SOME ASPECTS OF SULFUR-INDUCED EMBRITTLEMENT OF STEELS AT ELEVATED TEMPERATURES

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ABSTRACT

Recent evidence that sulfur re-distribution can lead to brittle behavior in ferritic and austenitic steels which have been heated to high austenitizing temperatures and rapidly cooled is reviewed. The brittle behavior can take the form of either intergranular cavitation or truly brittle intergranular decohesion, the mechanism of which is discussed. Cracking due to these factors can occur in the heat-affected zones of welds or in stainless steels in which sigma phase is formed in service. It appears that these problems can be treated by sulfur removal or scavenging by rare earths and by not allowing the creep strength of ferritic steels to be higher than necessary.

KEY WORDS

Sulfur, stress relief cracking, ferritic steels, austenitic steels, high temperature fracture, embrittlement.

Introduction

Virtually from the beginning of the modern age of steel it has been recognized that sulfur is one of the most deleterious impurities in iron and its alloys. One of the first problems to be overcome was that of "hot shortness", or the tendency for intergranular disintegration during hot working, due to the formation of the low-melting Fe-S eutectic liquid in the grain boundaries. This was eliminated by the addition of manganese which forms sulfides of much higher stability than FeS. However, in recent years as we have looked more carefully at high temperature intergranular fractures in steels, we have found that the effectiveness of sulfur-scavenging by manganese is inadequate for a number of applications.

Much of the difficulty is caused by the fact that MnS, although relatively stable, does dissolve appreciably in the austenitic phase at high temperatures, as indicated in Fig. 1. Here the effect of manganese content on sulfur solubility in iron is shown for the manganese contents of two steels that we will consider in some detail. When a steel is heated to a temperature significantly greater than 1100°C and then cooled fairly rapidly, dissolved sulfur can be re-distributed by segregation to austenite grain boundaries and by reprecipitation. The new grain boundaries sulfides are likely to be finely distributed, and they do not necessarily have the equilibrium composition; thus they are likely to be unstable. Both of these factors can lead to difficulties with ductility.

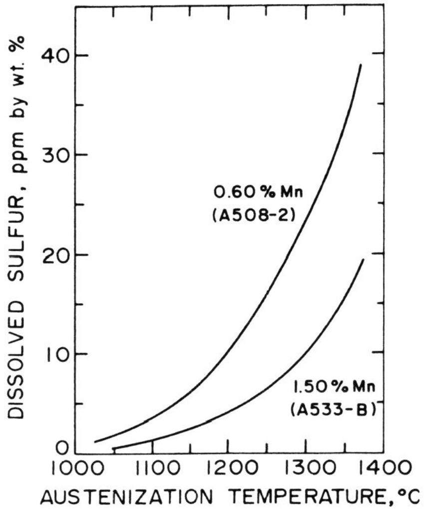

Fig. 1 Effect of manganese content on sulfur solubility in iron, calculated from Turkdogen et al(1).

In this paper we will consider several recent manifestations of brittle behavior at elevated temperatures involving steels which have received a high-temperature austenitizing treatment and in which redistributed sulfur appears to play an important role. These effects will be shown to occur in ferritic steels, particularly when they are treated to simulate the heat affected zone of a weld, and they may also be important for the long-time ductility of austenitic steels which are solution-treated at high temperatures.

Ferritic Steels

Rupture. It is becoming increasingly clear that the primary nucleation sites for creep cavities in ferritic steels given a high-temperature austenitizing treatment are re-precipitated sulfides in the prior austenitic grain boundaries. This was made particularly clear in the study by Middleton(2) of a series of CrMoV laboratory steels which were given a rapid, high-temperature austenitizing treatment and then tensile tested in vacuum at 873 K at strain rates in the range 10^{-6} to 10^{-1}/min. Middleton found that fracture in all cases of low ductility occurred by cavitation initiated at sulfides along the prior austenite grain boundaries, as indicated in Fig. 2. He reasoned that the fine sulfides had re-precipitated during the oil quench which followed the 2 min, 1600 K treatment in which the original sulfides had largely dissolved. Such a treatment is known(3-6) to produce intergranular rupture in room temperature notched-bar tests due to reprecipitated sulfides, a phenomenon known as the "overheating" effect when it is found in forgings austenitized at excessively high temperatures(3).

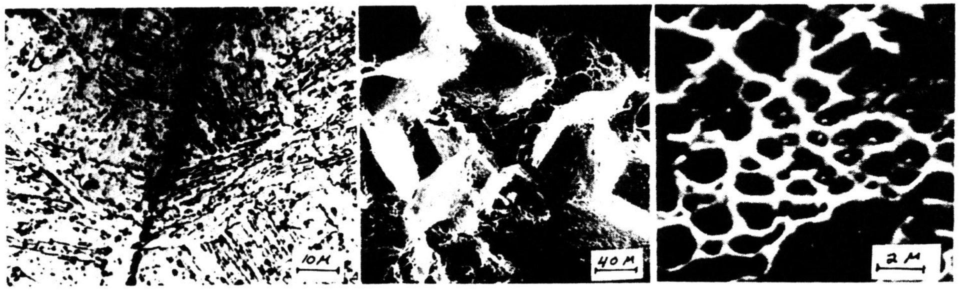

Fig. 2 (a) Intergranular cavities after 1% strain in a CrMoV steel.
(b) Fracture surface of same specimen.
(c) Sulfides found in cavities. After Middleton (Ref. 2).

Middleton used as his primary measure of the effects of impurities on ductility the "maximum local elongation" between fiducial marks placed at 1 mm intervals. He found that boron was necessary for low-ductility behavior and that the embrittlement could be eliminated by an addition of 0.06% cerium. The latter stabilized the sulfur and eliminated the dissolution and re-precipitation of sulfides; it also reduced the total amount of sulfur retained in the steel. The boron was found by autoradiography to have segregated to austenite grain boundaries. The role that it plays is unclear; Middleton(2) has speculated that it acts somehow as a nucleating agent for grain boundary sulfides.

Middleton found by varying the austenitization temperature that the reduction in ductility due to sulfide re-precipitation was separate from the effect of grain coarsening. He also found in interrupted tests that the sulfide particles lying in cavities tended to disappear with time at 983 K after cracking had occurred and that carbides tended to become visible, presumably by a thermal etching effect.

A contemporaneous study of MnMoNiCr (A508-2 type) laboratory steels given a similar austenitizing treatment was carried out by Fujii et al(7). They employed both constant-load, short-time (<18 h) rupture tests and fixed displacement stress-relaxation tests at 823 to 883 K. Fujii et al observed in their rupture tests the intergranular cavitation mode of fracture. Additions of 0.02 to 0.09% cerium or 0.06% zirconium were found to eliminate the low-ductility, and additions of 10 to 20 ppm boron were found to exacerbate it significantly. Observations with a scanning Auger microprobe on UHV fractures of partly-cracked specimens showed that the cavity surfaces contained elemental segregated sulfur, as well as some segregated nitrogen, and that surrounding grain boundary regions fractured in UHV contained some segregated phosphorus. They concluded that the sulfur and nitrogen had segregated after the cavities had formed and that the phosphorus came from intergranular segregation during austenitizing.

Fujii et al, like Middleton, connected the low ductilty to dissolution of MnS during the austenitization (at 1510 K); however, rather than ascribe it to cavitation around re-precipitated sulfides (which they apparently did not find in the cavities), they concluded that the sulfur remained in the elemental state during cooling from austenitization. They proposed that the low ductility was the result of rapid growth of cavities (nucleated in an unspecified manner) due to the presence of segregated sulfur on the cavity surfaces. They considered that this would reduce the surface free energy enough to sharpen the cavities significantly, so that less mass transport would be required for diffusive cavity growth.

An alternative interpretation of these results(41) would be that the cavities had been nucleated on re-precipitated sulfides which had then shrunk to below-detectable size, serving as sources of the sulfur which was later found on the cavity surfaces. This would bring their results and those of Middleton completely into consonnance and would eliminate the need to invoke an effect of sulfur on equilibrium cavity shape, which in any case would be rather small. For example, if we allow the solid/vapor surface free energy to be reduced by 50% and the grain boundary free energy by only 20% by segregated sulfur, the equilibrium dihedral angle at the cavity tip decreases only by about 18°.

A series of papers by Pope and coworkers(8-12) reporting results of creep-rupture and slow-strain-rate tensile tests on 2 1/4 Cr-1 Mo and CrMoV steels containing various combinations of manganese, phosphorus, and silicon have shown that ductility varies with austenitizing temperature in a way depending on composition. For example, Fig. 3 shows that a high-purity (HP) CrMoV steel lost ductility in a slow tensile test at 773 K as the austenitizing temperature was raised above 1175 K, whereas when manganese and phosphorus were added, the ductility was relatively unaffected. The heat containing only phosphorus was intermediate in behavior. Since grain size varied similarly in all three steels, the explanation must lie elsewhere. Observations by SEM and AES on cavitated fracture surfaces(12) showed sulfide particles in only some of the cavities and a high sulfur concentration in cavitated areas. This would be consistent with cavity nucleation by sulfides which later shrank as they supplied sulfur to the newly-created surfaces.

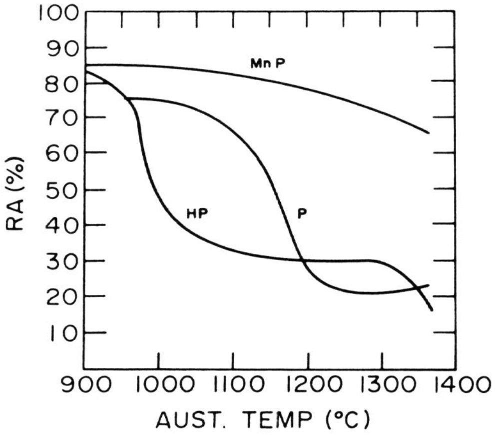

Fig. 3 Effect of austenitizing temperature on ductility in 773 K slow tensile tests (4x10^{-5}/sec) on CrMoV laboratory steels, comparing high purity, P-doped, and Mn+P doped. After Chen et al. (Ref. 12).

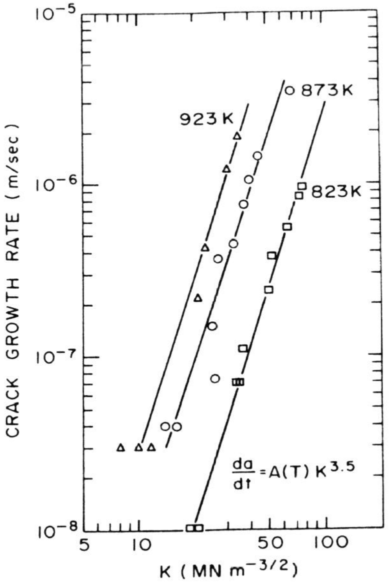

Fig. 4 K dependence of the brittle cracking rate in a MnMoNiCr steel. (Ref. 25).

The effect of manganese shown in Fig. 3 was interpreted(12) as one of sulfide stabilization, or raising of the "overheating" temperature. The effect of phosphorus in those steels has not yet been determined; suggested possibilities include: site competition with sulfur on austenite grain boundaries(12), and a reduction in the grain boundary diffusion coefficient, leading to a retardation of diffusive cavity growth(8). There does not seem to be any published information on the relative segregating tendencies of sulfur and phosphorus in austenite.

However, it may be noted that in nickel, which is also "austenitic", the presence of phosphorus has been found(13) to retard the segregation of sulfur to grain boundaries.

Brittle Fracture. Over the past ten years there have been a number of studies(14-26) of the fracture of steels given a high temperature austenitizing treatment in which notched or precracked specimens were used and in which brittle intergranular fracture, as distinct from rupture by cavitation, was observed. Initially, this was considered to be related to temper embrittlement and to be caused by the same impurities, principally phosphorus, tin, antimony, and arsenic(14,15,17,19). However, later it was recognized that, since the crack growth rate was many orders of magnitude slower than that of the brittle intergranular fracture associated with temper embrittlement, there must be some stress-induced, diffusion-controlled re-distribution of impurities during the cracking process(20-23,27). Recently, it was found(25,26) that the brittle mode, instead of being a lower-temperature alternative to rupture, is actually the higher-stress alternative and that it can occur at least over the temperature range 400 to 650°C (673-923 K).

The recent study(25,26) dealt with MnMoNiCr and MnMoNi steels (A508-2 and A533-B), and measurements of the growth rate of brittle cracks indicated a power law dependence on the stress intensity factor K, as shown in Fig. 4. The growth rates in the temperature interval 823 to 923 K ranged from 10^{-8}m/sec to almost 10^{-5}m/sec. High resolution TEM replica observations showed that the cracking occurred by intergranular decohesion, with virtually no sign of cavitation (Fig. 5). Thus, it now appears well established from the recent work at Pennsylvania(25,26) and at Cambridge and Harwell(20-22,24) that we have here a quasi-static form of true brittle cracking by intergranular decohesion*, which occurs at speeds at least eight orders of magnitude slower that the kinds of brittle fracture normally observed in metals. The rate of this cracking is highly stress and temperature dependent.

Since only a few measurements of crack growth rate have been made, and these on four different types of steel(18,24-26), the form of the K dependence is still open to question. Hippsley(24) has shown that the rate can be plotted as proportional to exp K; however, his data also appear to fit a power law plot. Some of the measurements on the several types of steels are compared in Fig. 6.

The early stages of cracking during stress relaxation of notched specimens at a fixed temperature and displacement in the MnMoNiCr and MnMoNi steels were shown to occur, first, by the formation of isolated intergranular microcracks ahead of the notch, followed by the development of patches of cracking, and finally the coalescence of these patches into a macroscopic crack(25,26). As the level of initial stress in the relaxation test was raised, the mode of microcracking shifted from rupture, presumably sulfide-nucleated, toward the brittle mode, as shown in Fig. 7(25,28).

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*no doubt accompanied by crack tip plasticity.

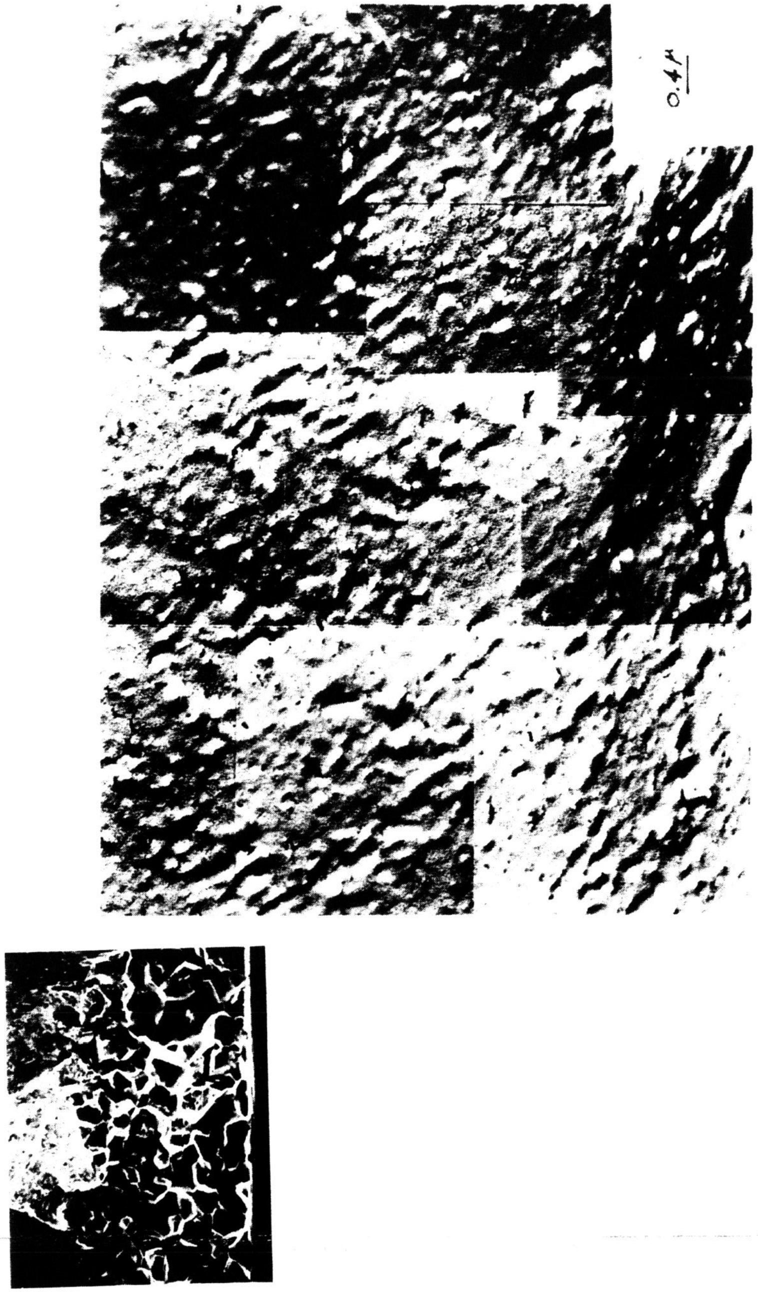

Fig. 5 Macrocrack extending from notch and TEM replica of high temperature brittle fracture surface of same steel as Fig. 4, showing absence of cavitation.

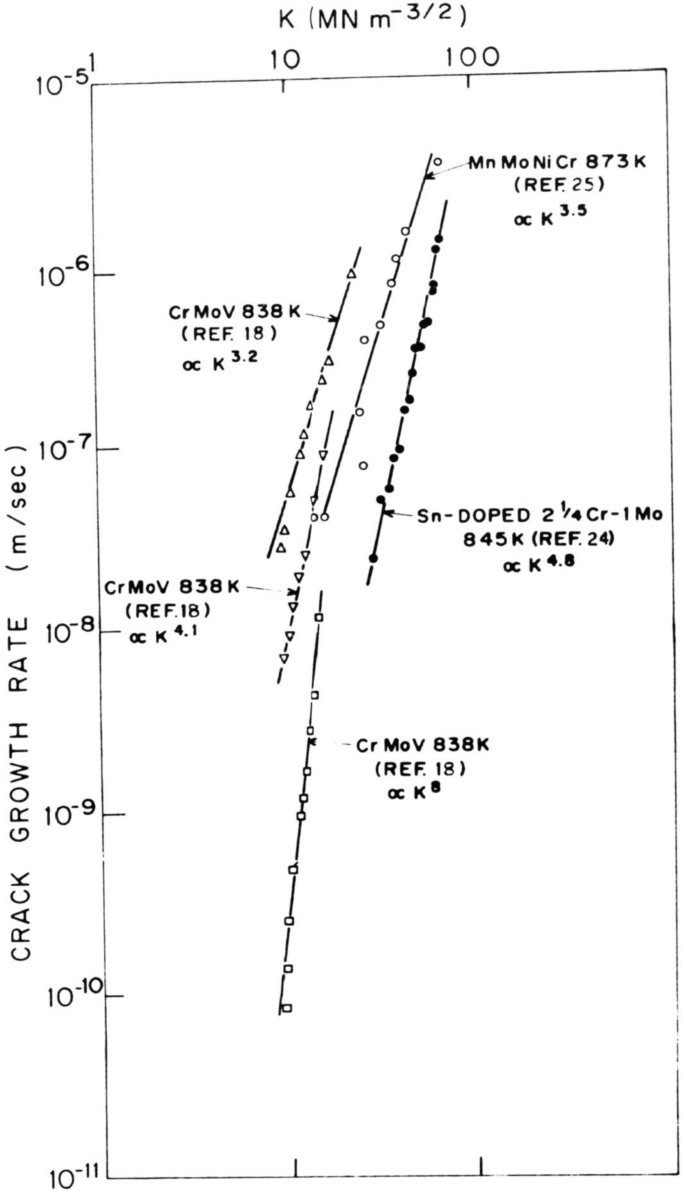

Fig. 6 Data of King[18] for 3 CrMoV steels at 838 K, compared with data for a MnMoNiCr steel at 873 K[25] and a CrMo steel at 845 K[24].

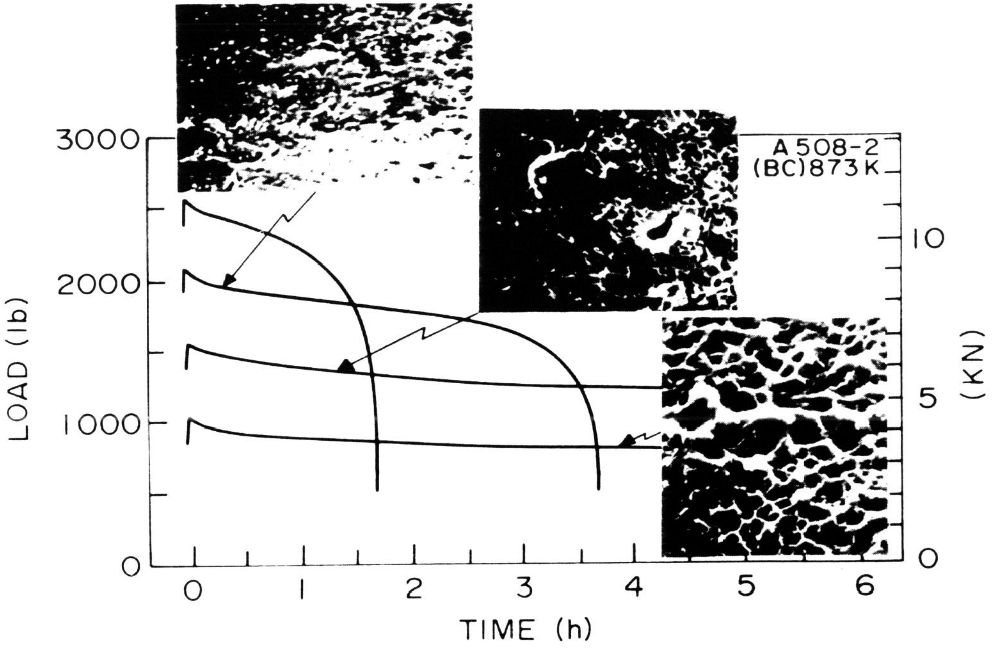

Fig. 7 Examples of load-relaxation curves for notched bars of a MnMoNiCr steel loaded to a fixed displacement at 873 K showing that mode of microcracking (ahead of notch) changes from cavitation to a brittle mode as the initial load is increased. (Ref. 25).

Since the initial microcracks were not contiguous with the notch tip, they were uncontaminated by the external environment. Hence, samples for Auger electron spectroscopy containing these buried microcracks could be machined from notched specimens whose load relaxation was interrupted after a few minutes. When such samples containing mostly-brittle-mode microcracks were fractured in UHV and Auger analysed, it was found that the microcracks contained large amounts of segregated sulfur and nitrogen and small amounts of phosphorus, tin, and antimony(25,26). An example of one such Auger spectrum is shown in Fig. 8. From surface segregation experiments on the same steels it was deduced that the sulfur had been present in the grain boundaries before the microcrack formed and that the nitrogen probably segregated afterwards to the new (internal) surface.

Based on the Auger studies, on the gradual transition from rupture to the brittle mode with increasing stress, and on recent work on creep cavity growth, particularly the effect of plasticity and the transition from equilibrium to crack-like cavities(29-35), a new model was proposed to explain the quasi-

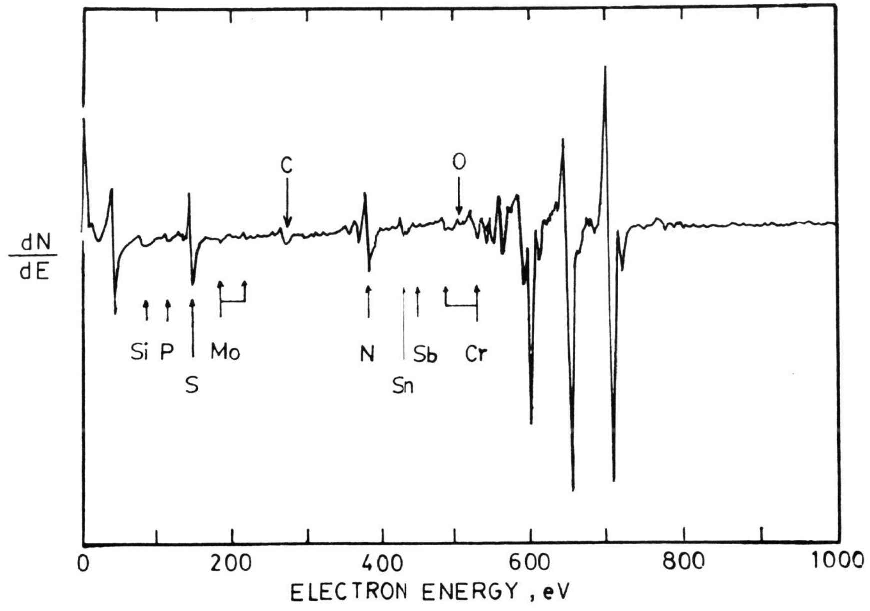

Fig. 8 Auger spectrum from brittle-mode intergranular microcrack formed ahead of notch in MnMoNiCr steel (heat BA) and exposed by fracture in UHV, showing presence of S, N, P, Sn and Sb, all of which were in the elemental form, as later demonstrated by ion sputtering. (Ref. 25).

static brittle cracking phenomenon(25). As outlined schematically in Fig. 9, it begins with a crack-like cavity whose surfaces contain adsorbed sulfur, supplied by the fine re-precipitated intergranular sulfides. As in the classical mechanism of cavity growth, atoms from the surfaces of the cavity are drawn into the surrounding grain boudnary, the driving force being the work done by the tensile stress normal to the boundary. In this case, of course, many of these atoms are sulfur.

Because of the high stresses involved, plasticity must be taken into account, and this can be done(33,34) by employing a plasticity-modified effective diffusion distance

$$L = \left(\frac{D\delta\Omega\sigma_\infty}{kT\dot{\varepsilon}_\infty}\right)^{1/3} \qquad (1)$$

which is the effective distance ahead of the cavity tip into which the diffusing atoms from the cavity surface are deposited. Here, $D\delta$ is the grain boundary diffusion coefficient, Ω the atomic volume of the diffusing atom, and σ_∞, $\dot{\varepsilon}$ the far-field

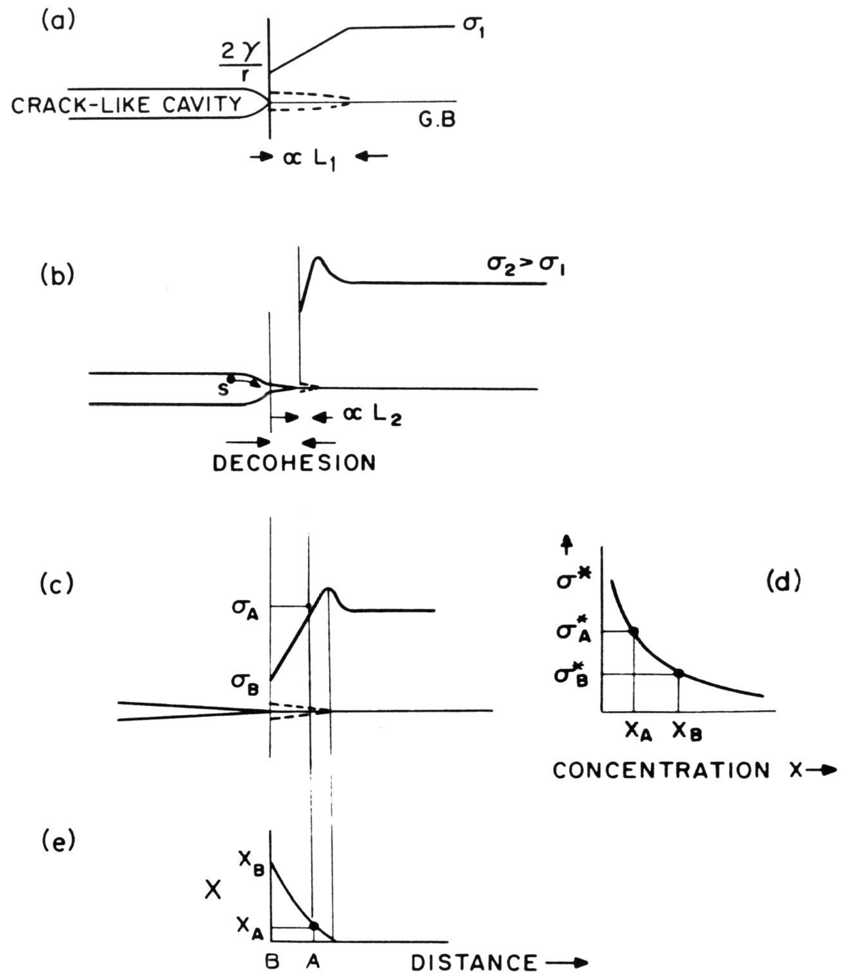

Fig. 9 Schematic representation of hypothetical transition from crack-like cavity growth (a) to decohesion (b,c) due to increase in stress, which shrinks the characteristic diffusion length L and causes the impurity (e.g., sulfur) concentration at the cavity tip to increase. (d) Represents cohesive strength σ^* vs impurity concentration X, and (e) the impurity profile ahead of the "peeling" crack tip. (c) Is drawn for the case where the stress at point A ahead of the crack tip (which is at B) is below σ^* for X_A. (Ref. 41)

stress and strain rate. The latter can be considered proportional to the stress raised to some power, but this power is probably greater than the steady state value 7 usually used for iron(36), because of the short times involved. Thus, L must be inversely proportional to σ_∞ raised to a power higher than two. Hence, as the stress is raised, L decreases, and the atoms from the cavity surface are deposited into an increasingly smaller region ahead of the cavity. This means that the sulfur concentration in this region must increase with σ_∞.

The essence of the model is that, since grain boundary cohesion in iron is known to decrease with increasing sulfur concentration(37,38), there must be a tensile stress at which L has decreased sufficiently to allow decohesion to occur at the cavity tip. The cavity then becomes a sharp crack which grows at a rate depending on the concentration of intergranular sulfur, the surface and grain boundary diffusion rates, and the values of σ_∞ and $\dot{\varepsilon}_\infty$.

While this model was being proposed, Hippsley and co-workers(39,40) were reporting on observations made by high-resolution Auger electron spectroscopy in the near-tip regions of intergranular brittle stress-relief cracks. An example is shown in Fig. 10. Although there may be some question about the exact location of the tip of the high-temperature crack and the interpretation of the Auger data(40,41), there is no doubt that there exists a region of increased sulfur concentration very near to the tip, as envisioned in the model.

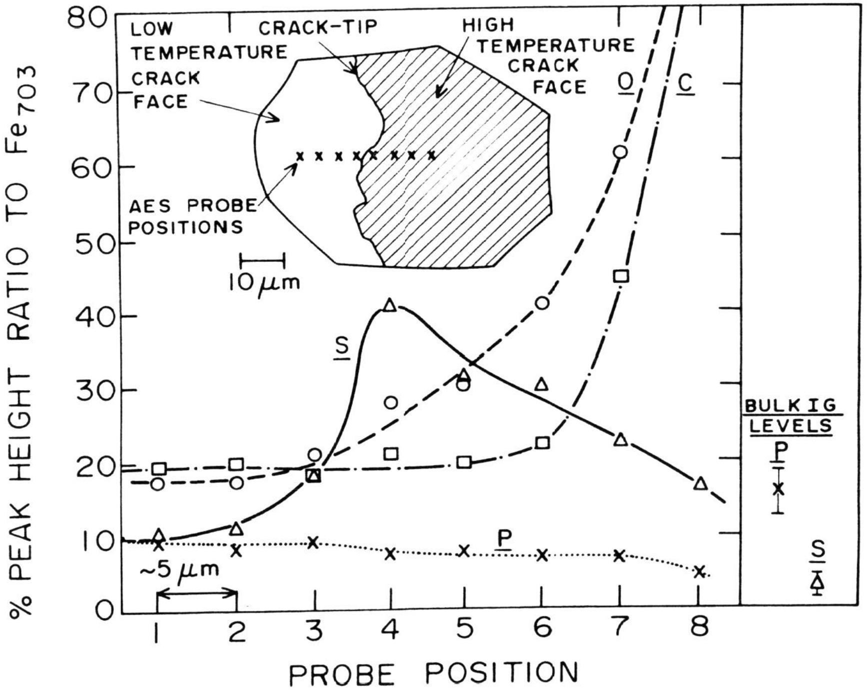

Fig. 10 Auger analysis at tip of intergranular brittle crack in P-doped 2 1/4 Cr-1 Mo steel tested at 750 K by Hippsley et al. (Ref. 40)

A number of investigations have observed effects of the temper embrittlement impurities as well as of copper and even aluminum on the tendency for stress relief cracking by both the cavitation(2,43) and brittle(15,19-22) modes. Examples of each are given in Figs. 11 and 12. As noted above, these elements can be found on some brittle intergranular facets (Fig. 8). Whether they were present originally in the grain boundary or segregated to the new surface after the crack had formed, they could play the same role as that described above for sulfur. Antimony and tin should have a large tendency to enter the grain boundary under stress from the cavity surface because of their large atomic volumes. However, antimony, the most potent embrittling element of this group, has been shown to be significantly less potent than sulfur in the embrittlement of nickel(42), and this is probably true also for iron. When cracking is carried out in air, oxygen should also be drawn into the crack tip in a similar way. This seems to have occurred in the specimens studied by Hippsley et al(39,40) (Fig. 10), and it could very well act as an additional factor in the grain boundary embrittlement.

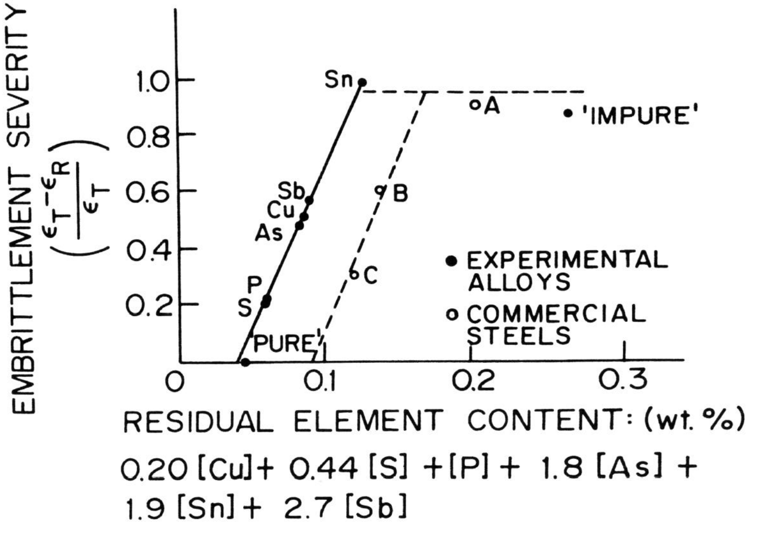

Fig. 11 The effect of residual elements on the cavitation mode of stress relief embrittlement of A533B/A508 steels, Brear and King. (Ref. 43)

The recent study(25,26) of the two pressure vessel steels succeeded in explaining why the MnMoNiCr (A508-2) is so much more susceptible to stress relief cracking then the MnMoNi (A533-B), as is well-known(44). There are two factors superimposed. The first is that the latter steel has 2 1/2 times the manganese content of the A508-2 and therefore its sulfides are more stable (Fig. 1). Hence, there should be less dissolution and re-precipitation of sulfur during the high-temperature austenitization in the A533-B steel. The second factor is the chromium content in the A508-2 steel. This provides additional creep strength and causes the stress to remain higher than in the A533-B steel during the stress relief process. Both these effects are illustrated in Fig. 13, which shows the effects on stress-relief cracking (13a) of the higher grain boundary sulfur (13c) and slower stress relaxation (13b) in the two A508-2 steels (BA and BC), compared with the A533-B steel (CC). The effect of chromium on the stress relaxation rate has been demonstrated also by Kanazawa et al(46).

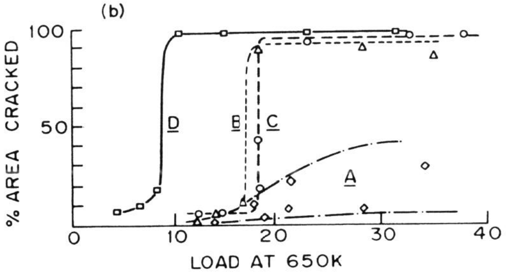

Fig. 12 The final percentage of the cross sectional area of the specimen cracked on heating to 975 K as a function of the applied load measured at 650 K in notched bars of 2 1/2 Cr-1 Mo steel: D-commercial, B and C-doped with phosphorus and tin, respectively, A-high purity, Hippsley et al. (Ref. 21)

Thus, there are at least two requisites for the brittle cracking phenomenon which causes the high susceptibility to stress relief cracking. One is that the creep strength be high enough; this is generally provided by the presence of strong carbide-forming alloy elements. The other is the presence of unscavenged sulfur, liberated by the high-temperature austenitization. This factor can be eliminated by rare-earth additions. The presence of boron may also be required, for the cavitation mode(2) as well as the brittle mode(15). Of course, the applied stress must also be high enough; this usually requires the presence of a notch or pre-crack, although a large, weakly-bonded inclusion may be just as effective.

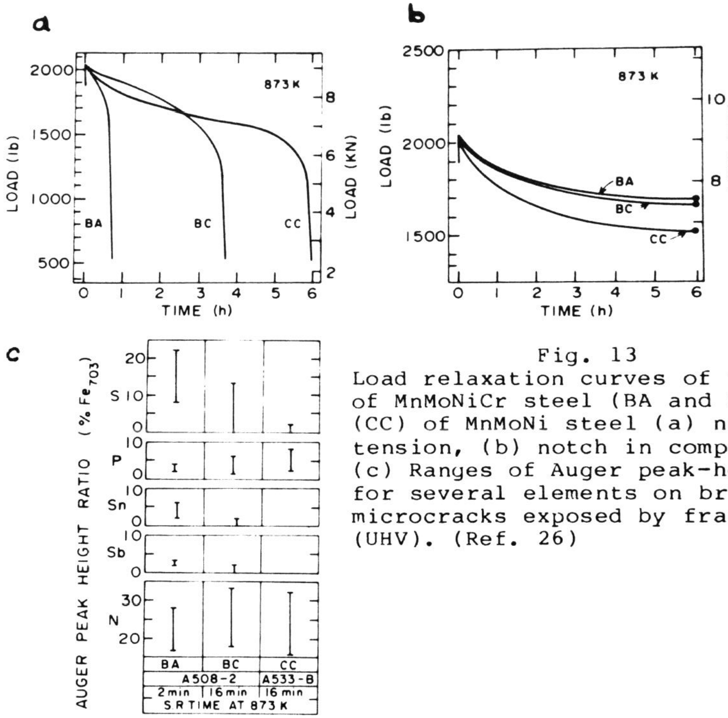

Fig. 13
Load relaxation curves of two heats of MnMoNiCr steel (BA and BC) and one (CC) of MnMoNi steel (a) notch in tension, (b) notch in compression. (c) Ranges of Auger peak-height-ratios for several elements on brittle-mode microcracks exposed by fracture in (UHV). (Ref. 26)

A recent survey(28,45) of a large number of heats of these two types of pressure vessel steels has confirmed the large difference in susceptibility to stress relief cracking, as shown in Fig. 14. This should provide convincing evidence for the need for attention to creep strength and sulfur scavenging in the design of steels intended for welding in thick sections.

Austenitic Steels

It has been known for many years that austenitic steels are subject to stress relief cracking and that this is exacerbated by the presence of strong carbide-forming elements, like tantalum, titanium, and niobium, which promote high temperature strength(47). It does not appear that mechanistic studies have been made recently in these steels in the manner discussed above for ferritic steels. However, two factors concerning austenitic steels should be noted. First, they usually contain about 16 to 20 pct chromium and about one pct manganese. This makes it likely that some of the sulfur in these steels will be present in the form of the less-stable chromium sulfide, especially of the steel is not close to equilibrium. Secondly, these steels are commonly solution-treated at high temperatures and rapidly cooled to prevent carbide precipitation. This

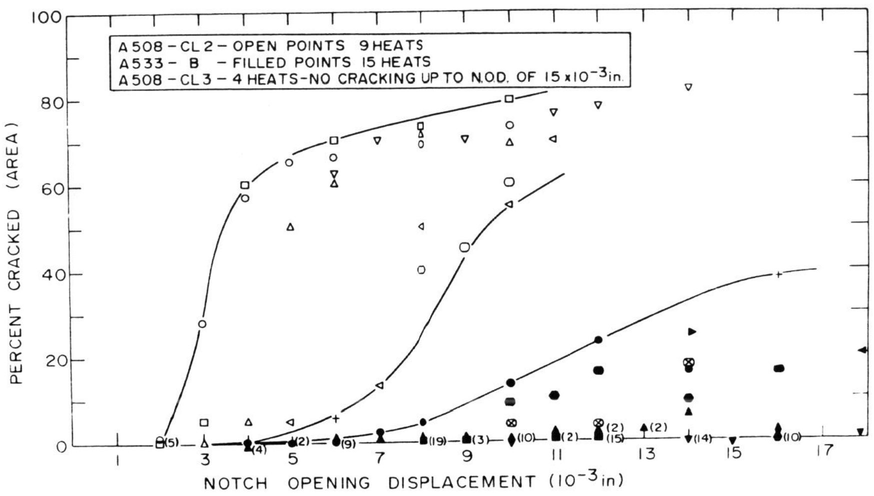

Fig. 14 Survey of stress relief cracking susceptibility of 26 additional heats of A508-2, A508-3, and A533-B steels tested anisothermally as 3-point-loaded Charpy specimens after HAZ simulation. Stress relief temperature 873 K. (Ref. 45)

should have the effect of redistributing sulfur to the grain boundaries, as in the case of the ferritic steels. For these reasons, it would not be surprising if stress-relief cracking in these steels were also sulfur-induced.

It has recently been shown(48) that, while creep cavitation in type 316 stainless steel which has been exposed for long times at elevated temperatures is associated with sigma-phase particles in the grain boundaries, not all steels with sigma phase are subject to this cavitation. This is fairly strong circumstantial evidence for an impurity effect. Still more recently, cavitated fracture surfaces of type 316 specimens which had been in service at 610 to 650°C for about 1.5×10^5 h were examined by Auger electron spectroscopy, and adsorbed sulfur was found, presumably on the surfaces of the creep cavities(49,50). A re-examination(50) of the Lai and Wickens(48) results showed that the one out of three sigma-containing steels which exhibited substantial caviation (in the sigma/austenite interfaces) contained the highest amount of sulfur and the lowest amount of manganese.

It was suggested(50) that, in a steel containing sufficient free, or chromium-precipitated, sulfur in the grain boundaries, the formation of chromium-rich sigma phase would result in sulfur rejection and non-equilibrium concentration in the sigma/austenite interface. This should reduce the cohesive strength of this interface between the plastic austenite and the relatively rigid sigma phase. Thus, there is reason to explore further the role of sulfur in the creep ductility of such austenitic steels.

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REFERENCES

1. E. T. Turkdogan, S. Ignatowicz, and J. Pearson, J. Iron Steel Inst., 1955, vol. 180, p. 349.
2. C. J. Middleton, Metal Sci., 1981, vol. 15, p. 154.
3. G. D. Joy and J. Nutting, in Effects of Second-Phase Particles on the Mechanical Properties of Steel, Iron Steel Inst. Lond., 1971, p. 95.
4. T. J. Baker and R. Johnson, J. Iron Steel Inst., 1973, vol. 211, p. 783.
5. B. J. Schulz and C. J. McMahon, Jr., Metall. Trans., 1973, vol. 4, p. 2485.
6. N. P. McLeod and J. Nutting, Metals Tech., 1982, vol. 9, p. 399.
7. T. Fujii, K. Yamamoto, and M. Ueno, Tetsu-to-Hagane, 1981, vol. 67, p. 117.
8. K. Abiko, R. L. Bodnar and D. P. Pope, in Ductility and Toughness Considerations in Elevated Temperature Service, G. V. Smith, ed., ASME, N.Y., 1978, p. 1.
9. D. P. Pope and D. S. Wilkinson, in Creep and Fracture of Engineering Materials and Structures, B. Wilshire and D.R.J. Owen, eds., Pineridge Press, Swansea, U.K., 1981, p. 531.
10. S. H. Chen, T. Takasugi, and D. P. Pope, Scripta Metall., 1982, vol. 16, p. 79.
11. T. Takasugi and D. P. Pope, Metall. Trans. A, 1982, vol. 13A, p. 1471.
12. S. H. Chen, T. Takasugi, and D. P. Pope, Metall. Trans. A, 1983, vol. 14A, p. 571.
13. S. M. Bruemmer, R. H. Jones, M. T. Thomas, and D. R. Baer, Scripta Metall. (1980), vol. 14, p. 137.
14. J. C. Ritter and R. McPherson, Metals Tech., 1974, vol. 1, p. 506.
15. R. I. Presser and R. McPherson, Scripta Metall. 1977, vol. 11, p. 745.
16. K. Kussmaul, D. Blind, and J. Ewald, Int. J. Pres. Ves. & Piping 1977, vol. 5, p. 159.
17. R. A. Tait and J. F. Knott, in Fracture 1977, ed. D.M.R. Taplin, Univ. of Waterloo, 1977, p. 671.
18. B. L. King, Phil. Trans. Roy. Soc, Lond., 1980, vol. A295, p. 235.
19. C. J. McMahon, Jr., R. J. Dobbs, and D. H. Gentner, Matl. Sci. and Eng., 1979, vol. 37, p. 179.
20. C. A. Hippsley, J. F. Knott, and B. C. Edwards, Acta Metall., 1980, vol. 28, p. 869.
21. C. A. Hippsley, J. F. Knott, and B. C. Edwards, Acta Metall., 1982, vol. 30, p. 641.
22. C. A. Hippsley, J. E. King, and J. F. Knott, in Advances in the Physical Metallurgy and Applications of Steels, Metals Soc., London, 1982, p. 147.
23. J. Shin, Jun Kameda, and C. J. McMahon, Jr., in Micro and Macro Mechanics of Crack Growth, ed. K. Sadananda, B. B. Rath, and D. J. Michel, TMS-AIME, 1981, p. 149.
24. C. A. Hippsley, Metal. Sci., 1983, vol. 17, p. 277.
25. J. Shin and C. J. McMahon, Jr., Acta Metall., 1984, in press.

26. J. Shin and C. J. McMahon, Jr., Metal Sci., 1984, in press.
27. B. C. Edwards, Int. Symposium on Defects and Fracture, Krakov, 1980, (Harwell Rept. AERE-R9930)(1980).
28. C. J. McMahon, Jr., J. Shin and D. H. Gentner, 2nd Intnl. Conf. on Creep and Fracture of Eng. Matls. and Structures, Swansea, 1984.
29. T. Z. Chuang and J. R. Rice, Acta Metall., 1973, vol. 21, p. 1625.
30. S. H. Goods and W. D. Nix, Acta Metall, 1978, vol. 26, p. 739.
31. G. M. Pharr and W. D. Nix, Acta Metall., 1979, vol. 27, p. 1615.
32. T. Z. Chuang, K. I. Kagawa, J. R. Rice, L. B. Sills, Acta Metall., 1979, vol. 27, p. 265.
33. A. Needleman and J. R. Rice, Acta Metall., 1980, vo. 28, p. 1315.
34. I-W. Chen and A. S. Argon, Acta Metall., 1981, vol. 29, p. 1759.
35. T. Takasugi and V. Vitek, Metall. Trans., 1981, vol. 12A, p. 659.
36. B. J. Cane and G. W. Greenwood, Metal Sci., 1975, vol. 9, p. 55.
37. C. Pichard, J. Rieu, and C. Goux, Mem. Sci. Rev. Met., 1973, vol. 70, p. 13.
38. K. S. Shin and M. Meshii, Scripta Metal. 1983, vol. 17, p. 1121.
39. C. A. Hippsley and B. C. Edwards, IAEA IWAFR Specialist Mtg. on "Mechanical Properties of Structural Materials Including Environmental Effects", Chester, England, 10-14 Oct. 1983.
40. C. A. Hippsley, H. Rauh, and R. Bullough, Harwell Rept. AERE R. 11120, Oct. 1983, to be published in Acta Metall.
41. C. J. McMahon, Jr., Zeitschrift fur Metallkunde, 1984, in press.
42. S. M. Bruemmer, R. H. Jones, M. T. Thomas, and D. R. Baer, Met. Trans. A 1981, vol. 12A, p. 1621.
43. J. M. Brear and B. L. King, Proc. Conf. on Grain Boundaries, Metals Soc., London, 1976.
44. A. G. Vinckier and A. W. Pense, Weld. Res. Council Bull. vol. 197, Aug. 1974.
45. C. J. McMahon, Jr. and D. H. Gentner, to be published.
46. S. Kanazawa, K. Yamoto, T. Takeda, and K. Hashimoto, J. Japan Weld. Soc., 1975, vol. 44, p. 791.
47. R. J. Christoffel, Weld. Jnl. Res. Suppl. June 1962, p. 251-S.
48. J. K. Lai and A. Wickens, Acta Metall., 1979, vol. 27, p. 217.
49. C. L. Briant, General Electric Co., 1983, unpublished research.
50. C. J. McMahon, Jr., Scripta Metall., 1984.