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VI. PERFORMANCE IN SERVICE: HIGH TEMPERATURE EFFECTS

The influence of purity on the strength and ductility in creep of CrMoV steels of varied microstructures

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Investigations into the effects of enhanced purity on the creep and rupture of CrMoV steels which have been carried out at the National Physical Laboratory are reviewed. Significant benefits in rupture life and ductility have been demonstrated, and these properties together with creep strength are described for steels in a variety of microstructural conditions and compositions. It has been shown that the rupture properties obtained reflect the influence of both purity and microstructure on the intergranular cavitation process leading to failure, and the importance of the interrelation between these factors is discussed.

1. Introduction

In this paper a synthesis has been made of extensive studies carried out over the past decade at the N.P.L. to discover the effect of enhanced purity on the behaviour during creep of CrMoV(CMV) steels. These steels were of the type used in steam power plant, and two compositions were examined, namely $\frac{1}{2}$Cr$\frac{1}{2}$Mo$\frac{1}{4}$V ($\frac{1}{2}$CMV) and 1Cr1Mo$\frac{1}{4}$V(1CMV). There were several reasons for initiating the programme. (i) These steels, when heat-treated to develop the maximum creep strength, usually had low ductility (Tipler *et al.* 1975), and although the ductility for a given high strength level could be improved by appropriate heat-treatment it was not always possible to achieve this microstructural control in practice so that some other route to secure the improvement had to be sought. (ii) The embrittling effect of trace elements such as oxygen (Rees & Hopkins 1952), phosphorus (Hopkins & Tipler 1958) and nitrogen (Hopkins & Tipler 1954) on the low-temperature brittleness of iron had been demonstrated, and the degree of embrittlement had been shown to be associated with the appearance and increased incidence of fracture along grain boundaries. (iii) Creep embrittlement in CMV steels had also been shown to occur by failure along grain boundaries (Tipler *et al.* 1970). (iv) Low temperature embrittlement due to phosphorus in iron (Hopkins & Tipler 1958) and creep embrittlement due to antimony in copper (Tipler & McLean 1970) had been shown by the use of radioactive tracer methods (Inman & Tipler 1958; Inman *et al.* 1963; Maji & Tipler 1972) to be associated with segregation of these elements to the grain boundaries, so that a reason for reduced grain boundary strength could be found in the effects of these impurity elements on grain boundary energy. (v) Bruscato (1970), in apparently the first studies on the effect of impurity elements on creep embrittlement in steels, had shown that 2$\frac{1}{4}$Cr1Mo weld metal had significantly higher rupture ductility for similar strength levels when impurities were reduced. (vi) Facilities for producing high purity alloys had been developed at N.P.L. (Hopkins *et al.* 1951). It was a logical step to follow up the evidence which pointed to the role of impurity elements in promoting grain boundary weakness by making use of these facilities to manufacture CMV steels in which impurities would be present to a much reduced extent compared with steels produced commercially. High purity versions of these steels were therefore prepared, and this marked the commencement, in 1968, of the studies which continued over the next 10 years and which are described in this paper. This was an extension of earlier work on commercial steels carried out in collaboration with the Electrical Research Association (Tipler *et al.* 1975).

A significant improvement in the rupture properties of the high purity steels over the commercial steels was demonstrated (Hopkins *et al.* 1971), and metallographic studies showed that this was related to an improved resistance in the higher purity steels to the formation of cavities leading to failure (Tipler 1972). To identify the impurities that were responsible for the inferior properties of the commercial steels, several high purity $\frac{1}{2}$CMV steels with selected impurity additions were made but they all had rupture properties similar to those of the high purity material. Consequently, it was not possible to attribute the inferiority of the commercial purity steels to the influence of any one of the impurity elements investigated.

The purpose in trying to identify the specific elements responsible for the inferior rupture properties of commercial steels was to take advantage of this information in the manufacture of steels of this type and to avoid the necessity of minimizing the content of all impurities. The results were therefore disappointing because it appeared to be essential to limit the properties of each potentially deleterious element, but despite this difficulty the possibility of achieving enhanced ductility and improved resistance to cavitation and cracking was an attractive proposition to the fabricators and users of CMV steels. An investigation was initiated, in collaboration with E.R.A., to establish the extent to which the superior properties obtained in laboratory high purity steels could be achieved by using the best melting procedures and materials available commercially.

The investigations into the properties of the high purity CMV steels prepared commercially and in the laboratory have shown that in the evaluation of the effect of increased purity the influence of microstructure must also be considered. The exposure of the interrelation of these factors with respect to rupture strength, ductility and the failure process during creep has been an important aspect of the results obtained in the studies of high purity CrMoV steels at N.P.L. during the past decade.

2. Materials and preparation

(*a*) *Manufacturing process*

The work has been carried out on steels of basic compositions $\frac{1}{2}$Cr$\frac{1}{2}$Mo$\frac{1}{4}$V and 1Cr1Mo$\frac{1}{4}$V with three levels of residual elements, namely (i) that typical of normal steel-making practice, (ii) a greatly reduced residual element content obtained by the use of high purity raw materials and vacuum refining in the laboratory, and (iii) similar to (ii) but manufactured by the best commercial practice. Details of the preparation of the normal commercial purity steels (C1 and C3, table 1) are given elsewhere (Tipler *et al.* 1975); bar stock of steel C1 was remelted in the laboratory without refining and was designated C2 (table 1). The high purity steels H1, H2 and H3 were made in the laboratory (Hopkins *et al.* 1951). The high purity steel H4,

Table 1. Chemical analyses of CrMoV steels (percentages by mass)

	C	Cr	Mo	V	Cu	S	P	As	Sb	Sn	O	N
commercial purity												
C1	0.14	0.41	0.54	0.29	0.08	0.006	0.008	0.025	0.007	0.009	0.0019	0.011
C2	0.12	0.41	0.54	0.31	0.12	0.01	0.009	0.031	0.007	0.014	0.0019	0.0044
C3	0.27	1.09	1.01	0.32	0.13	0.006	0.009	0.025	0.001	0.018	0.0014	0.009
high purity												
H1	0.11	0.39	0.50	0.26	0.003	0.003	0.003	0.003	0.001	< 0.003	0.0007	0.0013
H2	0.13	0.4	0.46	0.27	0.005	0.0023	0.0025	0.002	0.002	0.001	0.0004	0.0007
H3	0.30	1.04	0.97	0.30	0.003	0.004	0.003	0.003	0.001	< 0.003	0.0003	0.0018
H4	0.12	0.43	0.54	0.27	0.009	0.005	0.006	0.002	0.002	0.003	0.001	0.002

manufactured commercially, was cast as an ingot of approximately 4 t in mass, half of which was used for the production of 5 cm wall thickness × 36 cm outside diameter extruded pipe while the remainder was rolled by the steelmaker to 95 mm diameter bar. The chemical analyses of the steels are given in table 1.

A series of high purity $\frac{1}{2}$CMV steels with selected impurity additions were made in the laboratory; they contained one each of the following impurities at the level (percentages by mass) in which they were present in steel C1 : As, 0.03; P, 0.01; S, 0.007; Sb, 0.008; Sn, 0.01; N, 0.01. In other respects their analysis was similar to that of steel H2.

(*b*) *Fabrication and heat-treatment*

The ingots produced in the laboratory and the bar produced commercially were rolled at N.P.L. to 30 mm diameter bar at 950 and 1050 °C. These temperatures were chosen to match two of the austenitizing temperatures used subsequently and to achieve equilibrium solution of carbides at these temperatures.

In previous work on commercial purity steels (Tipler *et al.* 1975) with which comparisons were to be made, a range of structures typical of those occurring in different high temperature components of steam power plant were obtained by oil-quenching, air-cooling and furnace-cooling after austenitizing at 950 or 1050 °C for 30 min or at 1300 °C for 1 min, the last being chosen to simulate the structure occurring in the vicinity of a weld. For most of the steels in this work the same austenitizing temperatures and cooling rates were used with an identical tempering treatment of 4 h at 700 °C. However, the steel H4 that was extruded as pipe was austenitized at 960 °C for 1 h followed by cooling in air which, because of the large mass involved, was at a rate much lower than that obtained by air-cooling 30 mm bar; it was then tempered at 690 °C for 3 h.

(*c*) *Microstructure, hardness and grain size*

Significant differences in microstructure and hardness existed between commercial and high purity versions of steels of the same type that had received the same heat-treatment.

For $\frac{1}{2}$CMV steels the trend was for the high purity steels to have increased hardenability with respect to the commercial purity steel (cf. steel C2 with H2 and H4, table 2), and differences in hardenability were also apparent between high purity alloys that had received the same heat-treatment (cf. steels H1, H2 and H4, table 2). These differences could be partly the result of differences in grain growth characteristics. After the tempering treatment, many of the hardness differences between steels given the same austenitizing treatment were removed.

TABLE 2. MICROSTRUCTURAL CHARACTERISTICS, HARDNESS AND STRESS SENSITIVITY IN CREEP OF $\frac{1}{2}Cr\frac{1}{2}Mo\frac{1}{4}V$ STEELS AUSTENITIZED AS SHOWN AND TEMPERED FOR 4 h 700 °C

austenitizing temperature °C	steel type	cooling method†	grain size mm	hardness, HV30 as austenitized	hardness, HV30 as tempered	bainite content (%)	stress exponent n‡
950	C1	a.c.	0.02	205	209	14	6.4
	H2	a.c.	0.086	237	267	100	7.8
	C2	a.c.	0.024	186	203	20.8	9.9
	H4 (pipe)	a.c.	0.025	—	167	7.8	10.3
	H4 (bar)	a.c.	0.028	246	249	100	14.5
	H4 (bar in pipe)	a.c.	0.031	—	200	9.7	14.9
1050	C2	o.q.	0.088	—	262	100	7.8
	C1	a.c.	0.021	277	260	30	7.9
	H4	a.c.	0.104	260	252	100	8.1
	C2	a.c.	0.043	253	253	54	11.6
	H2	f.c.	0.074	205	218	16	12.0
	H2	a.c.	0.119	234	250	100	13.5
	H4	f.c.	0.083	145	149	15	16.3
	H1	a.c.	0.037	237	225	40	—
1300	C1	o.q.	0.143	294	282	100	5.4
	H4	o.q.	0.204	340	268	100	6.1
	C2	o.q.	0.151	311	267	100	6.7
	C1	a.c.	0.2	269	271	72	6.8
	H4	a.c.	0.235	247	263	100	7.0
	H4	f.c.	0.079	153	156	6.5	6.2
	H2	o.q.	0.167	305	266	100	9.7

† Abbreviations: a.c., air-cooling; o.q., oil-quenching; f.c., furnace-cooling.
‡ In $\dot{\epsilon} = A\sigma^n$.

These differences in hardenability between commercial and high purity $\frac{1}{2}$CMV steels occurred in all but one of the series of high purity steels to which single impurity additions had been made, the exception being the nitrogen-containing alloy which responded to heat-treatment in a similar way to commercial purity steel C2.

3. EXPERIMENTAL

(a) *Creep testing*

High sensitivity creep tests were carried out at 550 °C over a range of stresses to give lives of up to about 10 000 h. The specimen dimensions were 7.6 mm diam., 50.8 mm gauge length and 63.5 mm parallel portion. For a number of specimens the tests were stopped at various fractions of their rupture life so that the progress of creep cavitation damage could be related to the different stages of creep.

(b) *Creep cavitation measurement*

The extent and distribution of creep damage were determined by microscopic examination of a complete longitudinal section of partial or full-life creep-tested specimens. The number of cavities counted were averaged over the whole area examined with a limit of detection for cavities of 10^{-3} mm diameter at a magnification of $\times 1000$.

4. Creep properties

(a) *Strength and ductility at rupture*

(i) *Effects of purity*

$\frac{1}{2}$Cr$\frac{1}{2}$Mo$\frac{1}{4}$V *steels, austenitized at* 1050 °C *and tempered.* Values for the rupture life and rupture ductility of these steels in the fully bainitic condition are shown in figure 1. The high purity steels had superior rupture life and ductility although at times in excess of 1000 h their ductility decreased somewhat. In the ferrite–bainite condition (figure 2), the increase in life for a given reduction in stress was greater for the high purity steels than for commercial steels, so that at lower stresses the lives of the high purity steels were significantly greater. The enhanced ductility of the purer steels was retained to rupture lives in excess of 10000 h, even though it declined with longer lives.

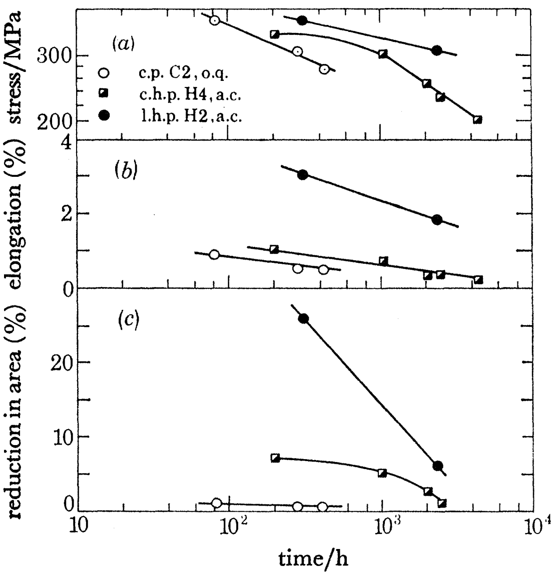

Figure 1. Rupture properties of $\frac{1}{2}$CMV steels obtained in a fully bainitic condition after austenitizing at 1050 °C followed by tempering. Abbreviations: c.p., commercial purity; c.h.p., commercial high purity; l.h.p., laboratory high purity; o.q., oil-quenched; a.c., air-cooled.

1Cr1Mo$\frac{1}{4}$V *steels, austenitized at* 1050 °C *and tempered.* Tests on commercial and high purity compositions showed (figure 3) that the improvements in rupture strength and ductility obtained for the high purity compositions were maintained over the range of stresses applied, i.e. for lives of up to 30000 h in spite of the gradual decrease in elongation at longer times. The highest curve for rupture life and ductility relates to a ferrite–bainite structure and the next lower curve to a fully bainitic structure, showing that the introduction of ferrite into the high purity steel improved the rupture ductility without impairing the rupture strength.

$\frac{1}{2}$Cr$\frac{1}{2}$Mo$\frac{1}{4}$V *steels, austenitized at* 950 °C *and tempered.* While the rupture properties for the commercial purity steels examined in this condition were very similar (figure 4), the high purity steels had a wide range of rupture properties such that they were higher than, the same as, or lower than for the commercial purity steels. However, by making comparisons between the commercial purity steels and steel H4 of similar rupture strength, increased purity was shown to be associated with enhanced ductility, especially at longer times. Conversely, steel H4 in

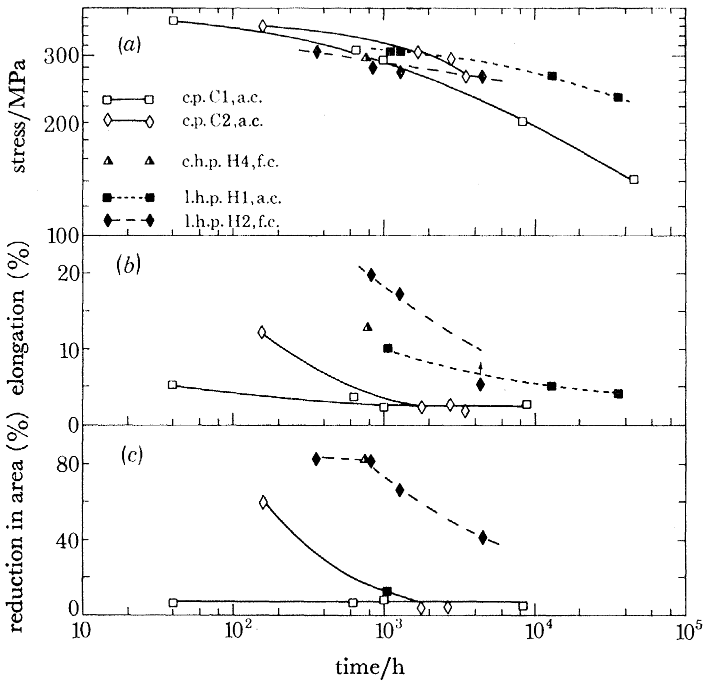

FIGURE 2. Rupture properties of ½CMV steels obtained in a ferrite–bainite condition after austenitizing at 1050 °C followed by tempering. Abbreviations as figure 1; f.c., furnace-cooled.

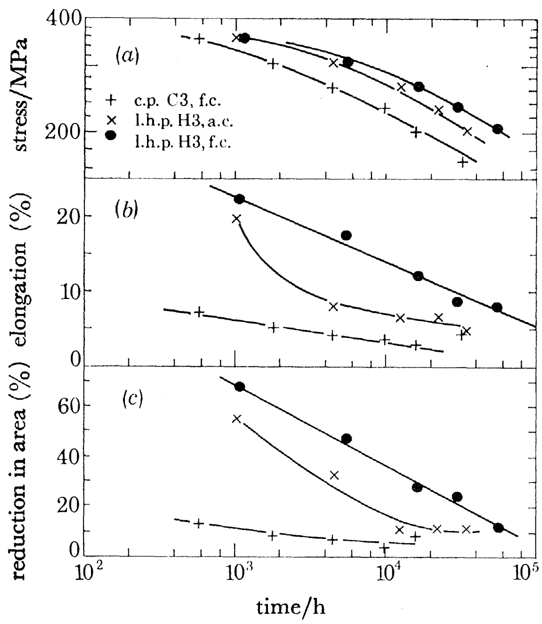

FIGURE 3. Rupture properties of 1CMV steels in conditions obtained by austenitizing at 1050 °C and tempering. Abbreviations as figure 2.

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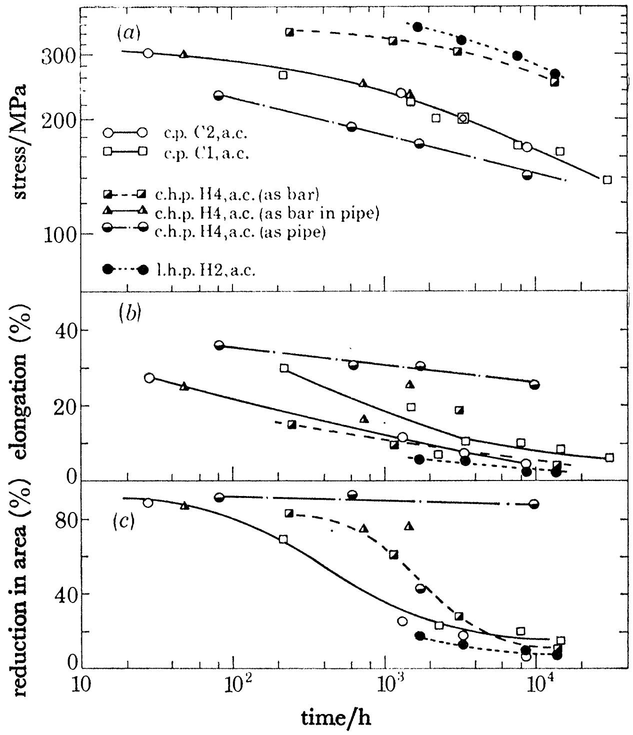

FIGURE 4. Rupture properties of ½CMV steels in conditions obtained by austenitizing at 950 °C and tempering. Abbreviations as figure 1.

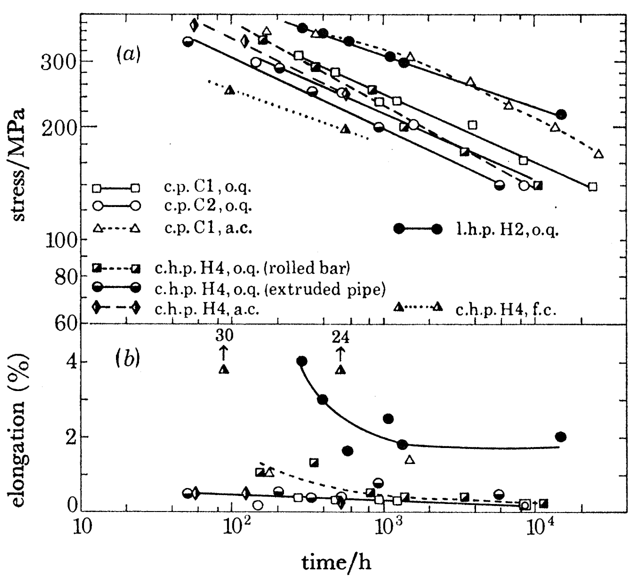

FIGURE 5. Rupture properties of ½CMV steels in conditions obtained by austenitizing at 1300 °C and tempering. Abbreviations as figure 2.

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a condition having similar ductility to those of the commercial purity steels had a significantly higher rupture strength, showing that it was possible to obtain improved strength by increased purity without impairing ductility.

The high purity steel with lower rupture strength than the commercial purity steels had correspondingly higher ductility, and this is considered to be more associated with the high temperature strength levels of the microstructure (cf. creep rates, figure 10).

$\frac{1}{2}$Cr$\frac{1}{2}$Mo$\frac{1}{4}$V *steels, austenitized at* 1300 °C *and tempered.* Examination of the results (figure 5) for steels in this condition showed that, with the exception of the steels H4 furnace-cooled from 1300 °C and H2 oil-quenched from 1300 °C, the rupture elongations were uniformly very low at 1 % or less although the range of rupture lives was about an order of magnitude. Some of the high purity steels had lower rupture strengths than the commercial purity steels and were extremely brittle, for reasons discussed later in the paper.

However, the properties of steel H2 suggested that, other things being equal, a reduction in residual element content could bring about improved ductility in a normally extremely brittle condition; this higher ductility in H2 was also accompanied by increased rupture strength. The reverse was true in steel H4 furnace-cooled from 1300 °C. Its considerably higher ductility appeared to be due to a weaker structure and it showed the lowest rupture strength and creep resistance (figure 11*b*) of steels austenitized at 1300 °C.

The introduction of a small amount of ferrite into the structure of steel C1 by air-cooling instead of oil-quenching from 1300 °C resulted in an increase in rupture life and ductility compared with the fully bainitic condition, which is consistent with the results for the steel H3 cooled at different rates from 1050 °C.

1Cr1Mo$\frac{1}{4}$V *steels, austenitized at* 1300 °C *and tempered.* From the results shown in figure 6 the benefits of increased purity on both rupture life and rupture ductility are again evident.

(ii) *Effects of microstructure*

While purity was an important factor in determining the results just presented, it was clear that other factors such as microstructure, grain size and hardness could also be influencing the relations observed between stress, rupture life and ductility. The criterion chosen for evaluating and comparing the rupture properties of the different materials and conditions was the stress to give rupture in 1000 h.

There was no correlation with room temperature hardness, but in figure 7*a* the bainite content of each microstructure has been plotted as a function of this criterion and a number of correlations can be drawn. As the bainite content increased to 100 % in mixed ferrite–bainite structures, the rupture strength increased progressively, and in this respect the results are similar to those of Murphy & Branch (1969) for cast CrMoV steels. In the ferrite–bainite structures, increased rupture strength was, in general, associated with increased purity for a given bainite content and with increased austenitizing temperature.

For fully bainitic structures the rupture strength was dependent on heat treatment and purity although for 1CMV steels and in most cases for $\frac{1}{2}$CMV steels the higher purity materials were stronger for a given austenitizing temperature. This was also true for the ferrite–bainite structures. However, as the austenitizing temperature was raised, the rupture strength of the fully bainitic structures decreased, but the opposite result was obtained for ferrite–bainite structures.

In figure 7*b* the rupture ductilities of the fully bainitic structures are plotted as a function of the rupture strength parameter, and it is evident that the weakest alloys were also the least ductile. Consequently ductility is providing an index of the brittleness in creep of the bainitic structures, and their rupture life was determined not by their strength characteristics but by their brittleness propensity, the reasons for which are discussed later. The importance of grain size is demonstrated in figure 8, where it is plotted against the elongation at rupture in 1000 h. This figure includes data for ferrite–bainite and fully bainitic structures and indicates a definite trend towards greater ductility with smaller grain sizes and with increasing purity for a given grain size. Thus it is anticipated that the grain size will have affected the rupture life of fully bainitic structures through the relation between rupture strength and rupture ductility demonstrated in figure 7*b*.

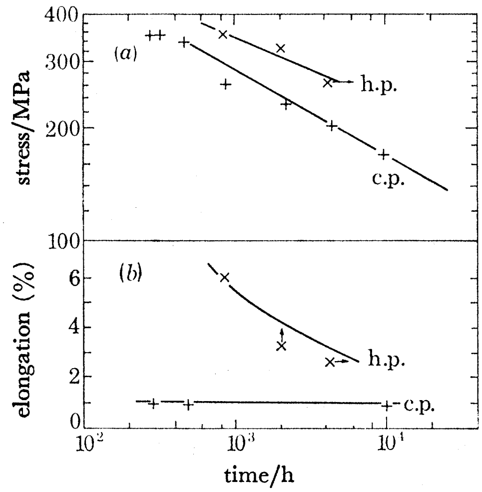

FIGURE 6. Rupture properties of 1CMV steels in the condition 1300 °C air-cooled and tempered. Abbreviations as figure 1.

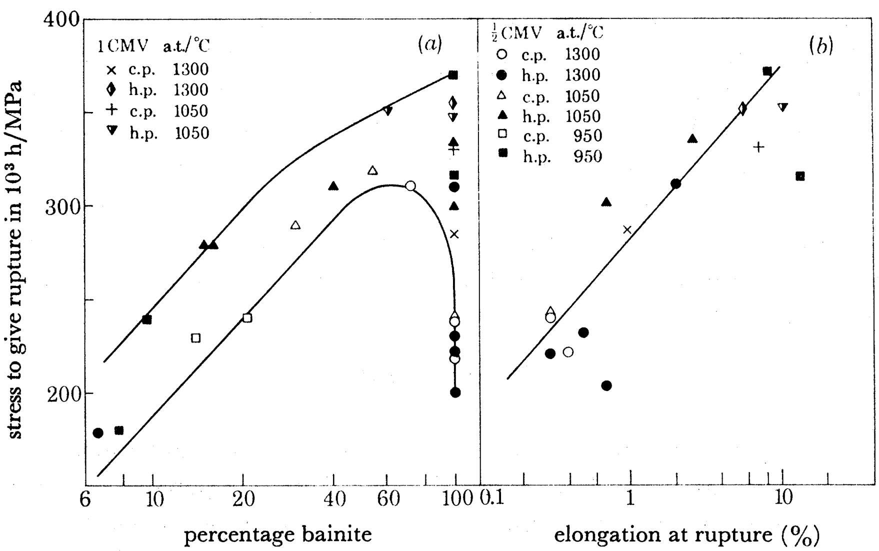

FIGURE 7. Influence of (*a*) bainite content and (*b*) ductility on the stress to give rupture in 1000 h for CMV steels. Abbreviations as figure 1; a.t., austenitizing temperature.

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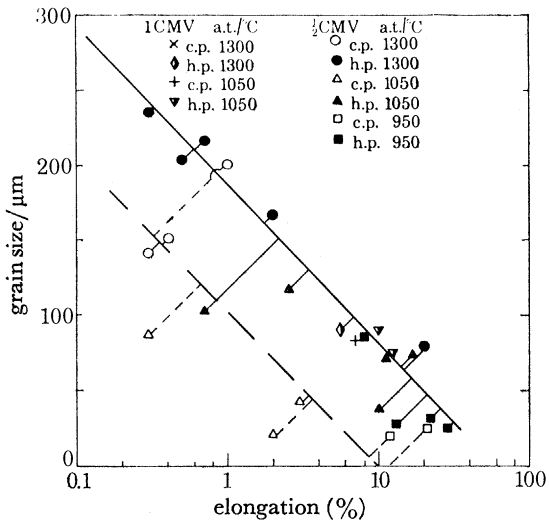

FIGURE 8. Influence of grain size on the rupture ductility of CMV steels. Abbreviations as figure 7. Broken line, commercial purity; solid line, high purity.

(iii) *Effects of added impurities*

$\frac{1}{2}$Cr$\frac{1}{2}$Mo$\frac{1}{4}$V *steels, austenitized at* 1050 °C *and tempered.* In figure 9*a*, *b* the rupture properties of a series of high purity base alloys to which single impurities have been added are compared with those of the high purity steel H2, and there appears to be no significant difference in the values obtained for rupture life and ductility.

$\frac{1}{2}$Cr$\frac{1}{2}$Mo$\frac{1}{4}$V *steels, austenitized at* 1300 °C *and tempered.* The rupture properties of the steels in this condition are given in figure 9*c*–*f* in which the lines drawn represent the behaviour of steel H2. The rupture lives were similar to that of the high purity steel but some scatter was apparent in ductility. Thus, while the Sb-containing steel (figure 9*d*) and the P-containing steel (figure 9*f*) had considerably higher reduction in area than the high purity steel for lives less than 1000 h, beyond this time their values dropped dramatically and became similar to that of the high purity steel. On the other hand the Sn- and As-containing alloys (figure 9*d*) had lower ductilities than the high purity steel at all times beyond 600 h.

The evidence from the results of tests on this series of alloys in two conditions of heat-treatment shows that at the levels to which the impurities have been added they have had no deleterious effect on rupture life or, with the possible exceptions of arsenic and tin, to any significant extent on ductility.

(*b*) *Creep strength*

(i) *Effects of purity*

The minimum creep rates for steels austenitized at 950 or 960 °C and tempered are shown in figure 10, and for those austenitized at 1050 and 1300 °C and tempered in figure 11*a*, *b*. The commercial purity steels had creep strengths similar to each other for the 950 °C condition and, with the exception of the steel H4 cooled slowly from 960 °C, the high purity steels had higher creep strengths. At each of the austenitizing temperatures 1050 and 1300 °C the strengths of the commercial purity steels were very similar while (except steel H4 slowly cooled from 1300 °C) the range of strengths of the high purity steels was narrower than at 950 °C and encompassed

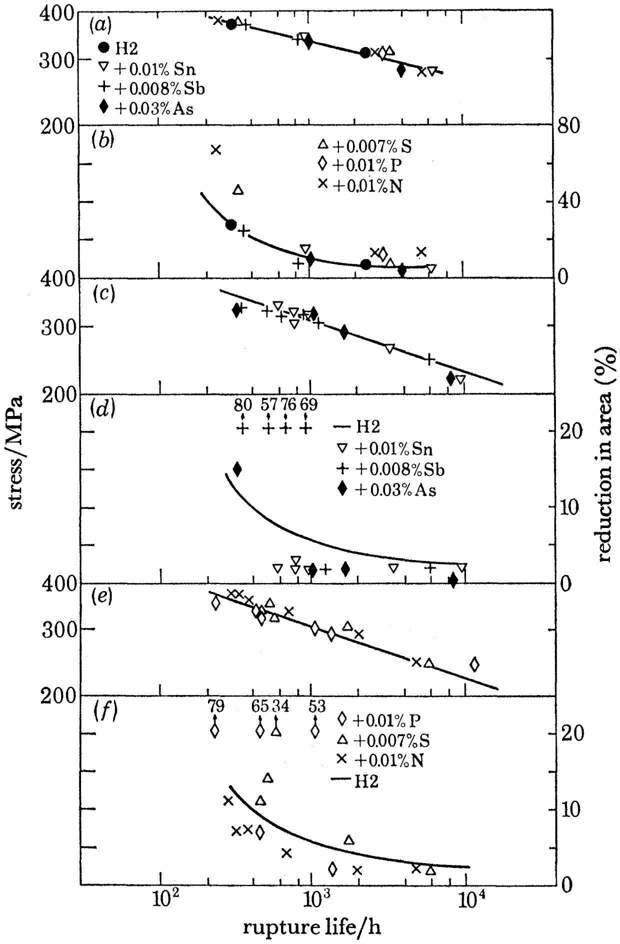

FIGURE 9. Rupture properties of a series of high purity based $\frac{1}{2}$CMV steels with single impurity element additions obtained in a fully bainitic condition by austenitizing at (*a*, *b*) 1050 °C and tempering; (*c*–*f*) 1300 °C and tempering.

the behaviour of the commercial purity materials. It appears, therefore, that any beneficial effects of purity on creep strength are most likely to occur in material austenitized at temperatures within the usual range for commercial normalizing treatments.

(ii) *Effects of microstructure*

As with the results on rupture behaviour the effect of microstructure must be considered in addition to the influence of purity. To demonstrate the effects of microstructure, the stress to give a minimum creep rate of 10^{-3}% per hour has been plotted in figure 12*a* against the proportion of bainite, and it is apparent that the creep strength as defined by this parameter increased with increase in bainite content up to 100%, which is contrary to the findings of Barford & Willoughby (1971). For the fully bainitic structures, the stress to produce a creep rate o 10^{-3}% per hour varied by as much as 100 MPa, which was more than the scatter in the ferrite–bainite structures. This variation could not be accounted for by differences in hardness, but the grain sizes of these fully bainitic structures have been plotted against the creep strength parameter in figure 12*b*. Without distinguishing austenitizing temperatures, the trend for lower strengths to be associated with coarser grain sizes was surprising, and is the reverse of the behaviour expected, namely that a material with fine grains would creep at the same rate as a coarse-grained material for a lower applied stress. This is a consequence of the larger contribution of grain boundary sliding to the creep rate for the fine-grained condition, assuming similar matrix deformation characteristics. It may be argued that for similar matrix deformation characteristics, bainitic structures austenitized from the same temperature should be compared, and if this is done for structures produced at 950 or 1050 °C it is found that the finer the grain

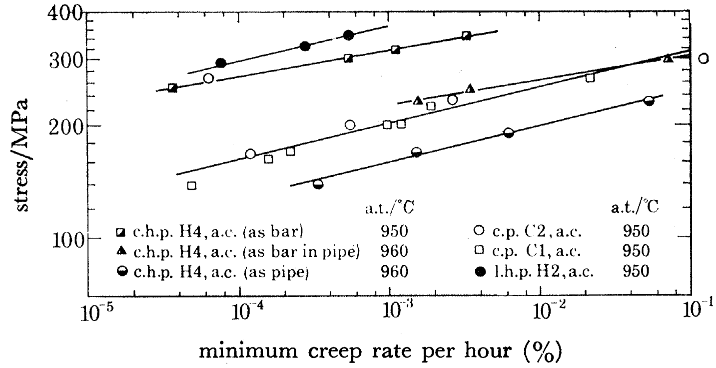

FIGURE 10. Creep strengths of ½CMV steels in conditions obtained by austenitizing at 950 or 960 °C and tempering. Abbreviations as figure 7.

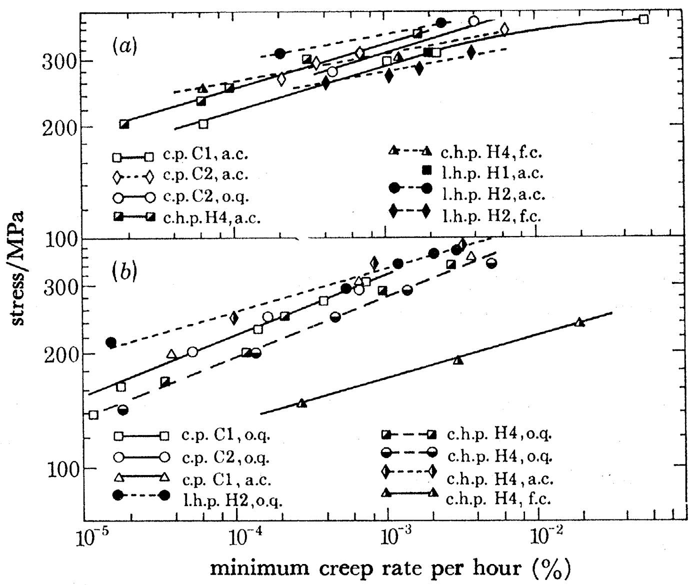

FIGURE 11. Creep strengths of ½CMV steels in conditions obtained by austenitizing at (*a*) 1050 °C and tempering; (*b*) 1300 °C and tempering. Abbreviations as figure 2.

size the lower is the stress to obtain a given creep rate. However, this means that for a given grain size the hardening of the matrix increases with decreasing austenitizing temperatures, which is contrary to the expected behaviour based on the precipitation hardening characteristics of these steels. Elucidation of these anomalies would entail a detailed examination of the fine microstructure and dislocation interactions in these alloys by electron microscopy so that the roles of matrix and of grain boundary features with respect to the deformation process could be identified.

The stress dependence of the minimum creep rate, $\dot{\epsilon}$, as given by n in the equation $\dot{\epsilon} = A\sigma^n$,

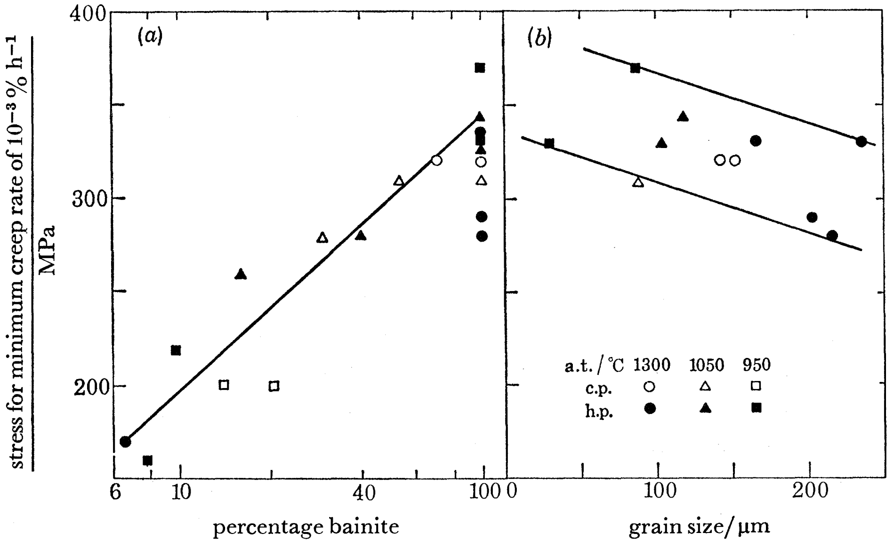

FIGURE 12. Influence of (*a*) bainite content, and (*b*) grain size in fully bainitic structures, on the stress to give a minimum creep rate of 10^{-3} % h^{-1} for $\frac{1}{2}$CMV steels. Abbreviations as figure 7.

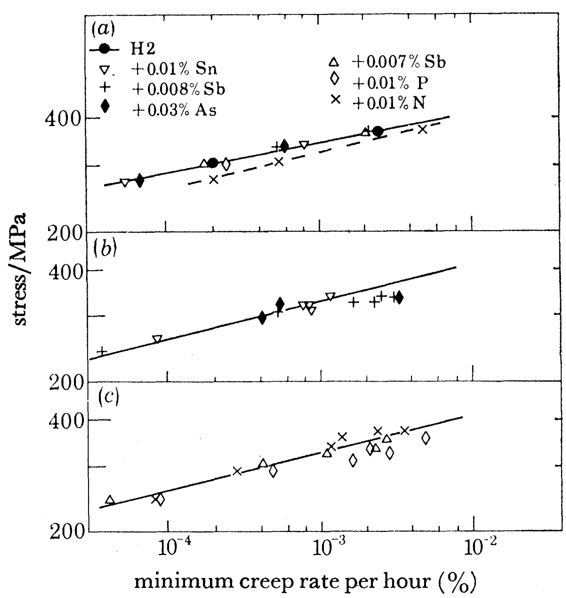

FIGURE 13. Creep strengths of a series of high purity $\frac{1}{2}$CMV steels with single impurity element additions obtained in a fully bainitic condition by austenitizing at (*a*) 1050 °C and tempering; (*b*, *c*) 1300 °C and tempering.

where σ is stress and A is a constant, has been determined from the results of creep tests shown in figures 10 and 11, and the values are given in table 2. Variations in microstructural conditions brought about by changes in austenitizing temperature appeared to play a more dominant part than purity in influencing n, and indeed many commercial and high purity steels had the same n. Thus, although there were conditions which gave different values of n for the same austenitizing temperature, the trend was for the highest austenitizing temperature to give lower stress exponents. It is of interest that at each austenitizing temperature there were conditions that had similar n values in spite of large differences in bainite content, microstructural differences appearing to alter A, i.e. the strength level over which the stress dependence applied.

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(iii) *Effects of added impurities*

The minimum creep rates of each of the steels with one added impurity were little different from those of the high purity base composition as figure 13 shows, and this applied to the two conditions of heat-treatment.

5. Cavitation characteristics

(*a*) *Threshold for first appearance of cavities*

The time and strain at which cavities first appeared during creep of commercial and high purity 1CMV steels when austenitized at 1050 and 1300 °C and tempered were determined according to the criterion of detection described earlier. In figure 14*a* lines have been drawn to indicate the detectable onset of cavitation relative to rupture life for the commercial purity steel over the range of stresses applied. For the high purity steel, tests were carried out at one stress only so that similar data are represented by individual points at the top of figure 14*a*.

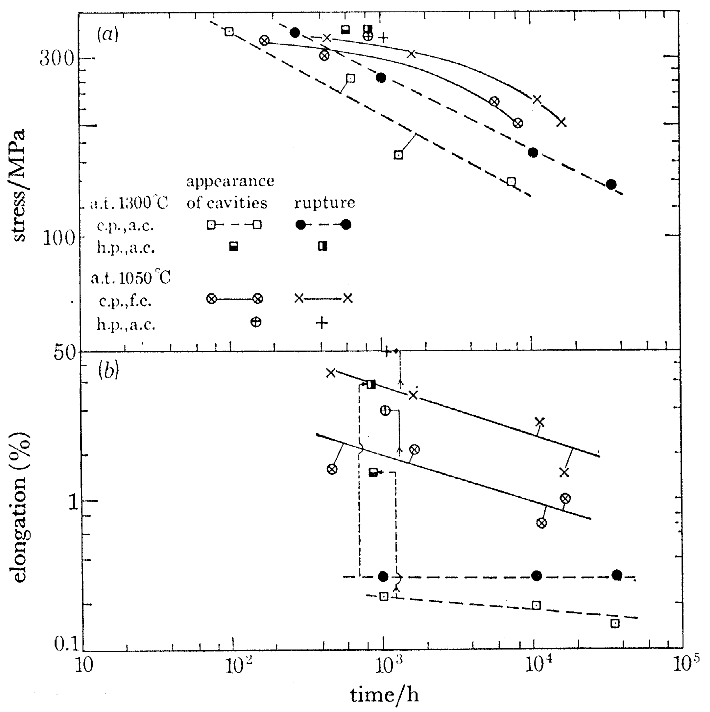

FIGURE 14. Influence of purity on (*a*) time and (*b*) strain for first appearance of cavities in a tempered 1CMV steel. Abbreviations as figure 7.

The observed increase in rupture lives has already been mentioned, but these results show that improvements in resistance to cavitation also occurred with an increase in purity. Furthermore, the extent to which cavitation was delayed compared with that to which rupture life was extended was in the ratio of about 2.5 : 1 for each condition, so that the proportion of life without cavitation was greater for the high purity steel.

In figure 14*b* similar data for the strain to the onset of detectable cavitation and to rupture are given, showing that the degree of strain accumulated before cavitation was detected was greater for the high purity steel. Also, of the two conditions examined, the proportional increases in the threshold strain for cavitation and the strain to rupture for the high purity steel compared with the commercial purity steel were greater for material austenitized at 1300 °C and tempered; the same was true if time rather than strain was used as the basis for comparison.

These results for 1CMV steels have been confirmed in steels of $\frac{1}{2}$CMV composition. In this instance the times for onset of detectable cavitation for commercial and high purity versions were 200 and 900 h respectively, while the corresponding rupture lives were 975 and 1058 h; the equivalent values for strain at onset of cavitation were 0.4 and 2.5 %, and at rupture 2.2 and 10 % respectively.

(b) Accumulation of creep damage

The measurements of the intensity of creep cavitation at various stages throughout the life of tested specimens enabled the accumulation of this type of creep damage to be related to the parameters of strain and time describing the creep behaviour. Previous work (Tipler & Hopkins 1976) had shown that throughout the portion of the creep test during which cavitation was

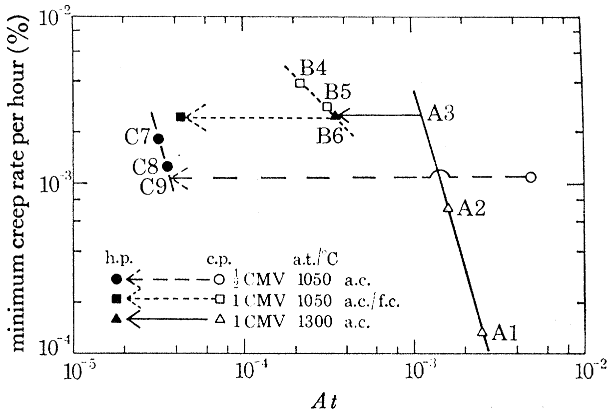

FIGURE 15. Influence of purity on the rate of accumulation of cavities during creep of tempered CMV steels. A is the areal density of cavities per unit creep strain and t the time in hours. Abbreviations as figure 7.

occurring, the areal intensity of cavitation was linearly related to the product of creep duration and creep strain, and the slope of the line has been used to express the rate of accumulation of cavities. The rates so determined for three conditions of commercial and high purity CMV steels are plotted in figure 15 against minimum creep rate, this parameter having been chosen to ensure that comparisons are made for characteristics of microstructure and creep deformation as nearly identical as possible. Thus for the commercial purity 1CMV steel air-cooled from 1300 °C and tempered, an extrapolation of the rates of cavity accumulation has been made from the determined values of the minimum creep rates at A1 and A2 to the value at A3 for comparison with the high purity version; similar extrapolations have been made from B4 and B5 to B6 and from C7 and C8 to C9 for the other results.

The comparisons made in figure 15 show that increased purity had a significant effect in reducing the rate of accumulation of cavities, such that for the same value of the product of strain and time which had accumulated during creep within the régime in which cavitation was occurring, the amount of damage present in the high purity steel would be one to two orders of magnitude less than that in the commercial purity steel for the same condition of heat treatment.

The trend for decreased accumulation of cavities with increasing creep rate is in keeping with a previously observed trend (Tipler *et al.* 1975, see fig. 23) in which the strain to first appearance of cavities also increased with increasing creep rate. The effect of decreasing austenitizing temperature for material having the same creep rate was to decrease the propensity to cavitation whether judged from delayed formation or reduced accumulation of cavities.

6. Discussion

(*a*) *Influence of purity on the tensile creep properties of* CrMoV *steels*

Despite the evident importance of microstructure some distinct trends associated with increased purity are observed. For example, at the two lower austenitizing temperatures there were improvements in rupture life for both types of steel for durations of 5000 h or more, and for some conditions of the high purity alloys these improvements increased with decreasing stress. For steels austenitized at 1300 °C and tempered there were examples of high purity $\frac{1}{2}$CMV and 1CMV steels which had rupture lives and ductility superior to those of the commercial purity steels. Although the rupture ductility of the high purity steels declined with increasing rupture life, there were examples for each austenitizing temperature where the improvements were maintained to lives of several thousands of hours for rupture strengths similar to, or in excess of, those of commercial purity steels.

While it has been shown that reducing the overall level of impurities has beneficial effects on rupture strength and ductility, the investigation into the effects of single impurity element additions has provided no firm evidence that any one of the added elements was responsible for creep embrittlement and hence has precluded any ranking of these elements in order of embrittling potency as has been done in other work (King, this symposium). However, as the same concentrations of impurity elements together do cause creep embrittlement, it follows that there is either an additive effect for the segregating species so that a minimum total concentration of impurities, in combination or individually, is required, or that there are interactions with the segregating species similar to the cosegregation effects proposed by Guttman (1975). Thus the permissible level of any one of them is likely to depend on the amount and nature of other species present, as well as on the major alloy elements. In other work (Viswanathan 1975) the addition of Sn, Sb and P to a $1\frac{1}{4}$Cr$\frac{1}{2}$Mo steel did not impair rupture properties, although increased concentrations of Sn, Sb, P, As, N and Al in a 1Cr1Mo$\frac{1}{4}$V steel caused a reduction in rupture ductility compared with the base melt but did not affect rupture life. These differences in behaviour emphasized the need for a more direct evaluation of the impurities that promote creep embrittlement, and for this purpose Auger analysis has been carried out on some materials investigated in this work. However, the difficulty of opening up, by fracture in the Auger apparatus, cavitated grain boundaries of creep tested specimens precluded direct measurements being made of the segregation which could have occurred before or during creep. As an alternative approach, Seah (this symposium) has measured the species which segregated to the free surface of samples of the steel C2 and three alloys from the series of high purity based steels to which single additions of tin, antimony and arsenic had been made. No preferential segregation of the elements Sn, Sb, As or P was found, and the element detected to the highest concentration was nitrogen. As described earlier, no deterioration in rupture properties was noted when nitrogen was present to a level of three times that in the commercial purity steel. In this instance the significance of surface segregation is not clear and indicates the necessity of obtaining direct measurements from the affected boundaries.

The conclusions that may be drawn from this investigation into the effect of added impurities are not entirely negative, however, because the fact that the properties of these steels, apart possibly from those containing arsenic and tin, were equal to those of the high purity version has confirmed that for another four steels austenitized at both 1300 and 1050 °C increased purity relative to that of a normal commercial steel is effective in securing increased rupture ductility and strength.

The effects of purity on creep strength are less clear, and indeed they would be expected to exert less of an influence on resistance to deformation than on resistance to failure because of the mechanisms involved. Thus, the minimum creep rate predominantly reflects the processes of deformation and recovery occurring within the grain structure and to a lesser extent those at the grain boundary, whereas in the fracture process events at the grain boundary would contribute to a greater extent and so influence the rupture life. Also, the segregation of impurities occurs primarily to interfaces such as grain boundaries. Consequently the creep strengths of these steels would be expected to reflect the influence of microstructure rather than of purity and this has been so through the relative amounts of bainite in the ferrite–bainite microstructure. However, for the lowest austenitizing temperature of 950 °C where intergranular failure would be less dominant the order in which the rupture strengths of the various conditions increased was the same as for that of creep strength. For those conditions of high purity steels which had improved rupture strength and ductility, or improved ductility for the same rupture strength as the commercial purity equivalent, the minimum creep rate was either similar or improved with respect to the commercial purity steel, so that there was no sacrifice of creep strength for improved rupture properties.

(b) *Influence of purity on cavitation in* CrMoV *steels*

Fracture during creep of these steels after austenitizing at 1300 and 1050 °C and tempering has been shown to be preceded by the formation and multiplication of cavities at grain boundaries (Tipler *et al.* 1970; Tipler & Hopkins 1976). The influence of increased purity has been to reduce the propensity to cavitation in two ways, namely (i) by delaying the onset of cavitation and (ii) by reducing the rate at which cavities multiply throughout the creep life.

The reasons for this behaviour are related to the effect of impurities on the stability of a new cavity nucleus. The radius r of a stable cavity is given by $r = (2\gamma/\sigma)$, and evidently a reduction in the appropriate interfacial energy term, γ, will enable a smaller cavity to be stable for a given stress, σ. The segregation of impurities to interfaces generally results in a reduction in interfacial energy so that if the impurities present in the commercial purity steels segregate to the grain boundaries it would be expected that smaller cavities would be stable in this material. Under continuous nucleation conditions, the effects of the impurities would apply at all stages during creep, thereby increasing the rate of accumulation of creep damage in the commercial alloy.

Although there is no direct evidence confirming that impurities reduce the size of stable cavities, the effect of Sb in lowering the interfacial energy of Cu by segregating to both free and grain boundary surfaces has been demonstrated (Inman *et al.* 1963) and shown to be associated with increased cavitation and reduced rupture life and ductility in a series of copper–antimony alloys (Tipler & McLean 1970). The similarity between this behaviour and that of CMV steels is apparent if one considers that the elements which are present to a greater extent in the commercial purity steels are those that have been shown to segregate to the grain boundaries in steel (Palmberg & Marcus 1969), to reduce the interfacial energies of iron (Hondros 1965; Seah & Hondros 1973) and thereby to reduce ductility as figure 16 shows. Seah (this symposium) has discussed in detail the effects of segregation on the kinetics of cavity nucleation and growth, and his results on the Auger analysis of surface and grain boundary segregation in a variety of CrMoV steels support the proposed role of impurities in enhancing cavitation.

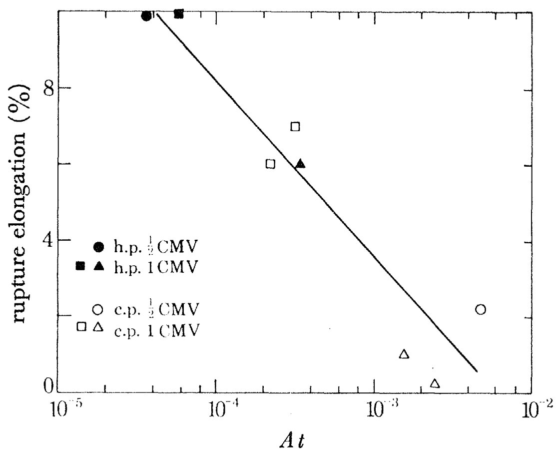

FIGURE 16. Influence of cavitation damage on creep rupture ductility. Abbreviations as figure 1.

(c) *Interrelation of rupture properties, creep strength, microstructure and cavitation*

In order to obtain some rationalization of the rupture behaviour of steels with the wide range of microstructural conditions considered here, it is desirable to find some quantity which can be readily measured and will realistically reflect the metallurgical condition of the different structures when under stress at high temperatures. A number of microstructural parameters are involved in the deformation and recovery processes that occur during creep, and variations in these parameters would be expected according to the temperature of solution treatment and the transformation product. It has not been possible to perform the electron microscopy necessary to quantify differences in precipitate dispersion, grain boundary and dislocation characteristics, for example, but their combined effects can be quantified according to the rate at which deformation occurs during steady state creep, i.e. by the minimum creep rate. This criterion, therefore, has been used as a basis for assessing the influence of metallurgical condition on the rupture behaviour of the ½CMV steels and has been plotted in figure 17 as a function of rupture strength, namely the stress to give a rupture life of 1000 h. Two general patterns of behaviour are evident and are found to depend on whether the microstructure is fully bainitic or contains ferrite, so that in figure 17 a vertical line separating these structural and behavioural types has been drawn.

In the ferrite–bainite microstructures the rupture strength decreased as the creep strength decreased. If identical processes were responsible for rupture and creep strength then these two properties would be expected to be directly proportional to each other although the degree of proportionality would depend on other intervening factors such as instability arising during tertiary creep. In general, the behaviour of the ferrite–bainite structures indicates that the rupture strength is largely determined by the resistance to deformation, i.e. its high temperature creep strength. From the pattern of behaviour shown in figure 17 it is also possible to make deductions about the ductility at rupture. At the lower stresses in the softer structures the creep rate is higher so that for the same rupture life there should be a higher strain to rupture and this is found to be so, the rupture elongation increasing from just under 10 % to about 30 %.

With the steels in the fully bainitic condition the rupture strength decreased as the creep strength increased. Also, with decreasing stress in the stronger structures with lower creep rates, the strain at rupture for the same rupture life should decrease, as it does from just under

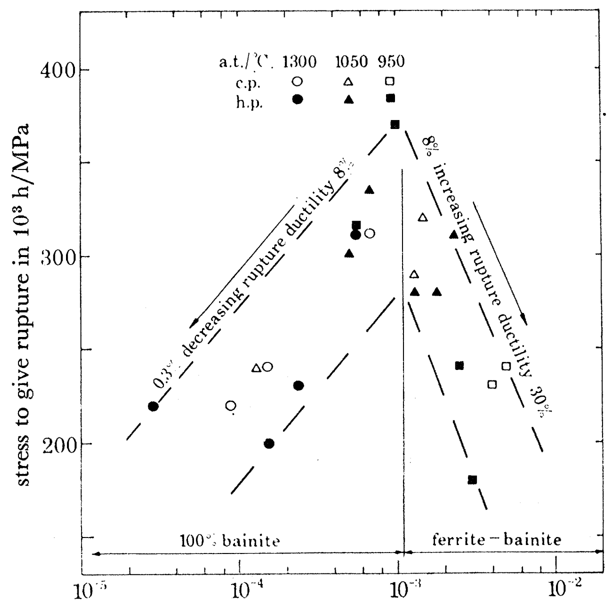

FIGURE 17. Interrelation of rupture strength, rupture ductility and microstructure for $\frac{1}{2}$CMV steels creep tested to the same rupture life. Abbreviations as figure 7.

10 % to about 0.5 %. The reversal in the trend of increasing rupture strength with increasing creep strength on changing from ferrite–bainite to fully bainitic structures indicates that some additional factor is intervening and competing with those influencing the matrix strength. The observed fall in ductility clearly indicates that cavitation is the important factor. Thus the lower rupture stresses for a given life are due to premature failure as a consequence of increased cavitation which progressively limits the strain and hence the life that can be attained. Thus, grain boundary cavitation rather than matrix creep strength becomes the limiting factor for rupture life in these conditions.

The increased cavitation in the structures with greater creep strengths is presumably related to the higher concentration of strain at the grain boundaries as a result of an increase in the deformation resistance of the matrix compared with the grain boundary. This increase may be so large as to override any effect of increased purity, so that this would account for the observation that the high purity steels show no benefits in rupture properties in the highest creep strength conditions. The reverse would be true for the mixed-bainite structures of decreasing creep strengths. At the highest creep rates and with elongations of 20% or more, the effects of segregating impurities on cavitation would be less significant because of the greater capability of the matrix to deform and so relax concentrations at the cavitated grain boundaries. The implication from this work and the behaviour demonstrated by the results in figure 17 is that the largest improvements to be expected from reducing the level of impurities would be for these conditions giving intermediate high temperature strength, i.e. there is an optimum metallurgical condition in which the benefits of increased purity may be displayed.

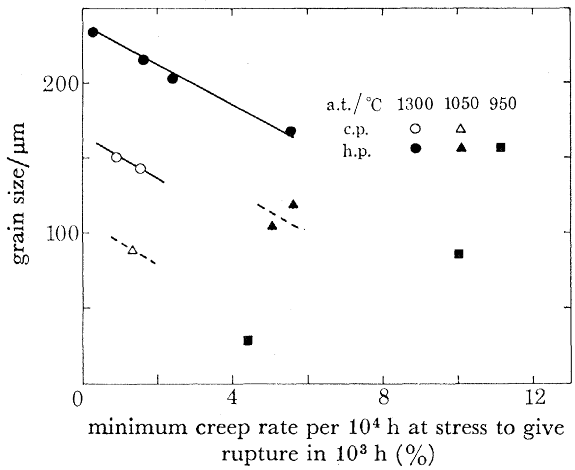

FIGURE 18. Influence of grain size on the deformation resistance of fully bainitic $\frac{1}{2}$CMV steels creep tested to the same rupture life. Abbreviations as figure 7.

For the range of creep rates shown in figure 17 the austenitizing temperatures would be expected to enhance the solution of carbides and increase the grain size. Sidey (1976) and Dunlop & Honeycombe (1977) have shown that a decreasing creep rate is associated with an increasing fineness of carbide dispersion; this is consistent with the general trend in figure 17 for the creep rate to decrease with higher austenitizing temperature for both the mixed ferrite–bainite and the fully bainitic steels. As shown in figure 18, the grain sizes of the fully bainitic steels increase with increasing austenitizing temperature, and for the same austenitizing temperature and purity the coarser grain size gives a lower creep rate; this is consistent with the expected effects of the austenitizing temperature on the microstructural parameters.

An additional aspect of the role of impurities in creep embrittlement is that their segregating potential may vary according to microstructure and hardness. Viswanathan & Joshi (1975) have shown that significant differences occur in the amount of phosphorus segregating to the grain boundaries of a 1CMV steel depending on whether the microstructure is bainitic or martensitic, and that the concentration of phosphorus at the grain boundary increases with the hardness of the microstructure. This effect may contribute to increased embrittlement as the strength of the fully bainitic structure increases.

7. Conclusions

(i) In a number of different melts of CrMoV steels, significant improvements in rupture strength and ductility, or in ductility for a given rupture strength, have been obtained by reducing residual impurities to 40 μg/g or less.

(ii) The creep strength chiefly reflects the influence of microstructural variables encountered in the series of steels rather than that of purity.

(iii) The improvements in rupture properties secured by increased purity may be mitigated by the microstructural and high temperature strength characteristics of the steel, especially in the structures produced by austenitizing at temperatures higher than normal. To optimize the benefits, some degree of microstructural control should be combined with a reduction in trace element content.

(iv) There is a marked diminution in the propensity to cavitation for steels of low residual impurity content.

(v) An increase in the degree of cavitation leads to a fall in rupture ductility. Increased cavitation may also be associated with a decrease in creep rate.

(vi) In mixed ferrite–bainite structures a progressive increase in both creep strength and rupture strength occurs with increasing bainite content up to about 100%. However, for fully bainitic structures the hardenability differences which exist between steels of similar composition give rise to a range of structures of increasing creep strength but decreasing rupture strength and ductility. These differences in behaviour reflect an increasing predominance of the influence of grain boundary cavitation as the rupture strength decreases for the fully bainitic structures, and in increasing predominance of the ability of the matrix to deform as the rupture strength of the ferrite–bainite structure decreases.

(vii) Strength at room temperature does not provide a consistent basis for predicting the effects of purity, heat treatment and microstructure on rupture properties for the range of steels and conditions studied; more reasonable correlations may be made by using strength at high temperature.

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