mode of solidification changed from ferritic to ferritic and austenitic with the amount of austenite determined solely by the amount of nitrogen. At a nitrogen content of 0.35 weight percent, no ferrite was

observed in the completed casting. At nitrogen contents greater than 0.13 weight percent, a number of second phase particles were observed primarily in interdendritic regions. These were identified as $M_6(C,N)$, $M_{23}C_6$, chi phase and small amounts of Fe_4N and Cr_2N . Two eutectic products were also identified. One of these, a chi phase-austenite eutectic had been observed in other systems and the authors therefore suggested that this reaction was not determined by nitrogen content. The other eutectic reaction, a $M_6(C,N)$ -austenite, was suggested to result from a supersaturation of nitrogen as a result of duplex solidification. This eutectic has a melting temperature of $1280 \pm 20^\circ C$.

Janzon (69) investigated the effect of nitrogen and nickel contents on the hot ductility of castings with nominal compositions similar to those of AISI 316. He found that in predominately austenitic alloys, increased nitrogen contents reduced the hot ductility by decreasing the rate of dynamic restoration. Increased amounts of nitrogen and nickel were found to increase the hot ductility of duplex (austenite-ferrite) alloys by reducing the amount of ferrite. The formation of the $M_6(C,N)$ -austenite eutectic upon exceeding the solubility of nitrogen in austenite was found to impair the hot ductility and to set an upper limit of $1280^\circ C$ on the hot working temperature.

Cullen and Davis (13) have investigated the effect of nitrogen on the elevated temperature tensile and stress-rupture properties of wrought 316 alloys. Tensile tests at temperatures from 200 to $1200^\circ C$ showed a beneficial effect of nitrogen on yield and ultimate tensile strength. Increased nitrogen contents were found to increase creep

strength and to decrease the minimum creep rates. However, analysis of long-term test results indicated that the long-term properties of these materials might be impaired by precipitation reactions.

Davis and Cullen (73) have also investigated the effect of nitrogen content on the stress-rupture properties of 308 weld deposits. They have tested welds with nitrogen content of 0.053, 0.14, and 0.29 weight percent after the deposits had been heat treated at 1190°C. They observed that the higher nitrogen deposit had slightly higher rupture strengths than those of the lower nitrogen content deposits. Ductilities of the higher nitrogen content deposits were lower than those of the lower nitrogen content deposits.

CHAPTER III

EXPERIMENTAL PROCEDURES

I. GENERAL NATURE OF THE EXPERIMENT

This investigation has been concerned with some of the aspects of the thermal stability of 316L. Since poor thermal stability in the austenitic stainless steels is most often linked to structural instability, this investigation was directed toward characterizing the structural changes in 316L weld metal after exposure to elevated temperature.

The concern with the effect of ferrite content on long-term elevated temperature behavior of weld deposits resulted in this investigation being devoted to the structural changes in welds of different ferrite contents. As Berggren et al. (63) have pointed out, the problem in determining the effect of ferrite content on mechanical properties is the need to vary either the chemical composition or the welding parameters to produce welds of different ferrite levels. The method used in this investigation was to introduce nitrogen into the weld shielding atmosphere. This technique had the benefit of producing welds with different ferrite contents with variations in only one chemical species which as pointed out by DeLong (55) is apt to be variable even under standard welding conditions.

An aging temperature of 650°C was selected for this investigation. This temperature represents a compromise between the actual service

temperature for this material of 538°C and the temperature of most rapid structural instability of about 750°C.

The observation that structural changes might be different for material aged under stress led to part of this investigation being devoted to assessing this effect in 316L weld metal. This was done by comparing the structural changes in specimens aged under creep conditions to those of samples aged without stress.

II. MATERIAL AND PROCEDURES

Four 304.8 mm (12 in) long vee butt welds made in 12.7 mm (0.5 in) 316 plate were furnished by Oak Ridge National Laboratory. One pair of deposits was made under an argon shielding atmosphere and the other using an atmosphere of 1% nitrogen in argon. The composition of the 1.59 mm (0.0625 in) diameter filler wire is given in Table 1.

TABLE 1
COMPOSITION OF 316L FILLER WIRE IN WEIGHT PERCENT

C	Mn	P	S	Si	Ni	Cr	Mo	Cu	Fe
0.025	1.84	0.013	0.022	0.38	13.60	19.12	2.17	0.09	balance

Radiographic analysis of the completed welds indicated that one of each type contained some small amounts of porosity.

A magnegage was used to determine ferrite numbers of the welds. Ferrite determinations were made over each of the weld lengths in the as-welded condition and after a 63 rms surface finish had been milled over the weld length. The welds were cut from the base plate and turned to 7.94 mm (0.3125 in) rods centered on the weld cross

section and tangent to the milled surface. The rods were cut into lengths for the stressed aging specimens insuring that the areas of porosity were confined to the grip sections. The remainder of these rods was cut into 15.9 mm (0.625 in) lengths for aging studies.

Using the data from Brinkman et al. (52), the average stresses for rupture times of 500, 1500, and 100,000 hours were determined. These data along with the density of stainless steel and the amounts of material needed for the various tests were used to determine the specimen dimensions for the stressed aging studies. Table 2 lists the stress values for these rupture lives along with the rod diameters selected for these stress levels.

TABLE 2
STRESS LEVELS USED IN STRESSED AGING STUDIES

Rupture Life (hours)	Stress Level (MPa) (psi)		Diameter for Stress Level Under a 1.78 kN (400 lb) Load	
			(mm)	(in)
500	185	26,865	3.51	0.138
1500	152	22,085	3.86	0.152
100,000	80	11,648	5.31	0.209

Figure 1 illustrates the two types of specimens used in the stressed aging studies. The longer of the two types of specimens has three different cross sectional areas so that when the 1.78 kN (400 lb) load was imposed, the specimen experienced the 500, 1500, and 100,000 hour rupture stresses. The shorter of the two specimens in Figure 1 has two different cross sectional areas. This type of specimen experienced

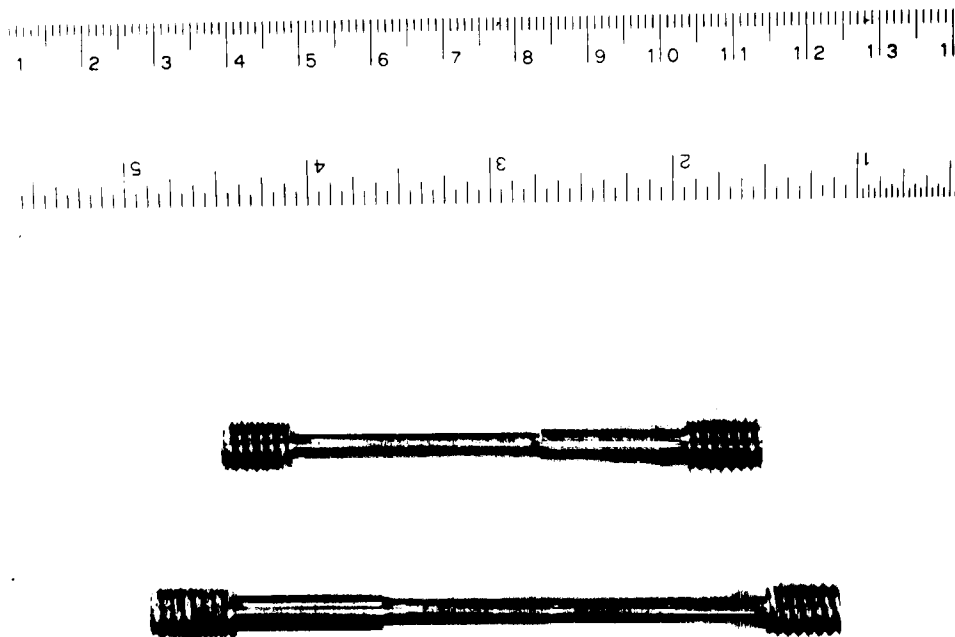


FIGURE 1. STRESSED AGING SPECIMENS

the 1500 and 100,000 hour rupture stresses when the 1.78 kN (400 lb) load was applied.

The stressed aging experiments consisted of aging samples of each composition under the 500, 1500, and 100,000 hour rupture stresses for 100 and 300 hours, and under the 1500 and 100,000 hour rupture stresses for 700 and 1300 hours. After the appropriate aging time, the furnaces were turned off and the samples were allowed to cool while still under load.

Samples of unstressed aging studies were aged in air in a horizontal tube furnace for 10, 100, 300, 500, 700, 1300, and 2000 hours. After the appropriate aging time, samples of each composition were removed from the furnace and water quenched.

Portions of each of the test specimens along with a similar piece of each type of the unaged welds were prepared for optical metallography using standard procedures. The limited amount of material allowed only transverse sections to be analyzed. The samples were etched electrolytically using a solution of chromic acid, water, and acetic acid. magnegage ferrite determinations were made on each of the optical metallographic specimens using standard procedures (55).

Samples for transmission electron microscopy were prepared in a Struers Tenupol unit marketed by Ladd Research Industries. An electrolyte of perchloric acid in acetic acid was used in preparing these samples. Here again, the limited amount of material allowed only transverse sections to be analyzed.

A bulk extraction technique was used to determine the amounts of second phase particles. This technique consisted of electrolytically

dissolving the austenite in a hydrochloric acid-methanol solution. Prior to dissolution, the sample was cleaned and weighed along with a specimen bottle which was later used to hold the extract. The specimen was supported by platinum wire and suspended within the electrolyte. Samples were dissolved at a potential of five to ten volts for about three hours. Following dissolution, the remaining portion of the sample was rinsed with methanol insuring that the residue fell into the beaker containing the electrolyte. The solution was then centrifuged to remove suspended particles. Following this, the majority of the solution was removed. The remainder of the solution was diluted with methanol, recentrifuged, and then the majority of the solution was removed. This was repeated until a clear solution was obtained. The extract was then transferred to the specimen bottle. After centrifuging, the methanol was boiled off by immersing the specimen bottle in a heated beaker of water. The bottle was then removed from the bath and allowed to dry until the next day when the undissolved portion of the sample and the dry specimen bottle containing the extract were weighed. The extract was determined by dividing the weight of the extract by the difference in weight of the specimen prior to extraction and the portion of the specimen left after extraction. The Debye-Scherrer x-ray powder diffraction technique was used to identify the phases present in the extracts.

III. STRESS-RUPTURE EQUIPMENT

An eight station stress-rupture laboratory was set up as part of this investigation. Figure 2 illustrates the nature of this



FIGURE 2. STRESS-RUPTURE LABORATORY

laboratory. Each of the eight units is composed of three main parts: the frame, the suspension system, and the furnace.

Figure 3 is a schematic diagram of the frame. The suspension system is supported by the upper plate. By using a heavy steel base plate and placing the load axis at the center of the frame, it was not necessary to secure the frame to the floor. The frame also supports the furnace in a rack which allows centering of the furnace about the suspension system. After centering, the furnace is held in position by set screws. The rigidity of the frame was increased by placing gussets in two orthogonal directions. To minimize the amount of vibration picked up by the frame, the laboratory was set up on the ground floor and each of the frames was mounted on cork pads.

Figure 4 is a schematic diagram of the suspension system. The leveling bushing is placed in a hole at the center of the upper plate of the frame. A rounded recess in this bushing meshes with the rounded end of the support nut allowing slight rotational and horizontal movement of the suspension system. This action insures that the sample will experience a uniaxial load. A 12.7 mm (0.5 in) rod connects the support nut to the extensometer. The extensometer, designed for threaded specimens, transforms increases in specimen length to increases in the spacing between two parallel plates outside the furnace. A dial indicator is used to monitor this spacing. The extensometer, the upper suspension rod, and the lower suspension rod all experience elevated temperatures and were therefore all fabricated from type 304 stainless steel. The stress that these parts experience is at least an order of magnitude less than that imposed on the specimen. A pair of

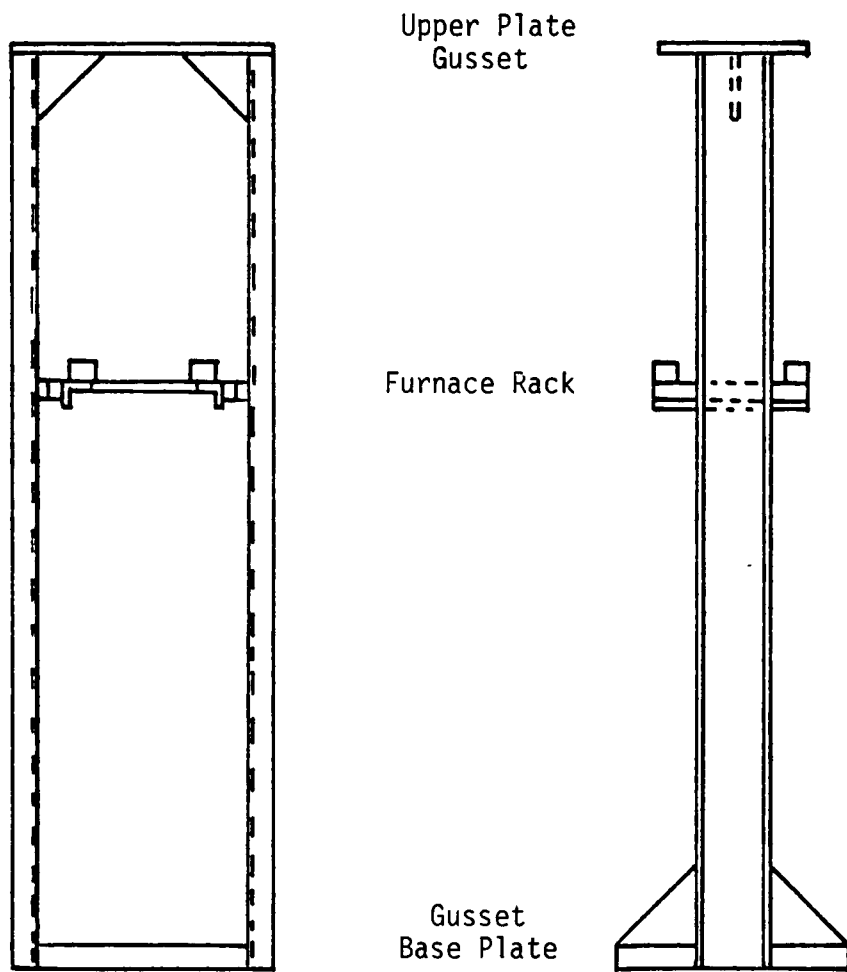


FIGURE 3. SCHEMATIC DIAGRAM OF THE FRAME

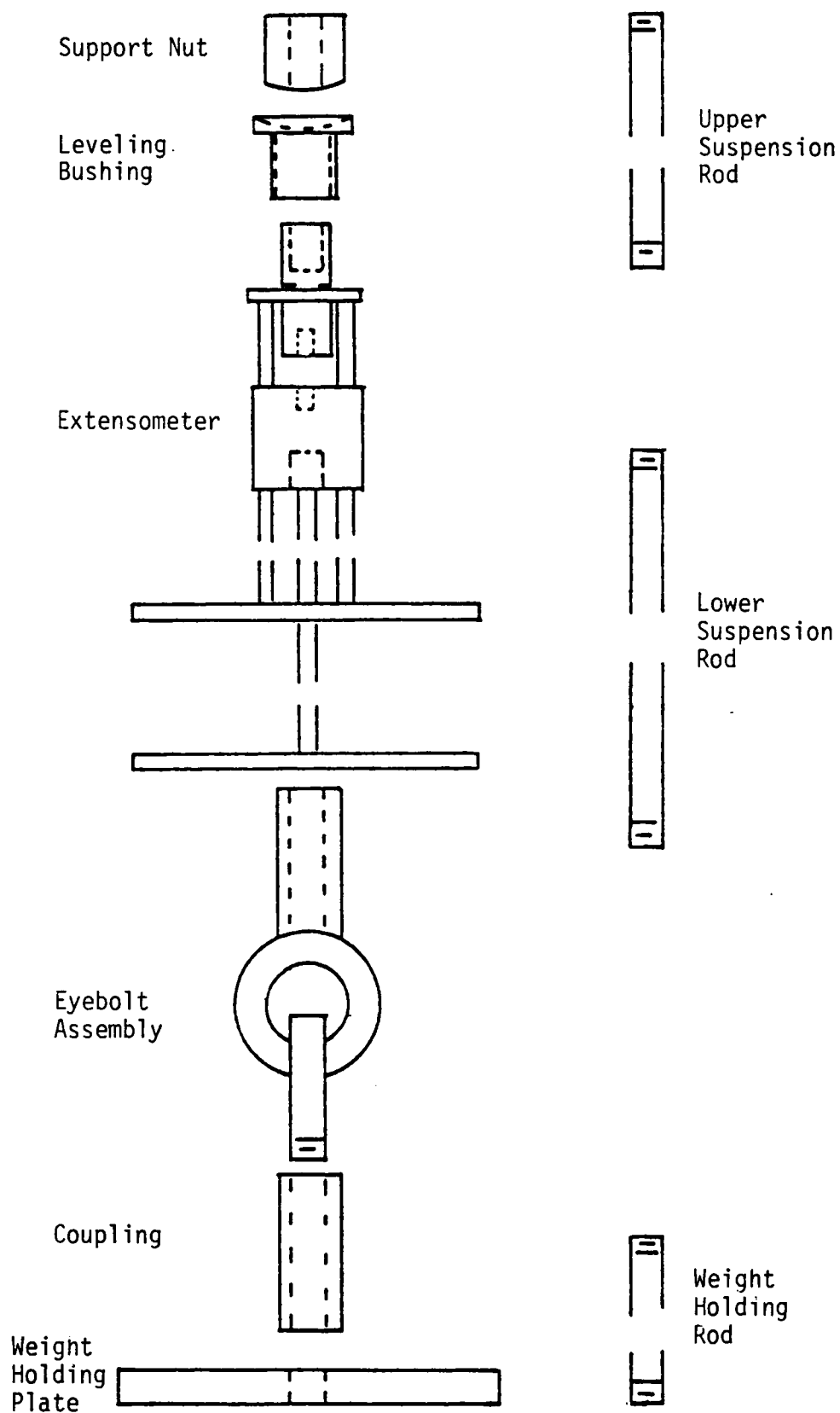


FIGURE 4. SCHEMATIC DIAGRAM OF THE SUSPENSION SYSTEM

interlocking eyebolts was attached to the lower suspension rod to allow the load to be removed from the specimen until the proper test temperature was obtained.

A three zone furnace design was used in constructing this equipment. The electronic shop came up with a scheme using triac phase fired relays in which the power to each furnace zone could be independently controlled while still using a single controller. The furnaces constructed for this equipment allowed a 76 mm (3 in) long zone to be maintained to within plus or minus two degrees Celsius of the desired temperature.

CHAPTER IV

RESULTS AND DISCUSSION

This chapter will present the results of the experiments described in Chapter III and compare these results to those of the investigations discussed in Chapter II. The initial section will characterize the as-welded materials. This will be followed by sections presenting the results of the aging and stressed aging experiments.

I. AS-WELDED MATERIALS

Since this investigation has been directed toward characterizing the aging response of welds of different ferrite contents, this section is directed toward comparing the two types of as-welded materials used in this investigation to establish a basis for future comparisons.

Figures 5 and 6 illustrate the variations in surface ferrite content over the four weld lengths in the as-welded and milled surface conditions. Table 3 indicates that the ferrite content over the as-welded lengths of the argon shielded deposits varied from 3.1 to 7.6 and from 0.5 to 0.0 for the argon-nitrogen shielded deposits. The transverse ferrite numbers determined from the optical metallographic specimens, oriented transversely to the welding direction, were 4.8 for the argon shielded deposit and 0.3 for the argon-nitrogen shielded deposit. These numbers will henceforth be referred to as the transverse ferrite numbers. These values are seen to be close to the averages that would be predicted from the surface ferrite measurements.

In a more rigorous assessment of ferrite variation, Gunia and Ratz (74) found that for an average ferrite content of 2.8, the actual

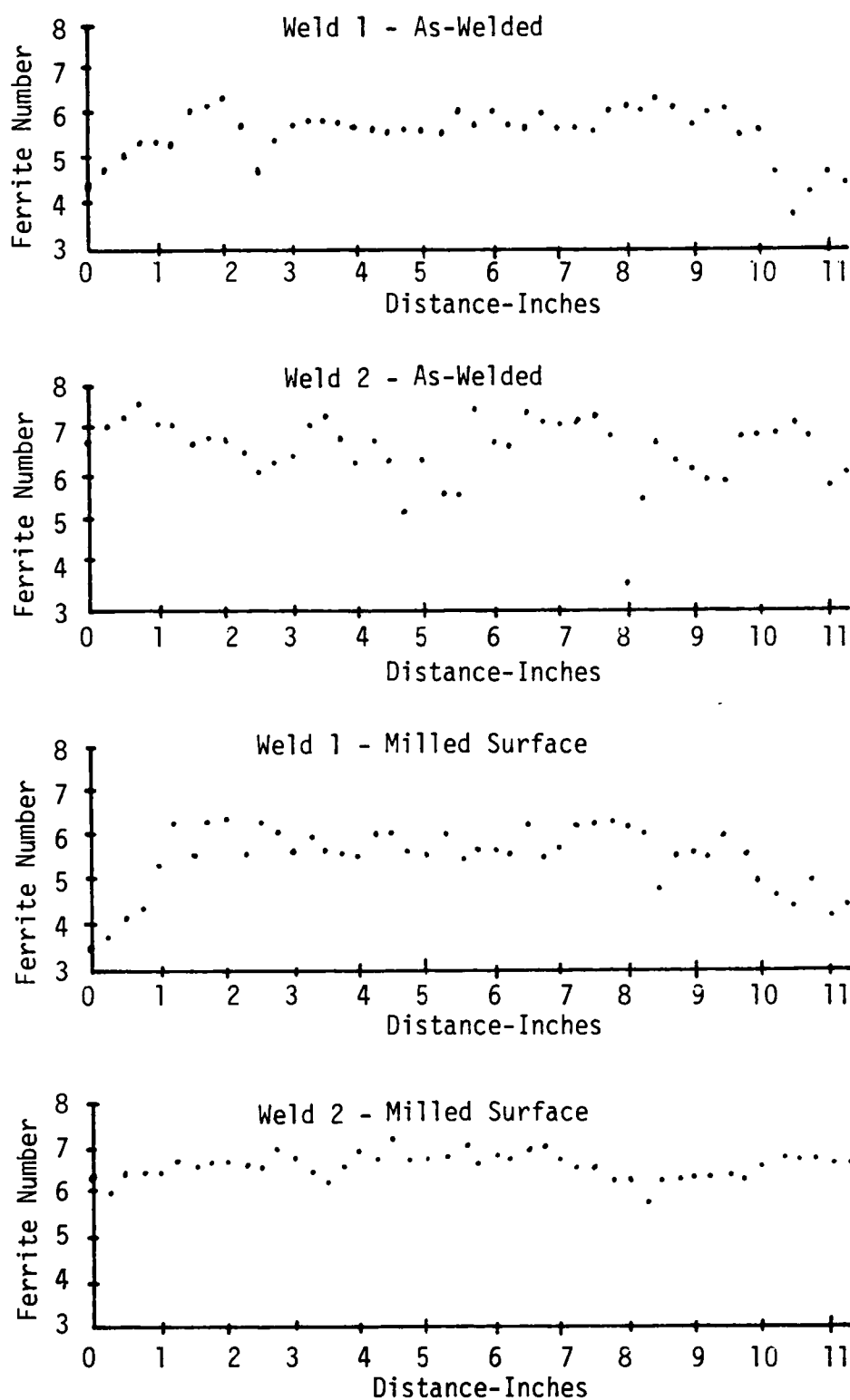


FIGURE 5. HETEROGENEITY OF FERRITE CONTENT IN AS-WELDED ARGON SHIELDED DEPOSITS

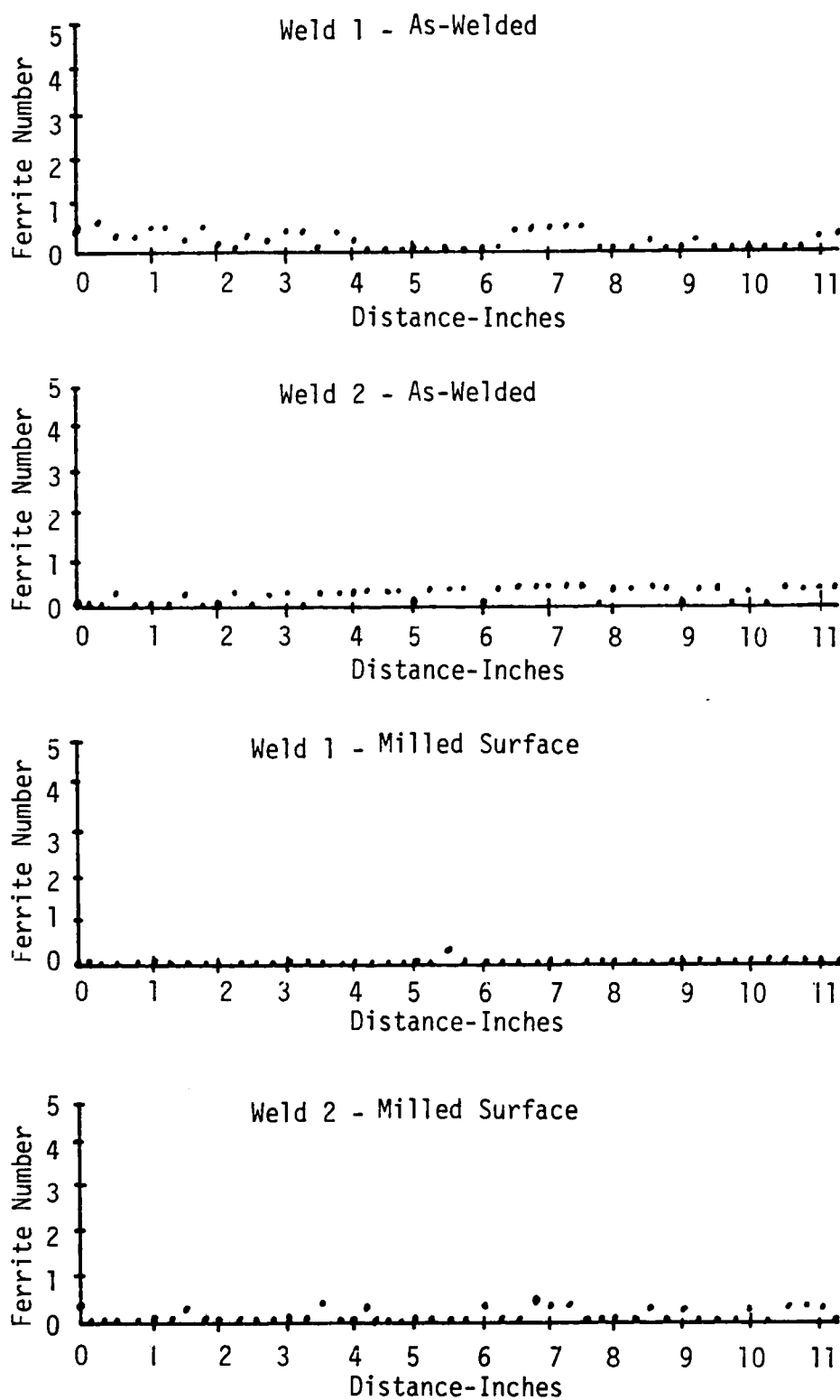


FIGURE 6. HETEROGENEITY OF FERRITE CONTENT IN AS-WELDED ARGON-NITROGEN SHIELDED DEPOSITS

ferrite content varied from 0.3 to 8.1%. Similarly, Goodwin et al. (62) have reported that a multipass 308 gas tungsten arc deposit had a variation in ferrite content from 4.9 to 10.2. DeLong (55) has noted that variations in ferrite content occur within the cross section of the bead, along the length of the bead, and from bead to bead, and that these variations are the result of differences in cooling and freezing rates, from changes in chemistry due to segregation and dilution effects, and possibly the result of variations in the amount of nitrogen picked up from the air as the weld progresses. (See Table 3.)

TABLE 3
EXPERIMENTAL RESULTS FOR THE AS-WELDED MATERIALS

Shielding Atmosphere	Variation in Ferrite Number Over the Weld Length		Transverse Ferrite Number	Extracted Weight Percent	Scatter in Extract (Percent) ^a
	As-Welded	Milled Surface			
Argon	3.1-6.2	3.4-6.2	4.8	0.842	9.0
	3.4-7.6	5.8-7.2		0.929	
Argon-Nitrogen	0.5-0.0	0.3-0.0	0.3	0.116	31.0
	0.4-0.0	0.4-0.0		0.167	

^aRatio of the smaller to the larger expressed as a percent and subtracted from 100.

The ferrite numbers reported in Table 3 do not show as much variation as those reported by Gunia and Ratz (74) and Goodwin et al. (62) probably because they were taken from areas which experience similar amounts of dilution and nitrogen pick up and most likely reflect the segregation due to the solidification process and variations in

freezing and cooling rate. The slightly tighter variations over the milled surfaces are probably the result of removal of some of the segregation effects when the last areas to solidify are removed during the milling operation.

If the composition of the weld deposit is assumed to be the same as that of the filler wire, i.e., neglecting variations due to dilution, element transfer, and atmospheric contamination, the DeLong diagram (55) would predict a ferrite number of 6.4 for these deposits. Using the composition of the filler wire, the formulations given with the DeLong diagram, and the transverse ferrite numbers, a calculated nitrogen content of 0.02% was determined for the argon shielded deposits and a value of 0.08% for the argon-nitrogen shielded deposits. These results are presented in Table 4. A more realistic conclusion would be that the nitrogen content of the mixed gas shielded deposits was about four times that of the argon shielded deposits.

TABLE 4
CALCULATIONS FROM THE DeLONG DIAGRAM

Chromium Equivalent	Nickel Equivalent	Predicted Ferrite Number	Calculated Nitrogen Content in Weight Percent	
			Argon Shielded	Argon and Nitrogen Shielded
21.86	15.32	6.4	0.02	0.08

Source: W. T. DeLong, "Ferrite in Austenitic Stainless Steel Weld Metal." Welding Journal, 53, 7, July 1974, 273s-286s.

Omsen and Eliasson (32) found that solidification changed from ferritic to ferritic-austenitic at nitrogen content of about 0.06% in 316L castings. Therefore the possibility exists that duplex solidification could occur in the argon-nitrogen shielded deposits. However, the more extreme solidification rates and stirring action experienced during weld solidification would make assessment of this possibility difficult. However, a somewhat different segregation pattern might be expected in the mixed gas shielded deposits.

Table 3 also lists the results of the bulk extraction experiments. Debye-Scherrer powder diffraction patterns of the extracted powders indicated that ferrite was the predominant phase present in both types of welds. This result was verified by the strong attraction of the powders to a magnet. One of the two extracts made of the argon shielded deposit exhibited a trace amount of sigma phase. This result seems possible due to the very rapid rate of transformation reported by Daemen and Dept (33). No evidence of carbides was seen in any of the patterns. Several lines which could not be identified were observed in these patterns. These lines are thought to be due to some type of metastable inclusions. Also of note was that the interplanar spacings of these unidentified phases were different in the two types of deposits suggesting that nitrogen played some part in their formation.

The extracted weight percentages are found to be significantly lower than the transverse ferrite numbers—about 20% for the argon shielded deposits and about 40% for the argon-nitrogen shielded deposits. This indicates that only a small part of the total ferrite is not dissolved by the electrolyte. The disparity in dissolution behavior of

ferrite particles within a given weld and between the two welds is probably linked to the variation in molybdenum content along the ferrite particles pointed out by Daemen and Dept (33). Efforts by our group to extract sigma phase using the hydrochloric acid-methanol solution from alloys which did not contain molybdenum indicated that sigma phase was dissolved in the electrolyte. Since Damen and Dept (33) found that the molybdenum content of ferrite particles in 316L showed substantial scatter, it appears feasible that this disparity leads to differences in dissolution rate of the ferrite in the electrolyte. The scatter in the amount of extract for each type of deposit, also given in Table 3, would appear to reflect the heterogeneity of the ferrite distribution; at the lower ferrite levels, there would be less likelihood of obtaining the same amount of ferrite from a given area, whereas at the higher ferrite level, a more statistical average would be seen. The significantly different ratio of the amount of extract relative to the ferrite number for the argon-nitrogen shielded deposits is probably due to the lower ferrite content allowing more of the ferrite particles to contain enough molybdenum so as not to be dissolved.

Figure 7 illustrates the nature of the structures of the two types of deposits as observed in the optical microscope. Ferrite in the argon shielded deposits is present as lacy, dendritic particles covering about half the cell boundaries and grain boundaries. Ferrite in the argon-nitrogen shielded deposit is present as isolated, elongated particles. The substructure size appears to have been unaffected by the nitrogen addition.



FIGURE 7. AS-WELDED OPTICAL MICROSTRUCTURES. (a) ARGON SHIELDED:
(b) ARGON-NITROGEN SHIELDED

Figure 8 presents typical structures for these two types of deposits as observed in the transmission electron microscope. No ferrite particles were observed in the limited number of samples available of the argon-nitrogen shielded deposits. Tilting experiments indicated that the dislocation density in the ferrite in the argon shielded deposits was significantly lower than that of the austenite. The orientation of the dislocations in the ferrite particle seen in Figure 8 could have resulted from the tensile stress imposed on the ferrite as the austenite cools. A random dislocation structure in the austenite is seen in both types of deposits.

II. AGED MATERIALS

This section will describe the changes in structure that occurred in the two types of deposits after aging at 650°C for 10, 100, 300, 500, 700, 1300, and 2000 hours. Table 5 lists the ferrite numbers and weight percentages extracted from specimens that had been aged under these conditions. Analysis of these results must be placed in the context of the inherent heterogeneity of the as-welded deposits. Some appreciation of this heterogeneity can be drawn from the ferrite determinations made over the weld lengths described in the previous section.

Figure 9 illustrates the effect of these exposures upon the ferrite contents of the two types of deposits. After ten hours, the ferrite contents of both types of deposits had been reduced to about half the original values. Further aging had no effect upon the ferrite contents of the argon-nitrogen shielded deposits. After 100 hours, the ferrite content of the argon shielded specimen was one-tenth that of

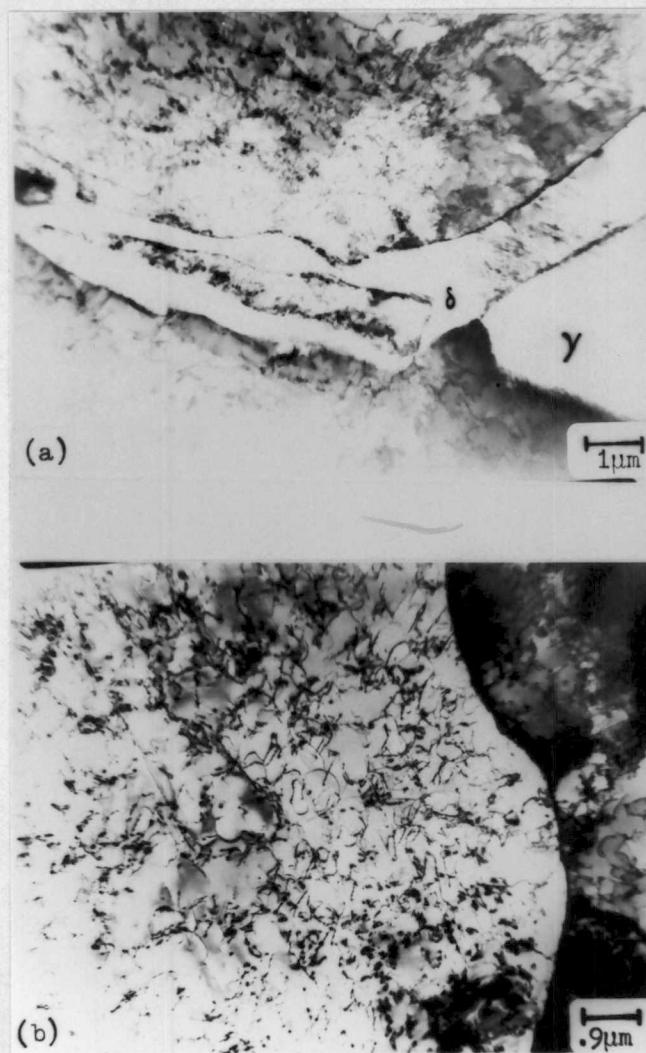


FIGURE 8. AS-WELDED TEM MICROSTRUCTURES. (a) ARGON SHIELDED:
(b) ARGON-NITROGEN SHIELDED

TABLE 5
EXPERIMENTAL RESULTS FOR AGED SAMPLES

Shielding Atmosphere	Aging Time (Hours)	Ferrite Number	Weight Percent Extracted	Scatter in Extract Percent ^a
Argon	10	2.30	1.06, 0.941	11.2
Argon-Nitrogen	10	0.15	0.315, 0.233	26.0
Argon	100	0.41	1.98, 1.50	24.2
Argon-Nitrogen	100	0.15	0.261, 0.220	23.4
Argon	300	0.20	2.42, 2.05	15.3
Argon-Nitrogen	300	0.15	0.406, 0.369	9.1
Argon	500	0.15	2.91, 2.22	23.7
Argon-Nitrogen	500	0.15	0.401, 0.397	1.0
Argon	700	0.15	3.01, 2.45	18.6
Argon-Nitrogen	700	0.15	0.599, 0.457	23.7
Argon	1300	0.15	3.34, 2.63	21.3
Argon-Nitrogen	1300	0.15	1.43, 1.19	16.8
Argon	2000	0.15	4.64, 3.21	30.8
Argon-Nitrogen	2000	0.15	1.16, 0.993	14.4

^aRatio of the smaller to the larger expressed as a percent and subtracted from 100.

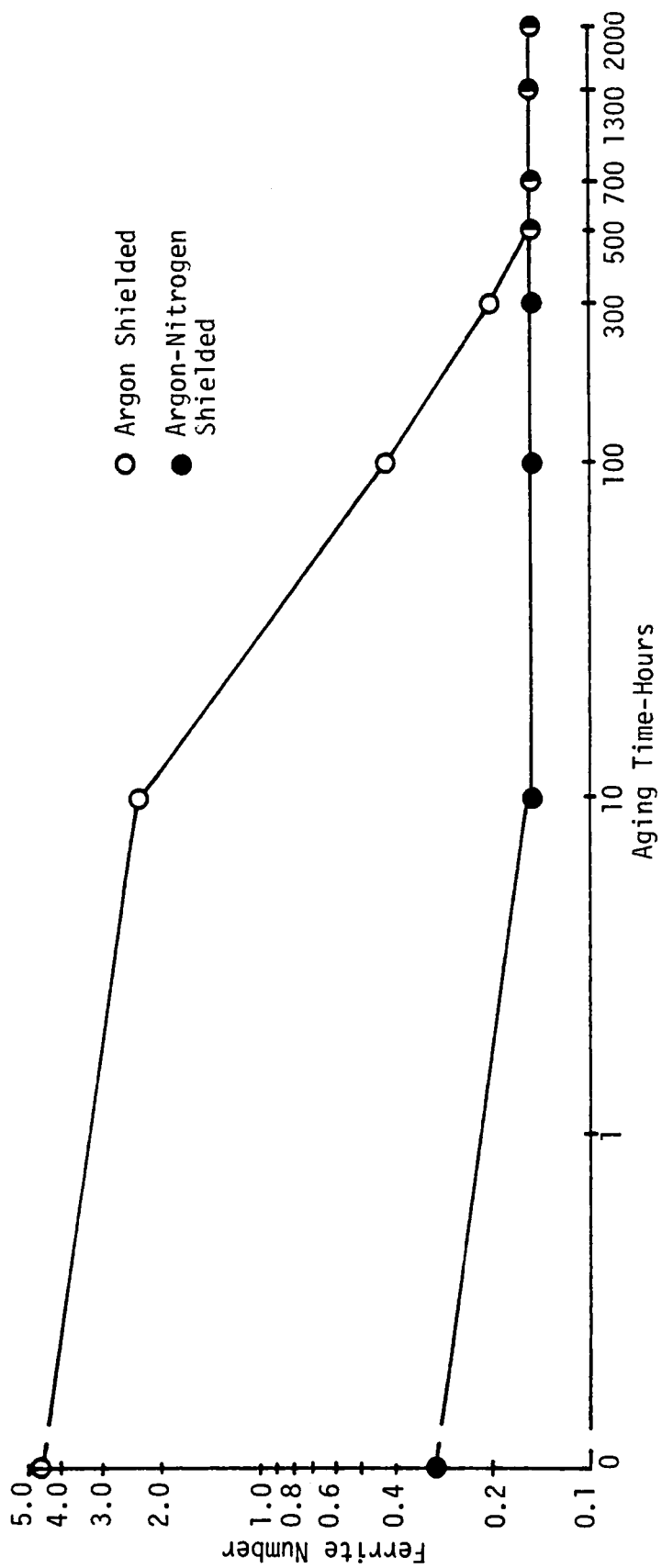


FIGURE 9. FERRITE CONTENT AFTER THERMAL AGING

the as-welded sample—one-sixth that of the specimen that had been exposed for ten hours. The ferrite content after 300 hours exposure was one-twentieth that of the original value—half the value after 100 hours. Further aging had essentially no effect upon ferrite content. These results are similar to those reported by Thomas and Yapp (51) who have reported that ferrite decay followed a sigmoidal transformation curve. Similar results have been reported by Spruiell et al. (75).

The small amount of ferrite present even after 2000 hours at 650°C could be the result of the sluggishness of the reaction at low ferrite levels or due to the composition of these materials being such that some small amounts of ferrite would be present in the equilibrium state. However, since both types of deposits contained about the same residual ferrite and the argon-nitrogen shielded deposits contain about four times as much of the powerful austenitizer nitrogen, it appears likely that the sluggishness of the reaction is responsible for this effect. Further support for this contention is seen in the response of the argon shielded deposit when it attains a ferrite content about equal to that of the argon-nitrogen shielded deposit in the as-welded condition. The 300 hour ferrite content of the argon shielded deposit is about half that of the 100 hour specimen which is very close to the difference in ferrite content of the argon-nitrogen shielded samples in the as-welded and ten hours at 650°C conditions. Therefore, it might be expected that after another 2000 hours at 650°C, the argon shielded deposit would still contain some trace amounts of ferrite. The possibility that strain induced martensite formed when the samples were quenched from 650°C could be responsible for this effect is unlikely

since the M_d temperature calculated from Hull's formulation (76) is considerably below the lowest temperature that these materials experience.

Figure 10 illustrates the results of the bulk extraction experiments. Debye-Scherrer x-ray analysis of the extracted powders for the argon shielded deposits indicated that sigma phase was the major constituent. Small amounts of $M_{23}C_6$ carbide were also observed. Thomas and Yapp (51) have reported that the maximum amount of $M_{23}C_6$ carbide that can be expected in 316L weld metal is about 0.6 weight percent. This result combined with the observations of the relative amounts of sigma and carbides present in the extracts would indicate that the reactions were occurring simultaneously. The amount of extract after ten hours exposure was about the same as that obtained from the as-welded specimen. This would appear to support the observation of Damen and Dept (33) who have suggested that ferrite transformation occurs first in those ferrite particles with the highest molybdenum contents. Further support for this contention is the lack of magnetic attraction of the extracted powder obtained from this sample and the absence of any indication of ferrite in the diffraction pattern.

The amount of extract obtained from the argon-nitrogen shielded sample after ten hours exposure was about twice that obtained from the as-welded specimen. The extract consisted primarily of $M_{23}C_6$ carbide but still contained some of the unidentified phase or phases described in the previous section. However, the extracted weight percentages were still only about a third of the maximum value that Thomas and Yapp (51) reported for standard 316L deposits which would indicate that the

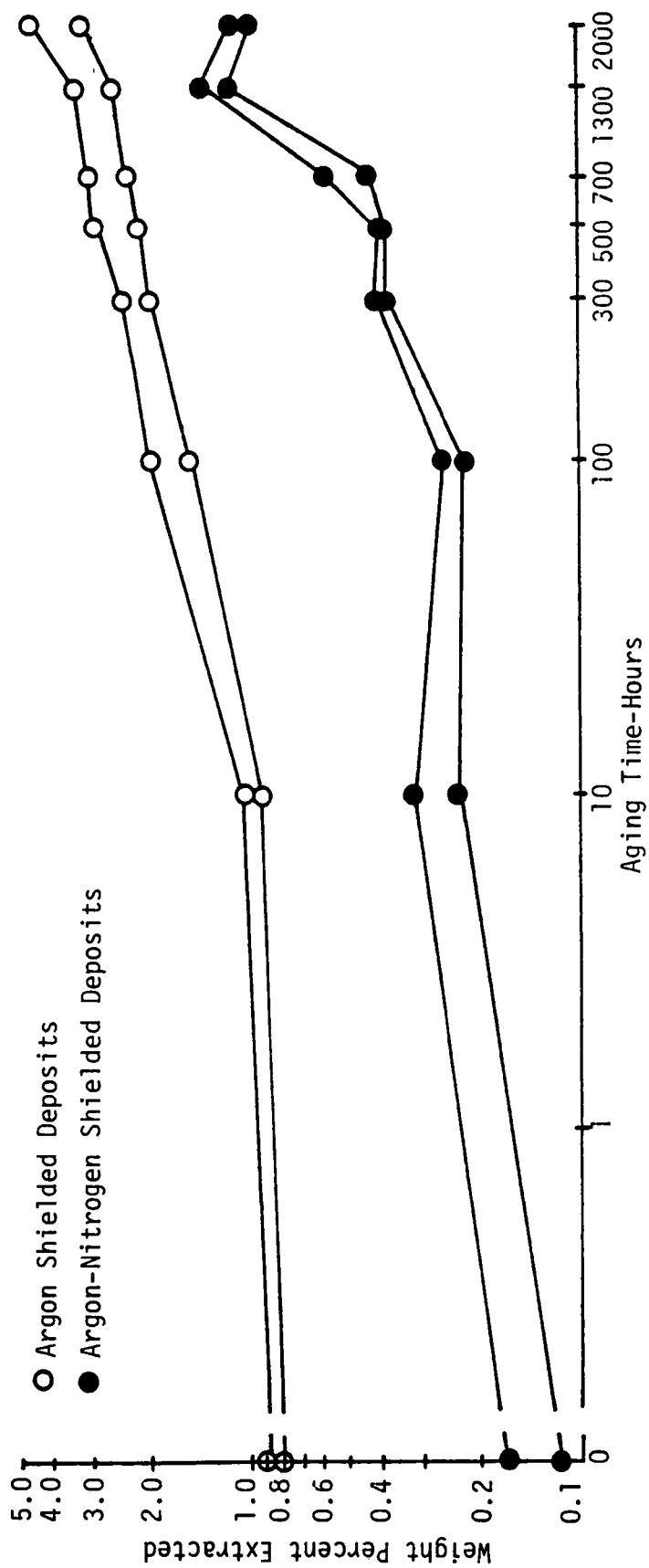


FIGURE 10. AMOUNT OF EXTRACT DUE TO THERMAL AGING

reaction had not been completed. No ferrite was observed in the diffraction pattern nor was the powder attracted to a magnet. Therefore, it appears that the effect of ferrite decay was carbide precipitation.

The sample of the argon shielded deposit that had been exposed for 100 hours showed about a 75% increase in the amount of extract. This result is similar to that observed for the change in ferrite content. However, the amount of extract is seen to be only about half the change in ferrite content. This would suggest that either the compositional variations among the sigma particles were such that a certain amount of sigma phase was dissolved during extraction or that as has been observed by other investigators, ferrite decomposes into sigma and austenite (6,34). The latter seems more likely due to the difference in composition of the ferrite and sigma phases.

Further aging of the argon shielded deposits is seen to have little effect upon ferrite content, but a gradual increase in the amount of extract is observed. Furthermore, the amount of sigma phase relative to that of carbide appeared to increase. This effect is most likely a reflection of the heterogeneity of the ferrite distribution in the as-welded deposits, but some effect due to carbide dissolution or changes in sigma composition might be expected.

The amounts of powder extracted from the argon-nitrogen shielded deposits that had been aged for 100, 300, and 500 hours were about the same as those extracted from the ten hour sample. However, after 700 hours exposure, the amount of extract had increased to near that reported as the maximum value in 316L (51). The 1300 hour exposure caused another doubling of the amount of extract. The amount of extract after 2000

hours was slightly less than that after 1300 hours exposure. This effect is probably due to the heterogeneity of carbide precipitation but might reflect some partial resolution. Also of interest was that the unidentified phase or phases observed in the as-welded pattern were still present although the amount of carbide precipitation reduced their relative intensities.

In summary, the results of the bulk extraction experiments appear to indicate that for the argon shielded deposits, the major effect of these exposures was the transformation of ferrite into sigma, carbides, and probably austenite. The argon-nitrogen shielded deposits when aged under these conditions formed only $M_{23}C_6$ carbides in amounts in excess of the maximum value consistent with the carbon content. This result would suggest that these were actually carbo-nitrides. Since no Cr_2N , Fe_4N , or M_6X were observed, it is likely that the actual nitrogen content was below 0.13 weight percent—the value that Omsen and Eliasson (32) reported as the nitrogen content for precipitation of these phases in 316L castings.

Figure 11 illustrates the effects of these exposures upon the optical microstructures. The sample of the argon-nitrogen shielded deposit that had been exposed for ten hours has an appearance very similar to that of the as-welded specimen suggesting that the majority of the reaction occurred in areas near or within the ferrite particles. The 500 hour specimen is seen to contain a fairly uniform distribution of grain boundary carbides. The sample that had been aged for 2000 hours reveals that the grain boundary carbide distribution had coarsened and a nonuniform distribution of carbides had formed in the cell



FIGURE 11. OPTICAL MICROSTRUCTURES AFTER THERMAL AGING. (a) ARGON-NITROGEN SHIELDED DEPOSIT AGED 10 HOURS; (b) ARGON-NITROGEN SHIELDED DEPOSIT AGED 500 HOURS; (c) ARGON-NITROGEN SHIELDED DEPOSIT AGED 2000 HOURS; (d) ARGON SHIELDED DEPOSIT AGED 10 HOURS; (e) ARGON SHIELDED DEPOSIT AGED 500 HOURS; (f) ARGON SHIELDED DEPOSIT AGED 2000 HOURS

boundaries. The argon shielded sample that had been exposed for ten hours reveals that ferrite decomposition occurred in patches within the ferrite particles. This effect further supports the observations of Damen and Dept (33). Increased aging time is seen to cause a more uniform distribution of sigma particles and some spheroidization of the individual sigma particles.

The limited amount of material, the inherent heterogeneity of the material, and the fine scale of the reactions prohibited comprehensive transmission electron microscopical analysis of these materials. However, a number of interesting observations were made.

Figure 12 illustrates some of the effects of these exposures on the dislocation substructures. A series of planar dislocation arrays are present in both micrographs. Yang and Spruiell (77) observed similar arrays in cold deformed wrought 316. They suggested that these arrays were the result of the low stacking fault energy preventing the formation of a cellular dislocation substructure. This result would suggest that either the stresses set up in the weld deposits during cooling or improper specimen preparation were responsible for these arrays. However, these arrays were not observed in the as-welded specimens which had been prepared in a similar manner as that of the aged specimens.

A possible explanation for this effect is seen in the observation that the aging temperature used in this investigation is about the same as that reported by Yang and Spruiell (77) as the recrystallization temperature for heavily deformed material. This would suggest that

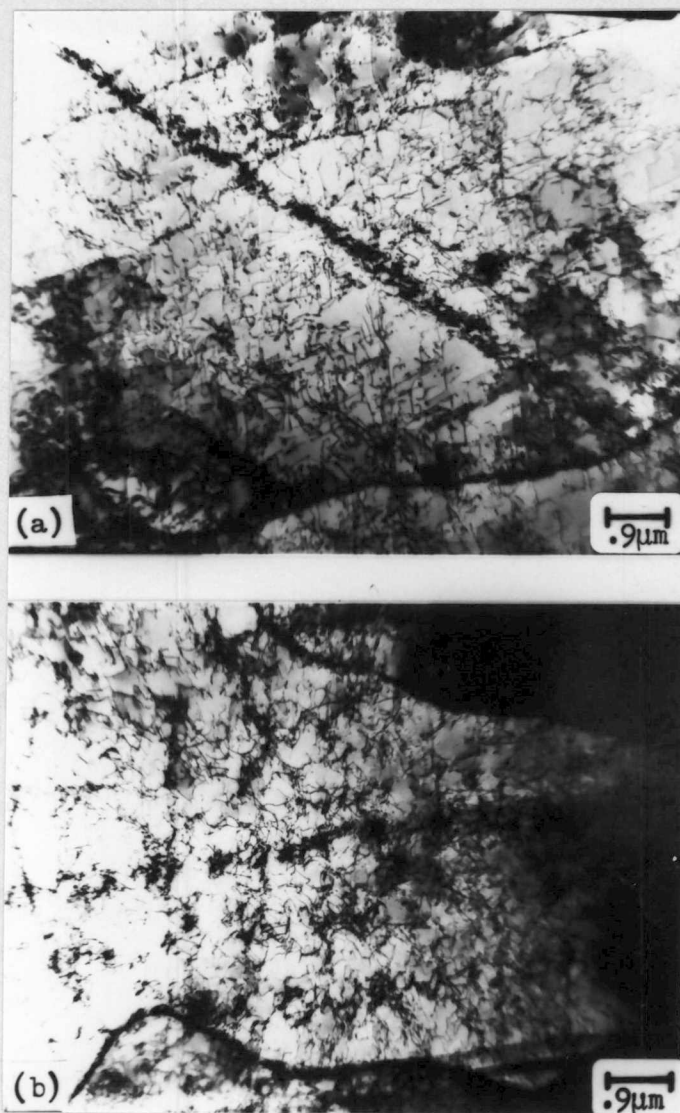


FIGURE 12. DISLOCATION SUBSTRUCTURES IN THE AGED MATERIALS. (a) ARGON-NITROGEN SHIELDED DEPOSIT AGED 10 HOURS; (b) ARGON SHIELDED DEPOSIT AGED 700 HOURS

diffusion rates would be high enough for substantial dislocation climb and that these arrays might be the result of recovery processes.

These dislocation arrays were most often observed in the argon-nitrogen shielded specimens which if nitrogen has a similar effect as that reported by Yang and Spruiell (77) for carbon would result in a higher stacking fault energy for these deposits. This would further support the contention that these arrays are the result of recovery processes. Also the number of such arrays appeared to increase with increased aging time. However, the limited number of samples and the higher residual stress pattern in the argon shielded specimens precludes a definitive assessment of the cause of these arrays.

Figure 13 illustrates the nature of carbide precipitation in the argon-nitrogen shielded deposits. Several morphologies of grain boundary particles are observed along with some intragranular carbide precipitates. In all cases, the carbide particles were found to have parallel orientations to the matrix. Figure 14 illustrates this relationship.

Figure 15 reveals a sigma particle and its diffraction pattern in the argon-nitrogen shielded specimen that had been aged for 100 hours. This result suggests that sigma phase forms in the argon-nitrogen shielded deposits but in amounts much less than those of carbide and in amounts too small to be detected in the extracts. Another possibility is that some sigma in this sample is dissolved by the electrolyte during the extraction process.

Figure 16 illustrates the nature of ferrite decay in the argon shielded deposits. The reaction is observed to occur at multiple sites

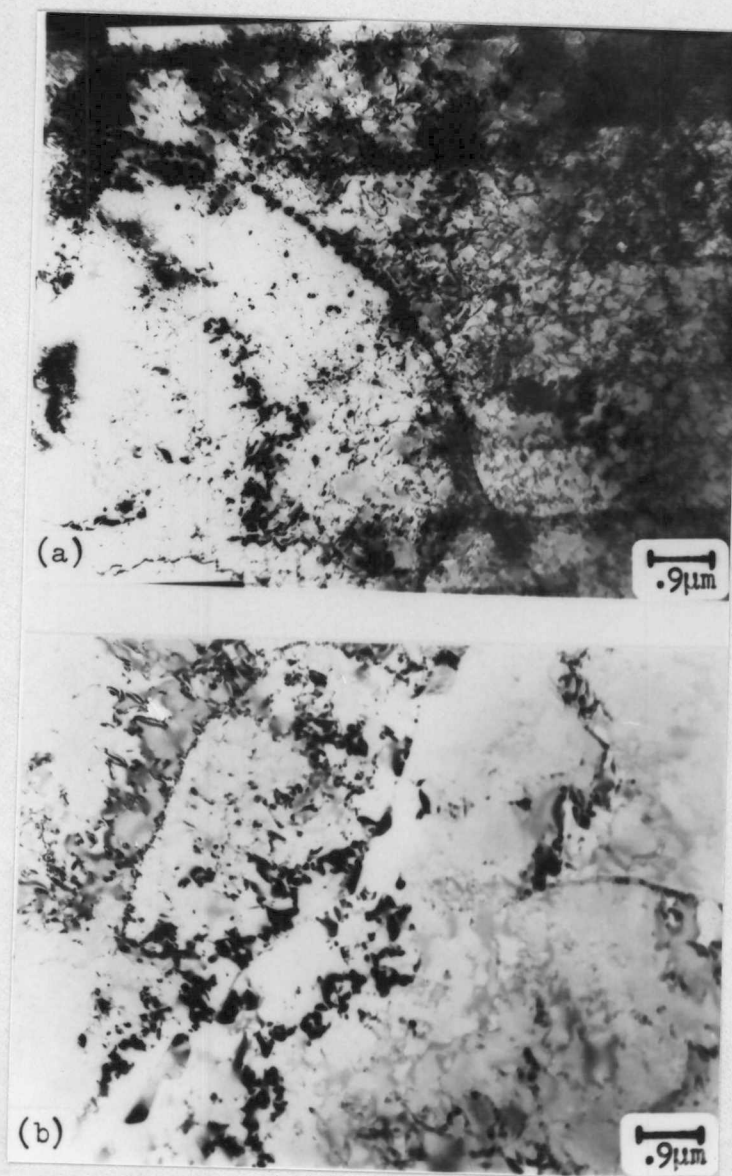


FIGURE 13. CARBIDE PRECIPITATION IN THE ARGON-NITROGEN SHIELDED DEPOSITS. (a) AGED 300 HOURS; (b) AGED 500 HOURS; (c) AGED 2000 HOURS; (d) AGED 2000 HOURS

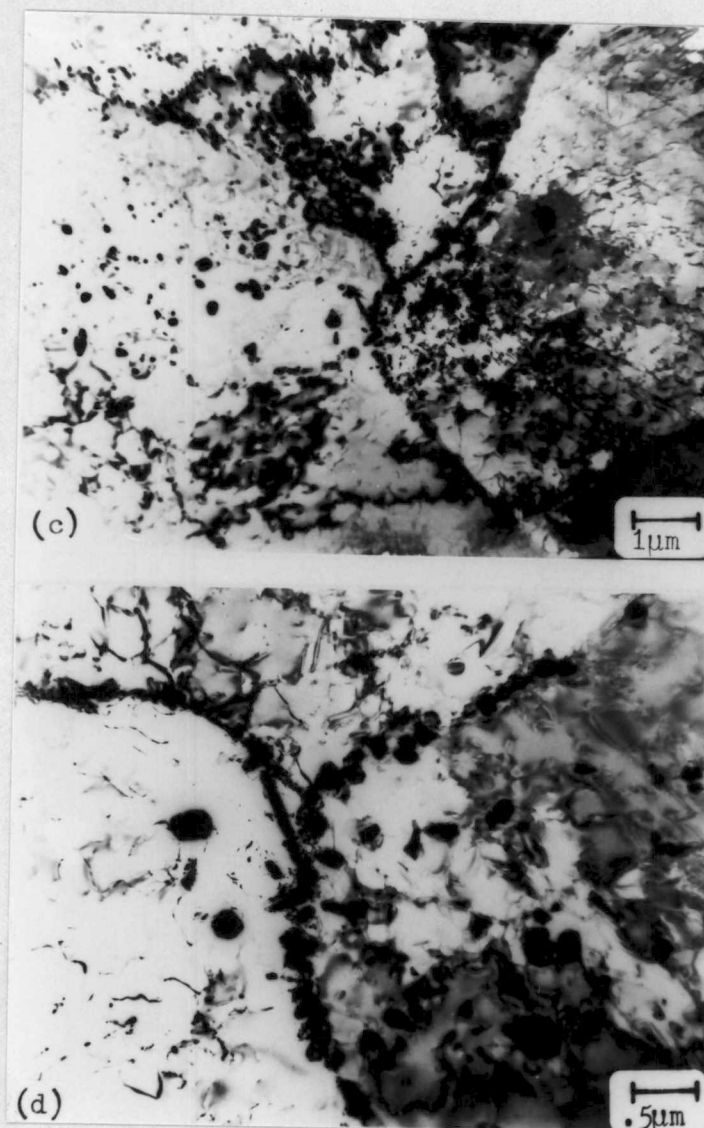


FIGURE 13 (CONTINUED)

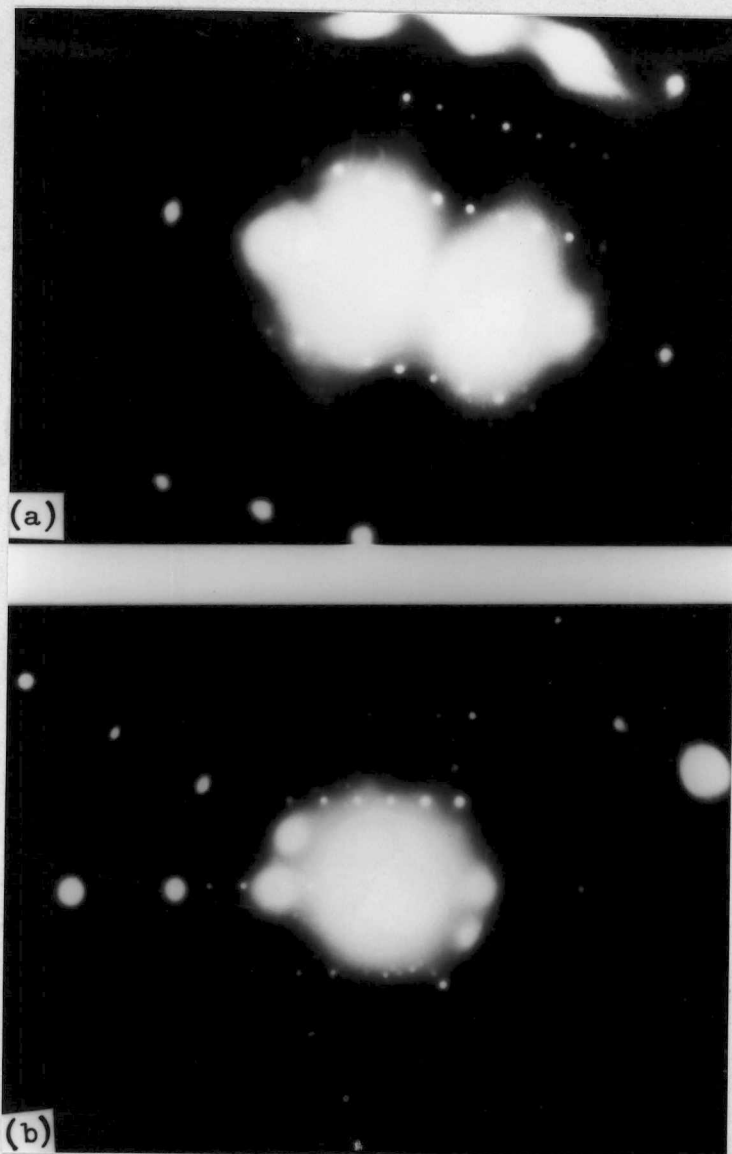


FIGURE 14. ORIENTATION OF CARBIDES TO MATRIX. (a) AGED 300 HOURS;
(b) AGED 500 HOURS

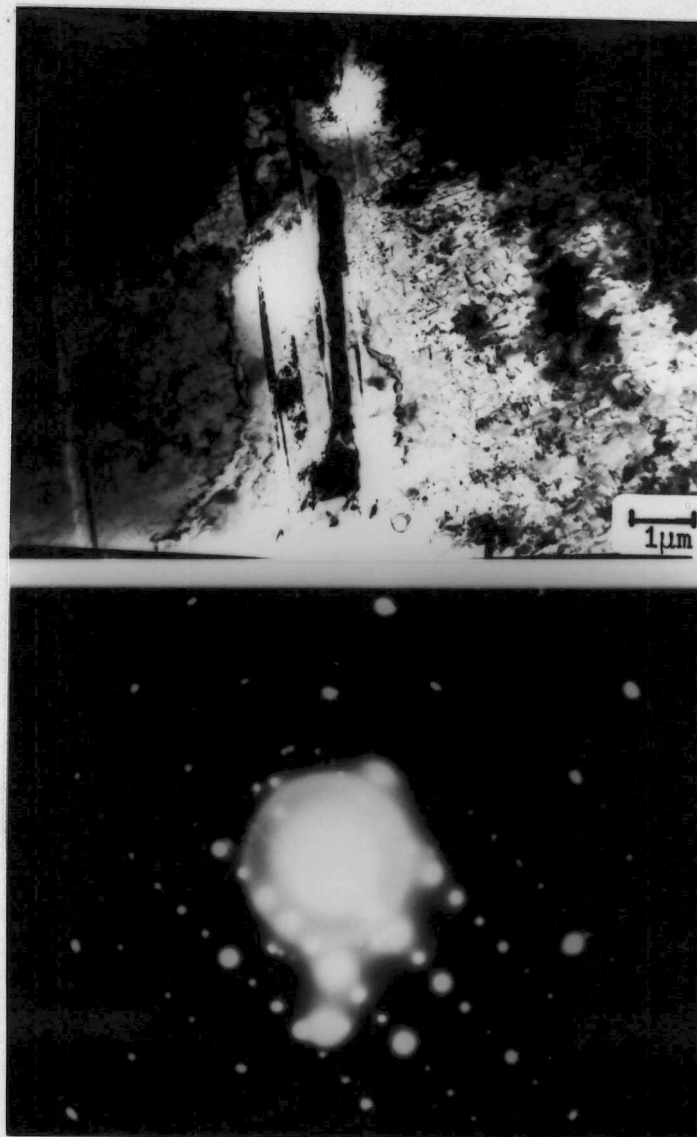


FIGURE 15. SIGMA PARTICLE AND ITS DIFFRACTION PATTERN IN ARGON-NITROGEN SHIELDED DEPOSIT AGED 100 HOURS

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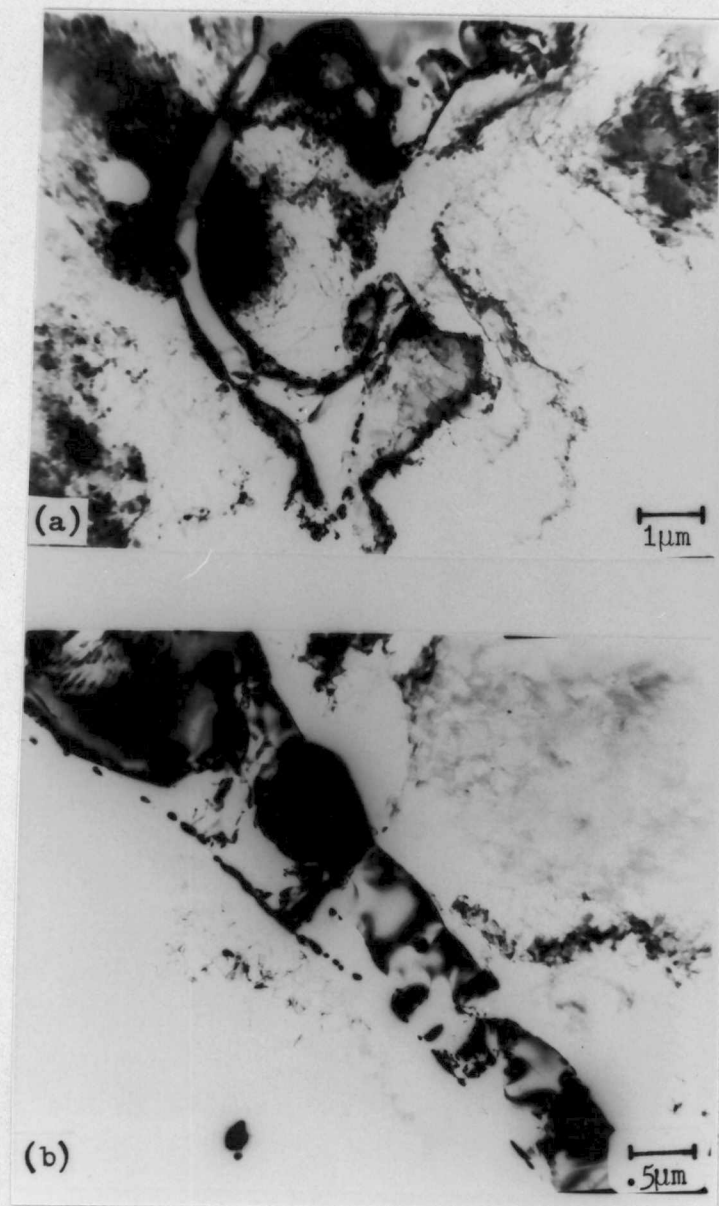


FIGURE 16. FERRITE DECAY IN THE ARGON SHIELDED DEPOSITS. (a) AGED 10 HOURS; (b) AGED 300 HOURS; (c) AGED 500 HOURS; (d) AGED 1300 HOURS

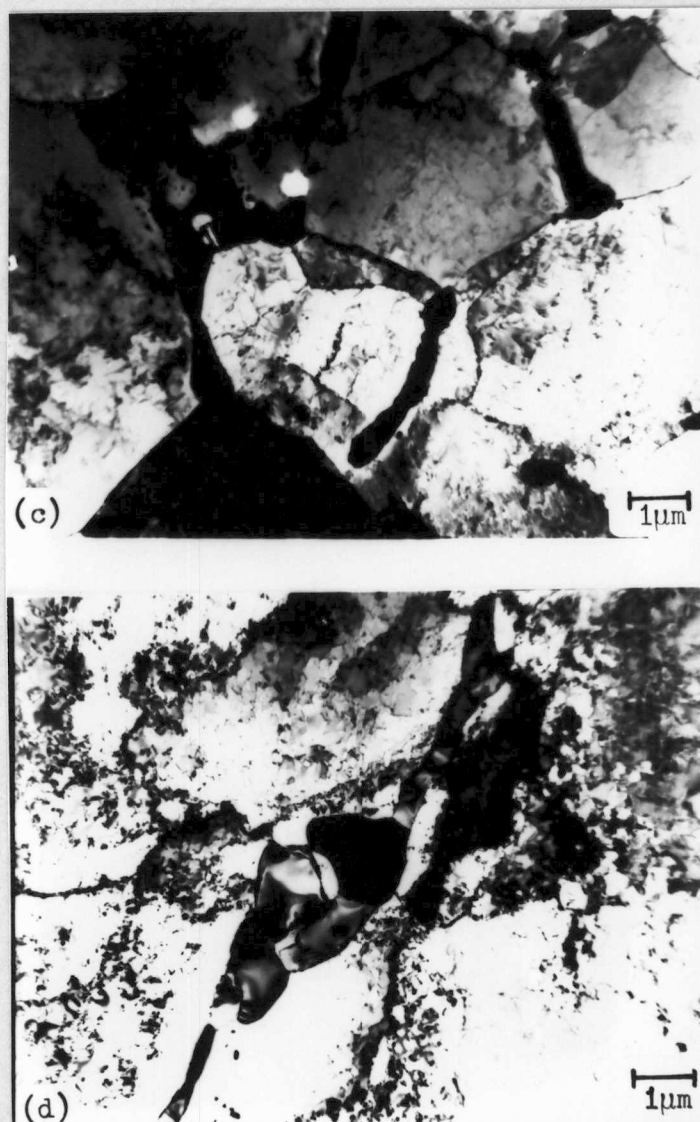


FIGURE 16 (CONTINUED)

within the ferrite with the end result being a chain of sigma particles. Also evident in these micrographs are isolated carbide particles.

III. MATERIALS AGED UNDER STRESS

This section will present the result of the stressed aging experiments and compare these results to those of the aging experiments.

A. Argon Shielded Deposits

Table 6 lists the ferrite numbers and weight percentages extracted from samples of the argon shielded deposits aged under the conditions described in Chapter III. In order to compare the results of the stressed aging experiments to those of the unstressed aging experiments, a parameter representing the variation in the amount of extract was calculated. This variation was calculated by taking the ratio of the amount of extract obtained from the stressed aging specimens to each of the amounts of extract obtained from the unstressed experiments aged for the same time, expressing these ratios as percentages, and then subtracting these percentages from 100. If the value obtained from the stressed aging experiment was greater than that from the unstressed experiment, the ratio was inverted.

Figure 17 graphically presents the effects of these exposures upon the ferrite numbers and weight percentages extracted. Lines were drawn to indicate the level of ferrite content and weight percent extracted in the unstressed experiments to facilitate comparisons between these results and the results obtained from the stressed aging experiments. These results when placed in the context of inherent heterogeneity of the material as described in the first section of this chapter indicate

TABLE 6
EXPERIMENTAL RESULTS FOR THE ARGON SHIELDED
DEPOSITS AGED UNDER STRESS

Aging Time (Hours)	Stress Value (MPa)	Ferrite Number	Weight Percent Extracted	Variation (Percent)
100	0	0.41	1.98, 1.50	24.2
100	80	0.68	1.14	42.4, 24.0
100	152	0.41	1.72	13.1, 12.8
100	185	0.28	1.89	4.5, 20.6
300	0	0.20	2.42, 2.05	14.9
232	80	0.28	2.19	9.1, 6.4
232	152	0.15	1.97	18.2, 3.9
232	185	0.15	1.74	27.8, 15.1
700	0	0.15	3.01, 2.45	18.6
700	80	0.15	2.77	8.0, 11.6
700	152	0.15	2.62	13.0, 6.5
1300	0	0.15	3.34, 2.63	21.3
1300	80	0.15	2.71	18.9, 3.0
1300	152	0.15	2.47	26.0, 6.1

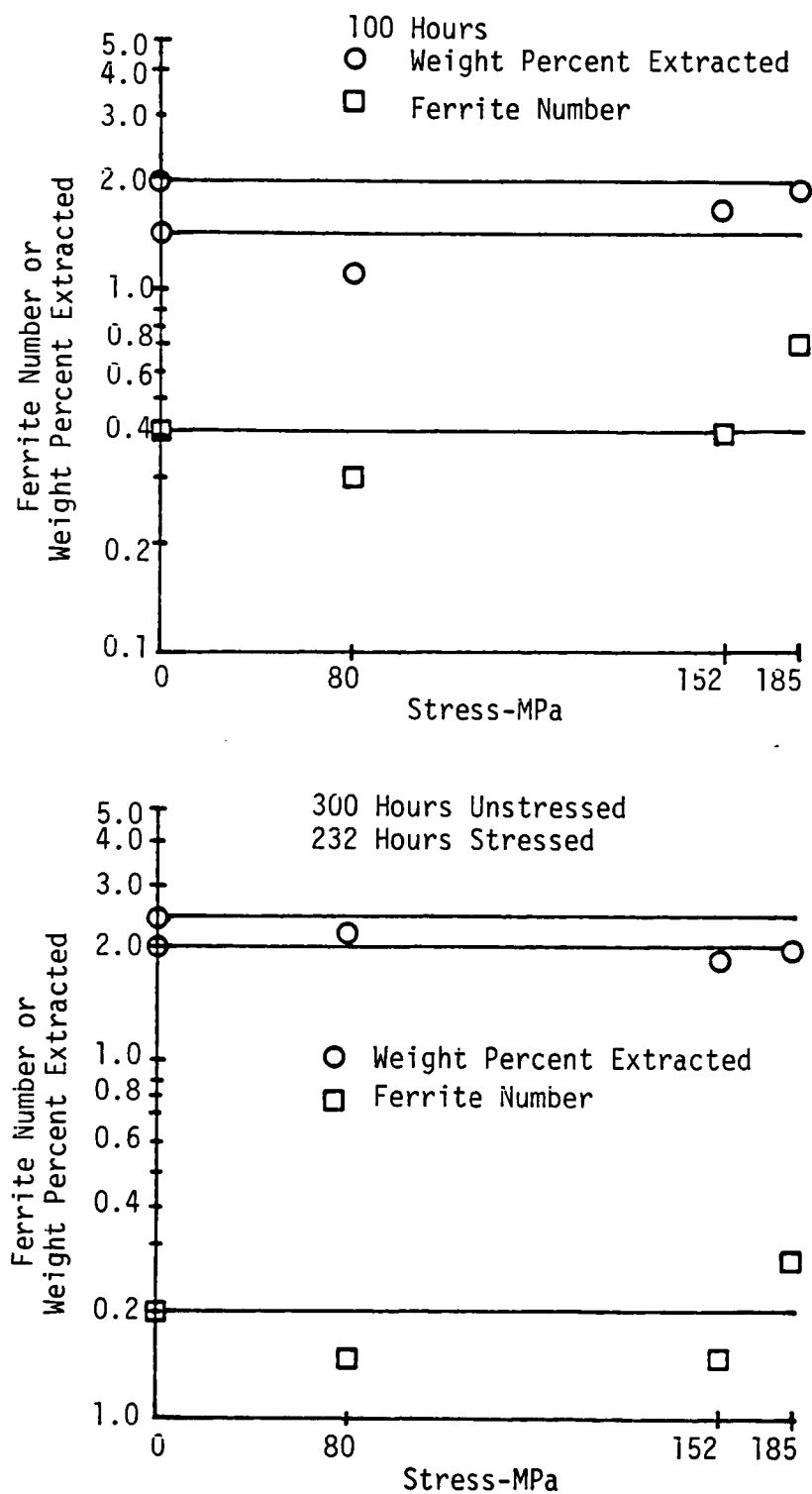


FIGURE 17. COMPARISONS OF STRUCTURAL STABILITY UNDER VARIOUS STRESS LEVELS FOR THE ARGON SHIELDED MATERIAL

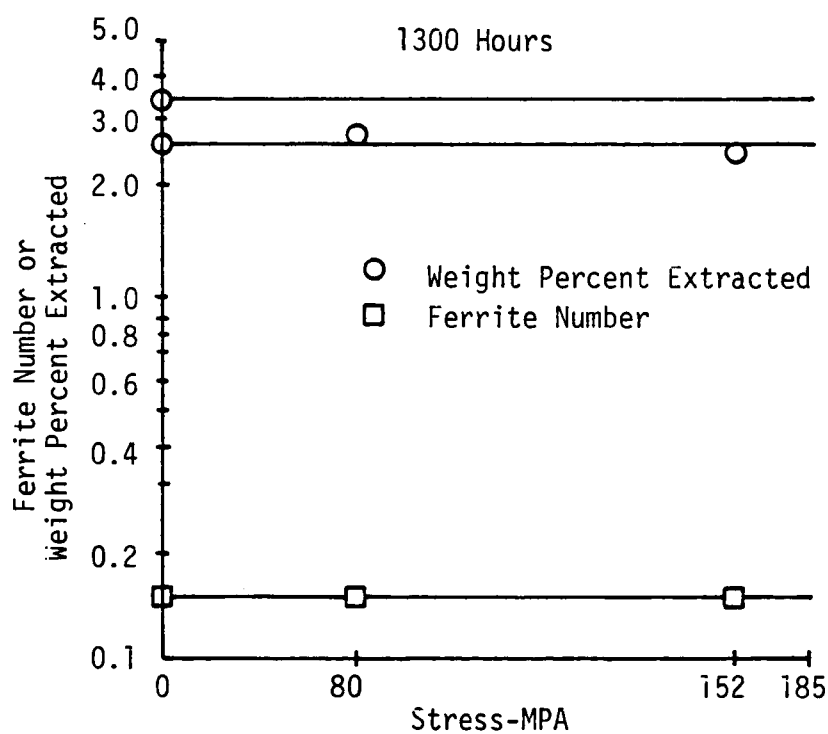
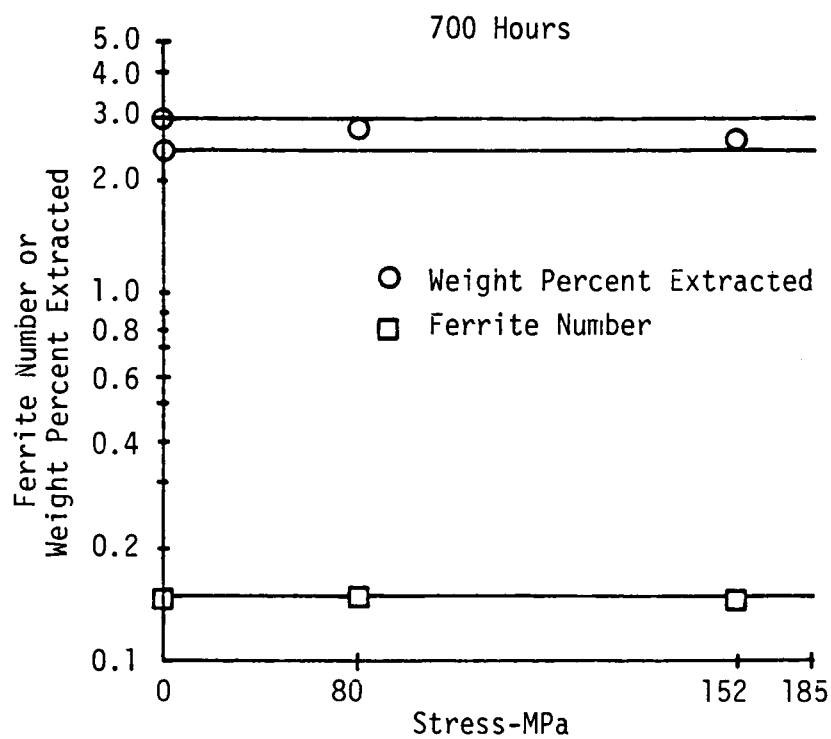


FIGURE 17 (CONTINUED)

no observable effect of stress on ferrite decay is present. The variations in weight percentages extracted are found to be similar to those of the unstressed experiments. Also no consistent variation is observed for a given stress level at different aging times—in some cases values are higher, in others about the same, and in others lower.

Figure 18 illustrates some of the optical microstructures of the aged and aged under stress specimens. These micrographs illustrate the heterogeneity of the ferrite distribution and that no significant effect of stress was evident in the optical observations. Figure 18 (a) and (b) represent the structures after 100 hour exposures in the unstressed and under the 185 MPa stress respectively. In both cases, ferrite decomposition is seen to occur in patches within the individual ferrite particles. Figure 18 (c) and (d) represent the effect of 1300 hours exposure in the absence of stress and under the 152 MPa stress respectively. These micrographs further demonstrate the heterogeneity of the material. Little difference is seen between these structures and those that had been aged for 100 hours which reflects the very slight difference in ferrite content as a result of the increased exposure.

Figure 19 illustrates the nature of ferrite decay during the stressed aging exposures. These micrographs are very similar to those obtained from the unstressed aging experiments. Sigma formation is seen to occur at several locations within the ferrite with the end result being a cluster of particles.

The sample that was to have been aged for 300 hours under the 500, 1500, and 100,000 hour rupture stresses fractured in the most highly stressed section after only 232 hours. A second sample aged in



FIGURE 18. COMPARISONS OF THE OPTICAL MICROSTRUCTURES OF THE ARGON SHIELDED AGED AND STRESS AGED SPECIMENS. (a) AGED 100 HOURS; (b) AGED 100 HOURS UNDER 185 MPa; (c) AGED 1300 HOURS; (d) AGED 1300 HOURS UNDER 152 MPa

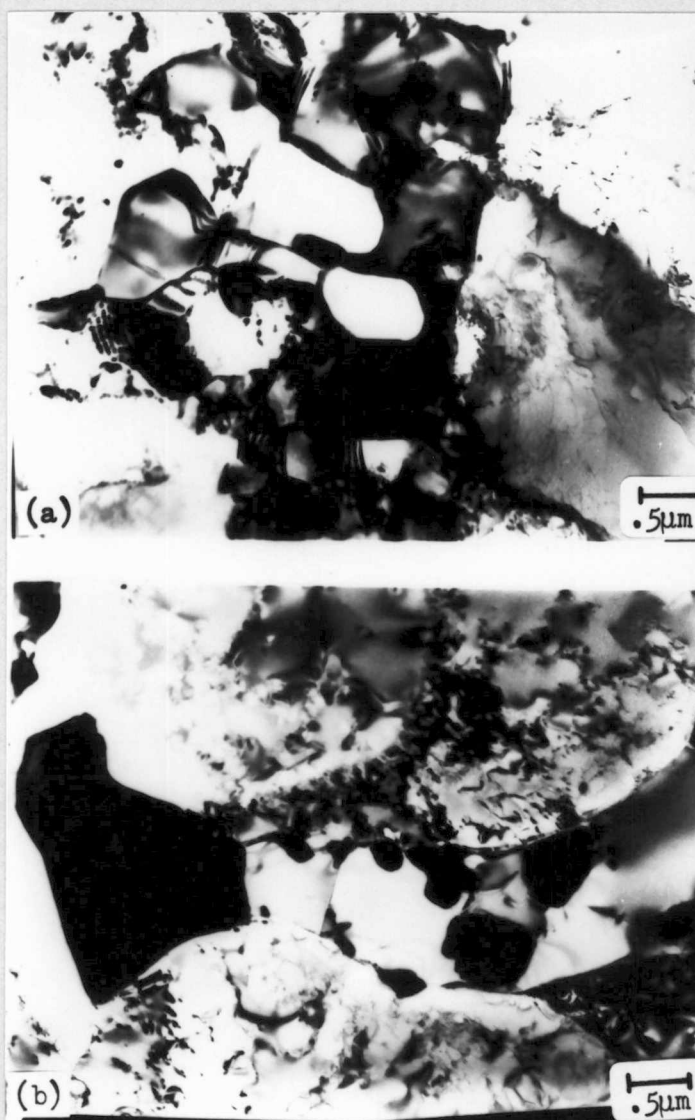


FIGURE 19. FERRITE DECAY IN THE ARGON SHIELDED DEPOSITS DURING STRESSED AGING. (a) 100 HOURS UNDER 185 MPa; (b) 232 HOURS UNDER 152 MPa

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the same frame and under the same load fractured after only 226 hours. A sample of the argon-nitrogen shielded deposit tested in the same frame and under the same load had not fractured after 300 hours. This result demonstrates the increased stress-rupture resistance of the argon-nitrogen shielded deposit which is similar to that reported by Cullen and Davis (73).

Figure 20 illustrates the nature of these fractures. The actual separation occurred away from the abrupt change in section which demonstrates the known notch toughness of this material. Also the sample shows evidence of necking indicating the ductility of the material. The actual fracture surface has a woody structure indicating that the substructure had a significant effect upon the fracture. Also seen in this micrograph are a number of surface cracks.

Figure 21 (a) reveals that the surface cracks show evidence of a link up of smaller cracks. Also some evidence of second phase particles within the cracks is seen. Figure 21 (b) reveals the ductile nature of the fracture surface. Figure 22 more clearly illustrates the ductile nature of the fracture.

B. Argon-Nitrogen Shielded Deposits

Table 7 presents the results of the stressed aging experiments and the unstressed experiments aged for the same times. Figure 23 graphically illustrates these results. The slightly higher ferrite content of the 100 hour 185 MPa sample is probably the result of the heterogeneity of the ferrite distribution. Otherwise, the ferrite numbers were identical under all aging conditions indicating no effect of stress on ferrite formation or decomposition. The extracted weight

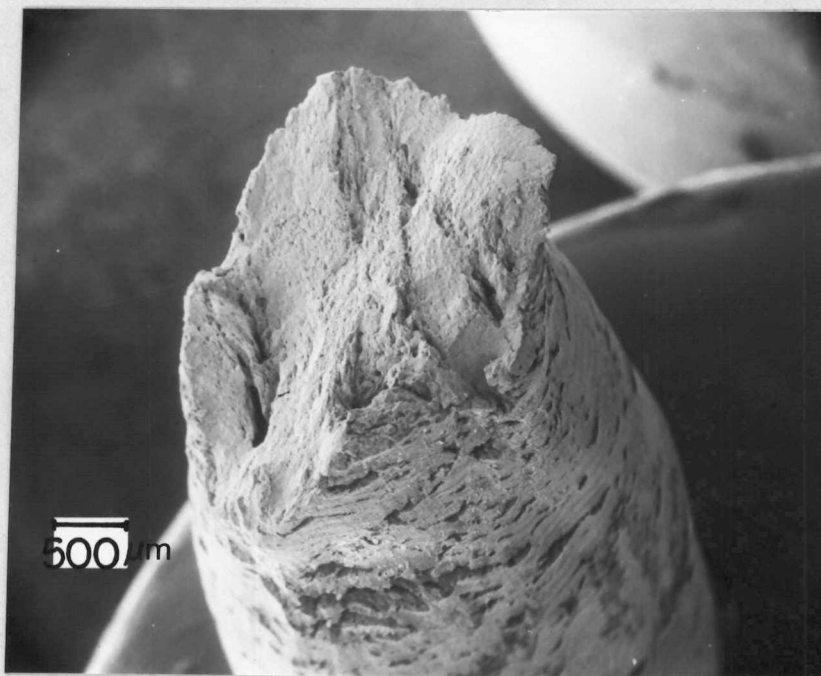


FIGURE 20. SEM MICROGRAPH OF THE ARGON SHIELDED SPECIMEN WHICH FRACTURED AFTER 226 HOURS

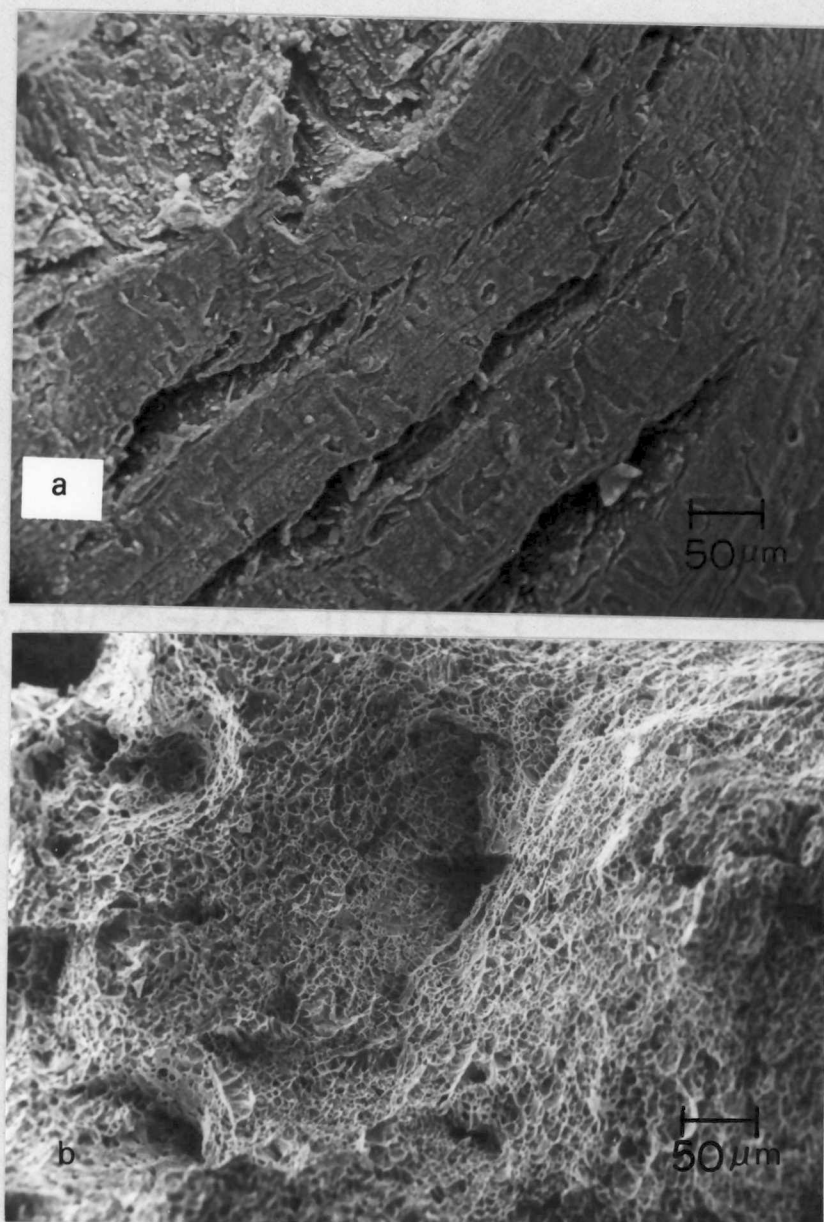


FIGURE 21. SEM MICROGRAPHS OF THE FRACTURED ARGON SHIELDED SPECIMEN.
(a) SURFACE CRACKS; (b) FRACTURE SURFACE

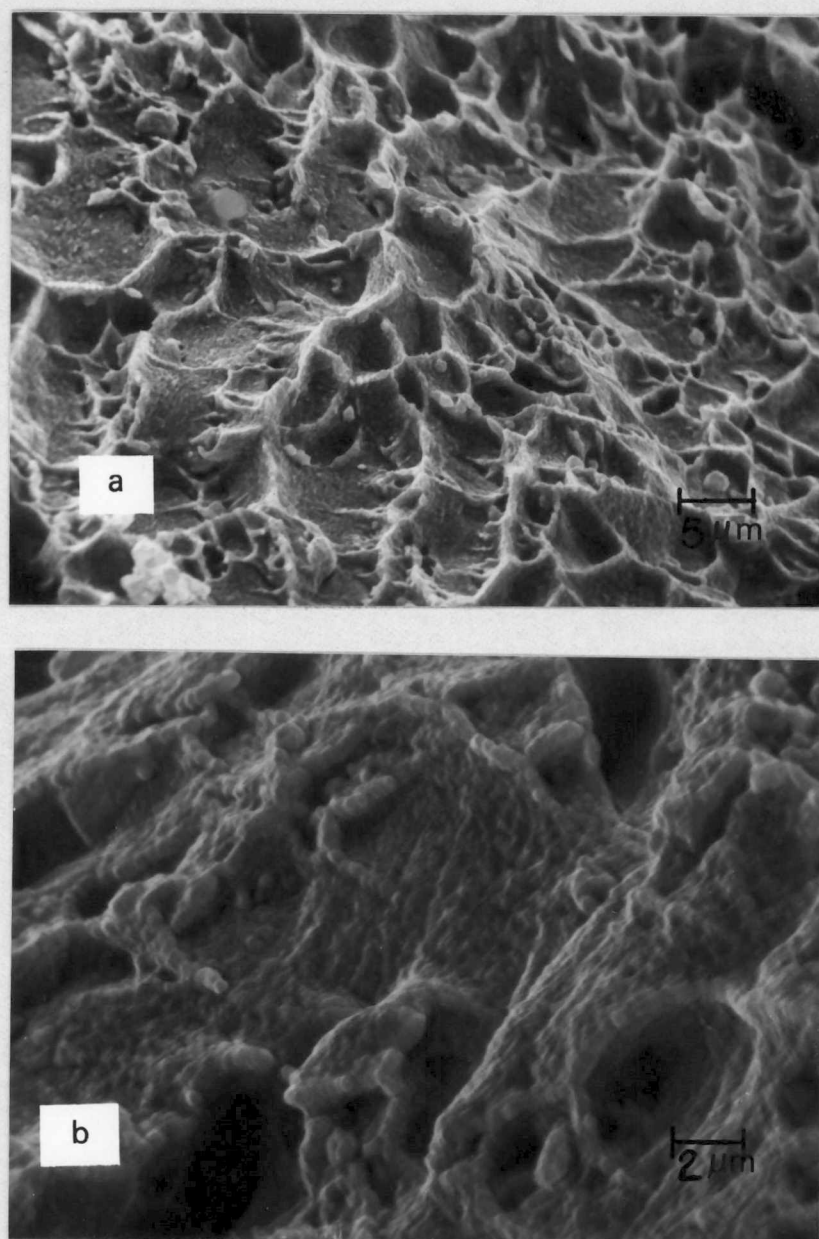


FIGURE 22. SEM MICROGRAPHS OF THE FRACTURE SURFACE. (a) 2000X;
(b) 5000X

TABLE 7
EXPERIMENTAL RESULTS FOR ARGON-NITROGEN SHIELDED
DEPOSITS AGED UNDER STRESS

Aging Time (Hours)	Stress Value (MPa)	Ferrite Number	Weight Percent Extracted	Variation (Percent)
100	0	0.15	0.261, 0.220	15.7
100	80	0.15	0.163	37.5, 25.9
100	152	0.15	0.388	32.7, 25.9
100	185	0.28	0.247	5.4, 10.9
300	0	0.15	0.406, 0.369	9.1
300	80	0.15	0.693	41.4, 46.8
300	152	0.15	0.458	11.4, 19.4
300	185	0.15	0.382	5.9, 3.5
700	0	0.15	0.599, 0.451	24.7
700	80	0.15	0.625	4.2, 27.8
700	152	0.15	0.391	34.7, 13.3
1300	0	0.15	1.43, 1.19	16.8
1300	80	0.15	0.404	71.7, 66.1
1300	152	0.15	0.399	72.1, 66.5

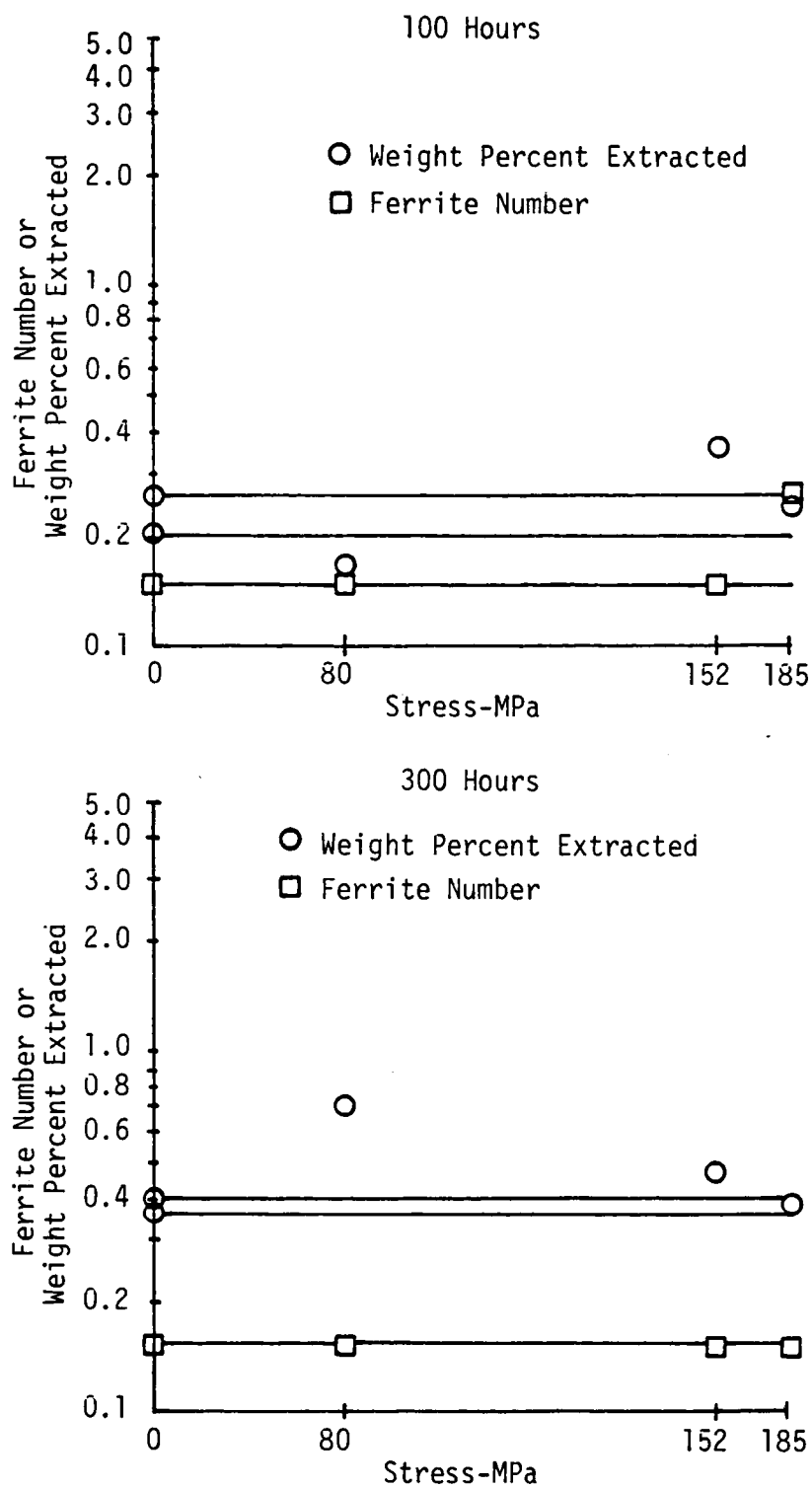


FIGURE 23. COMPARISONS OF STRUCTURAL STABILITY UNDER VARIOUS STRESS LEVELS FOR THE ARGON-NITROGEN SHIELDED MATERIAL

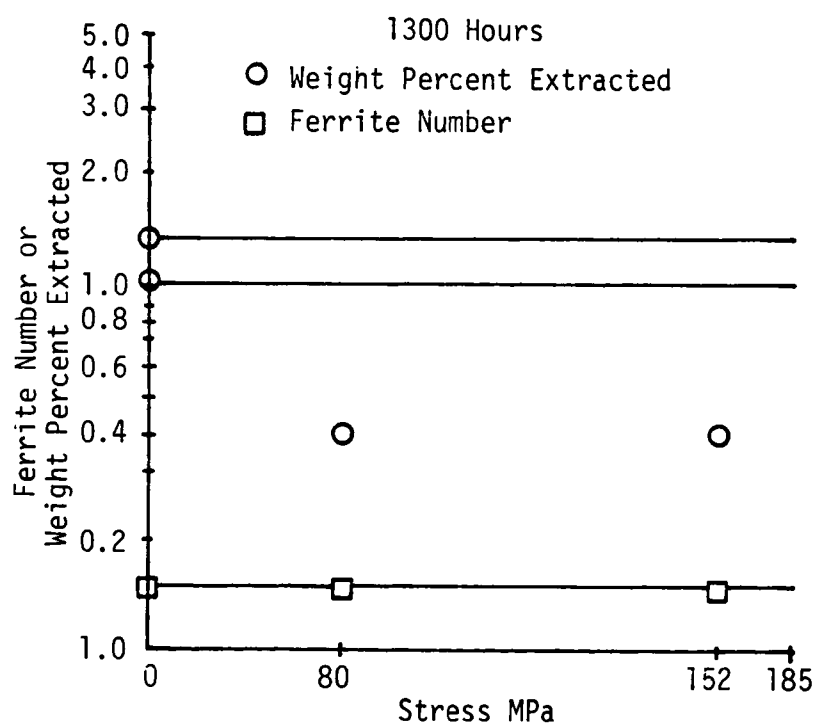
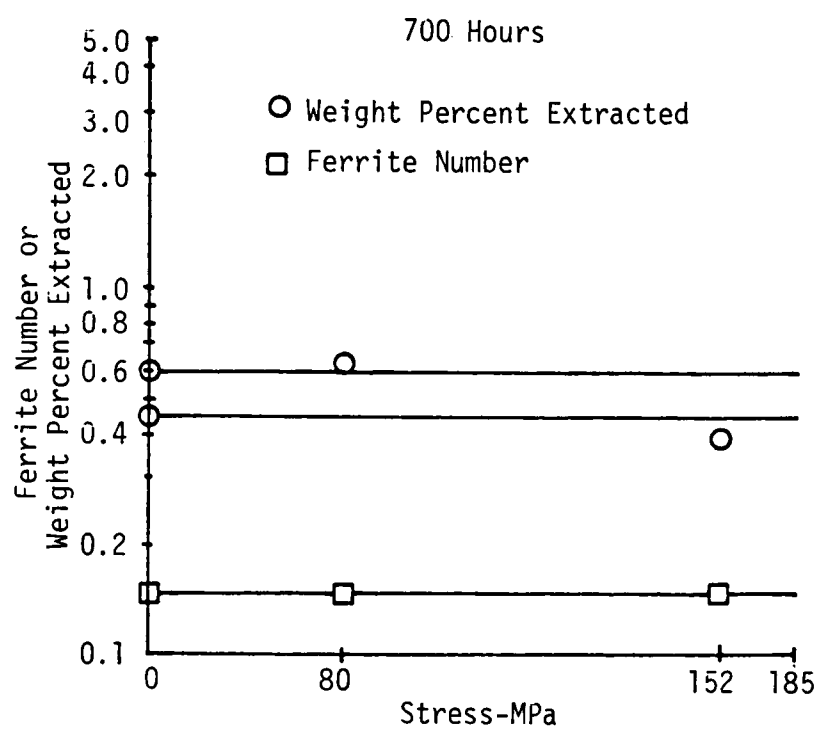


FIGURE 23 (CONTINUED)

percentages show about the same amount of variation as those of the argon shielded deposits for aging times of 100, 300, and 700 hours. However, the sample aged under both stress levels for 1300 hours contained only about one-third the amount of extract that was obtained from the unstressed specimen. X-ray analysis indicated that $M_{23}C_6$ carbide was still the only result of this exposure. It is difficult to rationalize this result on the basis of experimental error or heterogeneity of the material. There are at least two ways to explain this disparity. The first is partial carbide dissolution. However, since the amounts of extract after 1300 hours exposure are about the same as those obtained from the 700 hour exposure, it appears more likely that carbide formation was retarded.

Figure 24 illustrates the optical microstructures of the unstressed and most highly stressed specimens after aging for 100 and 1300 hours. The structures reveal no significant differences except that increased aging results in coarsening of the grain boundary carbide distribution and the precipitation of a nonuniform distribution of cellular carbide precipitates.

Figure 25 illustrates some of the observations made in the transmission electron microscope. Figure 25 (a) reveals the effect of aging under the 500 hour rupture stress for 100 hours on the dislocation substructure. This structure is similar to that seen in Figure 13 (a), page 96, and is probably the result of recovery processes rather than the applied stress. However, the limited number of samples precluded definitive assessment of this relationship. Figure 25 (b) and (c) reveal clustering of carbide precipitates which would suggest that the



FIGURE 24. COMPARISONS OF THE OPTICAL MICROSTRUCTURES OF THE ARGON-NITROGEN SHIELDED AGED AND STRESS AGED SPECIMENS; (a) AGED 100 HOURS; (b) AGED 100 HOURS UNDER 185 MPa; (c) AGED 1300 HOURS; (d) AGED 1300 HOURS UNDER 152MPa

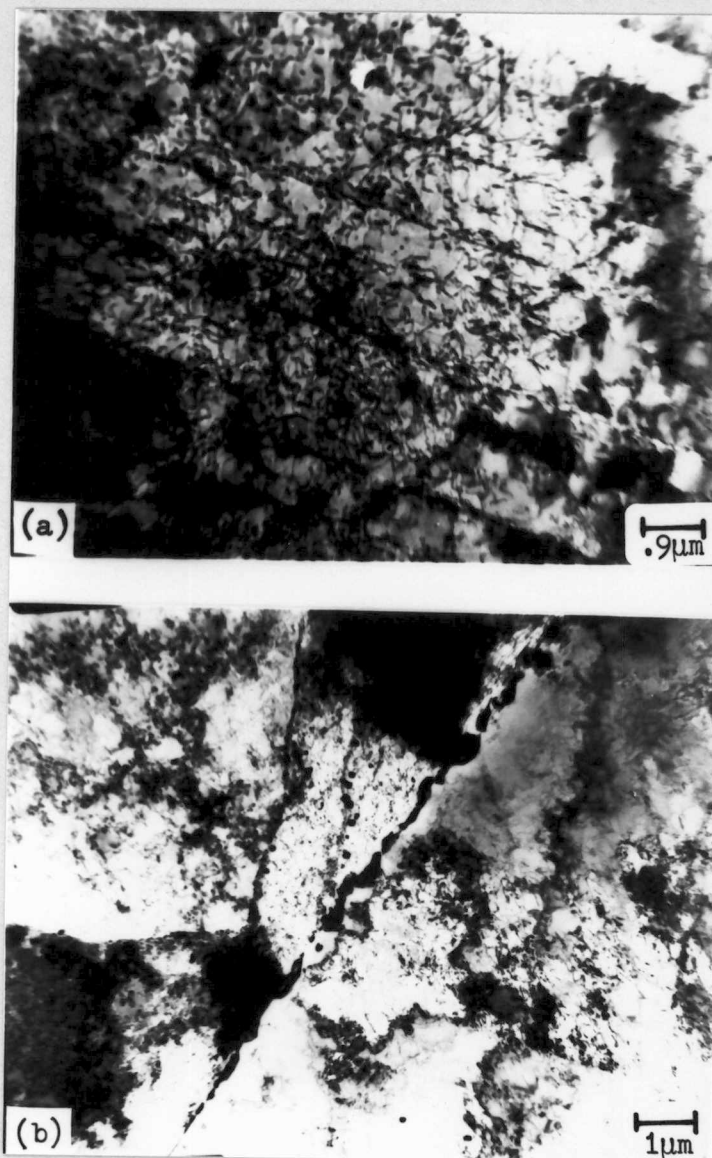


FIGURE 25. TEM MICROSTRUCTURAL OBSERVATIONS OF THE ARGON-NITROGEN SHIELDED DEPOSITS. (a) 100 HOURS UNDER 185 MPa; (b) 700 HOURS UNDER 80 MPa; (c) 700 HOURS UNDER 152 MPa; (d) 1300 HOURS UNDER 80 MPa

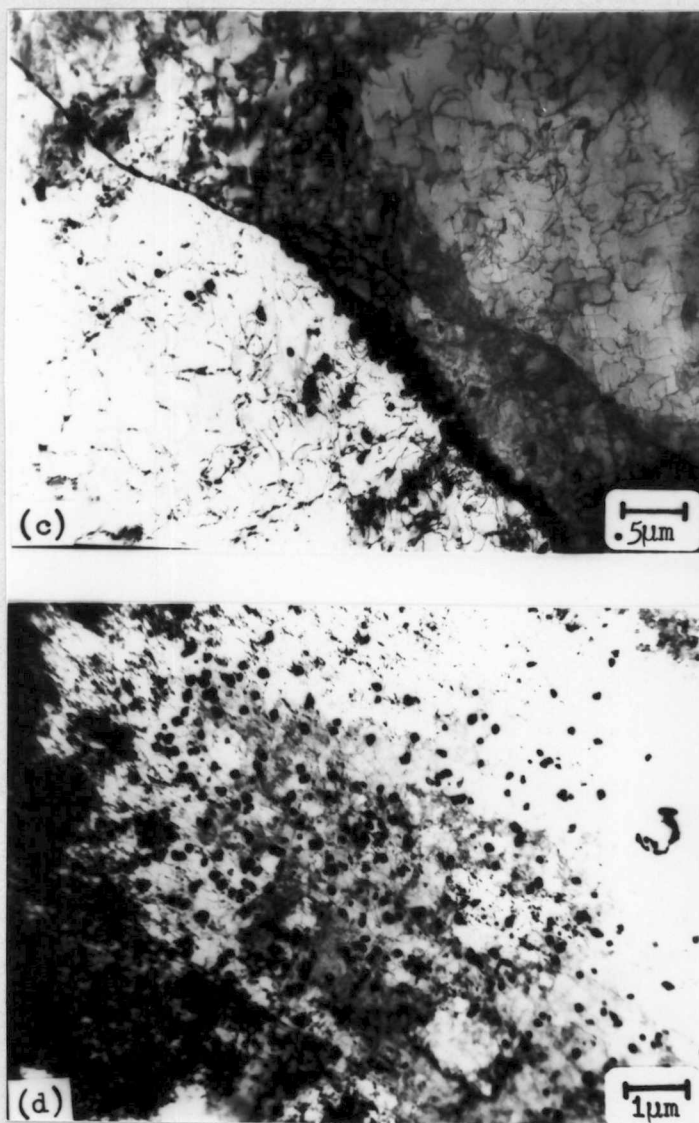


FIGURE 25 (CONTINUED)

coarsening of the grain boundary precipitation with increased aging time is the result of increased amounts of precipitation rather than from growth of the original particles. Figure 25 (d) illustrates the cubic shaped carbide particles which form intragranularly.

IV. SUMMARY

A 1% nitrogen addition to the shielding atmosphere is seen to greatly reduce the amount of ferrite present in gas tungsten arc 316L weld deposits and as a result change the structural stability observed due to elevated temperature exposure. The welds made in the standard manner (argon shielded) when aged at 650°C formed sigma phase, carbides, and probably austenite from the ferrite. The reaction was seen to be essentially complete after 100 hours at temperature. The mixed gas shielded welds when aged under similar conditions formed mainly carbides but in one instance sigma formation was observed. Also the reaction did not appear to have been completed until after at least 1300 hours at temperature. It therefore appears that by decreasing ferrite content, the addition of nitrogen to the shielding atmosphere effectively prevents sigma formation at least for the times of this investigation, but increases the amount of carbide or, perhaps, carbonitride precipitation. However, both deposits contained some residual ferrite after 2000 hours at temperature and the argon-nitrogen shielded deposit had about four times more of the powerful austenitizer nitrogen which would suggest that after aging times much greater than those of this investigation, additional reactions would occur.

Comparison of the response of materials aged under stress to those of the unstressed deposits indicated no significant effect for the standard deposits, but for the argon shielded deposits, stressed aging appears to have suppressed carbide precipitation to a value about equal to that which might be expected in standard deposits. Because of the paucity of data, this conclusion must be considered tentative until it is further substantiated.

The nitrogen addition was found to increase the creep strength of the material.

CHAPTER V

CONCLUSIONS

1. A 1% nitrogen addition to the shielding atmosphere effectively suppresses ferrite formation in 316L weld deposits.
2. The aging response of the deposit is found to depend upon the ferrite content—sigma, carbides, and probably austenite are formed in the argon shielded deposits, but only carbides with the possibility of some austenite are formed in the argon-nitrogen shielded deposits.
3. Carbides in the argon-nitrogen shielded specimens form in amounts greater than that expected based on carbon content suggesting that these are actually carbo-nitrides.
4. Stressed aging appears to have no effect upon the aging response of the argon shielded deposits.
5. Stressed aging appears to suppress carbide precipitation in the argon-nitrogen shielded deposits.
6. The argon-nitrogen shielded deposits appear to have greater creep resistance than the standard deposits.

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