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METALLURGICAL AND ENVIRONMENTAL FACTORS INFLUENCING CREEP BEHAVIOUR OF HASTELLOY-X

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Creep and rupture behaviours of Hastelloy-X and its modified version were examined with special reference to the effect of different test environments; i.e. air, high vacuum and the simulated HTR helium coolant. The respective environments showed different effects. The vacuum environment of about 10^{-8} torr. gave best reproducible behaviour with essentially no surface-to-volume ratio effect. Such size effect was significant in the other two environments. The simulated HTR environment was characterized in its potentiality of both oxidizing selected alloy constituents and carburization. The observed behaviour was attributed to the depletion of strengthning solute elements caused by the surface reactions and the associated solid state reactions.

Keywords : Hastelloy-X, Creep Properties, HTR coolant, Internal oxidation Carburization, Environmental Effect, Steady State Creep Rate, Tertiary Creep, High Vacuum,

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ハステロイーXの高温クリープ挙動に及ぼす冶金学的因子と環境の影響

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ハステロイーXの高温クリープ変形に及ぼす環境の影響について，大気，HTR近似ヘリウムおよび超高真空の各環境間で比較検討した。各環境の高温クリープに及ぼす影響は，異っており，クリープの時間依存がそれぞれの雰囲気で特有の形態を示す。超高真空中では，クリープ曲線の再現性が良く，表面積と断面積の比率の効果など，試験片の形状にも独立であった。一方他の環境では，定常クリープ速度および速度遷移点などのクリープ変形の時間依存傾向が試験片の寸法形状に大きく依存する。

高温ガスの一次系を近似したヘリウム環境では，Cr，Mnなど合金中の活性成分の選択酸化による表面近傍での欠乏と滲炭が原因で形成される粗大M_6C型炭化物の析出が促進される。その結果として基地合金中のCr，Moなどの置換型強化元素の欠乏を生じ強度低下が起る。終局には，これらの元素の欠乏と歪の蓄積の結果とみられる局部再結晶が粒界等の界面で生じ，著しくクリープが加速されることが分った。このようなクリープ変形過程の観察結果は，従来の高温でのヘリウム中クリープ試験データに見られる，第3期クリープが早期化し，破断延びが減少するなどの一般的知見を良く説明できる。

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environment-enhansed creep and embrittlement are among the major problems concerning the interaction of mechanical deformation and surface reactions for the structural materials of HTR. These subjects are not only simple matters of wall thinning effects but are the mutually activating synergistic actions of plastic deformations and surface reactions. In this field considerable efforts have been exercised in various laboratories in establishing a reliable experimental techniques by which essential simulation and proper acceleration of the process are to be made.

In this report, the role of the environment effects on creep at each deformation stage is analysed under controlled experimental conditions.

The essential features of a typical HTR environment is "oxidizing and carburizing" to the candidate structural alloys. Because of the low oxidizing potential, some Ni-Cr type austenitic alloys are known to show difficulty in establishing their protective oxide film with sufficient long time stability, and in a long exposure carburization can occur to cause more penetrating microstructural changes to influence the strain-time phenomena such as creep, fatigue and their interactions.

The authors[1] have demonstrated the evidence of strong interactions between the simulated HTR helium environment and the creep deformation-rupture properties through using specimens of a reduced diameter. In the course of the previous study, it was also pointed out that the use of specimens with a large diameter sufficient to the given experimental conditions could provide some reference results that were independent of the test environment.

2 EXPERIMENTAL METHODS

2.1 Materials

Hastelloy-X and its modified versions were used. (see table 1 for chemical analysis) The grain size of these materials was adjusted to ASTM No.4 in average. Small round bar specimens of 4 mm dia. were used for obtaining the results with the possible effects of environment in amplified manner, while those of 8 mm dia. were used to obtain the

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standard creep data based on their essential immunity to the influence of the environment. A series of several specimens from a large round bar of 8 mm dia. down to a thin plate of 1.5 mm thick were also used to monitor the trend of the size effects in terms of the surface area to volume or cross-sectional area ratio. A uniform length of the test section of 26 mm was the case for all specimens used in this experiments. The specimen sruface was prepared by polishing with diamond paste of 3 μm grid, ultrasonic cleaning in high purity methyl-alcohol and followed by drying in vacuum. Before starting the loading the specimen was heated for sufficient time at the test temperature to avoid the initial rapid change in the metallurgical structure to influence the results.

2.2 Test environments and apparatus

Creep tests were performed in environments with different oxygen and carbon potentials.(see table 2) The test apparatus used for the helium-base environment were connected to a helium recirculating system with continual purification and impurity injection operated at pressure of 1.5 kg/cm^2. The rate of supply to the test section was at least 10 times the theoretical expenditure rate of oxidizing impurities. The analysis of the test environment was made by gas chromatograph and hygrometer throughout the tests.

The use of the ultra high vacuum is to see the behavior under least influence of the test environment. The test apparatus use are equipped with continuous axial strain measurement with the minimum unit reading of 10 μm.

In the test sections for the case of the helium a core was exercised not to alter the compositional balance among the low level impurities by employing Mo for heaters and chucks and quartz or water-cooled steel containers for the chambers. The test temperature was maintained withing 5 °C at maximum fluctuation.

The specimens after removal from the test environments were examined through variety of metallographic techniques, in which the optical and the scanning electron (SEM) microscopy, the electron probe microanalysis (EPMA) and the secondary ion mass-spectrometric (SIMS) analyses were involved.

3 RESULTS

3.1 Influence of environment on time-deformation behavior — over all —

Use of thin 4 mm dia. rod specimen has revealed the influence of environment sharply in the range of test temperature around 900 to 1000 °C. A typical example of the comparison of the creep curves can be shown in Fig. 1. Sharp difference between the curves for 4 mm and 8 mm dia. specimens are noted in the helium environment. In contrast, the result from the ultra high vacuum environment with a 4 mm dia. specimen can be compared as nearly equivalent to the result with 8 mm dia. specimen.

The time to rupture data in various environments obtained by using the 4 mm dia. specimens were processed by the least mean square method to show in simplified lines and compared in Fig. 2. The actual data plots were already reported previously.[1] The trend shown is similar to that pointed out in Fig. 1. The reduction of the rupture life with decreasing the specimen diameter was found to be specific to the cases in corrosive environments i.e. air, the contaminated helium and lower vacuum. On the other hand, nearly complete independence to the size effect in the ultra high vacuum environment was confirmed as shown in Fig. 3 in comparison with the case in the helium environment.

3.2 The steady state creep and the environment effects

As already pointed out in the previous work, the creep rate measurements with reduced specimen diameter have shown a delicate reflection of the microstructural change in the specimen. A knick marked as t_2 in Fig. 1 for the curve obtained by the 4 mm dia. specimen tested in the simulated HTR helium was a sort of transition of the steady state strain rate to another steady state. Such an effect was observed neither in the larger diameter cases in the same helium or in the cases with air or vacuum environments.

In comparing the effect of the environment on the steady state creep rate the initial parts of the above mentioned curves were taken. Figure 4 gives such a comparison, where, again, some of the data for air and helium had already been reported previously, and hence are shown in lines to compare with the vacuum cases. In this simple comparison, the steady state creep rate was found to reflect the effect of the test

environment. From the figure, air is seen to be most aggressive environment. This is true, but referring to the occurence of the rate transition as noted earlier, the essential degradation in the creep properties is more significantly proceeding in the simulated HTR helium and the influence of the environment was seen to be more complex when the whole creep process was considered. An analysis of the creep rate as a simplified function of temperature and stress under various environments it can be stated that the followings can stand;

In the empirical expression of

$$d\varepsilon/dt = C \times \sigma^n$$

and

$$C \text{ and/or } n \sim B \exp(D/T)$$

where B and D are constants for a given material and an environment. The values n and C are compared in the order shown below

$$n : \text{UHV} > \text{medium vac.} > \text{HTR He} > \text{air}$$

$$C : \text{UHV} < \text{medium vac.} < \text{HTR He} < \text{air}$$

where medium vacuum means vacuum of the range $\sim 10^{-4}$ torr that was previously used in the work reported.[1]

3.3 Transition to the tertiary creep

The time and strain at which the creep deformation turns from the steady secondary stage into an accelerated stage are of particular significance in the engineering application of the creep data. The results obtained in this respect was also known to be under the influence of the test environment. In Fig. 5 the strain at the initiation of tertiary stage, ε_3, is plotted as a function of the applied stress. A large difference between the ultra high vacuum environment and the others is noted. The other features seen in the relative relations among each other also seem to reflect the nature of the effect. The difference observed in this case may be a result of cumulative material degradation rather than the synergistic effect observed in the secondary rate. In this sense, the decrease of ε_3 in the HTR helium relative to air is

interpreted as the reflection of possible substantial changes deep in the structure. This becomes more evident in the plot of rupture ductility as a function of stress in Fig. 6, where the HTR helium caused the largest drawback.

3.4 Material transport and the associated sturctural changes during creep

The change of chemical composition in the specimen can be a part of useful information in interpreting the phenomena. A small part of metal was sampled out from the fractured region of each specimen after tests in various environments. Figure 7 shows the carbon content as a function of applied stress. With decreasing stress the test duration was longer and, naturally, the trend of change due to the interfacial material transport is intensified. In the HTR helium, rather steep increase in carbon is apparent. This is a contrast to the decarburization in those tested in air. The substantial fracture ductility in air as shown in Fig. 5 and 6 can be due either to the decarburization or enforcement by rapid recovering of the cracked surface by adherent oxide or both.

The results of mass spectrometric analysis of the distribution of some key elements in the oxide film formed in the HTR helium clearly showed the evidence of carbon intrusion through the oxide film in Fig. 8. From this result the inner oxide layer adjacent to the metal was known to be an essential barrier to the carbon transfer, and the outer layer being also a supplementary one.

It has been observed in most experiments through EPMA scanning analysis that an extensive Cr-depleted layer is formed in Cr-Ni type austenite alloys after long exposure to oxidizing environments. The layer can also be detected by micro Vicker's hardness testing. Figure 9 indicate the existence of such layers in both air and the HTR helium environments. The slight shift in the results for the helium environment is interpreted as the influence of carburization, and perherps the associated carbide precipitation, superposed to Cr-depletion.

The carburization in this alloy, particularly at the Cr-depleted zone, causes the precipitation of carbide, M_6C.[10] The material loses strength with M_6C formation and the resultant local depletion of Mo can cause the recrystallization to eventually come to recrystallization.

The carburization through the grain boundary areas, where the protective oxide film was damaged locally due mainly to the integranular

attack and the tensile stress, was visualized by the observation of white spots, i.e. M_6C, appreared by the reflected electron image in an EPMA as shown in Fig. 10.

Figure 11 is an evidence of recrystallization due to M_6C precipitation in the HTR helium. Better stability of the microstructure of the specimens creep tested in air provide a support to the view that the most important means of protecting the material from the influence of the HTR helium environment is to combat the carburization as well as the oxidation.

In the specimens tested in the ultra high vacuum environment showed uniform structure. After close examination of the changes at different stages of creep, it was found that an extensive and uniform recrystallization, over the all gauge length under deformation took place at the time point when the tertiarly creep had started. Figure 12 show a typical case in different magnifications.

4 DISCUSSION

Among the experimental facts observed in the present work, the effect of surface to volume (or diameter) may have a generic significance in both interpretation and practical application of the creep test data. A typical application problem is the evaluation of the design strength of tube walls in the heat exchangers, which are exercised to be designed toward larger surface area with thinnest possible thickness. The difference in the strain vs. time curves among the data obtained under different environmental conditions throws another problem of converting the popular "rupture life" data to the estimation of strain limit. Further, the delayed but serious degradation of material due to carburization may make the extrapolation procedure more difficult and tedious because there can be a doubt for the applicability of the Larson-Miller type approximation, because of the complicated rate controlling mechanisms.

The reason for why the traditional creep data obtained in air have been handled by the simple empirical method can be understood when a plot like Fig. 13 is attempted. Those obtained in air and ultra high vacuum fell on a straight line despite the large difference in the minimum creep rates existing between these two cases. This concidence

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cames from the fact that the creep curves in both cases have high similarity. This was not the case in the simulated HTR helium, where the parallel occurence of oxidation and carburization causes extensive microstructural changes to deform the strain-time relationship significantly as already seen in Fig. 1.

One further significant aspect to be mentioned is the difference in the degree of the environmental effects dependent on the stress level. A typical one is the dependence of the strain rate transition on the stress level. Figure 14 shows the relation under different environment. In the helium environment, large reduction in the rupture life is observed in the low stress, i.e. long time exposure, which is in a sharp contrast to the straight relationship typical in the ultra high vacuum, where essentially no appreciable environment effect is involved.

The pronounced effect of the environment with low oxidizing potential and some substantial carburizing potential is further interpreted with the following sequence as shown in Fig. 15. The protective oxide film, (a), of inner Cr_2O_3 and outer $MnCr_2O_4$, is damaged upon deformation of underlying metal (b) which is frequently triggered by the selective attack at grain boundaries due to the existence of elements such as Aℓ and Ti.[1] In the crevice of the surface crack, the oxidizing impurities in the helium are skimmed out to leave only carburizing components to reach and react at the crack internals. This efficient carburization of the base metal is believed to be a mechanism most responsible to the observed effect. The synergistic part, which is typical in the acceleration of the steady state creep rate under oxidizing environment may involve the contribution from the outward diffusion of Cr toward the oxide forming interface. This diffusion should naturally be acompanied by the counter flow of lattice vacancies to the metal internals assisting the thermal activation process of the lattice defects to promote the deformation.

In any of the above mentioned mechanisms, the improvement of protective oxide film is considered to be one of the most effective way of enhancing creep resistance of materials in the HTR environment. This has been demonstrated to be true by the authors in their comparative evaluation of Hastelloy-X and its modified version, i.e. Hastelloy-XR, in the other series of work.[12]

5 SUMMARY

1) The strain-time relationship in the creep of Hastelloy-X under the influence of reactive environment is a strong function of the specimen geometry.
2) The observed dependence on geometry is the surface to volume ratio effect and is the result of surface reactions involving both oxidation and carburization.
3) In ultra high vacuum environment essentially no effect from the surface processes results, and hence no geometry effect was observed.
4) The selective diffusion of Cr toward surface was assumed to accelerate the steady state creep rate.
5) The rate transition to shift the deformation to more accelerated stage was found to be provided by carburization and the associated shortage in Mo from the austenite matrix to enhance the recrystallization and softening.

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Table 1 Specimen material

	Mn	Al		Co	P	N	GRAIN SIZE ASTM No.
HASTELLOY-X	0.55	0.16		0.67	0.012	0.027	4.5
HASTELLOY-XR	0.88	0.03		0.04	0.005	0.006	3.5

C	Si	Ti	S	Cr	Mo	W	Fe	B	Ni
0.07	0.31	0.01	0.005	21.51	8.71	0.50	18.06	0.001	BAL

Forged rod

Hastelloy-X ; 1160°C x 1 hr , WQ

Hastelloy-XR ; 1180°C x 1 hr , WQ

Table 2 Environmental variables.

1) Size effect(Ratio of surface area/volume)

8mm$^{\phi}$(0.50) , 4mm$^{\phi}$(1.00) ( )....mm^{-1}

2) Environment

a) AIR

b) Type B He-base mixture composition(μatom)

H_2	H_2O		CO	CO_2	CH_4
190~220	5~7		100~110	2~3	5~6

C) Ultra high vacuum

Turbo molecular pump , $<2 \times 10^{-8}$ Torr

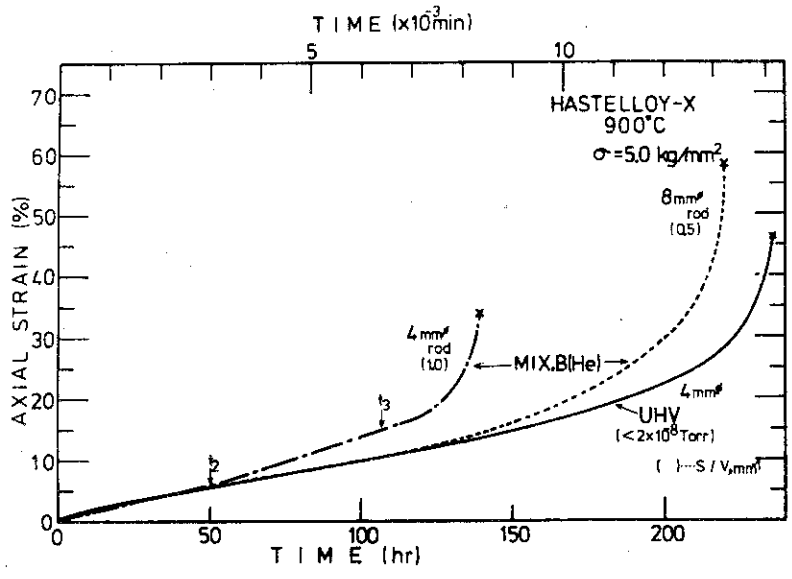

Fig.1 Effect of specimen size and environment on the strain-time relation in the creep of Hastelloy-X at 900°C.

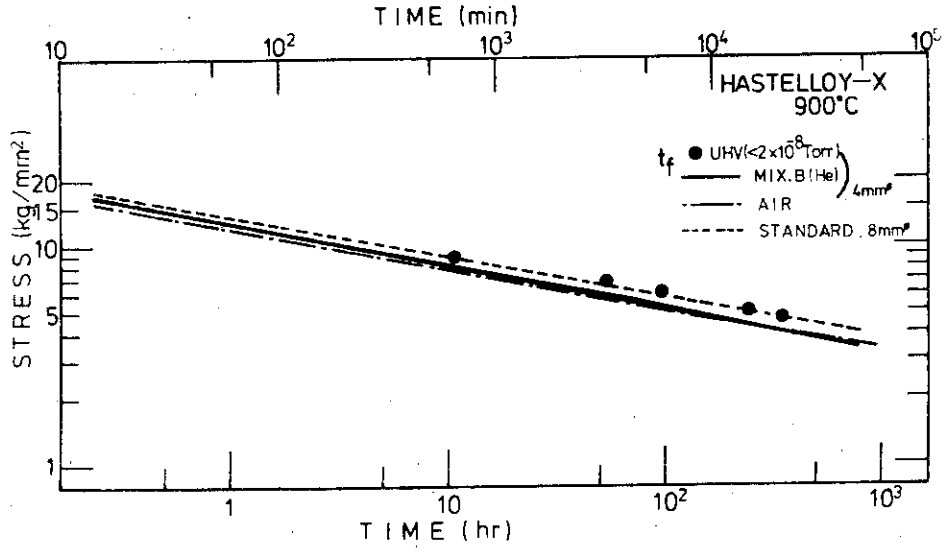

Fig.2 Effect of environment on creep rupture life of Hastelloy-X.

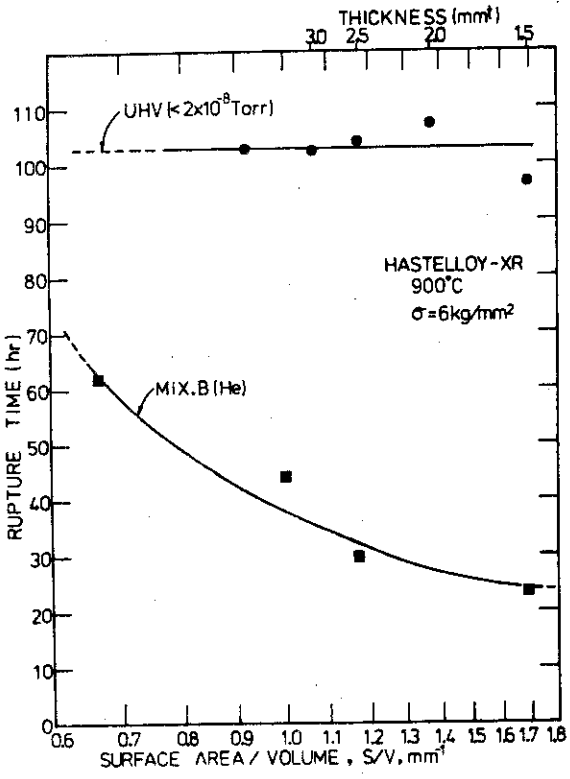

Fig.3 Effect of specimen size on creep rupture time of Hastelloy-XR.

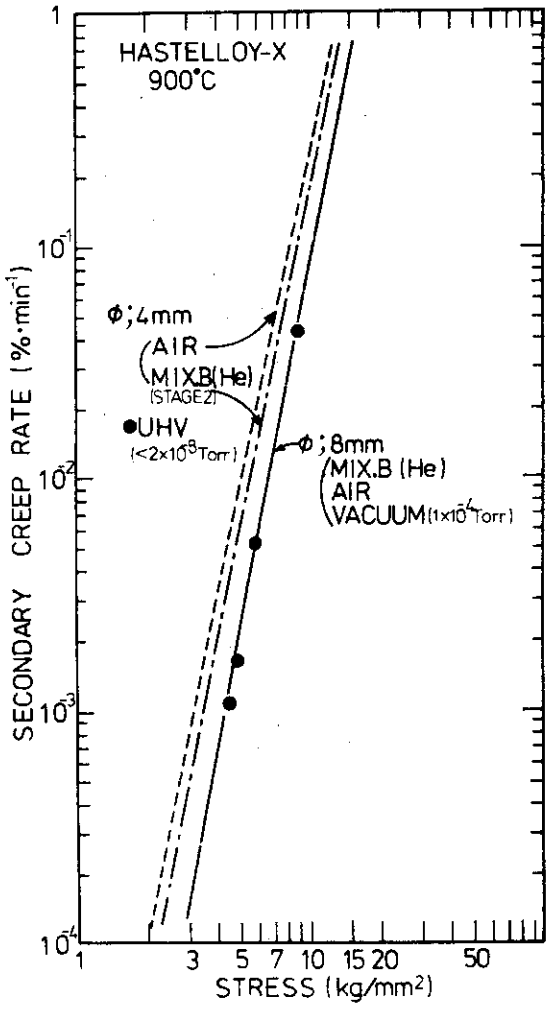

Fig.4 The dependence of steady state creep rate on applied stress at 900°C.

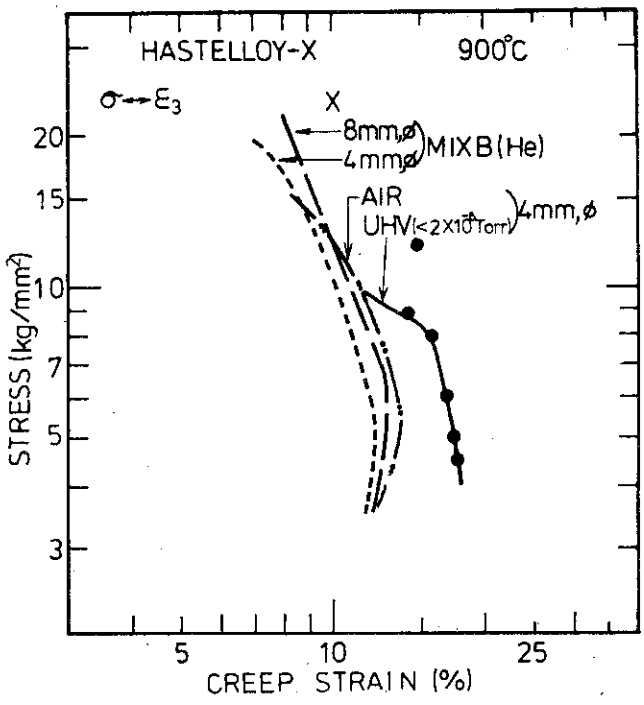

Fig.5 The effect of environment on the creep strain at initiation of tertiary creep.

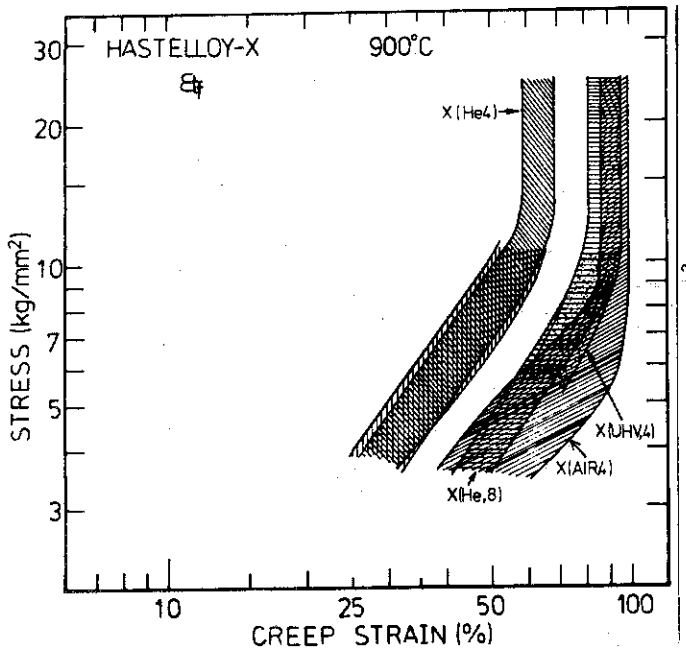

Fig.6 The effect of environment on the elongation at rupture at 900°C.

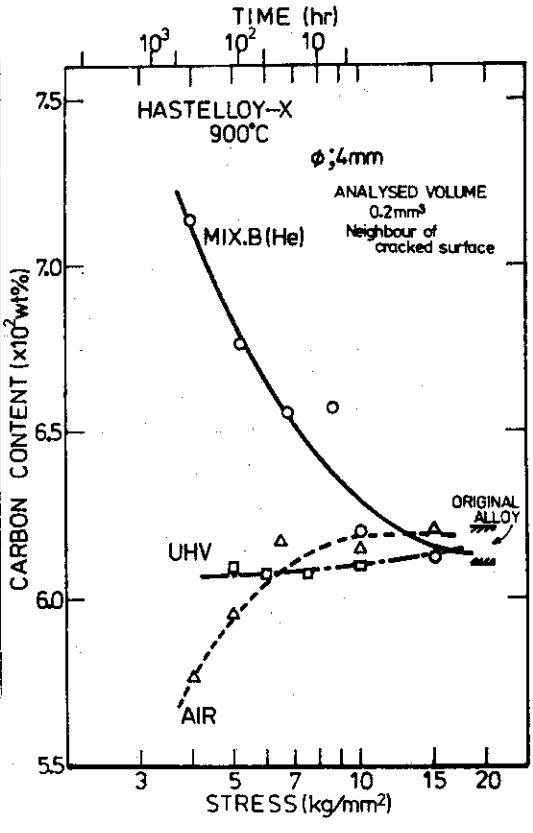

Fig.7 The carbon content near fracture surfaces in creep tested specimens of Hastelloy-X at 900°C.

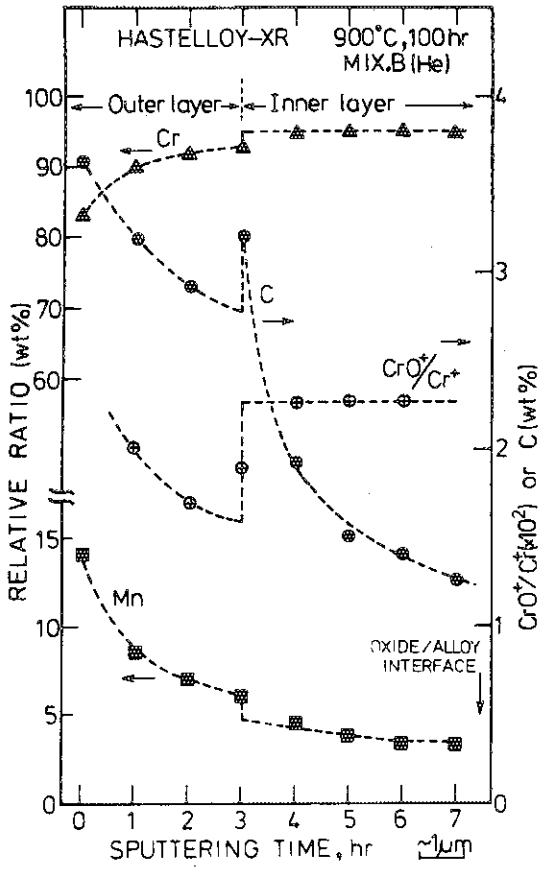

Fig.8 The depth profile of the concentration of several key elements across the oxide film formed on Hastelloy-X in the helium.

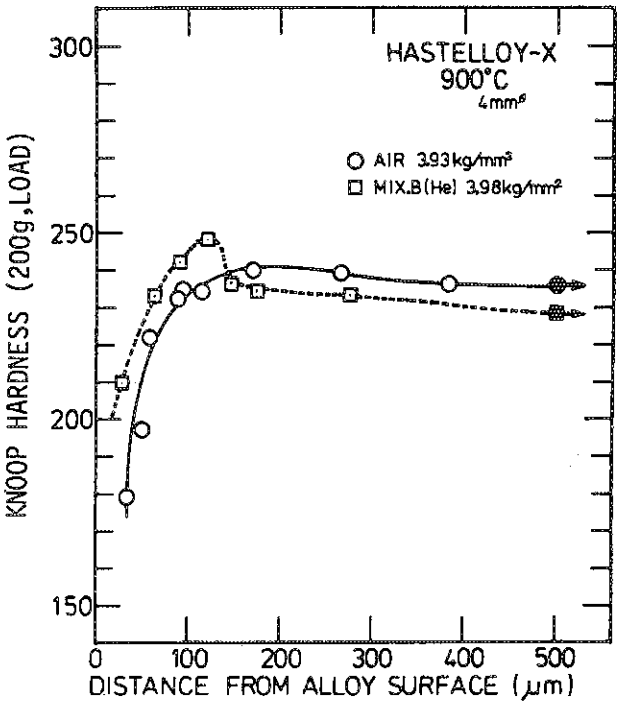

Fig.9 Microhardness near the oxide-metal interface after exposure to the test environments.

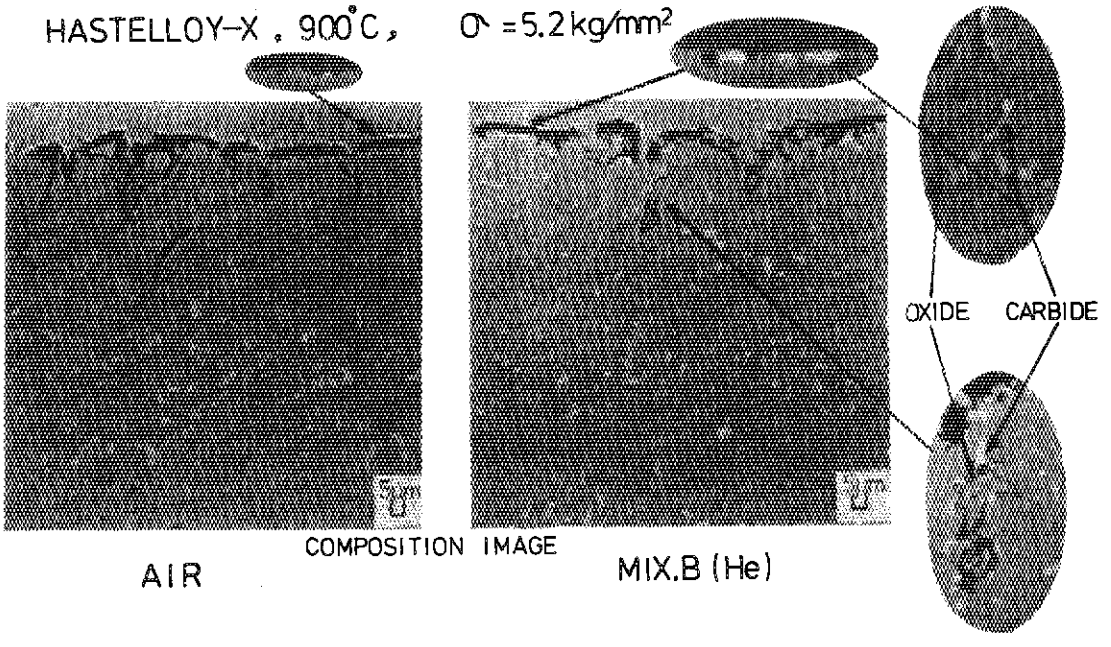

Fig.10 Effect of environment on the distribution of carbide(white spots) and internal oxide(black spots) observed by electron reflection image.

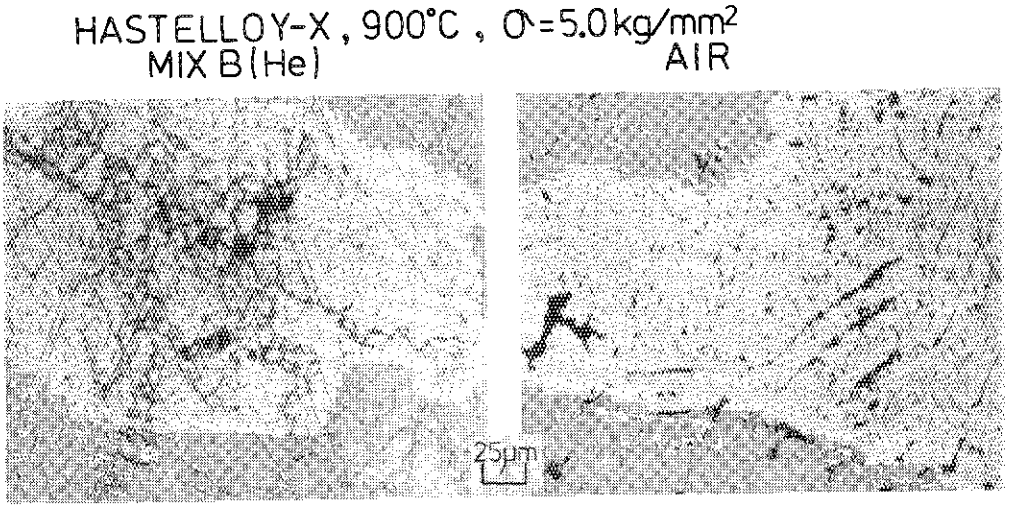

Fig.11 Effect of environment on the microstructure at uniform elongation regions after creep tests of Hastelloy-X at 900°C.

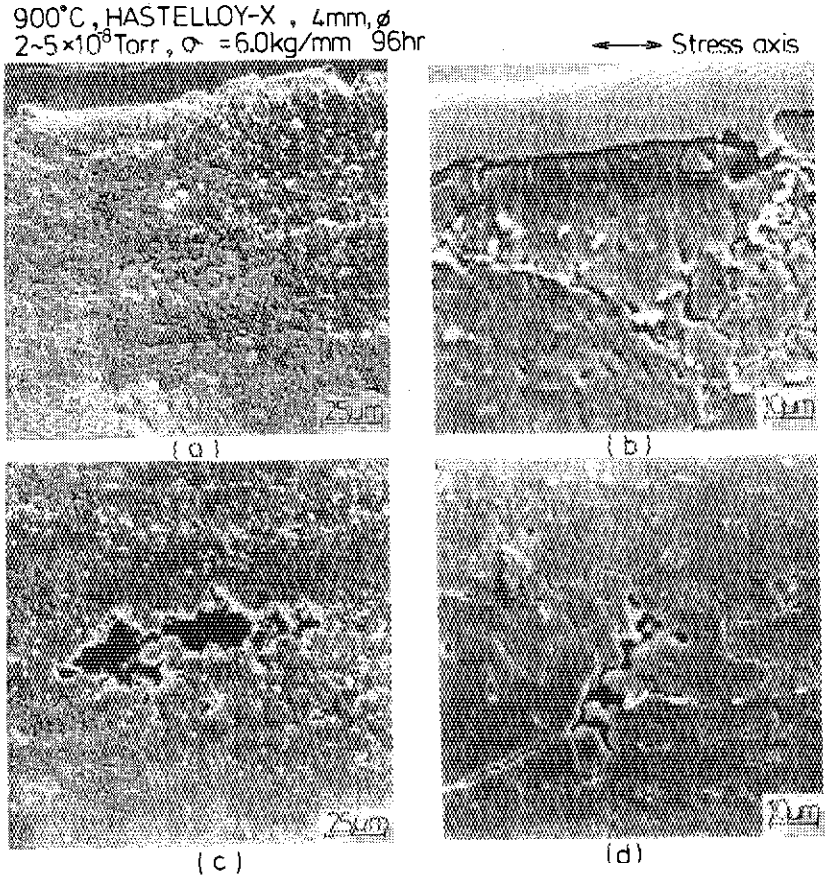

Fig.12 Microstructure at the vertical section of Hastelloy-X after creep tests in ultra-high vacuum at 900°C.

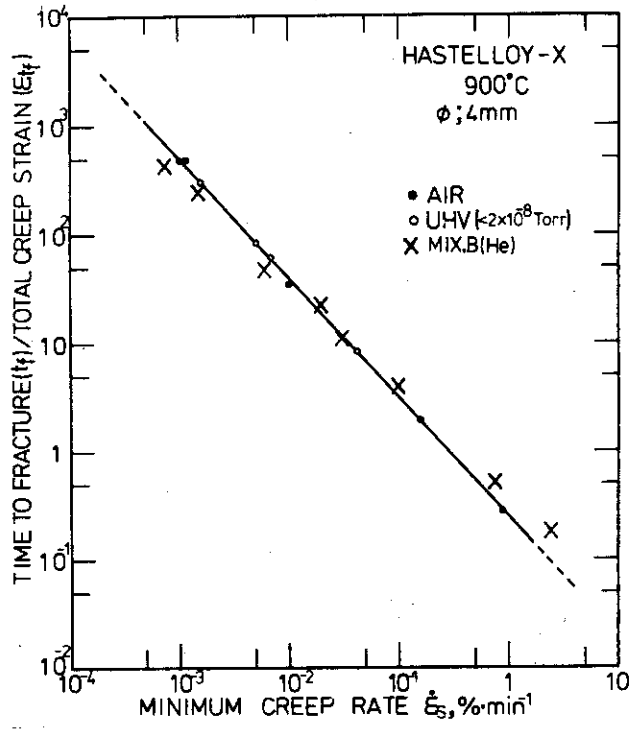

Fig.13 The relationship of the ratio of rupture time to rupture elongation and the steady state creep rate obtained in various environments.

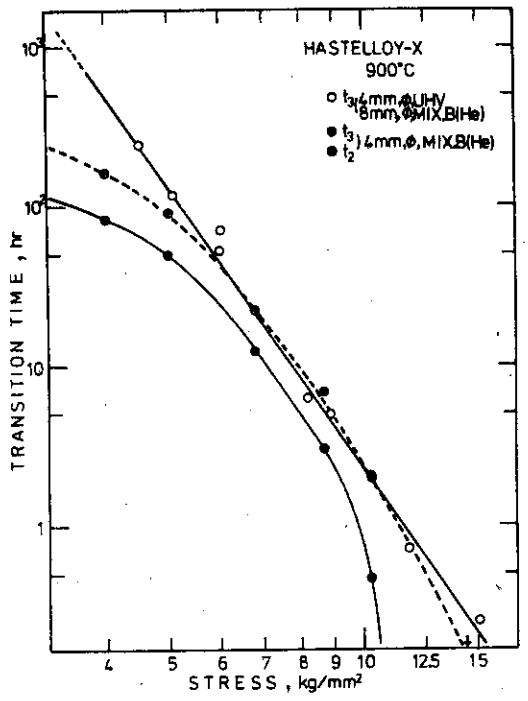

Fig.14 The dependence of the time of strain rate transition on the applied stress and the effect of environments.

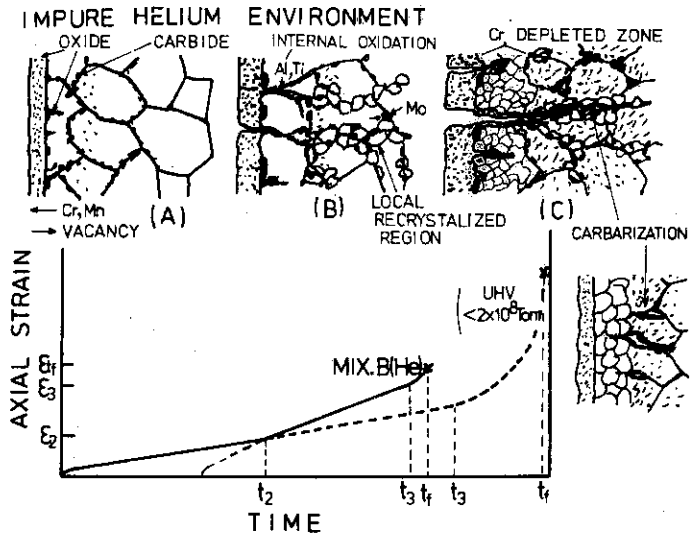

Fig.15 Schematic of a possible sequence of accelarated creep deformation and material degradation under the influence of a carburizing environment.