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Impurities, segregation and creep embrittlement

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[Plate 1]

Reported studies of creep embrittlement in low alloy steels at 550 °C and of stress relief cracking at 700 °C show conflicting evidence for the importance of residual impurities. Calculations of the relative effects of impurities, through segregation to grain boundaries and also to the internal surfaces of cavities, show that rupture life and ductility can be affected. Auger electron spectroscopic measurements of these segregations in commercial $\frac{1}{2}$CrMoV steels give the relative importance for all active elements. For stress relief cracking, the equilibrium surface segregation results agree with cracking measurements and allow extension to all important elements. Analysis of published data shows that, in practice, impurities are as important as microstructure in causing embrittlement, the most important impurities being, equally, tin, copper and arsenic. A similar analysis for creep shows that impurities are more important than microstructure with copper dominant and phosphorus and tin also detrimental. Here, the creep ductility falls but rupture life increases with impurity content, consistent with a model involving grain boundary segregation. The stress relief cracking and creep embrittlement are both sensitive to impurities but, involving different segregations, are dominated by different elements.

1. INTRODUCTION

During creep at high stresses, failure often occurs with good ductility; however, at intermediate or low stresses, failure with some low alloy steels can occur with very poor ductility. The failure often involves grain boundary cavitation with a subsequent intergranular fracture path. This behaviour has been associated with failures in industrial situations ranging from weld failures in the weld metal or heat-affected zone to creep failures in materials operating at temperature. It occurs particularly with some of the CrMoV steels widely used in the power generating industry.

For many years there have been indications that residual impurity elements could significantly reduce creep properties in the region of poor ductility. The evidence is not clear cut, as will be discussed below. In this paper, microstructure will be assumed to be held constant, although, as is well known (Stone & Murray 1965), microstructure is crucial in defining creep properties. Any effect of impurities on grain boundary cavitation is concerned with the interplay between the grain boundary and the grain. Thus, microstructures with the greatest creep resistance are likely to exhibit impurity effects most strongly whereas other microstructures may show little effect.

Many workers have sought to correlate intergranular creep embrittlement in low alloy steels with temper embrittlement (Bruscato 1970; Wolstenholme 1972; Batte 1973; Burns 1973; Viswanathan 1974), or with the sort of residual impurities that cause low temperature intergranular brittleness (Tipler & McLean 1970; Hopkins *et al.* 1971; Tipler 1972; Batte & Murphy 1973; Harris & Jones 1972; Viswanathan 1975*a*, *b*). The early work of Tipler &

McLean (1970) provided the greatest insight into the action of impurities on this creep performance in which grain boundary cavitation dominates. They showed that dilute levels of antimony in copper caused increases in both the grain boundary cavity generation and growth rates. Similar observations showed that oxygen caused the time to rupture at a given strain to be greatly reduced. The action of the impurity on the cavity growth rate was not explained but the easier nucleation was associated with the lowering of the energy required to create the cavities, γ', given by $2\gamma_s - \gamma_b$ where γ_s and γ_b are the surface and grain boundary energies respectively.

Little basic work has been completed since Tipler & McLean's but a number of studies have been made of the effects of various impurities in commercial alloys. Bruscato (1970), studying the creep embrittlement of $2\frac{1}{4}$Cr1Mo weld deposits, reasoned that the embrittlement, being intergranular, may be coupled to temper embrittlement which he related in turn by an embrittlement factor to the impurities P, Sb, Sn and As. The creep measurements for a high purity material indeed showed improved rupture ductility compared with commercial material at 565 °C, but not at 480 °C. Creep studies of $\frac{1}{2}$CrMoV steam pipe and 1CrMoV rotor forging material by Hopkins *et al.* (1971) showed that, at 550 °C, materials of high purity had improved rupture stress, life and ductility compared with a commercial material. The improvements were greatest in the low stress, long rupture time, region relevant to industrial applications, The high-purity material had low levels of the very wide range of elements: P, Sn, Sb, As, Cu, Pb, O and N, and it was not known which were important. More recently, Tipler (1972) has shown that purification delays the initiation of grain boundary cavitation and reduces the cavity density. These were thought to give the major contributions to the increased rupture life and ductility. Batte & Murphy (1973), studying creep in commercial casts of 1CrMoV, found results that supported the application of Bruscato's embrittlement factor. Here, however, the variation in the factor was mainly due to P. Similarly, Burns (1973) and Wolstenholme (1976) have correlated intergranular creep cracking in $2\frac{1}{4}$Cr1Mo weld deposits with temper brittleness due to phosphorus segregation, and Tait & Knott (1976) have shown that, in $\frac{1}{2}$CrMoV at 500 °C, the ductility was related to the total P, Sn, Sb, As and Cu content.

Contrary to the above observations, recent studies of creep ductility in $1\frac{1}{4}$Cr$\frac{1}{2}$Mo steels at 540 °C by Viswanathan (1974, 1975*a*, *b*), for rupture times up to 2000 h, show that P, Sn and Sb have little effect although B is very detrimental. This is supported by Tipler & Varma's (1976) findings for $\frac{1}{2}$CrMoV in which P, S, N, Sn, Sb and As were separately added to the earlier high purity steel, to commercial levels, without deterioration of the creep properties. They concluded that the impurity effect must be through mutual interaction.

A similar difference of opinion concerning the importance of impurities exists for stress relief cracking (s.r.c.) of these alloys, generally at 680–700 °C. Drinnan & Harris (1970) showed that the cracking in the weld heat-affected zone of $\frac{1}{2}$CrMoV could be related to the overall impurity content of Cu, Sn, As, Sb and P. Later, Harris & Jones (1972) confirmed the detrimental effect of Sn and Cu. King (1976), in a careful study, showed that the s.r.c. in $\frac{1}{2}$CrMoV at 550 °C is related to the impurity contents by the function

$$\mathrm{P} + 3.57\mathrm{Sn} + 8.16\mathrm{Sb} + 2.43\mathrm{As}, \tag{1}$$

where the element symbols represent their concentration in micrograms per gram.

Realizing the inaccuracy of drawing conclusions from a few steels which may have different microstructures, even for the same heat treatment, Miller & Batte (1975) measured the s.r.c. of 34 commercial casts of $\frac{1}{2}$CrMoV and 18 of $2\frac{1}{4}$Cr1Mo, at 700 °C. In contrast to the above results, they found no apparent correlation between crack susceptibility and residual element composition for the residuals P, Sn, Sb, As, Cu, Ni, Pb and Al.

Thus, for these steels, which regularly exhibit intergranular cavitation failure, there is strong evidence both for and against the importance of residual impurities in both creep embrittlement and in s.r.c. It may be that, for the microstructures used commercially, impurities are unimportant or it may be that the results are not always correctly interpreted. To try to resolve this difference, a number of ways in which residual impurities could affect creep cavitation are discussed in the next section so that the relative importance for different impurities in the various mechanisms can be established. Measurements of the activity of the various residuals at the appropriate surfaces and interfaces are then reported and related to the creep embrittlement and s.r.c. data.

2. THEORY

The various theories of rupture by creep cavity growth have been discussed at great length by many authors to evaluate the interrelation of the parameters of applied stress, σ, temperature, T, rupture time, t_r, and rupture strain, ϵ_r. The simple approach of Hull & Rimmer (1959) was subsequently modified by Speight & Harris (1967), Vitovec (1972), Weertman (1973), Harris *et al.* (1974), Raj & Ashby (1975) and Speight & Beere (1975) to allow for effects such as the rising net section stress as cavitation proceeds under a given applied load and also for the observed continual creation of cavities throughout creep. Thus, Skelton (1975) calculated the rupture time and strain for a model in which there is continuous creation of cavities at a rate N per unit area of grain boundary per second and where failure occurs as the cavities just coalesce:

$$t_r = (\tfrac{5}{16}G^{-1})^{\frac{2}{5}}N^{-\frac{3}{5}}, \tag{2}$$

$$\epsilon_r = 0.65d^{-1}(G/N)^{\frac{1}{5}}, \tag{3}$$

where $G = 2\pi D_{gb}\delta\sigma\Omega/kT$, D_{gb} being the grain boundary self diffusivity, δ the width of the grain boundary, Ω the atomic volume, k the Boltzmann constant and d the average grain diameter. In practice, ϵ_r is the grain boundary cavitation contribution to the total measured rupture strain. For our purposes a stress-dependent failure criterion may be more realistic than Skelton's; however, such changes do not alter the basic G and N dependences of ϵ_r and t_r and so do not affect the predicted relative effects of impurities. As will be shown later, the surface segregation of impurities can raise N, decreasing both ϵ_r and t_r, whereas grain boundary segregation can lower D_{gb}, again decreasing ϵ_r but increasing t_r. In both cases, as segregation increases, the fracture surfaces are predicted to exhibit a progressively higher and higher density of smaller and smaller cavities.

(a) *Segregation and cavity generation rate*

It now seems generally accepted that cavities are not spontaneously created by the condensation of vacancies (Raj & Ashby 1975; Dyson 1974) and that the most likely mechanism concerns decohesion at precipitate–matrix interfaces occurring at a steady rate throughout creep (Greenwood 1963; Tipler *et al.* 1970; Dyson & McLean 1972). Three segregation mechanisms which can affect the cavity generation rate at grain boundaries are discussed below.

(i) *Cavity surface segregation from the bulk*

It has been proposed that segretation of impurities to the cavity surface will lower the surface energy so that the critical stable cavity radius, r_c, given by the well known relation

$$\sigma_c = 2\gamma_s/r_c, \tag{4}$$

is also reduced with a consequent rise in cavity production rate (Tait & Knott 1976; Tipler & Varma 1976). Here σ is the local tensile stress normal to the boundary. Before surface segregation can occur there must, however, be a free surface, so here a model must be invoked whereby slip or some equivalent process rapidly generates a cavity with a radius of the order of r_c. This is likely to happen at grain boundary precipitates. If the cavity radius is greater than r_c, the cavity goes on to contribute to rupture directly, but if smaller, it begins to sinter. If the kinetics of surface segregation is sufficiently rapid, the fall in γ_s can be more rapid than the reduction of the cavity radius by sintering so that, after a short time, the cavity shrinkage ceases and the cavity, initially smaller than r_c, goes on to grow and contribute to rupture. Thus, provided the impurity is sufficiently surface active, it is the kinetics of surface segregation that is important. The analysis of the kinetics of surface segregation to flat surfaces has been treated at length elsewhere (Lea & Seah 1977). The build-up of segregation to the surface of a spherical cavity is faster than that to a flat surface because of the larger volume of material available to supply the impurity. Extension of Crank's (1975) analysis gives:

$$\Gamma_s = C\left\{\left(\frac{4Dt}{\pi}\right)^{\frac{1}{2}} + \frac{Dt}{r}\right\}, \tag{5}$$

where Γ_s is the segregation level in moles per square metre, C is the impurity concentration in moles per cubic metre, D is the solute bulk diffusivity and t the time elapsed.

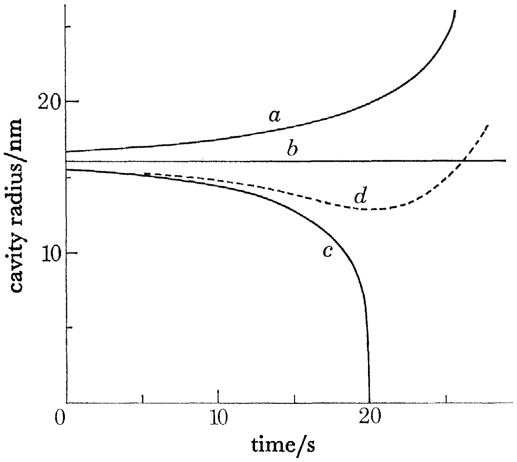

FIGURE 1. Cavity behaviour in creep at 550 °C with a local tensile stress of 250 MPa and surface energy 2 J m^{-2}. Curves *a*, *b* and *c* respectively show the time dependence of the cavity radius for an initial cavity larger than, equal to and smaller than the critical cavity size. Curve *d* shows the effect of surface segregation on curve *c*.

The normal behaviour of a cavity, according to Hull & Rimmer's (1959) analysis, is shown in figure 1. For $\frac{1}{2}$CrMoV steel undergoing creep at 550 °C, the applied tensile stress may typically be 250 MPa and the cavity surface energy 2 J m^{-2}. Thus, from (4) the critical radius is about 16 nm. If there are stress concentrating factors the critical radius will be smaller; however, its precise value is not important. Curves *a*, *b* and *c* therefore represent the cavity behaviour if its initial size is respectively larger than, equal to, and smaller than the critical size. With a segregate that can adsorb sufficiently in 20 s, curve *c* shifts to *d* and the effective critical radius becomes lowered. The lowering of the critical radius with bulk impurity content is calculated below for both phosphorus and nitrogen in iron as representing the substitutional and interstitial classes of impurity.

The adsorption isotherm for phosphorus on the surface may be reasonably described by the Langmuir theory (Hondros & Seah 1977) so that (Seah 1976)

$$\gamma_s = \gamma_s^\circ + \Gamma_{s0} RT \ln (1-X_s), \tag{6}$$

where γ_s° and γ_s are the surface energies of the clean surface and that with a fractional monolayer coverage, X_s, respectively. Γ_{s0} is the saturation coverage of the adsorbate in moles per square metre. Bearing in mind that $\Gamma_s = X_s \Gamma_{s0}$, (5) and (6) may be used with Hull & Rimmer's equation to generate curve *d* by an iterative computation. However, Hull & Rimmer's equation shows that a cavity with 1 % lower radius than the stable value will sinter in some 30 s. By using a phosphorus diffusivity of $1.58 \times 10^{-4} \exp(-219000/RT)$ m^2 s^{-1} (Gruzin & Mural 1964), and a typical commercial bulk phosphorus level of 0.017 %, (5) predicts that less than 2 % of a monolayer can have accumulated in this time. A full analysis shows that a negligible figure 2 require an order of magnitude more solute than is shown. The grain boundary activities of boron and nitrogen in iron appear to be around 10^4 (Seah 1975) and since the surface activity is between 2 and several hundred times that at the grain boundary (Seah & Lea 1975), the likely behaviour of boron and nitrogen is between that shown in figure 2 and values an order of magnitude weaker.

(ii) *Cavity surface segregation from a grain boundary source*

High diffusivities are also expected for substitutional elements residing at grain boundaries. As will be shown later, a typical average sample of $\frac{1}{2}$CrMoV material at 550 °C would exhibit the following segregation levels in percentage monolayers: P, 16; Cu, 7; Sn, 5; Sb, 1. Unfortunately the grain boundary diffusivities of these elements in iron are not known but, assuming that they are between that of iron at the grain boundary and a value an order of magnitude higher, their segregation to the cavity surface from the grain boundary would reduce the effective stable cavity size by about one-third with a corresponding increase in cavity production rate. Although the phosphorus would appear to be dominant here, having the highest grain boundary segregation and diffusivity, it is not as surface-active as copper and tin and so the main contributions will come from these latter two elements.

(iii) *Surface segregation at cavities stabilized by grain boundary precipitates*

A final way for surface segregation to affect the cavity source rate occurs for nucleation on a face of a grain boundary precipitate, as shown in figure 3. Under the applied stress, the interface decoheres and a cavity with a large but reducing radius starts to grow. The cavity height grows until the critical radius is reached, at which point the cavity is stable indefinitely. There is now sufficient time for the substitutional impurities to segregate to the cavity free surface and, for the typical commercial impurity levels, this segregation could halve γ_s and so halve the stable cavity radius. For the conditions used earlier for $\frac{1}{2}$CrMoV, therefore, precipitate faces of less than 32 nm diameter can progressively contribute to the nucleation of cavities that can contribute to failure. The lower limits of face size, at high impurity levels and ignoring stress concentrating mechanisms, appears to be around 10 nm.

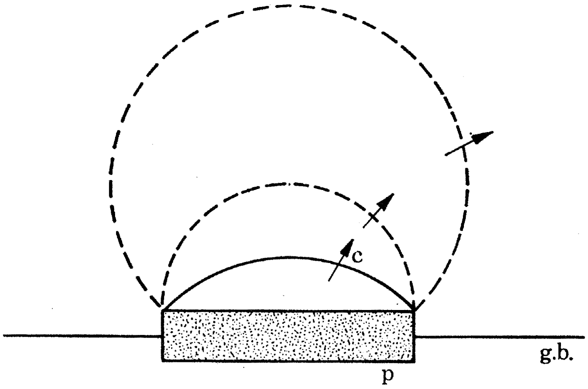

FIGURE 3. Nucleation of a cavity (c) on a grain boundary precipitate (p) face showing how the cavity radius falls as the cavity starts to grow.

(*b*) *Segregation and cavity growth rate*

As shown by experiments reported below, the grain boundary segregation in low alloy steels can be quite significant. This in turn can lead to a drop in the grain boundary energy, γ_b. A relation has been developed by Borisov *et al.* (1964) linking the grain boundary self-diffusivity, D_{gb}, with the excess free energy associated with the boundary, γ_b:

$$\gamma_b = \left(\frac{kT}{\alpha a^2}\right) m \left[\ln\left(\frac{D_{gb}\delta}{aD_L}\right) - \ln m\right], \tag{7}$$

where D_L is the lattice diffusivity, m is the number of atomic layers comprising the boundary, a is the interatomic spacing and $\alpha = 1$ for interstitial diffusion and $\alpha = 2$ for a vacancy mechanism. This relation has been tested by Pelleg (1966) for single-component systems and was found to be an excellent description of the experimental results if the grain boundary width was taken as one atom layer. Thus, for vacancy diffusion:

$$D_{gb}\delta/D_L = a \exp\,(2\gamma_b a^2/kT). \tag{8}$$

Although the above equations were derived for single-component systems, it is reasonable that segregants, improving the grain boundary order and reducing γ_b, will also reduce the self-diffusivity of grain boundary atoms. The effect of segregation may be included by substituting for γ_b, from the grain boundary analogue of (6), in (8). Recent studies by Gupta (1976) show that segregation does indeed produce precisely the behaviour expected in this way. Hence the effect of segregation on the rupture strain and time to rupture, in (2) and (3), may be calculated.

By using the example cited earlier with grain boundary segregation of, in percentage monolayers, P, 16; Cu, 7; Sn, 5; Sb, 1, a total fall in γ_b from 0.64 to 0.59 occurs so that D_{gb} falls by a factor of 1.6 causing t_r to rise by 20 % and ϵ_r to fall by 10 %. Clearly this effect is significant.

3. EXPERIMENTAL

Having established that both surface and grain boundary segregations were of possible importance in intergranular creep cavitation, measurements were made by Auger electron spectroscopy (A.e.s.) to determine the active species and their levels in both forms of segregation for commercial samples of ½CrMoV during creep at 550 °C or stress relief heating at 700 °C. Below, therefore, measurements are presented for equilibrium segregation to grain boundaries at 550 °C and to cavities at 550 and 700 °C. The materials used for the 700 °C treatment would not fail intergranularly without cavitation so there were no grain boundary A.e.s. measurements at 700 °C. The cavity segregation results at 700 °C were found to agree with equilibrium free surface segregation predictions and so the results were extended by the relatively easier direct equilibrium surface segregation measurements at 700 °C. At 500 °C, surface segregation measurements were made for both the fast acting species as well as for the species at equilibrium. From these measurements it was hoped that the controlling mechanisms could be established and the roles of all impurities predicted. The methods of measurement of the segregations are dealt with at length elsewhere (Seah & Hondros 1973; Seah & Lea 1975) and will not be described here.

(*a*) *Grain boundary segregation at* 550 °C

At 550 °C, equilibrium grain boundary segregation will be attained after a very small fraction of the creep life; thus equilibrium measurements could be made at any time after approximately a day at 550 °C. However, ½CrMoV and 1CrMoV do not appear to exhibit temper brittleness and so the grain boundaries could not generally be exposed for analysis by A.e.s. One commercial alloy of $\frac{1}{2}$CrMoV with a high tin level and one sample of 1CrMoV did fail on uncavitated grain boundaries. These measurements showed that an average commercial sample of $\frac{1}{2}$CrMoV steel† would exhibit a grain boundary composition of approximately, in percentage monolayers, P, 16; Sn, 5; Sb, 1; As, 5; Cu, 7; N, 11; B, less than 5. The results for phosphorus, tin and antimony are as predicted for pure iron (Seah & Lea 1975; Seah 1977*a*). The result for copper is similar to that observed for a wide range of steels and so these results seem fairly typical.

(*b*) *Cavity segregation at* 550 °C

Segregation to cavities formed early in creep cannot be measured by A.e.s. as the samples have to be opened up by fracture in the A.e.s. apparatus. The samples would only fail on heavily cavitated boundaries and so the measurements represent equilibrium cavity segregation. Measurements were only made on one alloy, which showed that the surface activities of Sn, Sb, Cu, N and B were high while P was even weaker than at the grain boundary. For the typical commercial material the segregation levels would be P, 1; Sn, 50; Sb, 20; As, less than 15; Cu, 22; N, 18; B, 31.

(*c*) *Cavity segregation at* 690–700 °C

The materials studied had crept to near failure or were internally cracked in stress relaxation tests (Miller & Batte 1975). The creep samples showed extensive cavitation over the whole fracture surface, as shown in figure 4, plate 1. In the stress relaxation tests highly cavitated

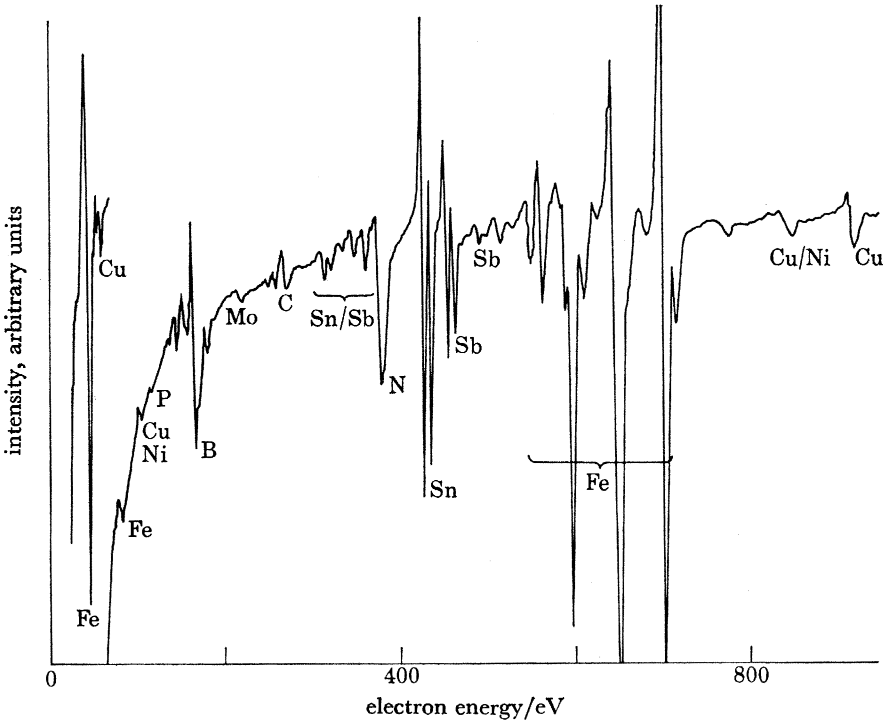

FIGURE 5. Auger electron spectrum of cavitation in $\frac{1}{2}$CrMoV after a stress relaxation test at 700 °C.

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† In this paper, as a convenient guide, an average commercial impurity composition is assumed to be, in micrograms per gram, S, 200; P, 170; Sn, 120; Sb, 30; As, 160; Cu, 1200; Ni, 1200; N, 100; B, 3.

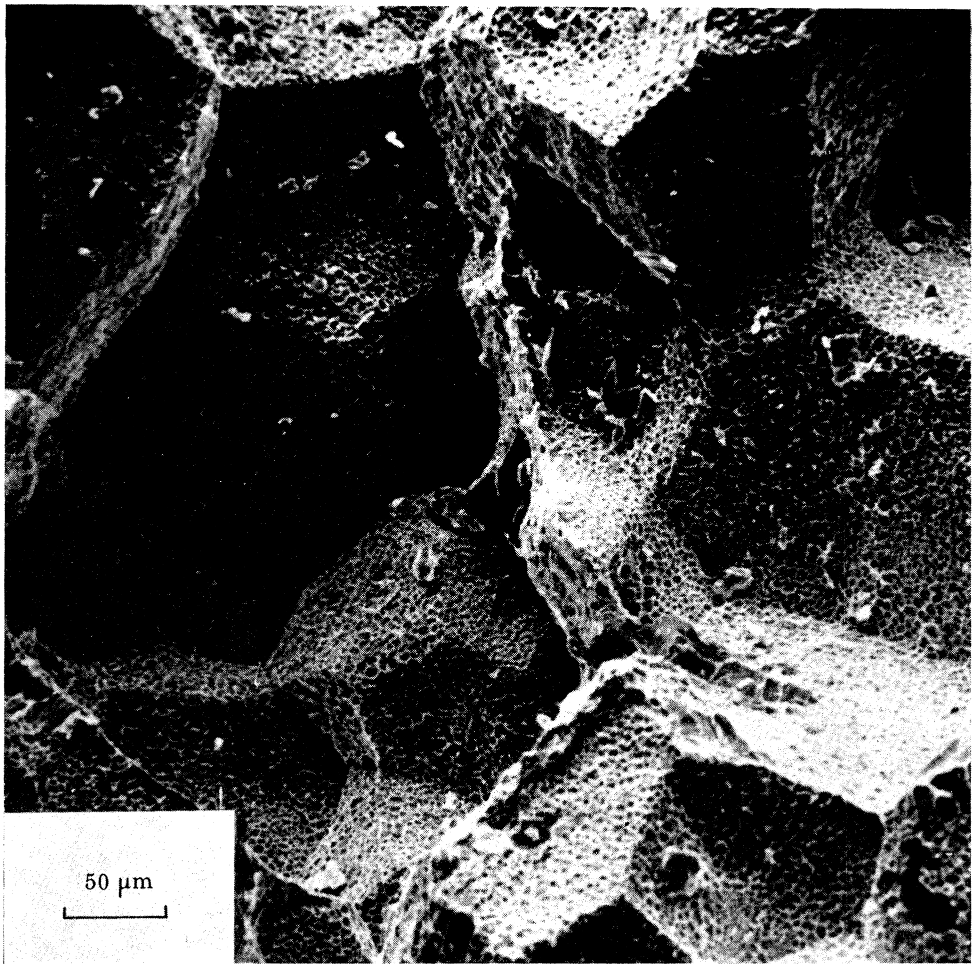

Figure 4. Cavitated grain boundary fracture surface of $\frac{1}{2}$CrMoV after simulated stress relief treatment at 700 °C.

regions were found only a grain or two ahead of the air exposed crack; however, measurements were fairly reproducible along the length of the crack front. A typical A.e.s. spectrum from such a cavitated region is shown in figure 5. The results for the cavity segregation of Sn and Sb agreed with the free surface segregation on pure iron (Seah & Lea 1975). In some cases the cavity segregation results are apparently low as the A.e.s. measurement averages over the cavity surfaces and any remaining ductile tearing required to fracture the sample. Ignoring this factor, for the average commercial composition cited earlier, the cavity surface segregation would be, in percentages of monolayers P, 4; Sn, 38; Sb, 13; As, 15; Cu, 14; N, 3; B, 3.

In view of the agreement of the above results with free surface segregation, the measurements were extended by studying the experimentally easier free surface segregation *in situ* in the A.e.s. apparatus.

(*d*) *Surface segregation at* 550 °C

For the surface segregation measurements Tipler & Varma's (1976) materials were selected. These were very thoroughly characterized in creep at 550 °C and showed the existence of improved properties for the high purity material but the anomaly of no loss in properties as each of the impurities was separately added. To study the rapid early segregation, measurements were made after 5 min at 550 °C, the time to achieve half the equilibrium level of, say, tin segregation being 10–100 h (Lea & Seah 1977). The experimental technique is presented elsewhere (Seah & Lea 1975), but briefly the surface of a cube of material of side 1 mm was cleaned by ion etching in the apparatus. The sample was then directly heated in the ultra-high vacuum for 5 min at 550 °C. The results showed that the most active species was nitrogen and not boron and that the high bulk level of copper enabled it also to build up rapidly. In Tipler & Varma's (1976) work, nitrogen was shown not to be very important but the effect of copper was not studied. Thus, it is possible that the main effect in Tipler & Varma's work was due to copper. The surface segregation, in percentage monolayers, may be expressed very roughly by the relation

$$X_s = 0.06\mathrm{P} + 0.2\mathrm{Sn} + 0.1\mathrm{Sb} + 0.02\mathrm{Cu} + 3\mathrm{N} + {<}\,2\mathrm{B},$$

where the element symbols represent the solute content in micrograms per gram.

Longer treatments of 1 h at 550 °C were given to four commercial alloys and segregation of Sn and As was seen to increase in addition to the high Cu and N levels. The results may be summarized by the equation

$$X_s = 0.12\mathrm{P} + 0.31\mathrm{Sn} + 0.15\mathrm{Sb} + 0.26\mathrm{As} + 0.04\mathrm{Cu} + \mathrm{N} + 3\mathrm{B}.$$

(*e*) *Surface segregation at* 700 °C

A range of six commercial $\frac{1}{2}$CrMoV alloys were studied after heating at 700 °C for 1 h, which time was sufficient for most segregants to reach equilibrium. The results may be expressed in the general equation for the total surface segregation:

$$X_s = 0.01\mathrm{P} + 0.43\mathrm{Sn} + 0.63\mathrm{Sb} + 0.17\mathrm{As} + 0.02\mathrm{Cu} + 0.09\mathrm{N} + \mathrm{B}. \tag{9}$$

The average commercial material would thus exhibit, in percentage monolayers, P, 2; Sn, 52; Sb, 19; As, 27; Cu, 26; N, 9; B, 3.

Full particulars of all of the alloy compositions and all of the A.e.s. measurements are presented elsewhere (Seah 1977*b*).

4. Discussion

(*a*) *Stress relief cracking at* 700 °C

The measurements for surface segregation and cavity segregation in $\frac{1}{2}$CrMoV at 700 °C show the same relative coefficients for the elements Sn, Sb, As and Cu. The surface segregation at cavities at 700 °C may be expressed as

$$X_s = 0.71\,(0.03\mathrm{P} + 0.45\mathrm{Sn} + 0.61\mathrm{Sb} + 0.13\mathrm{As} + 0.02\mathrm{Cu} + 0.04\mathrm{N} + 1.4\mathrm{B}), \tag{10}$$

which is very similar to the measurement for free surface segregation shown in (9). The lower factor outside the brackets is due, as noted above, to the A.e.s. sampling ductile failure and cavity surface; however, this does not alter the relative element ratios. The higher value of phosphorus here is the more likely value since the low value in (9) is caused by loss of phosphorus from the surface to the vacuum of the A.e.s. apparatus, phosphorus having an unusually high vapour pressure (Honig & Kramer 1969).

It is argued that each of the above elements segregates to the cavity surface and thereby cause a fall in γ_s according to (6), a rise in the cavity nucleation rate and a consequent fall in rupture elongation and life. From (6) and (10) the relative effects of the elements on rupture strain will be given by

$$-\Delta\epsilon_r \propto 0.7\mathrm{P} + 5.4\mathrm{Sn} + 7.7\mathrm{Sb} + 2.4\mathrm{As} + 0.4\mathrm{Cu} + 1.8\mathrm{N} + 33\mathrm{B}. \tag{11}$$

The closeness of this result, rather than that of the other measurements, to the measurements of the relative effects of impurities in stress relief cracking by King (1976), indicates that ϵ_r is controlled by surface segregation through the cavity production rate and that the relatively easy surface segregation measurements can be used to define all of the active species in a commercial alloy. For the typical commercial alloy the contributions for different elements are in the ratio P:Sn:Sb:As:Cu:N:B: of 1:5:2:3:4:1:1; attention should therefore be paid to tin, copper and arsenic, in order of importance, to improve the stress relief ductility.

Realizing the inaccuracy of deducing general behaviour from a study of a few alloys in which all parameters cannot be held constant, Miller & Batte (1975) analysed the stress relief crack

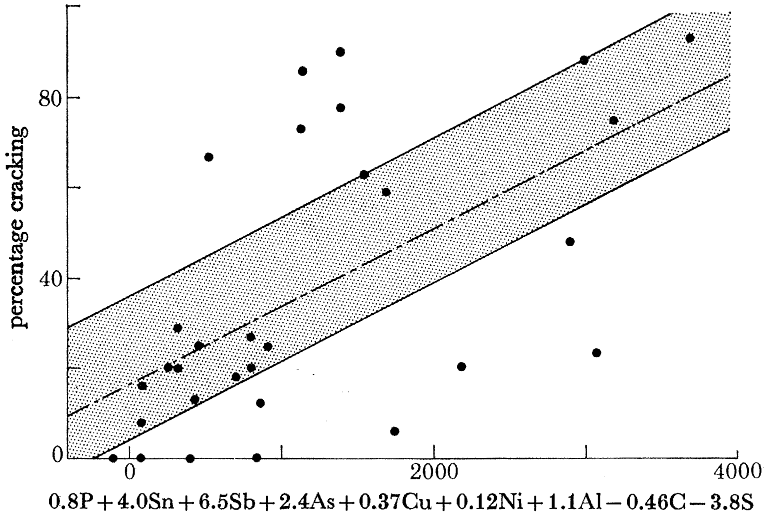

Figure 6. Analysis of Miller & Batte's (1975) results for stress relief cracking in $\frac{1}{2}$CrMoV steel, in relation to impurity content.

sensitivity of 34 $\frac{1}{2}$CrMoV commercial casts. They concluded that there was no correlation between cracking and residual element composition and that the microstructure was of overriding importance. This conclusion obviously implies either that (11) and (1) are incorrect or that the effect of impurities is only second-order compared with that of microstructure. Miller & Batte's results were therefore analysed for the relation between cracking and an average of (11) and (1). Their tables also provide the chemical composition in relation to nine other elements and so a regression analysis was applied for Ni, Al, C and S so that their effects could be removed. In figure 6 all their results, for which complete chemical analyses were available, are plotted against the function

$$0.8\mathrm{P}+4.0\mathrm{Sn}+6.5\mathrm{Sb}+2.4\mathrm{As}+0.37\mathrm{Cu}+0.12\mathrm{Ni}+1.1\mathrm{Al}-0.46\mathrm{C}-3.8\mathrm{S}, \qquad (12)$$

based on an average of (11) and (1) for the elements P, Sn, Sb, As, and Cu. Regression analysis shows that the cracking is indeed correlated with this function and that the broken line in figure 6 is the best straight-line description. The shaded zone includes 50 % of the points above the line, and 50 % below. The scatter about the line shows that the randomly varying microstructure's importance is approximately equal to that of impurity content, and is not overriding. A similar result occurs for their measurements on 2$\frac{1}{4}$Cr1Mo weld metals.

Thus, in commercial situations of stress relief cracking at 700 °C in $\frac{1}{2}$CrMoV steel, the impurity content is as important as microstructure and the relative importance of the tramp elements is given by (11) with the dominant mechanism acting through surface segregation to alter the cavity generation rate.

(b) *Creep embrittlement at* 550 °C

At 550 °C the situation changes. The rapid surface segregation in the typical commercial composition is dominated by copper, tin and nitrogen, whereas at 1 h arsenic is also important.

The experimental evidence for the effect of impurities on the creep of $\frac{1}{2}$CrMoV steel at 550 °C is quite contradictory. This is not surprising as the correlations so far published comprise two or three results and it is clear from figure 6 that any random small selection of results would not show any significant trend unless the microstructure could be properly controlled.

To try and assess the effect of impurities on creep a search was made for a set of results equivalent to figure 6. Such a set appears in *British Steelmakers Creep Committee high temperature data* (1973). A regression analysis was made for the effects of impurities on the measurements of rupture ductility (percentage reduction in area, A_d) and rupture life for all $\frac{1}{2}$CrMoV samples for which phosphorus, tin and copper chemical analyses are given. For a stress level of 108 MPa at 550 °C, the results for rupture ductility and rupture life are shown in figure 7 and 8. These show that impurities are very important in defining the creep properties and that any other variables, such as microstructure or other impurities, are of about half the importance of the impurity parameter plotted. Thus:

$$\left.\begin{aligned} A_d &= 132-0.059\,(1.5\mathrm{P}+1.2\mathrm{S}+0.36\mathrm{Cu}+1.6\mathrm{Sn}),\\ t_r &= -4571+5.7\,(1.3\mathrm{P}+1.7\mathrm{S}+0.34\mathrm{Cu}+2.1\mathrm{Sn}).\end{aligned}\right\} \qquad (13)$$

At 600 °C, A_d is still affected by impurities in the same way except that the coefficients of the elements are all increased by 30 %.

Some caution must be attached to regression analyses as it often occurs that the impurity contents are related to the bulk alloy levels and hence the microstructure and hardness. It is expected that the rupture ductility would reduce as the matrix hardness increases and so a regression analysis was made for the elements C, Cr, Mo, Ni and V associated with hardness. Significantly worse correlations than figures 7 and 8 were obtained but there was no general reduction of rupture ductility with increase in the hardening elements. The above impurity–creep relations (13) are therefore valid.

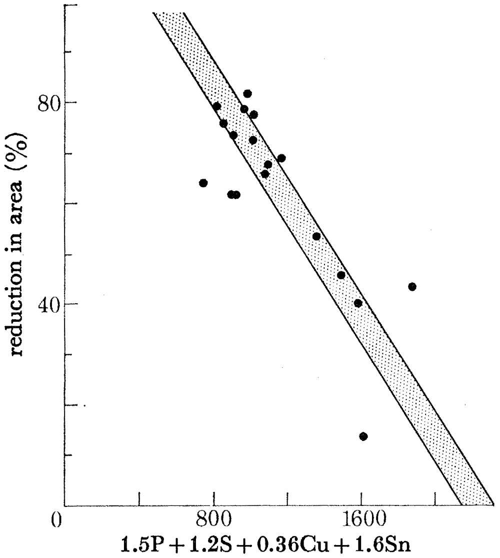

FIGURE 7. Analysis of creep ductility of $\frac{1}{2}$CrMoV steel at 550 °C and 108 MPa, from the B.S.C.C. data (1973), in relation to impurity content.

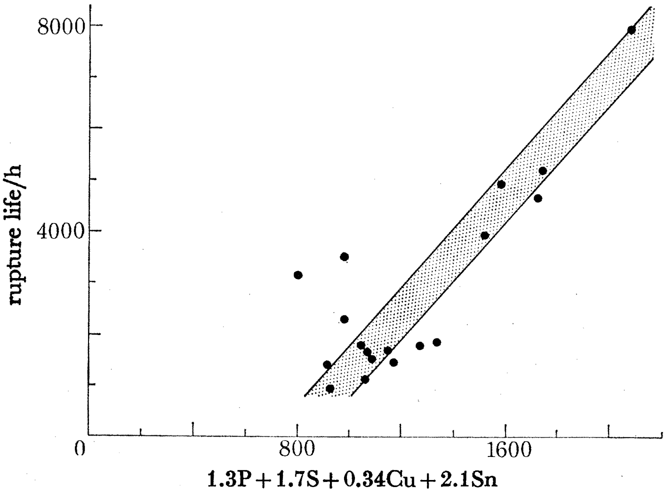

FIGURE 8. Analysis of the rupture life of $\frac{1}{2}$CrMoV steel at 550 °C and 108 MPa, from the B.S.C.C. data (1973), in relation to impurity content.

The above result for t_r is most striking and shows that in a uniaxial tension test the impurities actually *increase* the rupture life. This indicates that the impurities could be blocking the grain boundary diffusion and so slowing the cavity growth rate. Thus, if it is assumed that failure was by grain boundary cavitation in figures 7 and 8, in the creep of $\frac{1}{2}$CrMoV at 550 °C it is grain boundary segregation rather than surface segregation that is important. The same conclusion would hold if the failures were by the triple point wedge cracks of Burton & Heald (1975) or any mechanism involving the growth of voids involving grain boundary self-diffusivity. The grain boundary segregation causes the parameter G in (2) and (3) to decrease so that the rupture life increases but the ductility decreases. If the rather scant segregation data for grain boundaries at 550 °C are used to define the expected element ratios for this mechanism, use of (6) gives

$$G \propto 6.5\mathrm{P}+0.4\mathrm{Cu}+1.6\mathrm{Sn}+1.6\mathrm{Sb}+<1.6\mathrm{As},$$

which has similar copper and tin coefficients to A_d and t_r above, supporting the idea of action through grain boundary segregation. The different coefficients for phosphorus may involve its effect on microstructure (Hayes & Grieveson 1975).

5. Conclusions

In commercial ½CrMoV steel samples stress relieved at 700 °C, the effects of microstructure and impurity content are of about equal importance in defining the susceptibility to cracking. This cracking, due to grain boundary creep cavitation, is exacerbated by equilibrium segregation to the embryo cavity free surface. Analysis of free surface and cavity surface segregation by A.e.s. coupled with and extending a regression analysis of direct cracking data gives the relative effect of impurities as

$$0.8\mathrm{P}+4.0\mathrm{Sn}+6.5\mathrm{Sb}+2.4\mathrm{As}+0.37\mathrm{Cu}+0.12\mathrm{Ni}+1.6\mathrm{N}+30\mathrm{B}.$$

Thus, in the average ½CrMoV steel, where the Ni and Cu levels are an order of magnitude higher than the other impurities, the impurities in decreasing order of importance are Sn, Cu, As, Sb, Ni, P, with the first three dominant. Boron and nitrogen are of comparable importance to phosphorus in this mechanism, although their contribution though microstructural and hardness parameters, ignored here, may alter their importance.

The situation in creep at 550 °C is somewhat different. Regression analysis of accumulated data shows that the effect of impurities on rupture life and ductility is twice as important as any other parameter. Both show a relative element dependence of approximately

$$1.4\mathrm{P}+1.5\mathrm{S}+0.35\mathrm{Cu}+1.8\mathrm{Sn},$$

but with rupture ductility falling and rupture life increasing with impurity content. These dependences are explained in terms of grain boundary segregants blocking the grain boundary diffusion so that the cavity growth rate is reduced. For the typical commercial material the importance of impurities has changed in order from that for stress relief cracking to, in decreasing order of importance, Cu, P, Sn.

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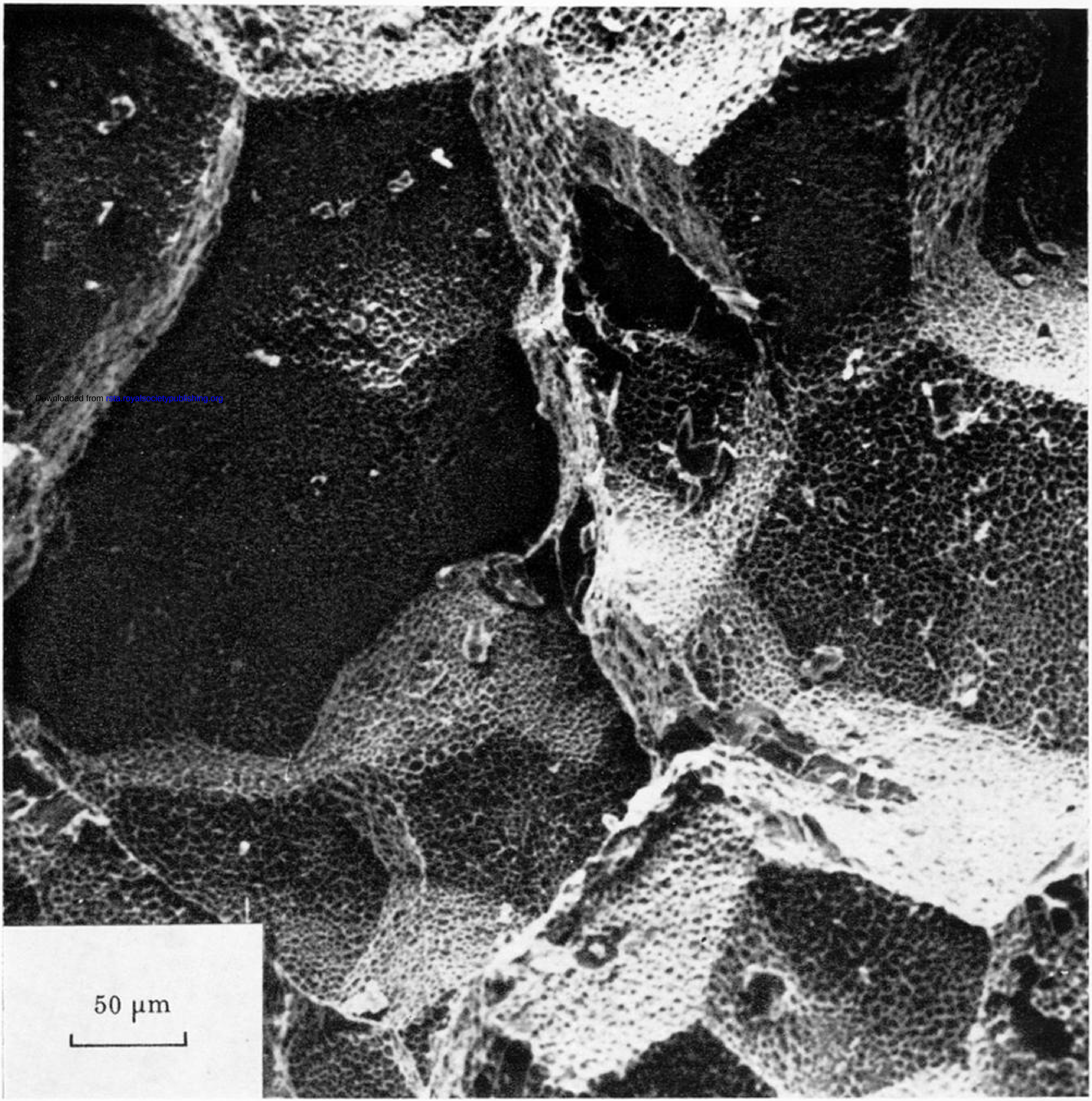

FIGURE 4. Cavitated grain boundary fracture surface of $\frac{1}{2}$CrMoV after simulated stress relief treatment at 700 °C.