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CHANGES IN THE MECHANICAL PROPERTIES OF HASTELLOY X WHEN EXPOSED TO A TYPICAL GAS-COOLED REACTOR ENVIRONMENT*

MASTER

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Abstract

The helium used in a gas-cooled reactor will contain small amounts of H_2, CO, CH_4, H_2O, and N_2 which can lead to oxidation and carburization/decarburization of structural materials. Long-term creep tests were run on Hastelloy X to 30,000 h at 649 to 871°C. It was found that extensive carburization occurred, the minimum creep rate and time to rupture were equal in air and impure helium environments, and the fracture strain was less in helium than in air. Thermal exposure in the temperature range of 538 to 871°C resulted in the reduction of ductility in impact and tensile tests at ambient temperature, and this reduction was greater when the exposure was in impure helium rather than in air. A modified alloy with lower chromium and 2% titanium resisted carburization.

Introduction

A number of gas-cooled reactor systems are in operation in this country and in Europe and several more advanced systems have been proposed. A common feature of all the systems is that they use pressurized gas as a heat-transfer medium, and the more advanced systems utilize helium. For reasonable efficiencies to be obtained, the proposed service temperatures have continued to increase to values

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in the 800 to 1000°C range. The systems generally contain graphite and other carbonaceous contaminants, so small amounts of contaminants such as CO, CH_4, H_2, H_2O, and N_2 would be expected in the gas stream.

Because of the high pressures and high temperatures involved, structural materials having good high temperature strengths are needed. The iron-base alloys such as the austentic stainless steels are too weak for consideration, and the solid solution-strengthened nickel-base alloys are the weakest and simplest alloys that can be considered. The precipitation-hardened nickel-base alloys are very complex, and it is questionable whether this strengthening mechanism is stable at the desired service temperatures. The cobalt base alloys offer the next increment of increasing strength, but their cost is already prohibitive and likely to increase further. Molybdenum is the next strongest usable alloy, but the low ductility associated with welding or any other fabrication process that causes recrystallization is a strong obstacle to the use of molybdenum in complex engineering systems.

The impure helium will react chemically with the structural materials in at least two ways. The first chemical reaction is oxidation and is associated with the fact that the traces of CO and H_2O present in the helium are oxidizing to most of the candidate alloys. The second reaction is carburization or decarburization and depends on the amounts of CO, CH_4, H_2, and H_2O present. In most of the candidate alloys, the activity of carbon is low enough that most conceivable environments would be carburizing. Alloys such as Fe-2.25% Cr-1 Mo steel could encounter conditions where decarburization would occur.

Although there are numerous alloys that may be useful for specialized applications in gas-cooled systems, the alloy that would currently be selected as the predominant structural material is a Ni-Cr-Fe-Mo alloy bearing the trade name of Hastelloy* X. The specified chemical limits of this alloy are given in Table 1 along with the specific composition of the two heats of material evaluated in the current study. Hastelloy X is a wrought nickel-base solid solution alloy of nickel-chromium-iron-molybdenum which relies mainly on molybdenum as the solution soltuion strengthener, although it also contains cobalt and tungsten. The alloy composition is such that it can form intermetallic compounds that can reduce the room temperature impact energy following long term aging. Despite this problem, Hastelloy X has been used extensively in making parts for jet aircraft and in the petrochemical industry.

Several studies[1–5] have been performed on Hastelloy X related to the gas-cooled reactor application, and many of the results of these studies are pertinent to the present discussion.

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*Hastelloy is a registered trademark of the Cabot Corporation.

a) Over the temperature range of 538 to 871°C Hastelloy X experiences reduction in ambient temperature ductility; primarily due to the precipitation of carbides, but some σ and μ phases formed at the high temperatures.

b) The extent of internal oxidation observed is shallow at 900°C and lower, being 10 to 20 µm in 10,000 h.

c) The kinetics of carburization become high at temperatures of 900°C and above so that carburization to a depth of about 10 mm would be predicted for 100,000 h.

d) The creep strength does not appear to be affected by carburization at the conditions studied.

e) There is considerable disagreement of test results as to whether carburization degrades the fracture strain below that caused by thermal aging. Studies at the same laboratory showed considerable heat-to-heat variation.

The purpose of the present study was to extend the data base for Hastelloy X, and particular emphasis was placed on ductility degradation during creep and aging studies. Aging times up to 20,000 h and creep test times to 30,000 h were involved. The details of the test equipment were reported,[5] but the most important feature is that helium test gas is premixed in standard cylinders and distributed to the test chambers through a manifold system. The composition of the test gas is monitored by on-line chromatography, and the flow rate is adjusted in the range of 15 to 100 cc/min to keep the gas composition constant through the test chamber. The helium composition in the test chamber is (in µ atmospheres) 337 H_2, 32 CH_4, 19 CO, 2 H_2O, and <0.5 N_2. Oxygen is reacted out with the H_2 by passing the gas through a furnace at 500°C. The test specimen used has a gage section 3.2 mm in diam by 2.5 cm long.

Test Results — Hastelloy X

The stress-rupture results of several tests on two heats of Hastelloy X are given in Fig. 1. Several tests are still in progress and the data points for these tests are noted with an arrow. Within the scatter of the results, the rupture life is unaffected by whether the test environment is air or helium. A significant downturn in rupture life occured at 760°C. Two of the points indicating this downturn have actually failed and two points represent tests still in progress. The two tests in progress will either help confirm the downturn or indicate that the two points obtained thus far are anomolous. The minimum creep rate data shown in Fig. 2 do not indicate the short fall. These data also do not indicate an effect of environment or a detectable variation in the properties of the two heats.

The fracture strains of the creep test specimens are plotted in Fig. 3. They show the expected trend of decreasing strain with decreasing rupture life. The creep strain for the tests run in impure helium is about a factor of 2 lower than that for tests run in air, but there are three points that show the opposite trend. However, the lowest strain noted was 12.5%, and this is more-than-adequate. It may appear inconsistent that environment did not have a detectable effect on minimum creep rate or rupture life, but did have an effect on creep strain. Since the minimum creep rate actually applies over one-half or less of the creep curve and a large part of the strain occurs during the last few hours of the test, it is quite reasonable that the creep strain be altered without either of the other two parameters being influenced.

Post-test carbon analyses are shown in Fig. 4 of entire sections of the test samples. At 760°C and down the kinetics of carburization are such that the section does not exhibit detectable carburization. At 816 and 871°C significant carburization is readily detected.

Several aging experiments were run and the most significant property changes were those associated with the ductility in short-term tests at ambient temperature. As shown in Fig. 5 the changes in the strength parameters were reasonably small at aging temperatures of 538 and 871°C. The most significant strength changes occurred at 704°C where aging 2500 h in inert gas caused a 40% increase in yield strength and aging 10,000 h in impure helium caused a 60% increase in yield strength. The maximum increase in ultimate tensile stress as a result of aging at 704°C was about 20% for the samples aged in inert gas and 40% for those aged in impure helium. Thus, the strength changes were greater in impure helium than in inert gas. The fracture strains for these samples are shown in Table 2 and the samples aged in impure helium generally fractured at lower strains.

A similar group of samples containing transverse welds was aged in inert and impure helium and comparative fracture strain data are given in Table 3. The fracture strains are lower for the samples annealed in impure helium at temperatures above 593°C than for those aged in an inert environment

Impact samples illustrate even more effectively the reduction in fracture toughness of Hastelloy X with aging. As shown in Fig. 6, the fracture toughness is reduced appreciably by aging at temperatures of 538 through 871°C in an inert environment. Although the reduction occurs in much shorter times at 871°C, the impact energy after aging at 704 and 871°C eventually gets below 13.6 J (10 ft-lb). The scanning electronmicrographs shown in Fig. 7 for impact samples aged 20,000 h show the transition of the fracture mode from ductile transgranular tearing in the as-received material to rather brittle intergranular fractures in the aged samples. Particularly at 704 and 871°C the fracture path seems to follow the grain-boundary carbide network. Elemental analysis of the fracture surface indicates a high concentration of molybdenum, the major constituent in the carbide. The numerous cracks running transverse to the fracture plane indicate the ease in nucleating cracks in these brittle samples. Unfortunately, duplicate samples were not aged in impure helium to assess whether carburization would result in even lower impact values.

Test Results — Other Materials

All of the alloys being evaluated for this application were actually developed for some other use, so it is quite possible that an alloy could be developed for use with impure helium that would be more suitable than Hastelloy X. Two basic trends in alloying suggest themselves. First reduce the amount of chromium in the alloy in an effort to reduce the thermodynamic driving force for the alloy to absorb carbon. Second add elements such as titanium or aluminum which are known to promote the formation of very tenacious and impervious oxides. Titanium-modified Hastelloy N which satisfies both of these requirements was at least partially developed for another application,[6] and the results of carburization tests on this alloy and Hastelloy X are compared in Table 4. Note that Hastelloy X was severly carburized whereas the carbon content of the titanium-modified Hastelloy N was essentially unchanged. The development of titanium-modified Hastelloy N was carried far enough to demonstrate that the alloy could be melted and fabricated into standard mill products by conventional techniques. Weldability and long-term stability also looked very good.

Discussion of Results

Long-term creep tests have been performed on Hastelloy X in impure helium and air to times up to 30,000 h. The results fail to show a detectable effect of environment on the minimum creep rate and the time-to-rupture, but the strain at rupture is less in helium than in air. It seems unusual that carburization extensive enough to increase the average carbon content of the entire cross section by about 50% would not cause a change in creep behavior. Since the matrix of the alloy is likely already saturated with carbon, the additional carbon would go to form carbides that may be too coarse to cause strengthening and would lead to the depletion of the matrix in molybdenum and cause a decrease in strength. It seems rather unusual that with all the possible effects that carburization could have on creep behavior, the net is no effect. Long-term tests should be continued to assume that there are not environment compositions and temperatures that could lead to significant creep effects.

The influence of impure helium on the fracture strain of Hastelloy X is significant. Although the lowest value of 12.5% observed thus far is adequate, the trend of decreasing fracture strain with increasing rupture life is obvious. Since the fracture path is likely defined by nearly continuous sheets of carbide particles, it is logical that extensive carburization will continue to decrease the fracture strain in helium below that observed in air.

A characteristic of Hastelloy X is that heating in the range of 500 to 900°C causes large reductions in the elongation and fracture toughness at ambient temperature. This reduction in ductility is attributed largely to carbide precipitation,[1] and it is difficult to imagine that extensive carburization would not make the degree of embrittlement more severe. In the current study there were only a few instances where identical tensile samples were aged in inert and impure helium, and the general trend was that the samples aged in impure helium had lower fracture strains in ambient temperature tensile tests than did those aged in inert gas.

Each of the processes just discussed which degrade the properties of Hastelloy X is thermally activated and its rate depends exponentially upon temperature. Thus, at some temperature the rate of degradation is tolerable with respect to the desired service life and material properties, and this temperature is the allowable service temperature. For Hastelloy X the temperature-limiting process will likely be the combined thermal aging and carburization which leads to unacceptable fracture toughness at lower temperatures encountered when the system is being started or shut-down.

Whereas the data scatter and inconsistencies noted by different experimenters for various heat of material are a source of confusion, they also offer hope that the degreee of degradation can be reduced somewhat by the control of residual elements in the Hastelloy X. Our very limited experiments with titanium-modified Hastelloy N show that carburization can be reduced by chemical modifications. Thus, if the allowable service temperature for standard Hastelloy X is too low, it is likely that chemical modifications can lead to an alloy with suitable properties.

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Heat Number	Content (wt %)											
	Ni	Cr	Co	Mo	Fe	Si	C	Mn	S	W	P	Other
Hastelloy X, Specified Limits	Bal	20.5–23.0	0.5–2.5	8.0–10.0	17.0–20.0	1.0[a]	0.05–0.15	1.0[a]	0.03[a]	0.2–1.0	0.04[a]	0.01 B[a]
Hastelloy X, Heat 4936	Bal	21.82	1.68	9.42	19.09	0.44	0.07	0.58	>0.005	0.63		
Hastelloy X, Heat 2792	Bal	21.25	1.94	8.99	18.96	0.41	0.10	0.57	>0.005	0.56		

[a] Maximum.

Table 2. Tensile Fracture Strains of Hastelloy X Samples Tested at Room Temperature

~~Material~~	Aging Conditions		Fracture Elongation (%)	
	Time (h)	Temperature (°C)	Aged in Inert Gas[a]	Aged in Impure He[b]
~~Hastelloy X~~	0	0	52	
	2,500	538	55	
	10,000	538	43	43[c]
	20,000	538	47	
	2,500	704	9	
	10,000	704	18	11
	20,000	704	10	
	2,500	871	15	
	10,000	871	15	10
	20,000	871	18	

[a] Test section 6.35-mm diam by 31.8 mm (1.4-in. diam by 1.25 in.) long.

[b] Test section 3.18-mm diam by 25.4 mm (1.8-in. diam by 1.00 in.) long.

[c] Aged at 593°C.

Hastelloy X

Table 3. Room-Temperature Tensile Fracture Strains for Transverse Welds Aged for 10,000 h

~~Alloy~~	Aging temp. (°C)	Elongation at rupture (%)	
		Inert environment	Impure He
~~Hastelloy X~~	593	18.5	30.7
	650	6.1	
	704		4.1
	760	6.5	
	871	10.6	4.6

Table 4. Carbon Concentration of 0.28-mm-Diam (0.011-in.) Wire Exposed to Helium

Exposure Conditions	Average Carbon Concentration (%)	
	Hastelloy X[a]	Titanium-Modified Hastelloy N[b]
As Received	0.0993	0.0208
100 h at 871°C	0.242	0.0242
1028 h at 871°C	0.438	0.0166

[a] Ni—22% Cr—18.5% Fe—9% Ni

[b] Ni—7% Cr—4% Fe—12% Mo—2% Ti

Fig. 1. Stress-rupture properties of Hastelloy X.

Fig. 2. Minimum creep rate of Hastelloy X.

Fig. 3. Relation of creep studies to rupture life for Hastelloy X.

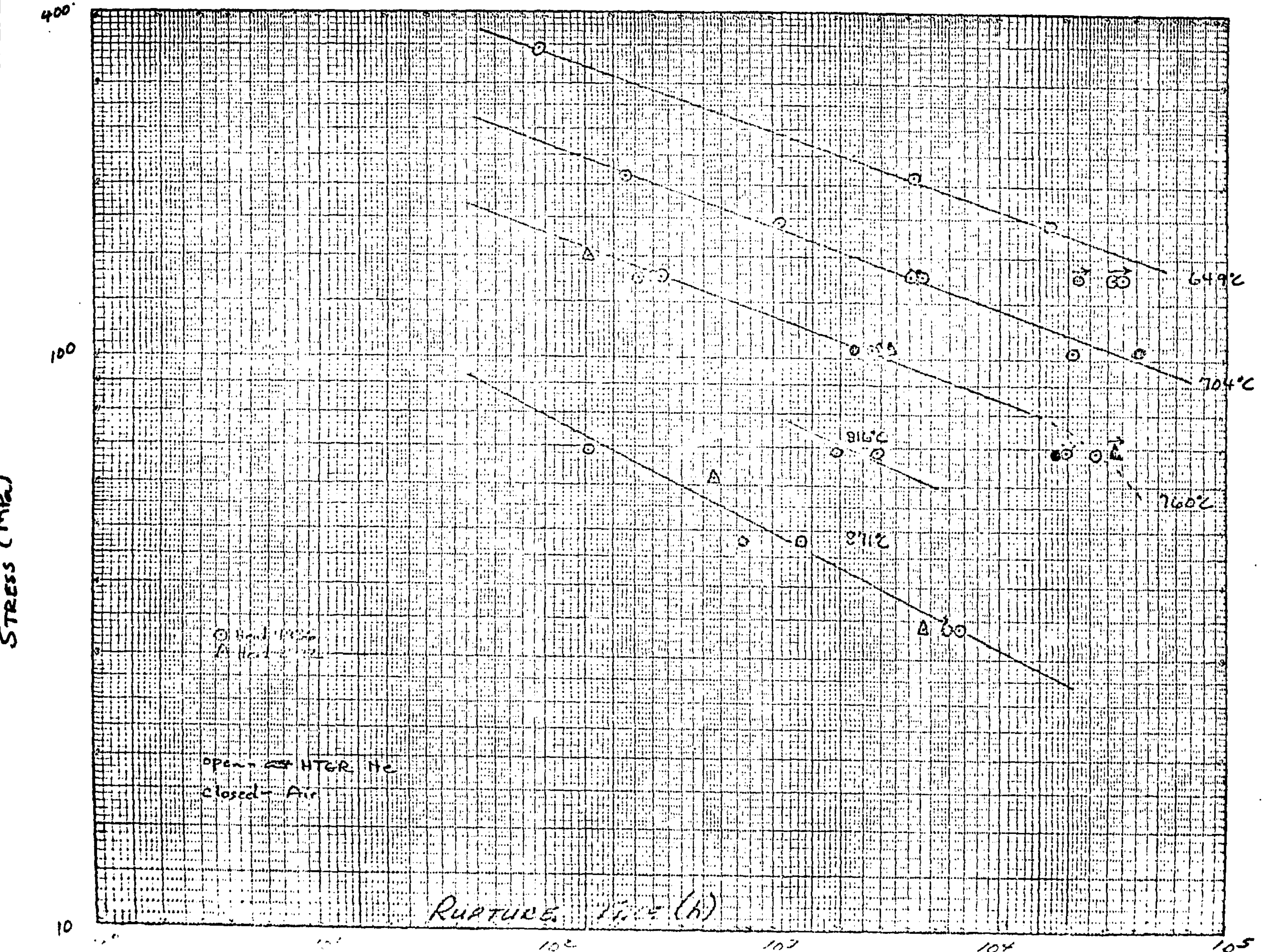
Fig. 4. Carbon content of Hastelloy X exposed to impure helium.

Fig. 5. Influence of aging on the tensile properties of Hastelloy X at 25°C.

Fig. 6. Effect of aging on impact properties of Hastelloy X.

Fig. 7. Fracture surfaces of Hastelloy X impact samples aged in inert gas and fractured at 25°C. a) as received, 55×, b) aged 20,000 h at 538°C 55×, c) aged 20,000 h at 704°C 55×, d) aged 20,000 h at 871°C 55×, e) 300× photomicrograph of surface in "d," but typical of "c" also.

①


400
100
10
649°C
704°C
760°C
816°C
871°C
Heat [illegible]
Heat [illegible]
open — HTGR He
closed — Air
STRESS (MPa)
RUPTURE TIME (h)
10^1
10^2
10^3
10^4
10^5

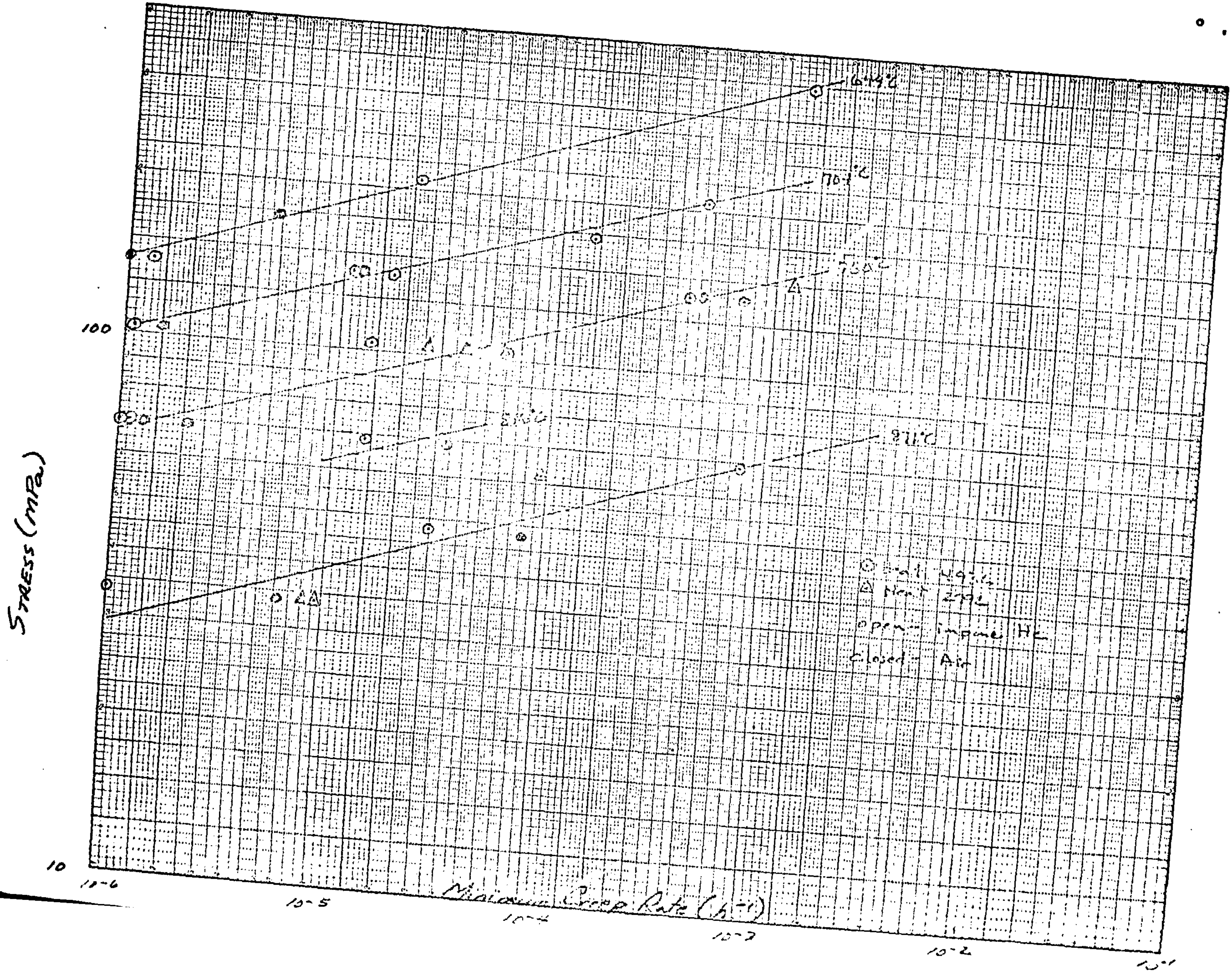

649°C
704°C
760°C
816°C
871°C
○ Heat 4924
△ Heat 2792
Open – Impure He
Closed – Air
Stress (MPa)
100
10
Minimum Creep Rate (h⁻¹)
10⁻⁶
10⁻⁵
10⁻⁴
10⁻³
10⁻²
10⁻¹

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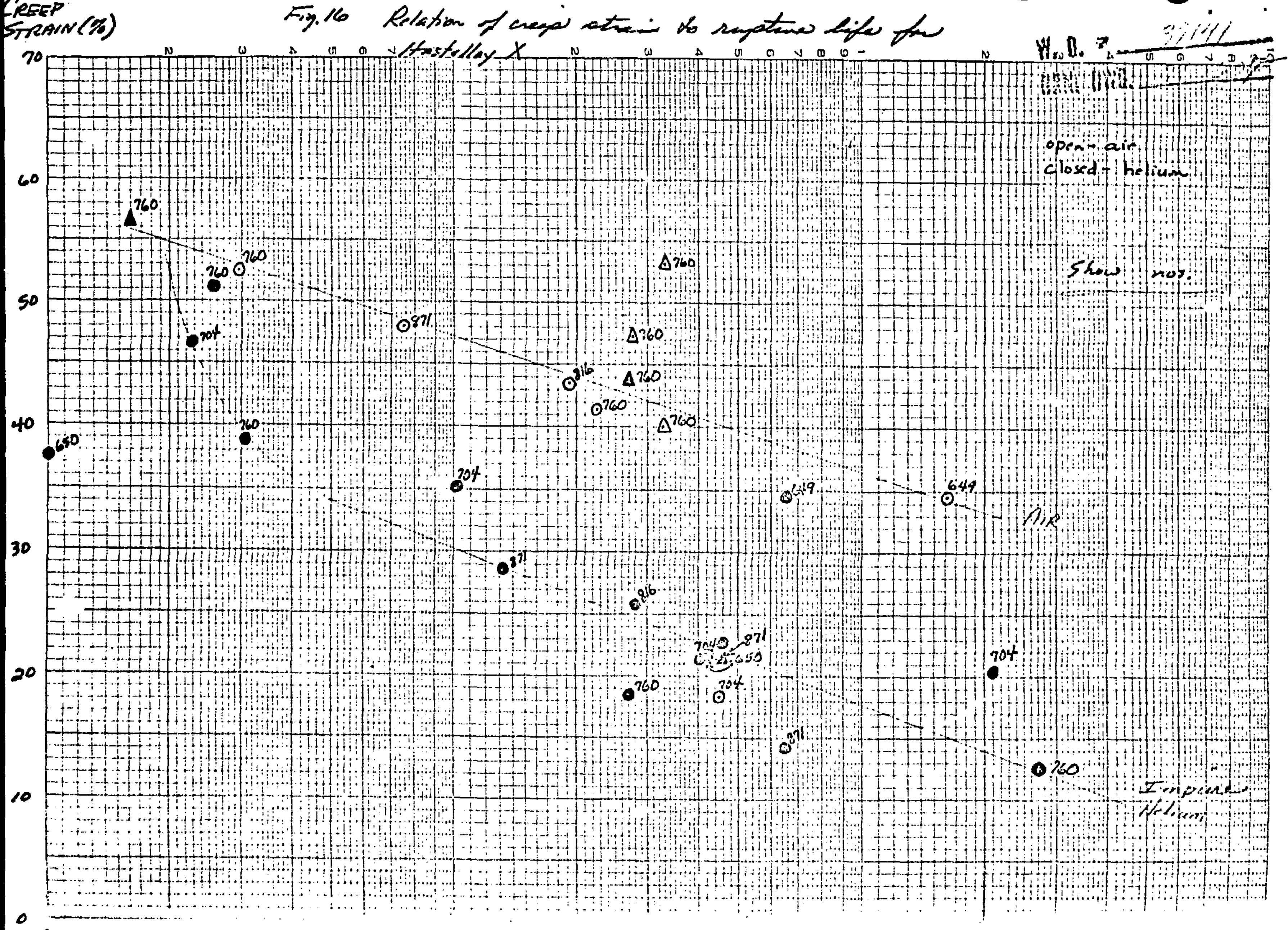
Fig. 16 Relation of creep strain to rupture life for Hastelloy X



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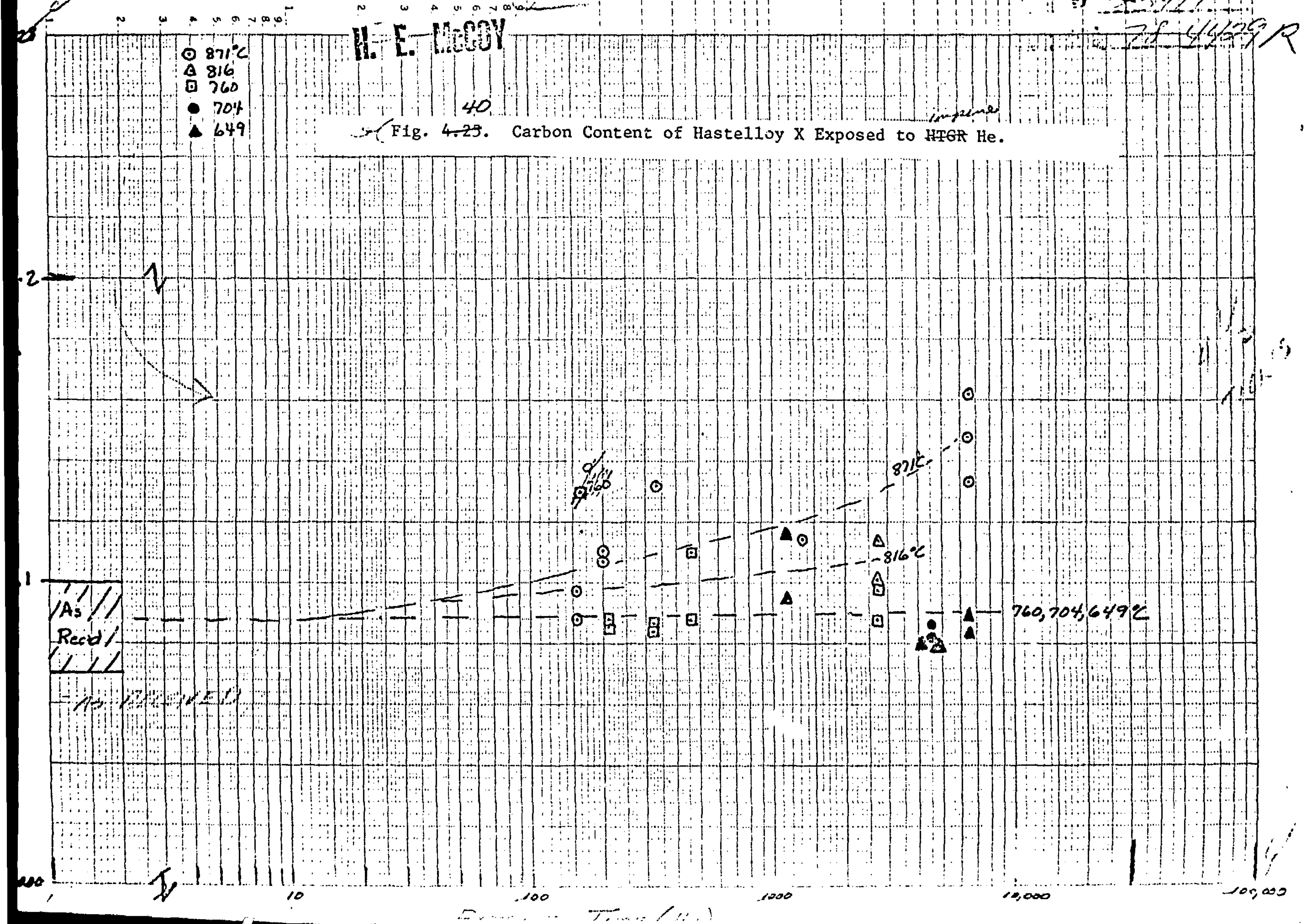
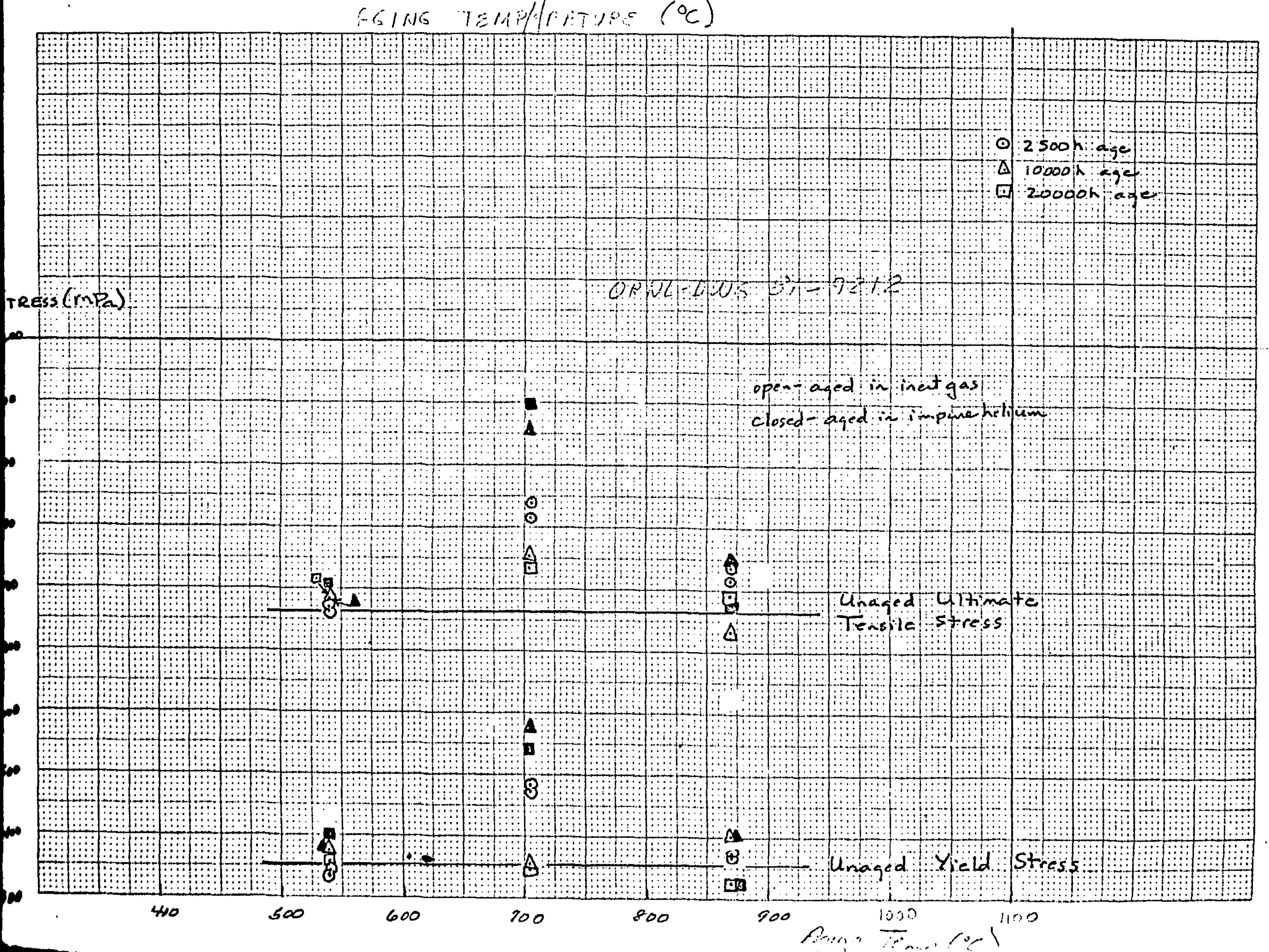
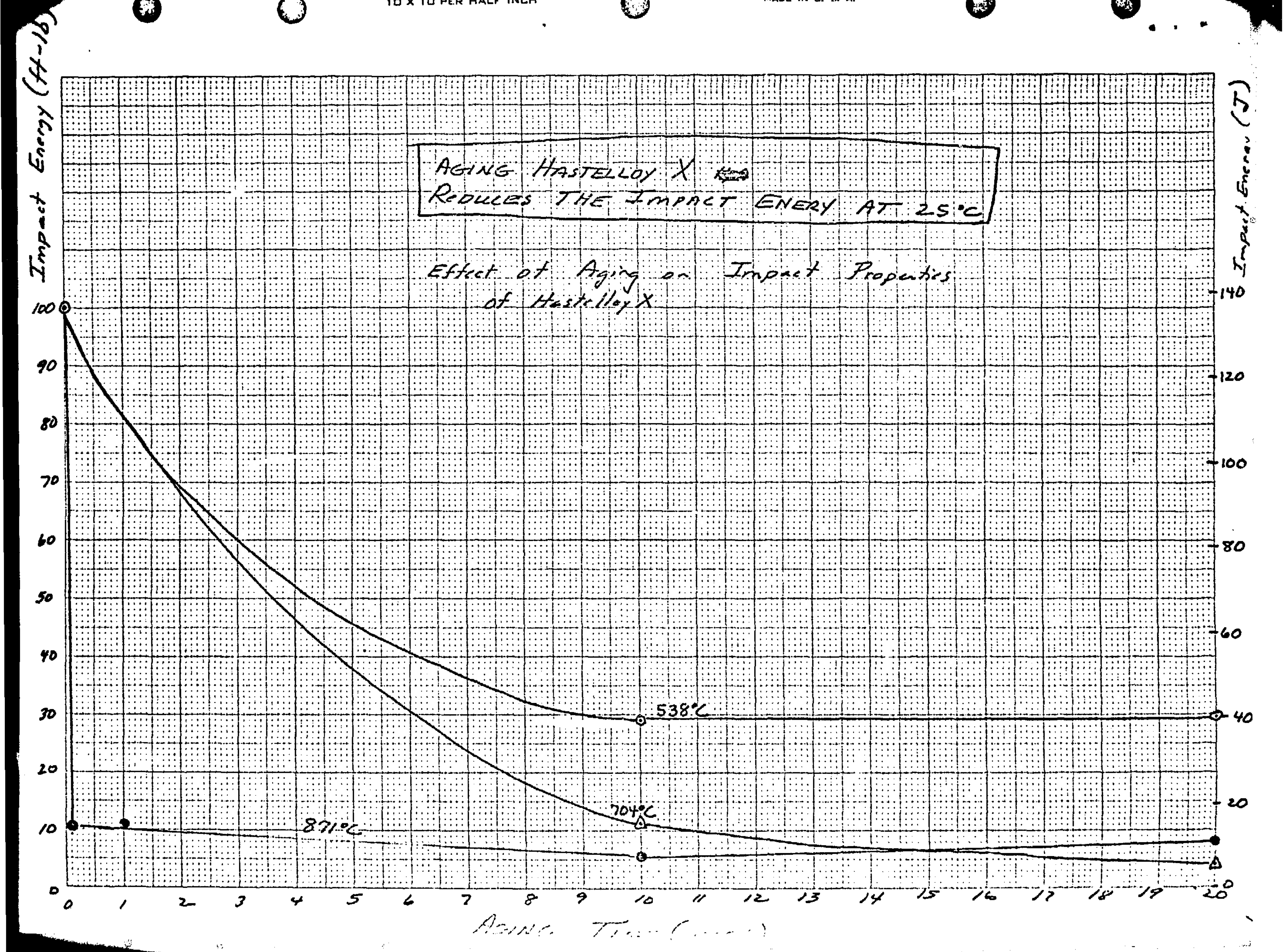


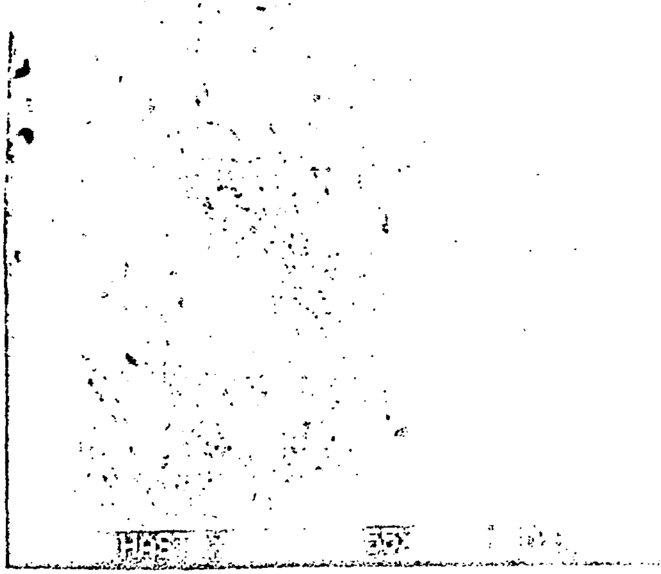
Fig. ~~4.25~~ 40. Carbon Content of Hastelloy X Exposed to ~~HTGR~~ impure He.

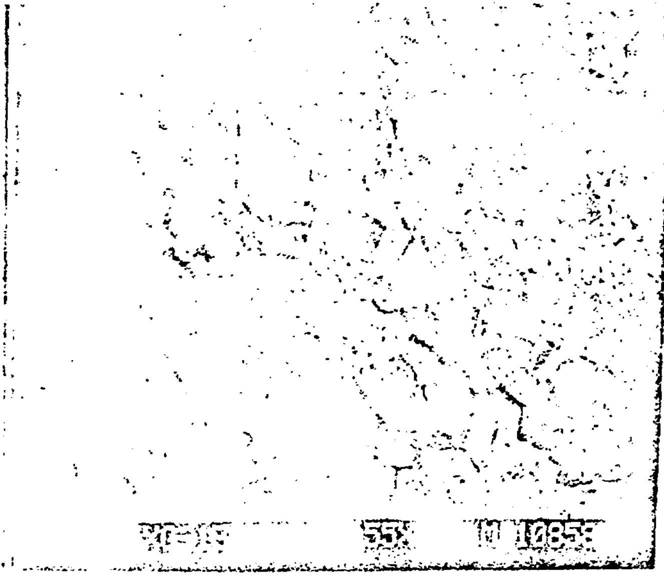

AGING TEMPERATURE (°C)
ORNL-DWG 87-9212
TRESS (mPa)
⊙ 2500h age
△ 10000h age
⊡ 20000h age
open - aged in inert gas
closed - aged in impure helium
Unaged Ultimate Tensile Stress
Unaged Yield Stress
400
500
600
700
800
900
1000
1100
Aging Temp (°C)



AGING HASTELLOY X REDUCES THE IMPACT ENERY AT 25°C

Effect of Aging on Impact Properties of Hastelloy X a





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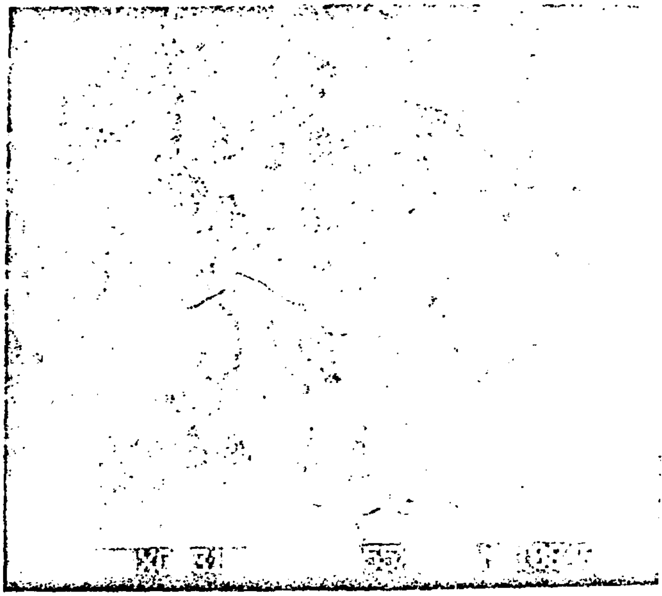

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