Development of substitute high temperature creep resistant alloys

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HIGH temperature creep resistant super strength alloys invariably contain considerable amounts of Ni, Co, W, etc. as alloying additions, in respect of which India lacks in raw material resources. Extensive work has been carried out on development of Cr-Mn-N type austenitic steels as substitute for 18 Cr 8 Ni austenitic stainless steel and their aging behaviour have been extensively studied at the National Metallurgical Laboratory in the last decade. The present work has been initiated to further study the high temperature creep behaviour of Cr-Mn-N type austenitic steels with a view to evolving suitable compositions and heat-treatment to obtain optimum high temperature creep strength and rupture ductility in these alloys. In this group of steel Mn and N are used as the chief austenitic stabilizers besides C.

Relationship[1,2] of minimum C+N required for austenite stabilization at different levels of Cr content for a range of Mn addition has been well established in these steels. Relative proportions of C and N excercise significant influence on the precipitations reactions in these steels on aging. Two types of reactions (1) grain boundary lamellar nodules and (2) uniform matrix precipitation have been observed. The grain boundary lamellar precipitation is predominant with higher N which should therefore be limited to 0·4% N with corresponding min. C required is ·4% although the border line between the predominantly grain boundary and general matrix precipitation is also strongly dependent on aging temperature-lower nitrogen favoured for higher temperature.

Recent work by Henry and co-workers[3,4] on electron metallography of these alloys have revealed the fine structure of the precipitation reaction products during high temperature aging treatment in low C-Cr-Mn-N steels. After aging at 650°C temperature grain boundary lamellar consists of alternate alyers of Cr_2 N and residual austenite which thereby gets depleted in N and Cr and enriched in Mn. This is why the steel remains fully non-magnetic showing stability of austenite structure on aging—a desirable feature for good high temperature creep properties. At the interface of the grain boundary lamellar nodule and primary austenite zone, the intermetallic Fe-Cr-Mn-Si δ phase appears. On aging at still higher temperature, there is predominantly general matrix precipitation of carbides (M_{23} C_6) and carbonitrides and also possibly intermetallic compounds probably due to enhanced volume diffusion at high temperature.

High temperature creep properties of alloys are highly structure-sensitive and as such, it is important that the steel should possess initially an optimum structure and show reasonable structural stability during subsequent creep aging under high temperature stress creep condition viz. under high stress and elevated temperature in service. The earlier work by Hsiao and Dullis[5] on Cr-Mn-N system of alloys showed that effect of solid solution hardening by substitutional elements viz. Cr and Mn was secondary in raising creep strength. C and N impart creep strengthening through precipitation reactions. Besides, C/N ratio of 1 : 1 for optimum creep properties and the initial structure of the steel, the precipitation reaction during creep conditions viz. stress, temperature and time were important.

Work[6] on Cr-Mn-N steel was taken up at Usines Henricot in Belgium in collaboration with one of the authors. This pertained to the steel with C 0·06, Mn 18·45, Cr 21·56, N 0·6%. Results of these investigations have been given in Tables A to D. In this investigation high solution treatment temperature was used viz. 1200°C presumably due to high Cr content, to dissolve all the precipitates. Severe loss of ductility was observed at 700°C/8 kg per sq. mm. test. Further notched rupture test results at 650°C showed again serious loss of ductility.

In investigations by Hsiao and Dullis[5] and Henricot[6] Laboratories high solution treatment temperature 1150°C–1200°C were employed for steel presumably to dissolve as much of carbides and nitrides in solution. Minimum solution temperature was found to increase with rising Cr and C content and appreciable decrease with increased Mn content. As the solution temperature of the steels has important bearing on high temperatures

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TABLE A Hot tensile test results

Test temp. °C	Tensile strength (kg/mm²)	Yield point (kg/mm²)	Elongation %	Reduction of area(%)	Mesnager impact strength (kg/cm²)
600	54	28	24	30	27
700	42	26	14	21	23
800	30	23	13	17	9

TABLE B Creep test results

Test temp. °C	Applied stress (kg/mm²)	Fracture time (hrs.)	Elongation %	Reduction of area (%)
600	25	75	10	17
	22	782	13	n.d.
	20	1935	11	20
	18	5200	10	18
650	18	297	22	17
	16	878	21	n.d.
	14	3048	19	19·6
	10	10258	18	(5)
700	16	32	12·5	22
	12	344	26	31
	8	3150	0	0

TABLE C Extrapolated values of rupture stress

Temp °C	Stress (kg/mm²) producing fracture in		
	1000 hrs.	10000 hrs.	100000 hrs.
600	23·5	18·2	15
650	16	11	6
700	10	6	n.d.

TABLE D Stress rupture test results on notched specimens

Temp. °C	Applied stress (kg/mm²)	Smooth test piece: Fracture time (hours)	Smooth test piece: Elong. %	Notch test piece: Fracture time (hours)	Notch test piece: Elong. %
650	18	297	22	687	0
	16	878	21	3 240	0

creep properties in not only taking precipitates into solid solution but also in promoting enhanced grain growth (presumably enhanced because of dissolution of the precipitates over certain temperature) and annealing of dislocations, it was thought desirable to extend the range of solution temperature from 1050° to 1200°C in this investigation.

Further the range of stress and temperature selected for creep tests in this work was such that appreciably long rupture times were obtained to correlate the relative effects of stress and temperature on structure and resulting creep properties.

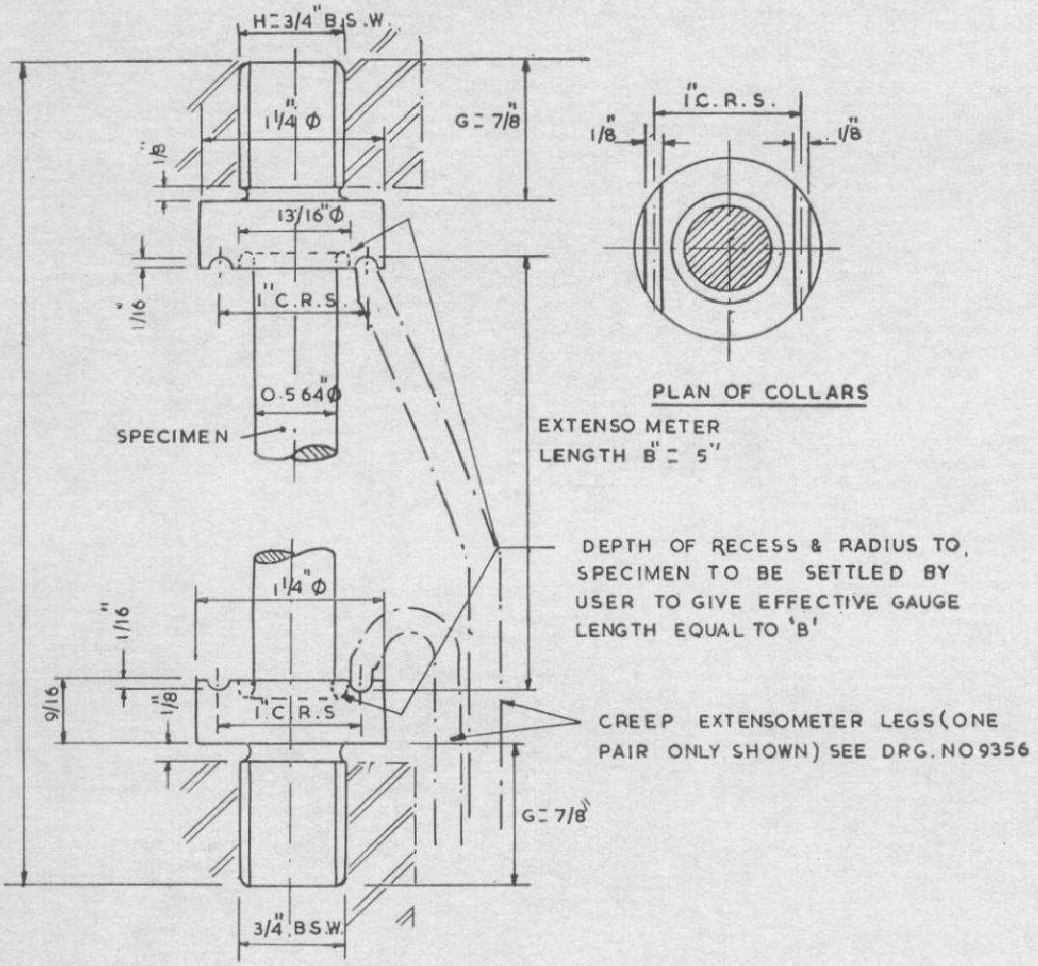
Experimental details

The three groups of steels taken up for this investigation were of the compositions, especially with respect to N and C, as given in Table I.

TABLE I Composition (%) of the three steels investigated

No.	C	N	C/N ratio	Cr	Mn	S	P
I	0·08	0·50	0·16	18	14	0·014	0·014
II	0·31	0·34	0·91	18	14	0·014	0·014
III	0·47	0·32	1·47	18	14	0·014	0·014

The steels were obtained as 4″ square ingots, cast from the steels made in a 0·8 ton experimental arc furnace. The ingots were hot-forged at 1180°C. For forging, the steel was slowly raised to soaking temperature and giving 2–3 hrs. soaking in the beginning and $\frac{1}{2}$–1 hr. in the intermediate reheatings during forging. The ingots were first forged to about 2″ square billets, which were surface machined and dressed to remove all surface defects before final hot-forging to $1\frac{1}{4}$″ square size bars. Finishing temperature for forging was



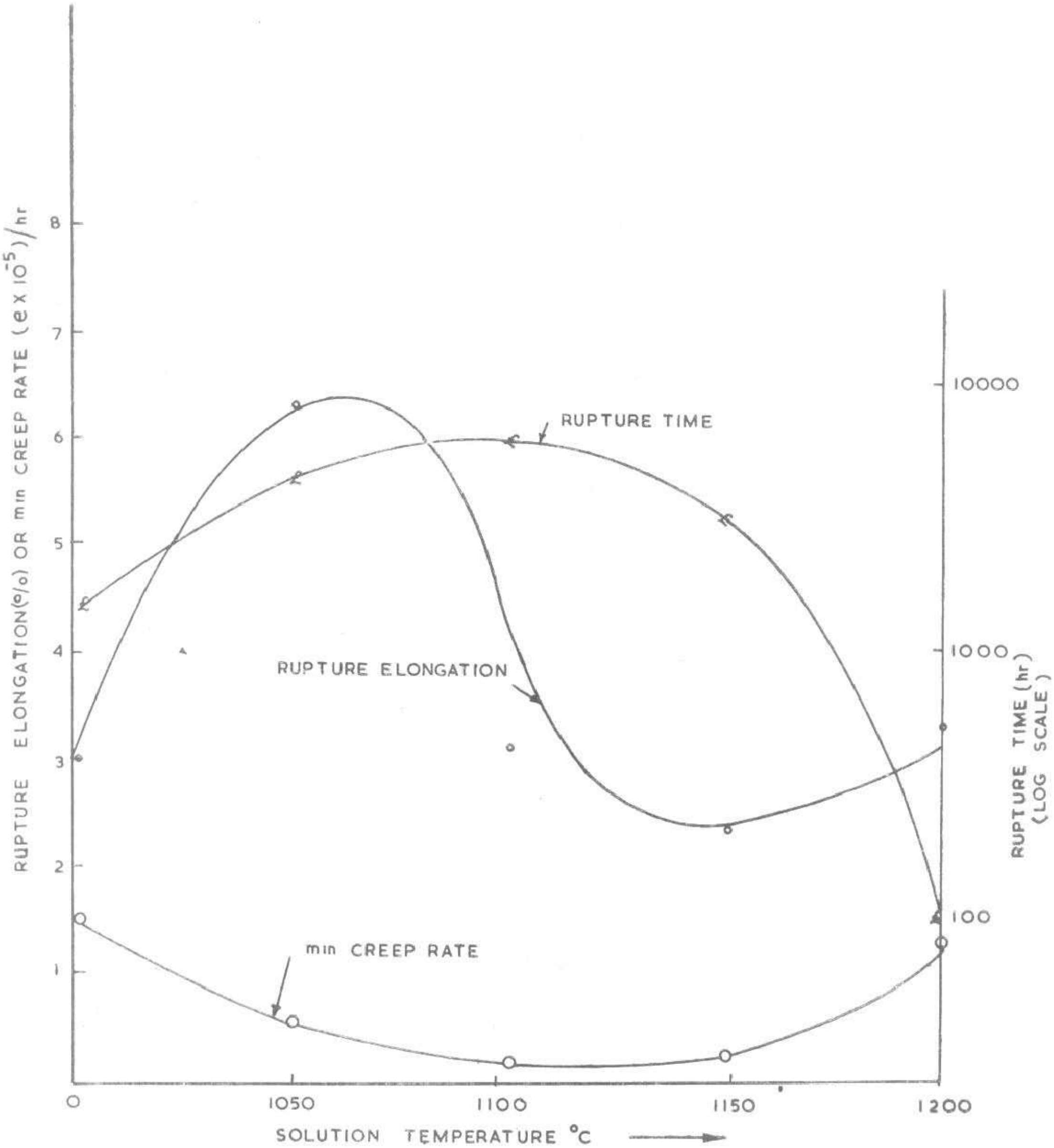
1 *Detail of creep test specimen*

controlled at 900°C–950°C. The forging of the materials was found to be highly satisfactory.

The material showed improved machinability after an aging treatment at 750°C for about 2 hrs. For this reason creep test specimens were in some cases first machined from bars heat-treated as above and then given solution treatment in nitrogen atmosphere. The creep test specimens were slowly raised to the specified solution temperature ranging from 1050°–1200°C soaked at the temperature for one hour, and finally water-quenched.

The creep test specimens had 2″ gauge length and 0·564″ diameter. At the two ends of the gauge length portion, solders $1\frac{1}{4}$″ dia. were machined with grooves (Fig. 1) for fixing the creep extensometer limbs, a pair of which was attached on the opposite ends of the diameter which helped in adjusting the axiality of loading as well as to obtain an average value of strain measured from the two sides of the specimen.

High sensitivity creep tests were performed using a battery of high sensitivity 5 tons and 5000 kg creep machines of N.P.L. design. The loading is achieved through a jockey weight sliding along the beam with graduated load scale and using a double lever system. Three zone nichrome wound 18″ long furnaces were employed together with sensitive temperature controllers of CNS-saturable reactor type in the new models. The temperature of the furnaces was controlled within $\pm 1{\cdot}5$°C of the test temperature. The temperature gradient along the specimens' length was maintained within 2°C during the entire period of testing. Pt-13%-Pt-Rh thermocouples were used, three thermocouples being attached to each specimen and the cold junction temperature being maintained at 0°C. Measurements were made thrice a day. Creep strain was measured by means of Martens mirror extensometer attached to the creep extensometer limbs. The sensitivity was of the order of 10^{-5}. Average value of strain was calculated from the measurements made from the extensometers attached on opposite sides of the specimens. Each extensometer consisted of one stationary mirror as reference and a telescope trolley system mounted with two telescopes was used for simultaneous observation of strain from two sides of the specimen, which assisted quick obser-



2 *Effect of solution temperature on creep properties at 650°C/15 kg per mm²*

vation of incremental strain during test loading.

Before start of the heating, loading system was carefully adjusted to ensure proper axiality of the test specimens as close as possible. Young's modulus of the material was calculated. The furnace was packed on both ends before switching on. Normally the specimen was loaded after 17–24 hours of the switching-on of the furnace; during this period the test temperature was controlled, special care being taken not to exceed the temperature. Creep tests were conducted at 650°C.

Test loading followed incremental steps viz. by increasing the load in steps and taking corresponding strain readings. Special care was taken to take the readings as quickly as possible especially in case of fast creep rates. On completion of test load, the creep strain was rapidly followed, especially in the beginning after a few minutes continuing until fracture.

Results and discussion

The results of creep tests on the various steels under different conditions of heat treatment and discussions thereof are given below.

Effect of solution treatment temperature

Table II gives the details of the results of creep tests conducted at 650°C and 15 kg/mm² stress and shows the effect of solution treatment on the creep properties. These values of rupture time, rupture elongation and minimum creep rate obtained for the Steel No. I (Table I) in as-hot-forged as well as solution treated materials at temperatures 1050°, 1100°, 1150° and 1200°C are shown in Fig. 2.

These curves show that the properties are strongly dependent on the solution treatment temperature. Rupture ductility is improved up to 1050°C and falls rather sharply after 1050°–1100°C. Even as seen from the fracture surface the material solution treated above 1100°C showed very coarse grain size and brittle fracture. Due to this reason, the earlier test specimens fractured in the screw threads. This necessitated reducing the section size of the parallel portion of the specimen and thus the tests had to be interrupted once as noted in Table II.

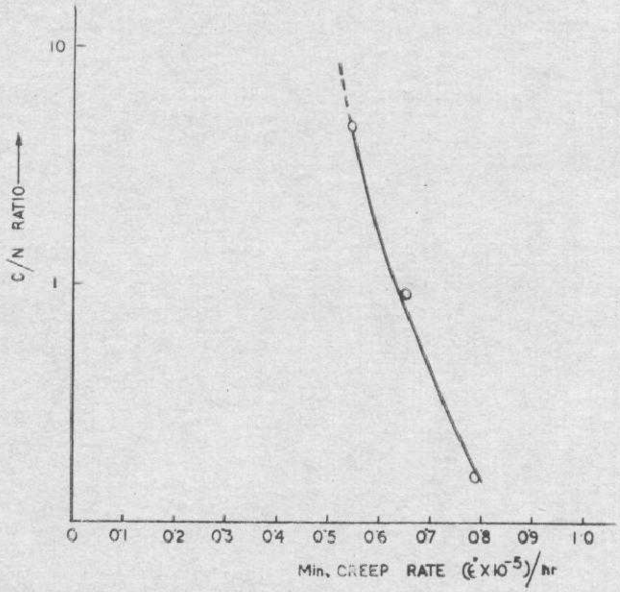
The curve of rupture life and minimum creep rate show similar trends in terms of creep strength. The rupture life is highest and the minimum creep rate is lowest for materials solution treated in the range of 1050°–1100°C. It will thus appear that this is the proper range of solution treatment temperature so far as the creep strength and rupture ductility is concerned.

The lower value of rupture life as well as higher creep rate of the material in the as-hot-forged condition is to be expected on the basis of less available carbides and nitrides for precipitation during creep testing as these are already as coarse precipitates and also due to finer grain size.

Effect of relative proportion of C and N on creep properties

The results of tests on three steels with different C/N ratios and practically similar Mn (14%) and Cr (18%) contents are shown in Table III and graphically represented in Fig. 3.

It is seen from Fig. 3 that the C/N ratio exerts pronounced influence on the creep rate. Below the C/N ratio of about 1 : 1 the creep rate increases at a relative faster rate; above this ratio the change in creep rate tails off, but since this investigation was limited to the three ranges of C and N contents only, it cannot be said with certainty whether much improvement is possible much above 1 : 1 ratio. As earlier referred to this ratio of 1 : 1 for C/N was found to be optimum by Hsiao and Dullis[5] also and this work more or less confirms their findings.



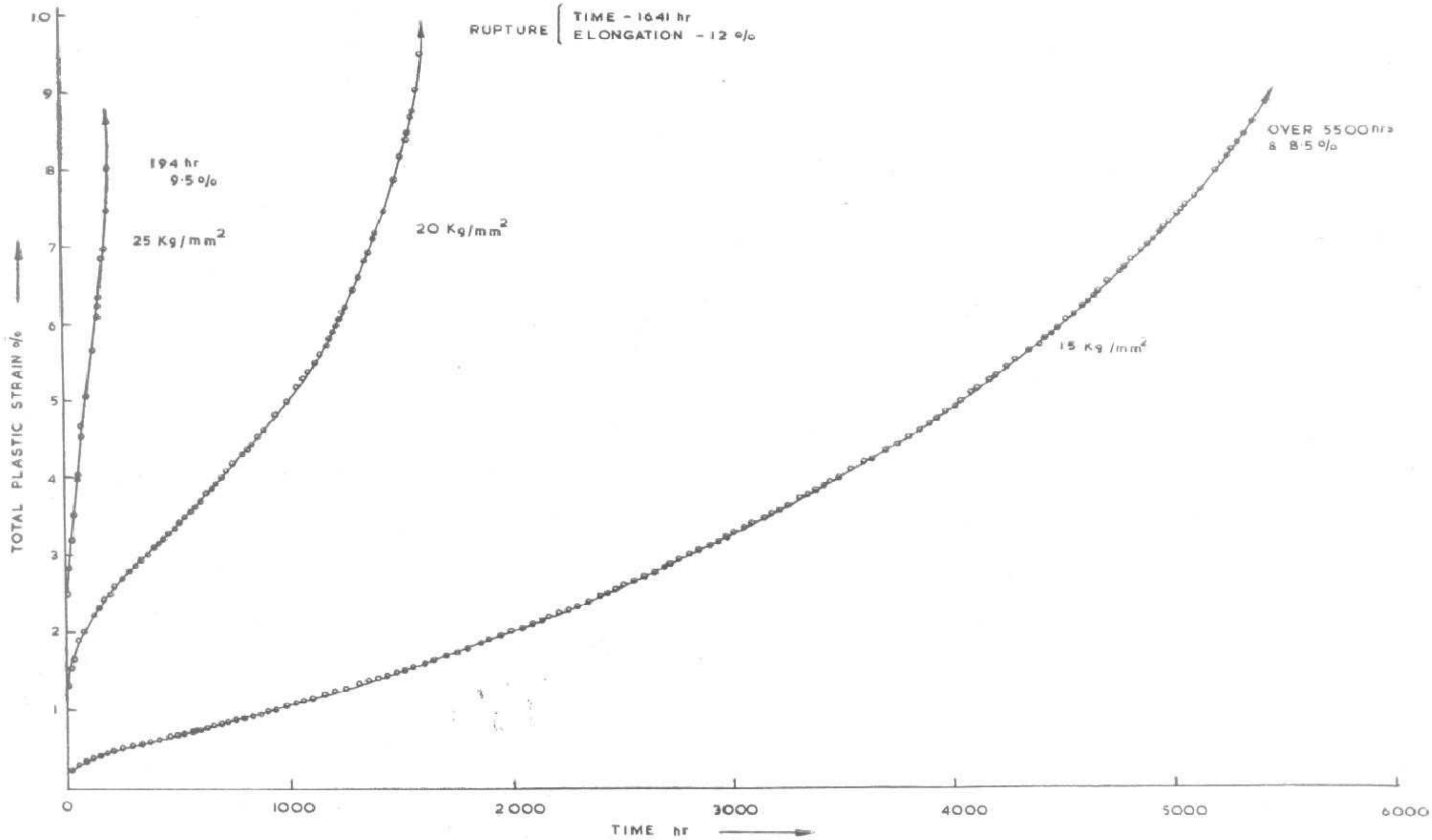
3 *Effect of C/N ratio on minimum creep rate*

General features of the creep curves and curve for rupture life and minimum creep rate

A set of typical creep curves for the steel in the lower

TABLE II Effect of solution treatment temperature on creep properties

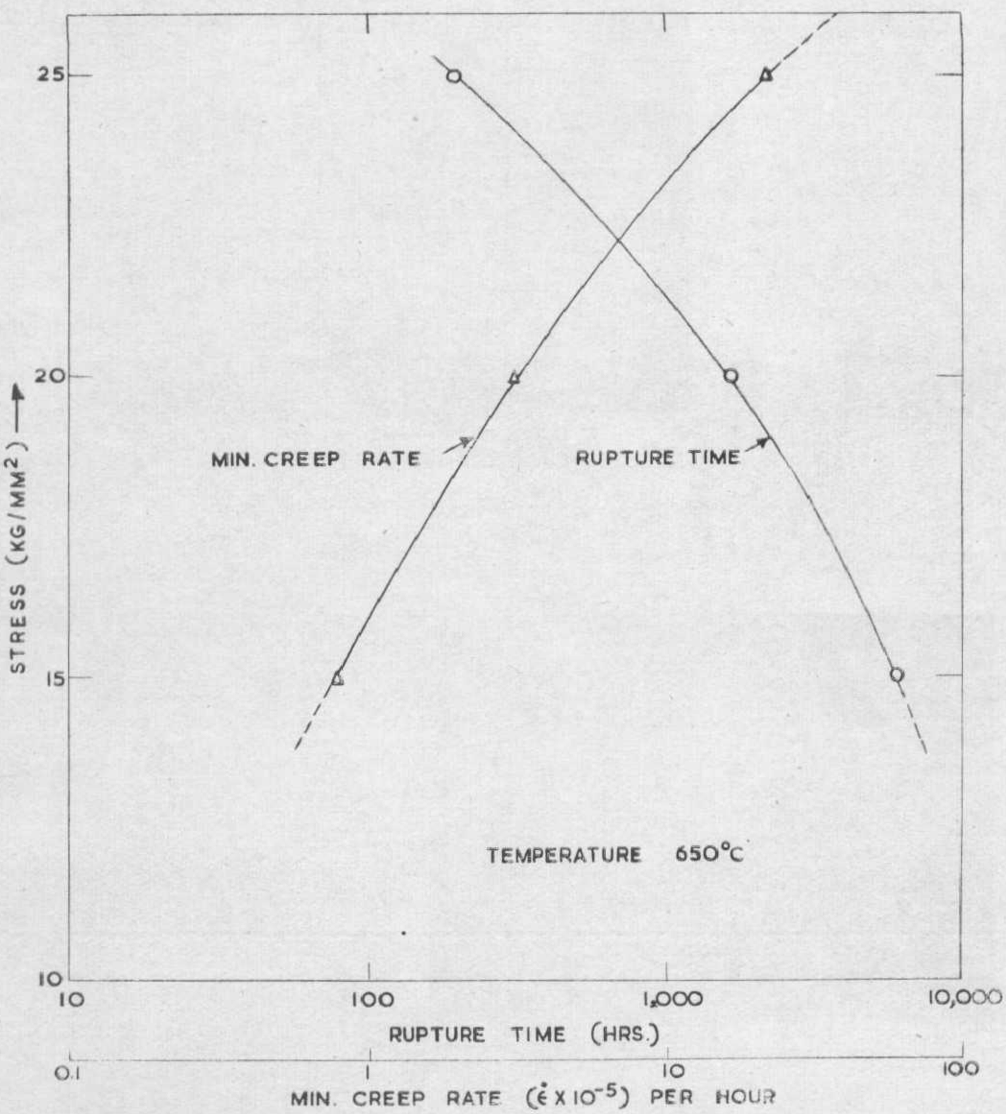
Test mark	Condition of material	Temp. of test °C	Stress kg/mm²	Rupture time (hrs.)	Rupture elong. %	Min. creep rate (per hour)
TF	As-hot-forged	650	15	1442	3	$1{\cdot}5\times10^{-5}$
TA	Solution treated 1050° 1 hr. W.Q.	650	15	4274	6·3	$0{\cdot}541\times10^{-5}$
TB	Solution-treated 1100°C 1 hr. W.Q	650	15	6658*	3·1	$0{\cdot}14\times10^{-5}$
TC	Solution-treated 1150°C 1 hr. W.Q.	650	15	3256*	2·3	0.21×10^{-5}
TD	Solution-treated 1200°C 1 hr. W.Q.	650	15	108*	3·3	$1{\cdot}8\times10^{-5}$



4 *A set of creep curves of low C austenitic steel at 650°C at various stress levels*

TABLE III Effect of C/N ratio on the creep properties of three selected steels with otherwise similar Cr and Mn contents

Test mark	Material C/N ratio	Heat treatment	Test temp. °C	Stress kg/mm^2	Min. creep ratio (per hr)	Rupture time (hr)	Elongation %
TA	C–0·47 N–0·32 C/N=1·47	Solution-treated 1050°C/lb. W.Q.	650	15	$0{\cdot}541\times10^{-5}$	4274	6·3
HT_2	C–0·31 N–0·34 C/N=0·91	do	do	do	$0{\cdot}65\times10^{-5}$	still running	—
L_1A_2	C–0·08 N–0·50 C/N=0·16	do	do	do	$0{\cdot}79\times10^{-5}$	5977	13

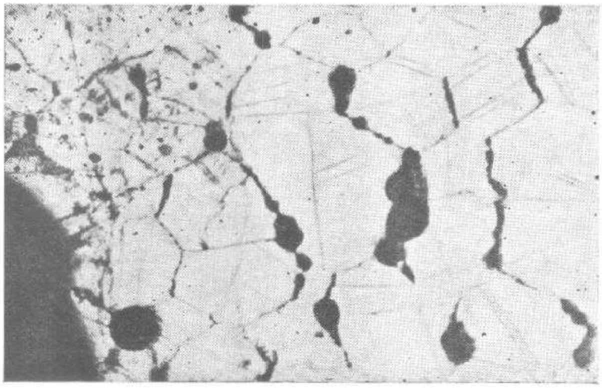


5 *Creep rupture time and minimum creep rate vs. stress curves*

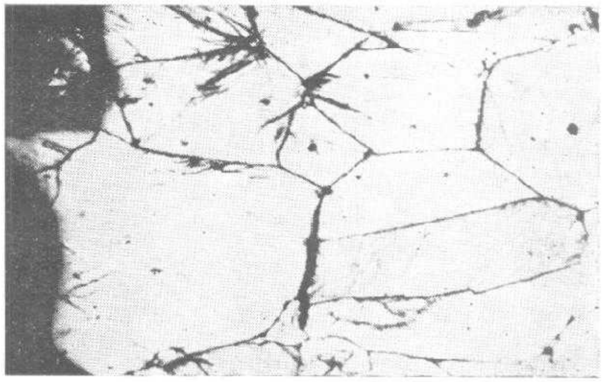
C series tested at 15, 20 and 25 kg per sq. mm. stress is shown in Fig. 4. The various creep values are given in Table IV. One prominent feature of these curves is that teritiary stage sets in at quite early periods of creep testing and lasts for long time till fracture. This is a desirable feature as it results in high rupture ductility as evident from the corresponding figures quoted along each curve. However, it is indicative of the process of precipitation and coarsening of the precipitate resulting in softening and thereby increasing creep rate. Examination of micro-structucture at the various stages of the creep curve could help in correlation of the overaging process with the increasing creep rate in the tertiary stage of creep. As expected, high initial plastic strain was obtained during loading to higher stresses and this would be useful information for design based on specific deformation in a given

TABLE IV Creep properties at different stresses at 650°C for the austenitic steel with relatively lower C content (Steel 1, Table I)

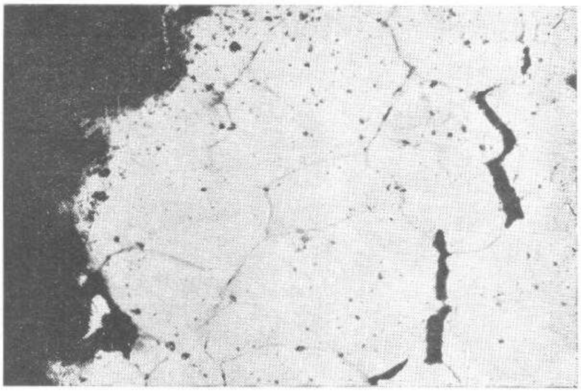
Test mark	Material heat treatment	Stress kg/mm²	Min. creep rate per hour	Rupture time (hr)	Elongation %
L_1A_2	Solution-treated 1050°C/1hWQ	15	$0{\cdot}79\times10^{-5}$	5977	13
L_1A_1	do	20	$3{\cdot}1\times10^{-5}$	1641	12
L_1A	do	25	$21{\cdot}8\times10^{-5}$	194	9·5



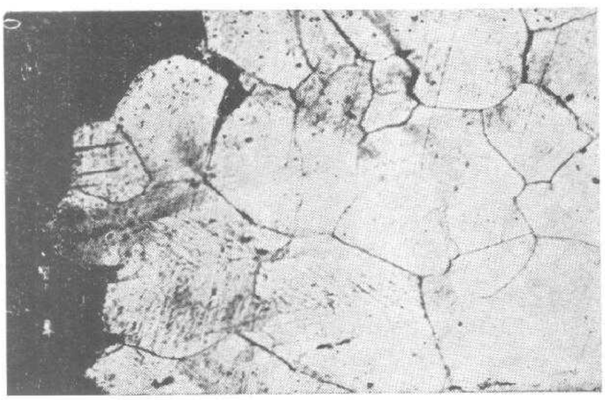
6a Sp. no. TF-as hot-forged ×150



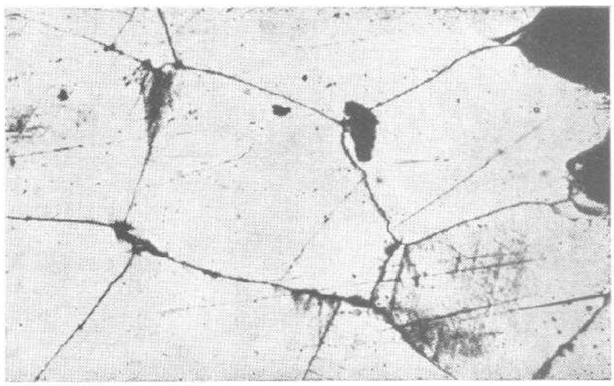
6b Sp. no. TA-solution treated at 1050°C ×150



6c No. 1 TB-solution treated at 1100°C ×150

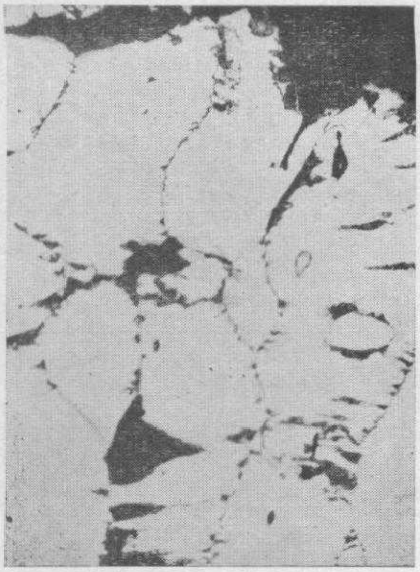


6d Sp. no. TC-solution treated at 1150°C ×150



6e Sp. no. TD-solution treated at 1200°C ×150

6 *Longitudinal section of creep fractured specimens of steel 3 (Table 1)*



7a (A) Stress 20 kg/mm², rupture time 2641 hrs ×150

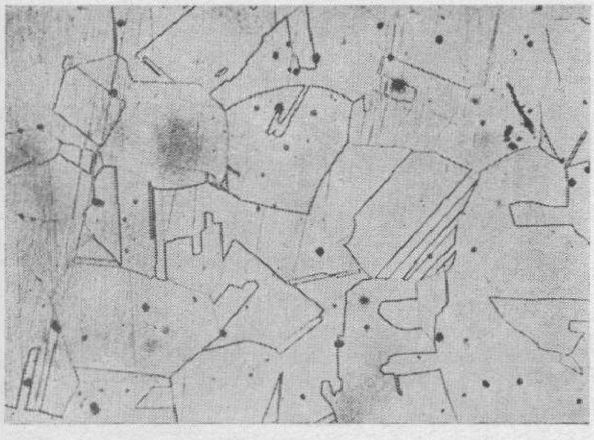
7b Stress 25 kg/mm², rupture time 194 hrs. ×150

7 *Longitudinal section of creep fractured specimens of steel I (Table I)*

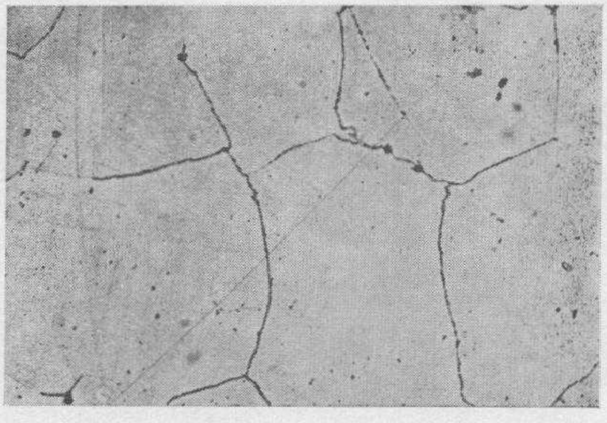
time. With this in view results of minimum creep rate and rupture life are plotted graphically against stress (Fig. 5) for tests conducted at 650°C for the steel with lower C content. These curves show uniform variation of these properties with stress within the conditions of test. Further tests to supplement the creep data are in progress.

Metallographic examination

The micro-structure of the longitudinal section of the creep fractured specimens have been shown in Figs. 6a to 6e. These show that practically in all cases the fracture is intergranular. One most important feature of the micro-structure was observed in case of steel with lower C and higher N content (Steel 1, Table I). These are shown in Figs. 7a and 7b for specimens tested at different stress levels. It is clearly seen that the precipitation process which starts from the grain boundary proceeds towards inside the grain and in the direction transverse to that of the load applied during testing. The intensity of the precipitation also seems to be dependent on rupture time, in turn dependent on the intensity of stress as is seen from the



8a Solution treated at 1050°C ×150



8b Solution treated at 1200°C ×150

8 *Effect of solution treatment at different temperatures for steel 3 (Table I)*

photomicrographs of the specimen tested at higher stress. Thus it can be concluded that the magnitude and the morphology of the precipitate is strongly dependent on the stress condition. This factor will be of great significance especially in case of notch rupture tests where localized plastic deformation will alter the precipitation structure and thereby the rupture properties. This same effect is not so prominently exhibited in specimens with relatively higher C contents (Fig. 6a to 6e). This shows that high nitrogen steels are more prone to that type of effect.

The photomicrograph Fig. 6a show that steel (specimen TF) in the as hot-forged condition was of finer grain size which was probably one reason for its poorer creep strength in addition to less solute available for precipitation during creep aging. The materials solution treated at higher and higher temperatures showed correspondingly larger grain sizes (Figs. 8a and 8b). Specimen TA (Fig. 6b) with solution-treatment at 1050°C showed considerable strain markings. Specimen TC (Fig. 6d) solution treated at 1150°C showed greater and uniform fine precipitation during creep testing in contrast to the specimen TD, solution-treated at 1200°C (Fig. 6e); probably because the rupture time in the latter case is too small as compared to the rupture time for specimen TC (Table II).

Conclusions

1. The solution treatment temperature has pronounced influence on the creep properties of these steels.
2. Preferred range of solution treatment temperature is 1050°–1100°C. Higher temperature leads to excessive brittleness resulting from coarse grain structure.
3. The optimum creep properties appear to be obtained at C/N ratio of about 1 : 1.
4. The precipitation process progressing during creep testing viz. under stress and temperature which may be termed as creep stress aging leads to stress induced precipitation following the direction transverse to the loading direction. This effect is more prominent in steels with higher N and lower C contents.
5. This limited investigation indicates that these Cr-Mn-N steels can be suitable for applications such as engine valves, operating at high temperature—say around 650°C. These are not recommended for application involving notch stresses.

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Discussions

Mr **P. B. Rao** (Electrosteel Castings Ltd., Calcutta): The authors have recommended this Cr-Mn-N alloy as suitable for applications at operating temperature of 650°C such as engine valves. I am interested to know the behaviour of this alloy under thermal fatigue and its resistance to carburizing atmospheres.

Mr **R. Choubey** (Author): The thermal fatigue behaviour of the Cr-Mn-N alloys has not yet been evaluated. But as stated in the text of the paper, since the precipitate structure in these alloys is influenced by stress, the thermal stresses are likely to affect the structure and thereby the porperties. Similar alloys have been found to resist corrosive conditions encountered by automotive engine valves. Their resistance to the attack of leaded fuels is particularly marked.