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SOME METALLURGICAL FACTORS AFFECTING STRESS CORROSION CRACKING OF AUSTENITIC STAINLESS STEELS

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ABSTRACT

Tests on stress corrosion cracking of 18-8 stainless steels in boiling 42% $MgCl_2$ (154°C) show that alloys containing .015% C or .01% N or less do not fail within maximum time of exposure (200-260 hours). Commercial 304 alloys, on the other hand, fail within 0.2 to 1.4 hour.

Stable austenitic 20% Cr, 20% Ni are similarly resistant if the nitrogen content is sufficiently low (about .002%). Carbon (.01 to .23%), contrary to its effect in 18-8, confers resistance to cracking.

Niobium (columbium) (0.5 to 1.3%) alloyed with 18-8 low in N and C is found to stabilize the γ-phase on quenching from 1050°C, and the alloy is susceptible to cracking as quenched, contrary to Nb-free alloys of similar composition. Titanium, on the other hand, neither stabilizes the γ-phase, nor is 18-8 containing 0.6% Ti susceptible. Alloys of Ti or Nb (.4 to .6%) with remelted commercial type 304 18-8 crack in about the same short time as commercial type 304, 321 or 347 alloys, indicating that these elements have no appreciable influence.

Silicon (1 to 4%) appreciably increases resistance to cracking of 18-8 compositions, and also of remelted commercial 25-20 (type 310) compositions. Cobalt (2 to 14%) is also beneficial. Boron (0.1 to .2%) is probably beneficial; limited data show that it is at least not detrimental to cracking resistance. Boron increases tendency of the alloys to work-harden.

It is concluded from present data that α-phase 18-8 is relatively resistant to stress corrosion cracking whether α-phase is produced by transformation on quenching from 1050°C or by cold work at room or below room temperatures. Austenitic 18-8, on the other hand, readily fails by cracking whether the γ-phase is stabilized by N, C or Nb.

The mechanism of cracking appears to involve formation of crack-sensitive paths by plastic deformation. Under conditions of lattice strain, nitrogen in particular readily diffuses to lattice imperfection sites, such as dislocations, forming cathodic areas which stimulate corrosion of the adjoining alloy, thereby favoring crack propagation. The beneficial effect of Si and Ni is one of altering the pattern of cathodic atmospheres or precipitates, or of inhibiting their formation in the same way as Ni and Si also inhibit nucleation of cementite in carbon steels.

It is shown that formation of quasi-martensite is not necessary to cracking, and is itself relatively resistant. A threshold stress below which cracking will not occur is not expected, because creep occurs at any level of applied stress and the accompanying plastic deformation is sufficient to form crack-sensitive paths through grains of the alloy. The important effect of plastic deformation accounts for almost immediate cracking of cold worked 18-8 on exposure to $MgCl_2$ solution, but an induction time before cracking occurs for alloys stressed elastically.

A major shift in susceptibility with control of impurities or specific alloy concentrations, as presently reported, provides reasonable hope that the problem of stress corrosion cracking in austenitic stainless steels can be solved by a metallurgical approach.

SOME METALLURGICAL FACTORS AFFECTING STRESS CORROSION CRACKING OF AUSTENITIC STAINLESS STEELS

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Although the metallurgical factors entering intergranular corrosion of austenitic stainless steels are reasonably well understood, a parallel understanding of factors entering the transgranular failure of these alloys by stress corrosion cracking is not yet established. Only a few metallurgical investigations have been reported. Rocha(1) stated that resistance to stress corrosion cracking of 18-8 stainless steels in a hot $CaCl_2$ solution increases with nickel content, and is a function of austenite stability, the less stable alloys failing sooner. In his experiments, optimum resistance of an 18-8 composition occurred at 0.045% carbon, shifting to higher carbon percentages the higher the nickel content of the alloy. Scheil et al(2) presented data showing that ferritic stainless steels do not crack in boiling 42% $MgCl_2$ for test periods up to 300 hours. This was confirmed by Edeleanu(3) in tests lasting up to 1000 hours. The latter also showed that austenitic

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(1) H. J. Rocha, Stahl u. Eisen, 62 1091 (1942)

(2) M. Scheil, O. Zmeskal, J. Waber and F. Stockhausen, Welding Journal Res. Supplement, October 1943

(3) C. Edeleanu, J. Iron and Steel Inst., 173 140 (1953)

*Present address: Standard Oil Company of California, San Francisco, Calif.

stainless steels containing 12 to 21% Ni are more resistant than 8 to 10% Ni stainless steels. Scheil(4) stated that austenitic stainless steels become immune to stress corrosion cracking in magnesium chloride when the nickel content is about 45% or more. Edeleanu and Snowden(5) reported that a 30% Ni stainless steel marks considerable improvement over a 12% Ni stainless steel in resistance to cracking in steam or hot water.

Leu and Helle(6) found that alloying additions of 0.3 to 3.0% Si increased the number of observed cracks which form, which they interpreted in terms of a brittle oxide film forming on the alloy surface in presence of Si. But the results of this paper show an opposite effect, namely that Si additions to stainless steels are beneficial. It has been proposed that susceptibility(3) of 18-8 stainless steels to stress corrosion cracking or sites for initiation of cracks(7) are related to presence of quasi-martensite (ferrite) formed by plastic deformation. This idea has been criticized(8)(9) on the grounds that austenitic steels crack by stress corrosion even when

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(4) M. Scheil, J. Iron and Steel Inst., (correspondence), 174 218 (1953)

(5) C. Edeleanu and P. Snowden, J. Iron and Steel Inst., 186 406 (1957)

(6) K. Leu and J. Helle, Corrosion, 14 249t (1958)

(7) J. Hines and T. Hoar, J. Iron and Steel Inst., 184 166 (1956)

(8) S. Heger and E. Dulis, J. Iron and Steel Inst. (correspondence), 175 390 (1953)

(9) H. Nathorst, Ibid., 175 390 (1953)

the composition precludes transformation on cold working to quasi-martensite, or when the temperatures are too high for the austenite-ferrite transformation to occur. Edeleanu(10) emphasized later that quasi-martensite is the path of easy corrosion across grains only in some but not all cases.

Graf(11) showed that susceptibility of some Au-Ag and Au-Cu alloys to intergranular stress corrosion cracking is an intrinsic property of the plastically deformed alloy, independent of impurities. Robertson and Bakish presented data for Au-Cu alloys leading to the same conclusion(12). However, in the case of austenitic stainless steels, Uhlig et al reported that impurities, e.g. C and N, play an important role(13). Experiments along these lines have been continued and are reported herewith, including observations on relatively pure (1) 18% Cr-8% Ni alloys which transform in part to ferrite on quenching from elevated temperatures or on cold working, and (2) 20% Cr-20% Ni compositions which remain austenitic on quenching or cold working.

Experimental Procedure and Results

Stress corrosion cracking tests were carried out in boiling 42% $MgCl_2$

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(10) "Stress Corrosion Cracking and Embrittlement", C. Edeleanu, pp. 126-39, Edited by W. Robertson, J. Wiley and Sons, Inc., New York (1956)

(11) L. Graf, Ref. 10, pp. 48-60.

(12) W. Robertson and R. Bakish, Ref. 10, pp. 32-47

(13) H. Uhlig, R. White and J. Lincoln, Jr., Acta Metallurgica, 5 473 (1957)

solution (154°C) which Scheil(14) showed to be a suitable medium for accelerated tests. A detailed description of the test apparatus has been published elsewhere(15) in connection with a description of chemical factors affecting stress corrosion cracking of 18-8 stainless steels. In brief, a specimen measuring 1-3/4" x 3/16" x 0.040" (4.45 x 0.48 x 0.10 cm) was bent in a vise beyond the elastic limit to the shape of a C until it just fitted into a notched standard specimen holder having a span of 1-5/8" (4.1 cm). The specimen was immediately transferred to the test apparatus, the sliding arm tightened and the notched holder released. The span of the bent specimen was then adjusted between two porcelain insulators to a final 1-7/16" (3.65 cm) and held to this dimension by means of a compression spring.

The specimens in test, therefore, were all plastically deformed the same amount and were under continuous and relatively constant load, marking an improvement over a clamped C type specimen for which the elastic load decreases as the specimen creeps or begins to crack. Specimens were totally immersed in 250 ml boiling 42% magnesium chloride and cracking times were recorded electrically.

Magnesium chloride was chemically pure, but cracking times for a given alloy differed from batch to batch, making it necessary to check each shipment using a series of standard specimens held in reserve for such purpose. A correction was then applied to bring all cracking times to the same standard value. Mean cracking times of commercial 18-8 were found to differ

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(14) M. Scheil, "Symposium on Stress Corrosion Cracking of Metals", ASTM-AIME, pp. 395-410, Philadelphia (1945)

(15) H. Uhlig and J. Lincoln, Jr., J. Electrochem. Soc., 105 325 (1958)

from batch to batch by as much as 0.7 hour where the normal cracking time was 1.5 hours with standard deviation for a single batch of magnesium chloride equal to ± 0.2 hour. Reproducibility, in general, of stress corrosion cracking tests even under best of conditions is inherently not good, making it necessary to average several specimens for any single set of experimental conditions.

Alloys before testing were either annealed at 1050°C and water quenched, then sheared to size (annealed-sheared) or were sheared to size first, then annealed (sheared-annealed). In general, specimens that were "annealed-sheared" cracked in shorter time than specimens "sheared-annealed". Reproducibility of annealed-sheared specimens was better perhaps because these specimens supported a greater spring load than did the softer annealed specimens, and hence the corresponding percentage experimental variation of load in any single test was less. All specimens were pickled by a standard procedure immediately before tests. This consisted of a preliminary pickle in 25 vol % HCl, 25 vol % H_2SO_4 of the commercial concentrated acids at 90°C to remove visible oxide scale. Specimens were next pickled in 15 vol % nitric acid, 5 vol % hydrofluoric acid, based on the commercial acids, at 90°C for 5 minutes where each specimen was contained in individual test tubes maintained at temperature by a surrounding water bath. This procedure insured uniform surface treatment.

Specimens of commercial materials were prepared from the sheet as received after cold rolling to proper thickness. Alloys prepared in the laboratory were melted in a vacuum furnace in 1-1/2 pound lots using high purity alumina crucibles. After melting, a purified helium atmosphere (passed through liquid N_2 traps and over Ti sponge at 600°C) was introduced, and ingots were cast by drawing the melt into 9 mm diameter Vycor tubing, then water quenched. The ingots were homogenized in helium at 1050°C for 24 hours, and cold rolled to appropriate thickness.

The sources of materials used for the laboratory melts were as follows:

Nickel - electrolytic (courtesy of International Nickel Co.)
Iron - electrolytic or vacuum melted electrolytic[*]
Chromium - electrolytic (Electro Metallurgical Company)
Columbium - 99.7% (courtesy of Electro Metallurgical Company)
Titanium - duPont Sheet (E. I. duPont de Nemours Company)
Boron - 99.2% (courtesy of U.S. Borax and Chemical Company)
Cobalt - commercial reagent grade
Silicon - high purity (E. I. duPont de Nemours Company)

Nitrogen, when added, was supplied by exposure of the melt to the purified gas at 1 atm for several minutes. Carbon was introduced by addition of previously carburized iron produced by passing H_2 plus benzene over pure iron at 1000°C. No deoxidizers were used in any of the melts, and conditions otherwise were chosen to insure relatively pure compositions.

Results for annealed-sheared and cold-rolled specimens together with standard deviations from the average cracking times are summarized in Table I. Data for sheared-annealed specimens of several alloys are given in Table II. In general, cracking tests were carried out to not more than 200-250 hours because of the corrosive action of $MgCl_2$ solution on the test apparatus. The indication of cracking time in hours preceded by $>$ means that the specimen

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[*] Ferro-vac, purchased from National Research Corporation.

did not crack within the time specified. The few instances where circumstances led to arbitrarily choosing a maximum time of test greater or less than 200 hours have no special significance. It is significant that an alloy surviving even 100 hours represents improvement over commercial type 304 alloys by a factor of 30 to 500.

Effect of Temperature of Bending

For regular tests, specimens were bent to the required span at room temperature. Experiments were also carried out by bending specimens either above or below room temperature using a commercial type 304 specimen (304A), annealed-sheared and "stress relieved" at 375°C for two hours. Specimens were first heated or cooled to a specific temperature, then rapidly transferred with tongs at the same temperature to a vise, and immediately bent to fit a metal specimen holder having a span only slightly larger than that required for the test apparatus. After reaching room temperature, the specimen was transferred without spring-back to the test apparatus. Bending in liquid nitrogen was accomplished by a special jig which deformed the specimen the proper amount while the specimen was completely immersed in the refrigerant. Averaged results for 2 to 4 specimens at each temperature are plotted in Fig. 1. It is noted that bending specimens above room temperature had no effect, but for specimens stressed below 0°C (32°F), cracking times became increasingly longer as the temperature was lowered. For specimens bent at liquid nitrogen temperature (-196°C), average cracking time was 5 times longer than for specimens bent at room temperature*. For

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*These results were obtained by John Lincoln, M.I.T. Thesis, 1955. Cracking times shown are for large size test specimens (5 x 3/8 x 1/16"; 12.7 x 0.95 x 0.16 cm) used originally for which absolute cracking times are longer than for the smaller size specimens used presently. Cracking times are in qualitative agreement for both size specimens.

sheared-annealed specimens, the final anneal eliminating cold-worked edges produced by shearing as contrasted with annealed-sheared specimens having cold-worked edges, the process of bending at -196°C produced complete resistance to cracking within maximum time of test equal to 250 hours. Similar specimens bent at room temperature, then refrigerated in liquid nitrogen for some time showed normal cracking times.

Further deformation at room temperature of specimens bent at -196°C caused cracking to occur, but the failures were observed at places removed from maximum curvature where deformation predominated during low-temperature bending and where cracking otherwise took place. Constraining further bending to regions of maximum curvature resulted in continued resistance to cracking. Also, cold-worked specimens bent in liquid nitrogen were not greatly improved compared to similar specimens bent at room temperature. Apparently the beneficial effect of low temperature stressing applies largely to annealed 18-8 specimens.

The effect of low temperature stressing was found to be sensitive to composition. A second commercial 18-8 (304B), sheared-annealed, and bent at -196°C cracked within 4.7 hours, compared to 1.5 hours when bent at room temperature, a ratio equal to about 3. This alloy remained essentially non-magnetic after bending at -196°C, whereas 304A became slightly magnetic in the region of the bend indicating partial transformation to ferrite. Specimens of commercial types 321, 347B and 310B tested as sheared-annealed, and stressed at liquid nitrogen temperatures cracked within 6.5, 4.2 and 14.7 hours with ratios equal to 3.8, 2.5 and 1.7 respectively. On the other hand, relatively pure 18-8 compositions sensitive to stress corrosion cracking when bent at room temperature (alloys 5, C, J, Cb-2) resisted cracking when bent at -196°C for the maximum time of test, in accord with the improvement described above for the commercial 18-8 (304A) first tested (Table II).

Results

Effect of Nitrogen, Carbon, and Nickel

It will be noted that compositions of about 18% chromium, 8% nickel containing .015% C or .01% N or less (alloys A, B, 1, H45) did not crack within maximum time of test (200 to 260 hours). On the other hand, relatively pure 18-8 alloys, annealed-sheared, containing 0.15% C or more, low in N (alloys I, J, H44) cracked within 2.4 to 3.4 hours. Similarly alloys C and 5 containing .15% and .24% N, and relatively low in C, failed within 1.2 hours. Two commercial type 304 alloys, 304A and 304B, containing .04% and .05% N, and .08% and .06% C respectively, cracked within 1.4 and 0.2 hour. Cracking susceptibility of these two alloys differs despite similar N and C contents. The complete analyses of the two commercial alloys as supplied by the manufacturer (except for nitrogen which was carried out at M.I.T.) are given in Table III. Commercial extra low carbon type 304L also cracked within a relatively short time, although the time to cracking was longer than for the two type 304 alloys.

The stable austenitic 20% Cr, 20% Ni alloys do not crack if the nitrogen content is sufficiently low. When annealed-sheared or cold rolled they tend to resist cracking within maximum times of test equal to 20 or more hours (alloy D2, NRL 29-19). However, some specimens of alloy D failed in long time tests even though analysis showed a low C and N content. Alloy E containing .05% nitrogen, when annealed-sheared, showed only edge cracks after 290 hours, but failed completely in the cold rolled condition. On increasing the nitrogen content to 0.115% (alloy E2), complete failure occurred both in specimens annealed-sheared and cold rolled, the cold-rolled specimens cracking in shorter time. It is interesting that alloy H containing 0.17% carbon is resistant both in the annealed-sheared and cold-worked states, as is alloy G containing 0.23% carbon*. This behavior is contrary to that of carbon in the 18-8 compositions.

Two commercial type 310 alloys, 310A and 310B, with a nitrogen content of 0.04% and .05% respectively, cracked in shorter times than any of the laboratory melts of similar composition. Cold rolling of these alloys decreased cracking times only of 310A which is the more resistant of the two.

Effect of Niobium (Columbium) and Titanium

Data of Table I show that niobium (columbium) increases susceptibility of pure 18-8 compositions to cracking. Alloys 31, 32 and Cb-2, annealed-sheared, failed despite low carbon and nitrogen contents, whereas without niobium additions, these alloys would have resisted cracking for the maximum period of test.

On the other hand, commercial 304B vacuum remelted with addition of 0.55% Nb as sheared-annealed (alloy Cb-1), cracked in 1.7 hours, which is approximately the same as the cracking time of 1.5 hours for sheared-annealed specimens of 304B without addition of Nb (Table II). Commercial type 347B alloy cracked in about the same short time as did commercial 304B (sheared-annealed) or Cb-1. Commercial 347A is somewhat more resistant than 347B but

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*The maximum time of test for 4 specimens of alloy G equal to 170 hours is arbitrary. These specimens would probably also have survived the 335 hr. test of the fifth specimen.

the difference is small.

Cold working of 347B had no appreciable effect on cracking time, but cold rolling of Cb-1 made it more susceptible. Cold working of laboratory melts 31, 32 and Cb-2, on the other hand, conferred immunity up to the maximum test period of 200 or 230 hours. The latter alloys readily transformed to α phase on cold working unlike the commercial alloys which resisted transformation.

Titanium, contrary to niobium, when alloyed with a low-C, low-N 18-8, resisted cracking whether annealed-sheared or cold rolled (alloy Ti-1). This alloy is strongly magnetic as quenched, indicating that α-phase predominates. As with columbium, addition of titanium to vacuum remelted commercial 304B appears neither to increase nor decrease cracking time (alloy Ti-2). Sheared-annealed specimens of commercial 321 cracked in about the same time as vacuum remelted 304B with addition of Ti (Ti-2) or Nb (Nb-1). The present evidence, therefore, is that Nb and Ti additions to commercial 18-8 compositions have no appreciable effect on susceptibility to cracking.

<u>Effect of Si, Co and B</u>

Silicon (1.35%) added to 0.03% C, low N, 18-8 (alloy M) did not fail by cracking, nor did both alloy N containing 2.7% Si, 0.03% C, 0.05% N, and the remelted commercial 304A (alloy LN) containing 3.7% Si, 0.07% C and 0.03% N. These three alloys, as quenched, are slightly or moderately magnetic and hence contain a mixture of α and γ phases. If only 1.1% Si is present in the remelted 304A (alloy LM), the alloy is still a mixture of α and γ, but now cracks in the annealed-sheared condition, but not when cold rolled (moderately magnetic)nor as sheared-annealed. When 1.3% Si is alloyed with a high nitrogen alloy (alloy P), the alloy is non-magnetic as quenched, slightly magnetic as cold rolled, and cracks both in the annealed-sheared and in the cold rolled condition.

Presence of 2% Si in vacuum remelted commercial 310A (alloy Si-2) which is entirely γ-phase appreciably increases resistance to cracking of both annealed-sheared and cold-rolled specimens. The effect is marked, quite apart from the inadvertent lowering of C and N content by the remelting procedure. For commercial alloy 310B to which Si was similarly added (alloy Si-1), the improvement is also definite but not as pronounced as for 310A.

Cobalt increases to some extent the resistance to cracking of remelted 304B, but the effect, even for a 13.7% addition, is not large. The cold-worked alloys became moderately magnetic and cracked in shorter times than did the annealed alloys which are non-magnetic.

Addition of 0.2% boron to a low C, low N, 18-8, in comparison with carbon, neither effectively stabilizes the austenite phase nor does it alter the inherent resistance of α-phase 18-8 to cracking (alloy B-1). When 0.2% B is added to a low C, low N, 20% Cr-20% Ni composition (alloy B-2), the alloy likewise is resistant to cracking, as is alloy B-3 containing less boron and more nitrogen. Several alloys were also made up of remelted commercial 304B and commercial 310B with additions of about .05, 0.1 and 0.15% boron. The effect was one of increasing resistance to cracking the greater the boron addition, both for annealed-sheared and cold worked specimens. The effect was not large, however, and accompanying reduction of C and N contents made it uncertain to what extent boron is beneficial, especially in view of apparent analytical difficulties for N and B when both are present in the alloy. It can be concluded that at least boron is not detrimental to cracking resistance of 18-8 or 20-20 alloys. Boron increased the work-hardening characteristics of both 18-8 and 20-20 alloys.

Discussion

Apparently either C or N alone can induce susceptibility to cracking in an 18-8 composition, but with N accounting for somewhat shorter cracking times than C. Both these elements inhibit the γ-α phase transformation on quenching from 1050°C, whereas alloys low in both C and N are partially or almost wholly ferritic (α) as quenched (alloys A, 1, H45) as was described by one of us some years ago(16). Alloy B is mostly austenitic, but very readily transforms to ferrite when plastically deformed (x-ray examination), and hence the convex surface of the deformed test specimen is probably mostly ferrite. Alloys 31, 32 and Cb-2 demonstrate that Nb can also stabilize the γ-phase on quenching, but like alloy B they easily transform to α-phase when plastically deformed. These alloys crack as quenched, but become resistant when cold worked.

The overall evidence is that α-phase 18-8 resists stress corrosion cracking in $MgCl_2$ solutions whether formed by transformation on cooling, or by plastic deformation at room or below room temperatures. On the other hand, γ-phase 18-8 alloys crack, and this is true whether the alloying element responsible for stabilizing the face-centered cubic lattice on cooling from elevated temperatures is N, C, or Nb. This result is in line with observations

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(16) H. H. Uhlig, Transactions ASM, 30 947 (1942)

of others(2)(3) that ferritic stainless steels do not crack in the $MgCl_2$ test, and points to the further conclusion that lattice type in this instance is the important factor rather than the Cr or Ni content. To what extent, if any, the hexagonal close packed phase, as formed by quenching from elevated temperatures or by deformation of 18-8 at room temperature(17) or at low temperatures(18) may enter the mechanism of stress corrosion cracking has not yet been established. X-ray examination of alloys B, P, 5, N, Si-2, and Cb-2, as quenched, revealed only α or γ phase, or both.

Alloying additions of nickel above 8% in presence of nitrogen delay cracking, but cracking apparently is inhibited only when the amount added approaches 50% or more(2). Although increased nickel both stabilizes γ-phase and delays cracking, the present results do not bear out the supposition expressed by some investigators that a more stable γ-phase 18-8, whatever the stabilizing elements, is more resistant to cracking. For example, the relatively easy-to-transform austenitic alloys 31, 32, Cb-2 and partially austenitic LM did not crack at all after cold rolling. Furthermore, commercial 304B sheet on cold rolling from .063" to .040" transformed to α-phase less than did cold rolled commercial 304A sheet, as indicated by magnetic tests, yet annealed 304B cracked in about 1/4 the time of annealed 304A; and, when cold rolled, in less than 1/2 the time of cold rolled 304A.

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(17) B. Cina, J. Iron and Steel Inst., 177 406 (1954); Acta Metallurgica, 6 748 (1958)

(18) W. O. Binder, Metal Progress, 58 201 (1950)

Cracking of the stable γ-phase, pure 20% Cr, 20% Ni alloys is associated mainly with nitrogen content; carbon, contrary to its effect in 18-8, appears to be beneficial. Alloy D cracked despite a relatively low nitrogen content (.005%), but when the C to N ratio was increased, as in alloy H containing .005% N and in alloy G containing .016% N, resistance to cracking was restored. Commercial 25% Cr, 20% Cr alloys (310A and 310B) cracked in shorter times than any of the laboratory prepared alloys, indicating that elements in addition to nitrogen participate in the cracking mechanism. The difference in cracking times of 18-8 compositions 304A and 304B, both with about the same C and N contents, leads to the same conclusion. What these additional elements may be remains for further study.

The major detrimental effect of nitrogen in 20% Cr, 20% Ni alloys, in contrast to carbon, suggests the possibility that nitrogen is also the damaging interstitial component in 18-8, but that carbon and Nb may lower the threshold concentration of nitrogen needed to induce susceptibility. This could be proved by testing alloys for cracking essentially free of nitrogen but containing enough carbon or Nb to ensure that the alloys are austenitic at room temperature. The results presented in this paper cover only alloys for which nitrogen content, although low, is present in analyzable amounts.

Silicon is definitely beneficial to 20% Cr, 20% Ni alloys. It is apparently also beneficial to 18-8 compositions, quite apart from the tendency of Si to favor the γ-α transformation. Alloy P, for example, containing .09% N and 1.3% Si cracks in about 41 hours (annealed-sheared specimens, Table I), whereas in absence of Si a similar alloy would be expected to crack in much shorter time. Also, commercial alloy 304A as received, containing 0.3% Si cracks within 5.5 hours (sheared-annealed specimens, Table II). When melted with additional Si to bring the percentage to 1.1% (alloy LM), cracking of sheared-annealed specimens no longer occurs within the test period of 210 hours (Table II). But the same alloy cracks if the specimens are sheared from the annealed sheet (Table I), the shearing process introducing cold work at the edges. Further cold work, however, transforms most or all of the alloy to α-phase, and it again becomes immune to cracking. This behavior suggests that Si is beneficial to 18-8, both because it inhibits formation of crack-sensitive paths, and also because it favors the γ-α transformation during plastic deformation.

Increased resistance to cracking by cold working of occasional stainless steels that transform readily has been noted by Edeleanu(10) and by Rocha(1). The present results clarify the reason for this increased resistance, namely the complete or almost complete transformation of the alloy surface to α-phase during plastic deformation, whereas if transformation is resisted the alloy cracks. Similarly the beneficial effect of low-temperature straining is in part explained by the increased formation of cold work ferrite or α-phase at low temperatures. Magnetic tests of several alloys, and also x-ray patterns of tensile specimens of 304A extended in tension both at room temperature and at -196°C, proved the existence of a greater amount of α-phase in specimens deformed at the low temperature. Annealed alloys sensitive to transformation on cold work, therefore, such as 304A, 5, C, J, and Co-2 were much more resistant to cracking when stressed at -196°C. Furthermore, annealed commercial 304A which transforms more readily than 304B did not crack at all within the maximum test period when stressed at -196°C, representing an improvement in cracking resistance of more than 45 fold, whereas 304B was improved only 3 fold.

But a second factor quite apart from increased phase transformation accounts for improved resistance of 20% Cr-20% Ni or 25% Cr-20% Ni alloys stressed at -196°C since these compositions do not transform at all. Commercial 310A and 310B, for example, were improved about 65% when annealed specimens were bent at liquid nitrogen temperature. It is probable, therefore, that the responsible factor is a retarded diffusion rate of nitrogen, or an altered pattern for precipitation of nitrides at low temperatures, either effect altering the nature and extent of crack-sensitive paths through the grains. This factor probably also enters the observed increase in resistance of 18-8 compositions such as 304B which when stressed at low temperatures do not readily transform to α-phase.

Formation of α-phase or quasi-martensite during plastic deformation is not necessary to either crack initiation or crack propagation. Certainly alloys that are all or predominantly quasi-martensite do not crack at all within limits of the test, as results of this investigation prove. And 18-8 compositions that form quasi-martensite more readily, such as 304A, do not necessarily crack more readily. This places the major responsibility for cracking susceptibility on impurities, especially nitrogen which is a component of all the austenitic stainless steels whether of 18-8, 20-20, or 25-20 composition.

The necessary and important role of tensile stress to the cracking mechanism and lack of corrosion along crack-sensitive paths in absence of stress suggests that crack-sensitive paths are established largely while the alloy undergoes plastic deformation. The corrosion paths induced by deformation account for almost immediate observation of cracks in plastically deformed alloys(15) stressed beyond the elastic limit upon immersion in $MgCl_2$, but for an observed induction period when the alloys are stressed elastically(7), the latter situation probably requiring creep (a lower rate of plastic deformation) before the crack-sensitive paths can form. The apparent sensitivity to cracking even for small amounts of plastic deformation accounts for the observed lack of a critical applied stress below which stress corrosion cracking will not occur, because creep occurs in time at any applied stress. On this basis, the time of cracking is expected to be shorter the higher the applied stress, as is observed. The initial appearance of corrosion locallized along traces of slip planes at the surface of plastically deformed 18-8 has been described by Leu and Helle(6).

The present results, therefore, favor a mechanism of stress corrosion cracking based on strain-induced precipitates or incipient precipitates (e.g. N atmospheres at dislocations, with diffusion of N being accelerated by strain and by temperatures slightly above room temperature). Crack-sensitive paths are formed accordingly by the deformation process at the apex of the growing crack. Incipient or real precipitates are expected to be the cathodes, and the adjoining alloy the anodes of electrochemical cells entering into progressive corrosion and crack propagation. The beneficial role of silicon and nickel, according to this point of view, is one of altering the pattern of cathodic atmospheres or precipitates, or of actually inhibiting their formation in the same manner as Ni and Si also inhibit nucleation of cementite on quenching of carbon steels.

Obviously, more work remains to be done in order to establish the details of the above or any other proposed mechanism of stress corrosion cracking in the stainless steels. The large effect of interstitial impurities on susceptibility to cracking provides an important clue to the problem. Work is now underway on the effect of heat treatment on susceptibility which will probably help separate some of the several factors that enter the mechanism. The data presented in this paper provide hope, perhaps for the first time, that the frustrating problem of stress corrosion cracking in these commercially important alloys can be solved by a metallurgical approach.

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TABLE I

Cracking Times of Stainless Steels in 42% $MgCl_2$ Boiling at 154°C

							Annealed and Sheared		Cold Rolled, Sheared		
	Alloy	Magnetic Properties as Quenched	% Cr	% Ni	% C	% N	No. of Test Spec.	Cracking Time	Reduct. of Thickness by** Cold Rolling	No. of Test Spec.	Cracking Time
	Code				**Effect of Nitrogen and Carbon**						
	A	Mag.	18.4	8.7	.012	<.001	2	>260 hrs	80%	2	>260 hrs
	B	Sl. mag.	18.8	8.5	.015	.009	2	>200	80%	2	>200
	1	Mag.	17.5	8.3	.007	.001	1	>260			
	H45	"	18.4	8.1	.004	.005	3	>260	80%	3	>260
	C	Non-mag.	18.5	8.5	.013	.15	13	1.2 ± 0.3			
	5	"	17.7	8.0	.007	.24+	2	1.2			
	I	"	20.4	9.5	.34	—+	9	3.4 ± 0.9			
	J	"	19.8	9.0	.15	—	12	2.5 ± 0.7			
	H44	"	18.6	8.0	.15	.002	4	2.4 ± 0.6	80%	3	0.8 ± 0.4
	304A	"	18.4	8.6	.08	.04	37	1.4 ± 0.4	35%	11	0.7 ± 0.2
Com. 18-8	304B	"	18.8	9.2	.06	.05	4	0.2 ± 0.1	35%	4	0.3 ± 0.1
	304L	"	18.6	10.0	.02	.02	7	3.0 ± 2.6			
	D	"	18.5	20.1	.008	.005	1 1	300 ⊛ 183	50%	1 1	245 55
	D2	"	21.1	17.6	.015	.001	-	—	80%	3	>255
	NRL 29-19	"	18.7	20.6	.01	.002	3	>200	30%	3	>200
	E	"	18.6	20.0	.010	.051	6	>290 ⊛	80%	2	91 ± 26
	E2	"	21.3	17.5	.01	.115	5	149 ± 49	30%	3	59 ± 16
	G	"	21.9	19.0	.23	.016	3	>250	80%	4 1	> 170 > 335
	H	"	18.2	20.4	.17	.005	2	>300	80%	2	> 300

TABLE I (cont'd)

							Annealed and Sheared		Cold Rolled, Sheared		
Alloy	Magnetic Properties as Quenched	% Cr	% Ni	% C	% N		No. of Test Spec.	Cracking Time	Reduct. of Thickness by Cold Rolling**	No. of Test Spec.	Cracking Time
Code											
Com. 25-20 310A	Non-mag.	24.7	21.4	.05	.04		5	20 ± 3 hrs	30%	13	5.3 ± 1.5 hrs
Com. 25-20 310B	"	24.8	19.5	.03	.05		4	5.5 ± 1.8	30%	4	5.2 ± 1.2
Effect of Niobium and Titanium											
31	"	19.1	9.1	<.002	.005	0.46%Nb	7	60 ± 17	80%	2	>230
32	"	18.9	9.0	<.002	.008	1.3% Nb	8	22 ± 9	80%	2	>230
Cb-2	"	19.0	9.0	.004	<.002	1.0% Nb	4	29 ± 13	80%	4	>200
Com. 347A	"	18.5	10.7	.07		0.8% Nb	16	2.6 ± 1.7			
Com. 347B	"	17.3	10.5	.06	.05	0.77%Nb	7	1.4 ± 0.4*	20%	4	1.2 ± 0.1
Cb-1(304B+Nb)	"			.03$^{\Delta}$	.04$^{\Delta}$	0.55%Nb$^{\Delta}$	4	1.7 ± 0.5*	80%	4	0.8 ± 0.1
Ti-1	Mag.	18.2	8.3	.01	.004	0.62%Ti	3	>200	80%	2	>200
Ti-2(304B+Ti)	Sl. Mag.			.03$^{\Delta}$	.03$^{\Delta}$	0.41%Ti$^{\Delta}$	4	1.5 ± 0.7*	80%	4	0.5 ± 0.1
Com. 321	Non. Mag.	18.1	10.1	.05	.05	0.49%Ti	6	1.7 ± 0.4*	20%	6	1.2 ± 0.2
Effect of Silicon											
LM(304A+Si)	Sl. Mag.			.08$^{\Delta}$	.03$^{\Delta}$	1.1% Si$^{\Delta}$	3	30.9 ± 8.7	80%	2	> 250
LN(304A+Si)	"			.07$^{\Delta}$	.03$^{\Delta}$	3.7% Si$^{\Delta}$	2	>250	80%	2	>250
M	"	17.8	8.3	.03	.01	1.35%Si	2	>250	80%	1	>200
N	"	16.7	8.7	.03	.05	2.7% Si	2	> 250	80%	1	>200
P	Non. Mag.	17.8	9.1	.008	.09	1.3% Si	5	41 ± 11.7	80%	2	9 ± 2.2
Si-2(310A+Si)	"			.03$^{\Delta}$	.03$^{\Delta}$	2.0% Si$^{\Delta}$	4	>200	80%	4	> 200 ●
Si-1(310B+Si)	"			.02$^{\Delta}$	.02$^{\Delta}$	2.0% Si$^{\Delta}$	3	13 ± 7	80%	2	15 ± 3

TABLE I (cont'd)

Alloy	Magnetic Properties as Quenched	% Cr	% Ni	% C	% N		Annealed and Sheared No. of Test Spec.	Annealed and Sheared Cracking Time	Cold Rolled, Sheared Reduct. of Thickness by Cold Rolling[**]	Cold Rolled, Sheared No. of Test Spec.	Cold Rolled, Sheared Cracking Time
Code					**Effect of Cobalt**						
Co-1 (304B+Co)	Non. Mag.			.05[Δ]	.03	1.8% Co	3	1.5 ± 0.5[*] hrs	80%	3	0.8 ± .5 hr
Co-2(304B+Co)	"			.05	.03	6.0% Co	3	3.1 ± 1.2[*]	80%	3	1.1 ± 0.3
Co-3(304B+Co)	"			.04	.03	13.7% Co	3	5.5 ± 1.1[*]	80%	3	2.6 ± 0.5
					Effect of Boron						
B-1	Sl. Mag.	18.7	9.3	< .002	—[+]	0.2% B[□]	2	> 200	50%	2	> 200
B-2	Non. Mag.	29.1	20.3	< .002	—[+]	0.2% B[□]	2	> 200	75%	2	> 200
B-3	"	20.4	19.0	< .002	.015	.08% B[□]	3	> 200	75%	3	> 200

[*] Sheared and annealed.

[**] Approximate values.

[□] Added amount. Analyses not available.

[+] Not analyzed. Estimated to be below .01% N.

[@] Edge cracks noted.

[Δ] Analysis after remelting of commercial alloy.

[●] One specimen cracked at 200 hrs.

TABLE II

Effect of Stressing at -196°C on Cracking Time of Sheared-Annealed Specimens

Code	Alloy	Stressed Room Temp. No. of Test Spec.	Stressed Room Temp. Cracking Time, Hours	Stressed -196°C No. of Test Spec.	Stressed -196°C Cracking Time, Hours	Ratio Cracking Times
304A	Com. 18-8	4	5.5 ± 1.8 hrs.	5	> 250 hrs.	> 45
304B	Com. 18-8	4	1.5 ± 0.4	4	4.7 ± 2	3
310A	Com. 25-20	3	21 ± 5	2	34 ± 4	1.6
310B	Com. 25-20	4	8.5 ± 2.3	4	14.7 ± 2.7	1.7
5	18-8, .007% C, .24% N			2	> 70	
C	19-9, .01% C, .15% N			2	> 250	
J	20-9, .15% C, low N			2	> 140	
347B	Cb-stabilized 18-8	4	1.7 ± 0.5	2	4.2 ± 0.2	2.5
Cb-1	304B + 0.55% Cb	4	1.7 ± 1.8	2	7.8 ± 3	4.6
Cb-2	19-9; low C, N; 1.3% Cb	3	4.5 ± 1.7	2	> 260	> 58
321	Ti-stabilized 18-8	6	1.7 ± 0.4	2	6.5 ± 1.5	3.8
Ti-2	304B + .41% Ti	4	1.5 ± 0.7	2	23 ± 2.7	15
Co-1	304B + 1.8% Co	3	1.5 ± 0.5	2	7.8 ± 2.1	5
Co-2	304B + 6.0% Co	3	3.1 ± 1.2	2	38 ± 8.4	12
Co-3	304B + 13.7% Co	3	5.5 ± 1.1	2	62 ± 3.1	11
LM	304A + 1.1% Si	2	> 210	2	> 260	
Si-2	310A + 2.0% Si	2	> 200	2	> 200	

TABLE III

Analysis of Commercial Types 304 and 310 Stainless Steels

	Cr	Ni	C	N	Mn	P	S	Si	Cu	Mo
304A	18.42	8.63	.08	.04	1.16	.024	.018	0.30		
304B	18.77	9.20	.06	.05	1.54	.029	.026	0.69	0.28	0.42
304L	18.62	10.04	.02	.02	1.23	.029	.01	0.58		
310A	24.68	21.42	.05	.04	1.81	.025	.007	0.70		
310B	24.84	19.54	.03	.05	1.72	.026	.015	0.53	0.44	0.14

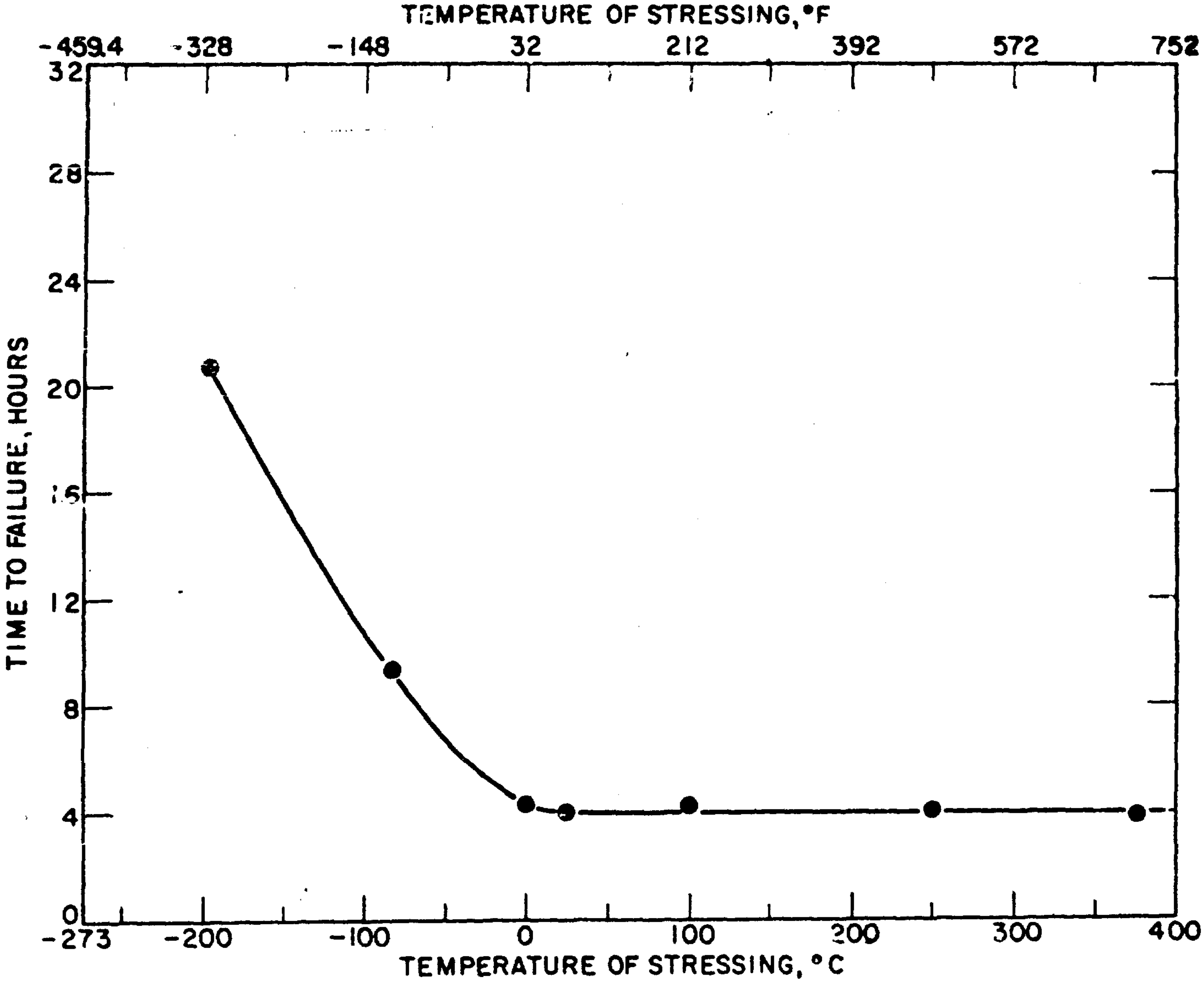

Fig. 1. Effect of Temperature of Stressing on Time to Failure of Sheared 18-8 Specimens in 42% $MgCl_2$ at 154°C.