77 to 1200 K Tensile Properties of Several Wrought Superalloys after Long-Term 1093 K Heat Treatment in Air and Vacuum

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The 77 to 1200 K tensile properties of approximately 1.3 mm thick wrought sheet Co-base Haynes alloy 188 and Ni-base Haynes alloy 230 and Inconel 617 have been measured after heat treatment in air and vacuum for periods up to 22,500 h at 1093 K. Significant changes in structure were produced by prior exposures, including precipitation of second phases and, in the case of heat treatment in air, oxide scale and surface-connected grain boundary pits/oxides, as deep as 50 to 70 μm, in all three superalloys. Due to the geometry of the experiment, the vacuum-exposed samples were protected from loss of volatile elements by evaporation; hence, such specimens were simply given 1093 K anneals in an innocuous environment, which produced very little surface attack. Compared to the properties of as-received alloys, prior exposure tended to reduce both the yield strength and ultimate tensile strength, with the greatest reductions at 77 and 298 K. The most dramatic effect of heat treatment was found in the low-temperature residual tensile elongation, where decreases from 40 to 5% at 77 K were found. Ductility is the only property that was found to have a consistent dependency on environment, with air exposure always yielding less tensile elongation than vacuum exposure.

Keywords

cobalt based alloys, heat treatment, nickel based alloys, tensile properties, vacuum, superalloys

1. Introduction

AS part of materials support for a proposed solar dynamic power system[1] to convert heat to electricity for Space Station Freedom, several superalloys were subjected to long-term exposure at 1093 K to molten LiF-22CaF_2, its vapor, and vacuum.[2,3] Interest in this salt stems from its consideration as a thermal energy storage media, where the solid to liquid phase transformation is used to store heat.[4] Although the primary source for potential failure of the containment alloys would involve reactions between the F-based salt and superalloys, elevated temperature exposure of Cr-rich alloys in vacuum for long periods of time could also affect mechanical properties. In this case, the volatile elements evaporate from exposed surfaces and lead to changes in structure and behavior.[5]

Because the potential corrosion problems associated with the solar dynamic system are nontraditional, the superalloys also have been annealed in air for long periods of time. Comparison of the behavior after air exposure with the results from salt or vacuum exposures would then permit assessment of any extraordinary effects due to salt corrosion or evaporation of the volatile elements. To this end, the Co-base alloy Haynes Alloy 188™ (HA 188) and the Ni-base alloys Haynes Alloy 230™ (HA 230) and Inconel 617™ (IN 617) have been annealed for 4900, 10,000 and 22,500 h at 1093 K in air. Upon completion of these heat treatments, changes in the near-surface and subsurface microstructures were evaluated and reported in Ref 6. As outlined in Table 1, oxidation leads to weight gains and surface-connected grain boundary pits/oxides in all three superalloys, with both the weight gains and depths of intergranular attack being dependent on the square root of time. In terms of visible damage, grain boundary attack at the surface was particularly significant, where after 22,500 h the depth of the grain boundary pits reached from ~50 μm for HA 188 and HA 230 to ~70 μm for IN 617. Although precipitation of second phases, mainly carbides, occurred in all three materials, the degree was less in IN 617. No change in grain size was observed in HA 230 and IN 617; however, HA 188 did appear to exhibit some grain growth.

The 77 to 1200 K tensile properties of HA 188, HA 230, and IN 617 have been measured after long-term heat treatment in vacuum and air at 1093 K in an effort to assess the influence of prior exposure on mechanical properties. Because of the geometry of the experiment, the vast majority of the superalloy samples were not subjected to any surface attack during vacuum heat treatments.[6] Hence, the tensile data for vacuum-exposed alloys generated in this study simply characterized the influence of prolonged heating on residual mechanical properties. This article compares the tensile properties and microstructures of exposed and tested materials to those determined for as-received alloys.

2. Experimental Procedures

Approximately 1.27 mm thick by 0.6 m by 1.2 m sheet of HA 188, HA 230, and IN 617 were purchased for this study; specific chemistries, vendor, and heat numbers are reported in Table 2. For simplicity and ease of fabrication, pin and clevis tensile-type specimens (108 mm long by 19 mm wide with a 31.8 mm by 9.8 mm gage section) were directly punched from

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Table 1 Summary of weight change and microstructural results for superalloys exposed to air at 1093 K

Alloy	Observation
HA 188, HA 230, IN 617	Weight gain increased with $\sqrt{t}$; depth of surface-connected grain boundary pitting/oxidation increased with $\sqrt{t}$
HA 188, HA 230	Significant grain boundary and intragranular carbide precipitation
IN 617	Minor carbide precipitation
HA 188	Grain growth (20 to 30 μm in 22,500 h)

Table 2 Characterization of starting materials

Material	Vendor	Heat/lot	Composition, wt%
HA 188	Cabot Corp.	188061773	0.005B-0.11C-21.69Cr-1.95Fe-0.048La-0.72Mn-23.03Ni-0.013P-<0.002S-0.38Si-14.02W-Co
HA 230	Cabot Corp.	1830557171	0.004B-0.3Al-0.10C-22.00Cr-1.22Fe-0.009La-0.61Mn-1.29Mo-0.01P-<0.002S-0.39Si-14.01W-Ni
IN 617	INCO Alloys International, Inc.	XX0130UK	1.05Al-0.002B-0.06C-13.46Co-21.83Cr-0.08Cu-1.66Fe-0.14Mn-9.25Mo-<0.001S-0.11Si-0.24Ti-Ni

Table 3 Summary of exposures at 1093 K

	Vacuum	Air
HA 188	400, 2500, 4900, 10,000, and 22,500 h	4900, 10,000, and 22,500 h
HA 230	400, 2500, and 10,000 h	4900, 10,000, and 22,500 h
IN 617	400, 2500, and 7914 h	4900, 10,000, and 22,500 h

the alloy sheet with the gage length parallel to the sheet rolling direction for HA 188 and HA 230. Due to a misinterpretation of the sheet orientation, the IN 617 samples were punched with their gage lengths perpendicular to the sheet rolling direction.

Tensile samples were exposed in air at 1093 K in groups of ~50 specimens arranged in racks that maintained about a 3 mm separation distance between individual samples. Three racks of samples for each of the superalloys were placed in a large muffle furnace at room temperature and then heated over a period of 5 h to 1093 K. With completion of one of the planned exposures, the furnace was allowed to cool to room temperature prior to removal of the rack of samples. In addition to these furnace shutdowns, unplanned interruptions in the heat treatments also occurred due to the loss of electrical power.

Concurrent with the air exposures, racks of tensile-type specimens were also being exposed in vacuum. These heat treatments were undertaken at 1093 K in a cryogenically pumped vacuum of ~1.3×10^{-4} Pa or more. As was the case for the air exposures, none of the vacuum heat treatments were continuous due to planned shutdowns to regenerate the cryogenic pumps or remove racks of specimens. Although many unexpected disruptions in the vacuum heat treatments also occurred due to loss of utilities, the vacuum-exposed superalloy samples were never in contact with air at high temperatures. A summary of all the air/vacuum exposure conditions for each

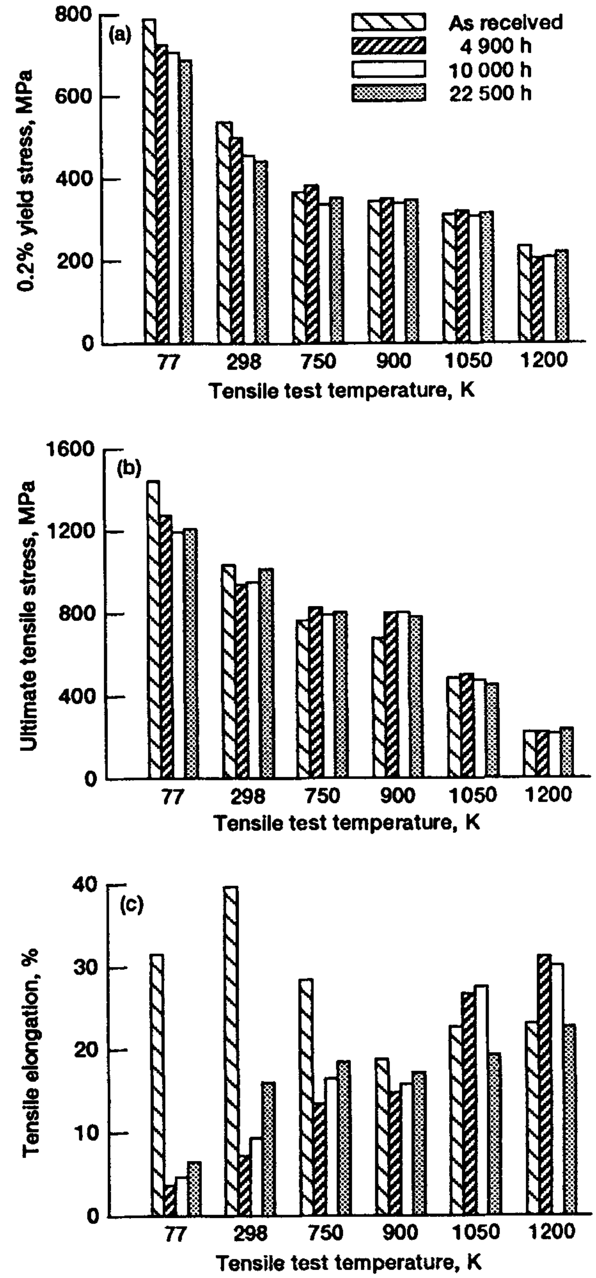

Fig. 1 0.2% yield stress (a), ultimate tensile strength (b), and tensile elongation (c) of HA 188 after long-term heat treatment in air at 1093 K.

alloy during the course of this program is presented in Table 3. Although 1093 K air exposures of all three alloys were conducted to 22,500 h, only HA 188 was given the longest heat treatment in vacuum. Shorter term vacuum heat treatments of HA 230 and IN 617 were undertaken due to a redirection of the overall Space Station program.

Following either air or vacuum exposure, the specimens were carefully removed, weighed, and then sent to a contractor for testing. Triplicate tensile tests at 77, 298, 750, 900, 1050, and 1200 K were conducted under contracts at the Surface En-

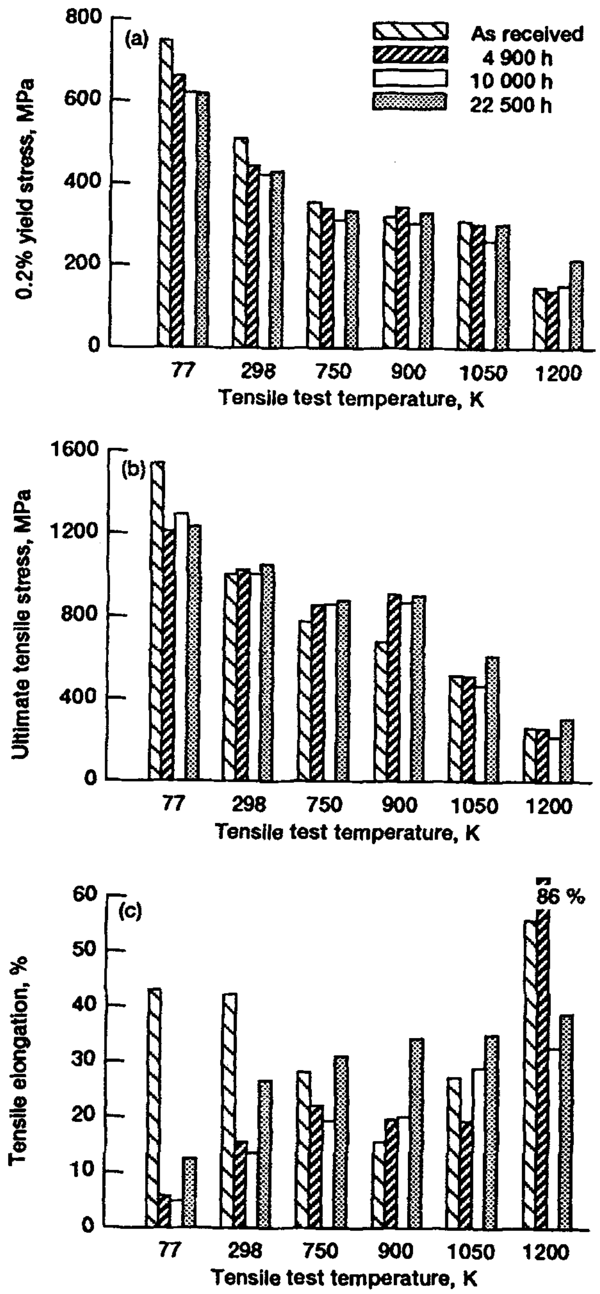

Fig. 2 0.2% yield stress (a), ultimate tensile strength (b), and tensile elongation (c) of HA 188 after long-term heat treatment in vacuum at 1093 K.

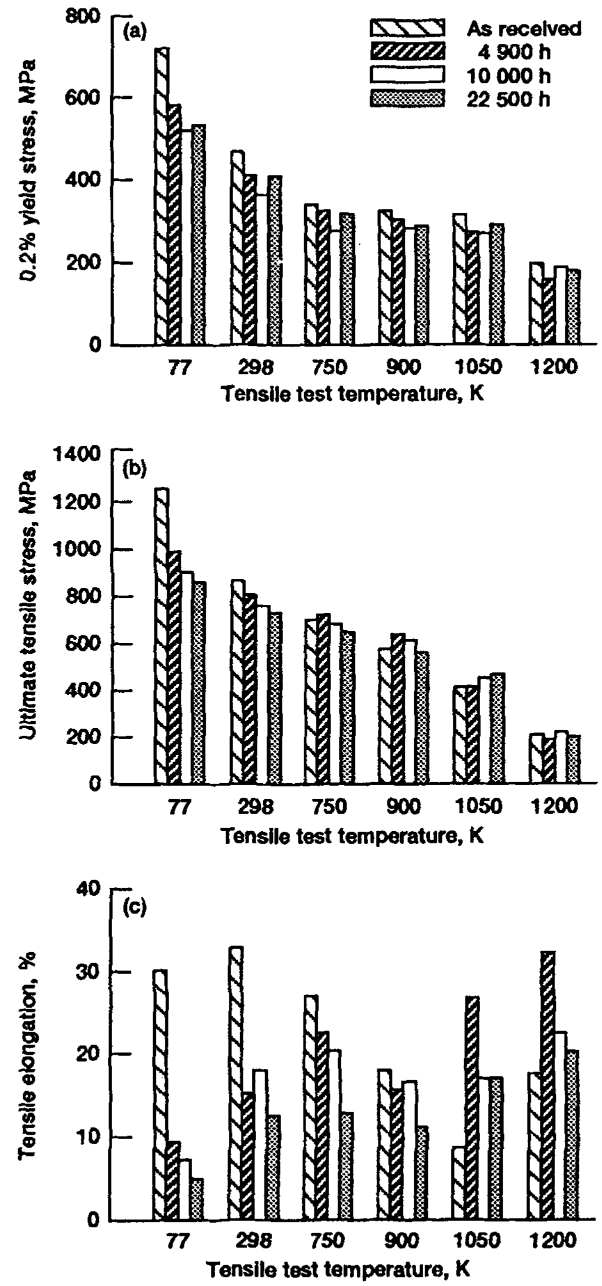

Fig. 3 0.2% yield stress (a), ultimate tensile strength (b), and tensile elongation (c) of HA 230 after long-term heat treatment in air at 1093 K.

gineering Center of the IIT Research Institute (NAS3-24976) and the Cortest Laboratories, Inc. (NAS3-25759) on vacuum-exposed, air-exposed, and as-received specimens. All 77 K tensile tests were conducted in liquid N_2, whereas the 298 K tests were undertaken in air. For testing at and above 750 K, the vacuum-exposed samples were tested in vacuum ($<10^{-3}$ Pa), whereas the air-exposed samples were conducted in air. As-received alloys were tested both in air and in vacuum at and above 750 K. Typical test data included 0.02 and 0.2% offset yield strengths, ultimate tensile strength (UTS), and elongation at failure; all mechanical properties were calculated on the basis of the original (pre-exposure) dimensions.

Standard metallographic procedures and X-ray methods were used to characterize the starting and tensile tested materials. Polished metallographic sections of as-received HA 188 were immersion etched with a mixture of 80 mL HCl and 8 mL H_2O_2, whereas exposed material was electrolytically etched at 4 V and 0.5 A in 95 mL H_2O + 5 mL HCl. All forms of HA 230 were electrolytically etched at 4 V and 0.5 to 0.75 A in slightly diluted acid solution consisting of 33 mL HNO_3, 33 mL acetic

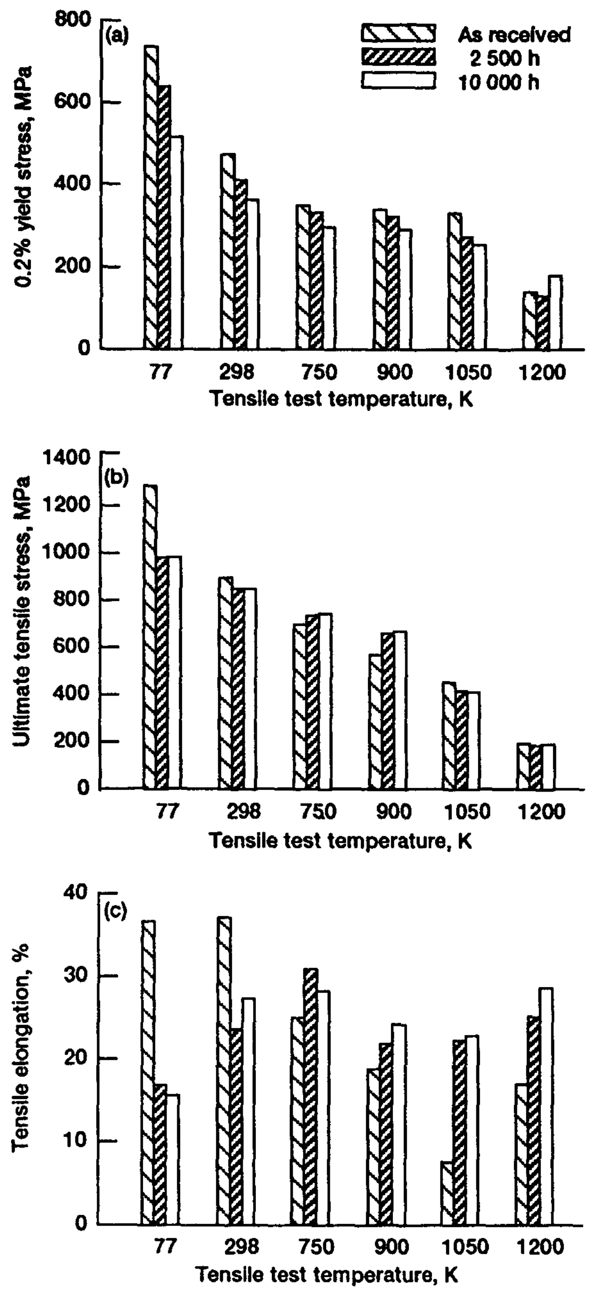

Fig. 4 0.2% yield stress (a), ultimate tensile strength (b), and tensile elongation (c) of HA 230 after long-term heat treatment in vacuum at 1093 K.

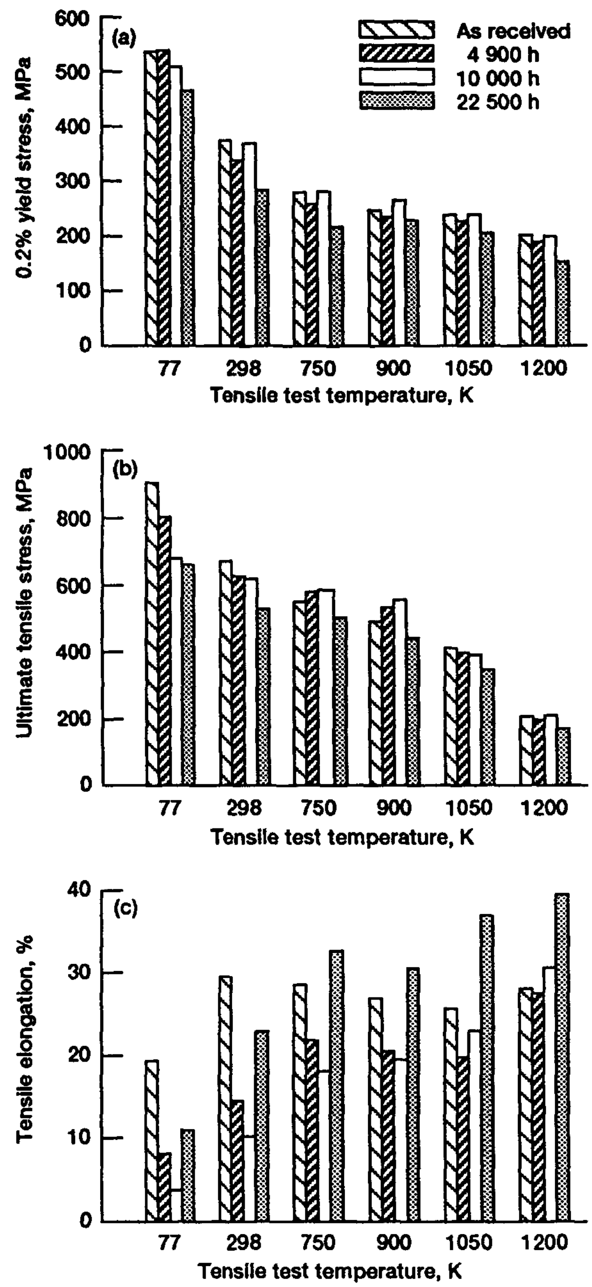

Fig. 5 0.2% yield stress (a), ultimate tensile strength (b), and tensile elongation (c) of IN 617 after long-term heat treatment in air at 1093 K.

acid, 33 mL H_2O, and 1 mL HF. IN 617 was also electrolytically etched at 4 V and 0.5 A for 2 to 3 s in a mixture consisting of 95 mL H_2O + 5 mL HCl.

3. Results

3.1 *Alloys*

A complete description of the effects of prolonged 1093 K air/vacuum exposure on the condition of each superalloy is given in Ref 6; the following briefly characterizes the structure of the three alloys prior to and after exposure.

3.1.1 As-Received Condition

The Ni-base alloys HA 230 and IN 617 and the Co-base alloy HA 188 sheet were supplied in a solution treated condition. Although HA 188 and IN 617 sheet possessed a normal silver metallic sheen, the HA 230 specimens had a dull oxide-like gray color due to the black anneal + pickling surface finish processing. Polished and etched metallurgical sections revealed that the Haynes alloys had reasonably uniform,

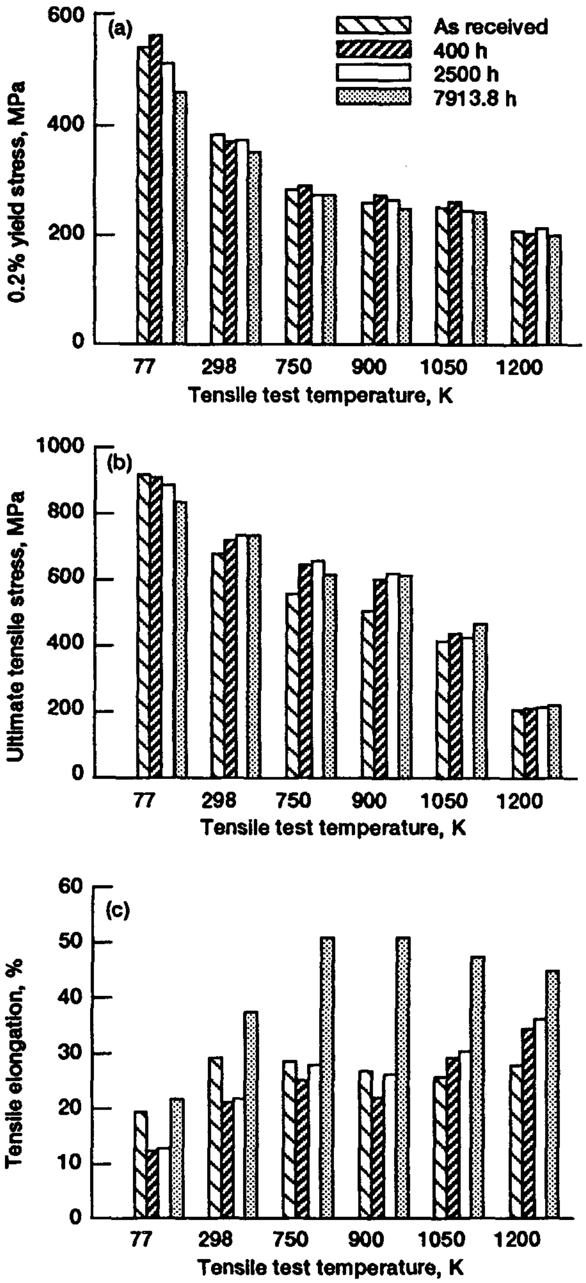

Fig. 6 0.2% yield stress (a), ultimate tensile strength (b), and tensile elongation (c) of IN 617 after long-term heat treatment in vacuum at 1093 K.

equiaxed grain structures with average diameters of about 20 μm for HA 188 and 35 μm for HA 230. HA 188 possessed a consistent structure comprised of grains with numerous twins and relatively few second-phase particles, whereas HA 230 had a relatively uniform dispersion of second-phase particles. A thin layer of ~10 μm grains was found at the IN 617 sheet surface, with a much larger grain diameter (~85 μm) in the sheet interior. Both IN 617 and HA 188 had relatively flaw-free, smooth surfaces; however, the surface of HA 230 contained pits as deep as 10 μm that formed at grain boundary/surface junctions due to the pickling process.

3.1.2 Air Exposure

After 1093 K air exposure, the surfaces of the three superalloys were covered with a dark, blackish scale that was comprised of Cr_2O_3 and Ni-based spinel for HA 230 and IN 617 or Co-based spinel for HA 188. For all three alloys, the weight increases could be described as a function of the square root of time at temperature, hence oxidation in air at 1093 K followed diffusion-controlled kinetics. Examination of the near-surface structure indicated that pits developed along the surface-connected grain boundaries in all three alloys. The depth of this pitting increased with time of exposure, where quantitative measurements of the depth of the intergranular pits (perpendicular to the sheet surface) indicated a square root of time dependency for all three superalloys.

3.1.3 Vacuum Exposure

The original bright, shiny surfaces of HA 188 and IN 617 were changed to a silvery, matte metallic finish after 1093 K vacuum exposure, whereas HA 230 retained its original dull, gray appearance after vacuum heat treatment. Because of the geometry of the specimen racks, the majority* of specimens lost little mass, as elements volatilized from the surface of one specimen were directly deposited on the surface of its nearest neighbor.

Such shielding effects negated major chemistry changes in the vast majority of vacuum-exposed samples; therefore, these specimens were simply given 1093 K heat treatments in an innocuous environment that produced very little surface attack even after 22,500 h at temperature. Subsequent evaluation of these vacuum-exposed samples would then allow assessment of the effect of prolonged thermal exposure without any interference from surface attack mechanisms.

3.2 *Tensile Properties*

The averaged residual 0.2% yield stresses, ultimate tensile strengths, and residual tensile elongation for air and vacuum-exposed HA 188 are presented in Fig. 1 and 2, respectively. In a like manner, the tensile properties for HA 230 and IN 617 after air exposure are illustrated in Fig. 3 and 5, whereas the data after vacuum exposures are given in Fig. 4 and 6 for these two alloys. With the exception of IN 617, the as-received condition for each alloy was tested both in air and vacuum, thus the designation "as-received" in Fig. 1 and 3 represents the results from air tensile testing, whereas "as-received" in Fig. 2, 4, and 6 signifies properties obtained in vacuum. As-received 617 was only tensile tested in vacuum; hence, the properties reported in Fig. 5 and 6 for the "as-received" material are identical. In general, the test environment had little effect on the tensile behavior of the as-received alloys. Compilations of the average tensile properties and their standard deviations for all alloy/exposure/tensile test temperature combinations are given in Tables 4 to 9. Because the figures and tables represent an enormous amount of data, only the major differences in proper-

*The two end specimens in each rack were the exceptions, where their outer surfaces did not have neighbors. Hence, volatilized elements from these unshadowed areas were lost to the furnace heat shields.

Table 4 Tensile properties of HA 188 after air exposure at 1093 K

Temperature, K	0.02% yield stress Avg MPa	0.02% yield stress Std dev MPa	0.2% yield stress Avg MPa	0.2% yield stress Std dev MPa	Ultimate tensile strength Avg MPa	Ultimate tensile strength Std dev MPa	Elongation, % Avg	Elongation, % Std dev
As-received								
77	677.5	25.1	790.4	25.8	1435.4	73.8	31.5	3.9
298	430.3	73.6	540.3	7.5	1027.1	7.2	39.8	1.2
750	331.2	5.9	362.5	1.5	755.0	3.4	28.6	0.8
900	313.8	2.5	335.4	5.9	667.8	3.7	19.1	0.7
1050	286.7	5.3	309.6	3.7	489.3	12.5	23.1	5.3
1200	210.5	6.3	234.2	8.4	235.6	9.1	23.7	3.5
4900 h								
77	607.7	91.4	725.6	72.2	1272.5	61.1	3.4	0.5
298	408.2	60.7	506.4	27.0	956.6	50.9	6.9	1.0
750	336.0	12.5	380.5	6.4	822.3	28.0	13.7	2.2
900	318.8	10.5	348.5	8.7	805.8	27.7	15.1	0.3
1050	278.4	13.9	318.0	21.2	510.4	8.4	27.3	1.5
1200	180.6	3.3	202.1	3.2	233.2	4.7	32.0	0.8
10,000 h								
77	579.2	19.2	708.6	35.9	1187.9	12.1	4.4	0.2
298	388.3	32.5	458.0	19.3	951.7	45.6	9.3	0.5
750	306.2	4.3	335.8	1.5	789.9	20.5	16.6	3.7
900	315.2	13.0	336.9	11.8	810.1	7.7	15.9	1.4
1050	275.3	17.4	306.9	18.1	484.5	6.0	28.2	1.9
1200	189.3	3.8	206.3	2.2	229.5	5.2	30.8	2.4
22,500 h								
77	581.3	50.5	690.2	21.1	1200.3	64.9	6.3	1.9
298	392.4	29.4	441.8	26.0	1009.1	25.8	16.1	1.3
750	317.3	25.6	348.7	20.5	798.1	37.4	18.6	1.7
900	310.5	33.6	345.0	29.9	777.5	9.4	17.6	1.1
1050	287.9	11.1	312.2	14.7	447.3	10.4	19.7	1.8
1200	202.1	30.6	214.2	41.0	236.2	42.6	23.3	1.6

ties due to exposure time and/or environment will be highlighted.

For purposes of documentation, it should be noted that (1) the triplicate 750, 900, 1050, and 1200 K tensile tests (Fig. 2) conducted on 10,000 h vacuum-exposed HA 188 samples were inadvertently conducted in air instead of vacuum and (2) the tensile data (Fig. 4) obtained for 2500 h vacuum-exposed HA 230 are results from smaller gage section (25.4 mm by 6.3 mm) specimens.[2]

3.2.1 HA 188

Any prior exposure at 1093 K for at least 4900 h reduces the 77 and 298 K yield stresses about 15% from the as-received condition. At higher tensile test temperatures, however, little differences between as-received and air or vacuum-exposed yield strengths were found (Fig. 1a and 2a). At 77 and 298 K, the yield stress levels, particularly after air exposure, tended to decrease with increasing time at temperature; a similar tendency did not occur at any of the four higher tensile test temperatures. The as-received and 4900 h and 10,000 h air-exposed specimens displayed much higher yield strengths at 1200 K (Fig. 1a) than their counterparts (Fig. 2a) exposed in vacuum. However, after 22,500 h of either air or vacuum exposure, the 1200 K yield strengths were essentially equal.

In terms of ultimate tensile strength, annealing of HA 188 at 1093 K reduced the 77 K value about 20% compared to the as-received condition (Fig. 1b and 2b). Prior exposure to either air or vacuum also induced some strengthening (up to 25%) at 750 and 900 K, but had little effect at 298, 1050, or 1200 K on the UTS of HA 188. The trend of decreasing 77 and 298 K yield stress (Fig. 1a and 2a) with increasing time of exposure is not followed in the 77 or 298 K ultimate tensile strength data. Comparison of the results after identical lengths of air or vacuum heat treatment indicates that the ultimate tensile strengths are similar; hence, changes in UTS cannot be related to a specific environment.

The most dramatic effect ascribable to exposure is found in the 77 and 298 K residual tensile ductility (Fig. 1c and 2c) where the ~40% elongation for as-received stock are reduced to about 5% at 77 K and approximately 10% at 298 K. Elongations at 750 K are also decreased by prior exposure; however, in these instances, the losses are only about a factor of 2 (28 to ~15% at 750 K) at worst. In opposition to such degradations, the 900, 1050, and 1200 K ductilities of exposed HA 188 generally are equal to or better than the as-received condition. Although the 77 and 298 K yield strengths tend to decrease with increasing time of exposure (Fig. 1a and 2a), the residual tensile ductility at these two test temperatures (Fig. 1c and 2c) basically increases with time at temperature. Some differences due to environment and, perhaps, time of exposure appear to exist in the tensile elongation data. The results from vacuum-exposed alloy specimens indicate that they consistently possess better ductility than the equivalent air-exposed samples (for example testing at 750 K, Fig. 2c versus 1c). Irrespective of this tendency, no instances, however, exist where the air-exposed alloy is "brittle" and the vacuum-exposed material is "ductile."

Table 5 Tensile properties of HA 188 after vacuum exposure at 1093 K

Temperature,	0.02% yield stress		0.2% yield stress		Ultimate tensile strength		Elongation, %	
	Avg	Std dev	Avg	Std dev	Avg	Std dev		
K	MPa	MPa	MPa	MPa	MPa	MPa	Avg	Std dev
As-received								
77	759.0	66.5	844.0	37.6	1527.7	6.6	43.3	2.4
298	531.7	102.6	573.0	85.2	1002.3	25.8	42.3	4.8
750	373.7	10.2	395.3	6.2	767.3	13.7	28.3	0.9
900	332.3	11.5	357.3	8.8	671.7	15.5	15.3	5.2
1050	317.7	11.0	345.7	5.2	507.7	4.8	27.3	1.7
1200	141.0	10.8	163.7	11.3	243.3	4.2	56.0	27.0
4900 h								
77	660.0	38.8	748.0	32.8	1199.7	5.6	6.0	0.0
298	411.0	13.1	490.3	18.8	1012.3	31.7	15.7	2.1
750	316.3	42.5	381.0	14.2	844.3	20.1	22.0	3.7
900	350.7	21.7	385.7	21.8	887.7	37.9	22.7	0.9
1050	289.0	4.3	320.3	1.2	505.7	8.7	19.7	1.7
1200	134.3	10.1	154.7	14.1	243.7	20.8	86.0	6.5
10,000 h								
77	594.6	83.0	699.6	83.8	1281.1	73.1	5.3	1.2
298	387.7	15.2	457.4	10.2	993.7	24.0	13.4	0.8
750	285.4	13.3	347.6	7.1	840.3	8.6	19.3	0.4
900	306.4	12.3	343.6	8.4	844.9	3.1	23.0	0.6
1050	249.1	9.1	293.5	7.8	449.3	6.9	29.1	0.1
1200	150.9	6.9	173.1	7.5	201.9	4.3	32.6	0.3
22,500 h								
77	607.6	43.3	702.3	24.2	1230.0	39.0	12.7	0.8
298	417.8	34.4	479.0	21.2	1039.8	30.8	26.6	2.3
750	345.1	7.0	375.6	8.0	867.8	8.4	31.1	1.3
900	333.8	8.5	370.6	3.7	892.5	3.9	34.4	0.3
1050	314.3	7.0	338.8	4.9	588.7	11.3	35.0	0.9
1200	223.8	5.3	241.2	3.4	279.2	7.6	38.8	3.3

3.2.2 HA 230

Long-term exposure of HA 230 at 1093 K reduces 0.2% yield stress at all test temperatures (Fig. 3a and 4a), where the maximum loss occurs at 77 K with the ~700 MPa value for the as-received alloy lessened to about 500 MPa. Based on the 10,000 h vacuum- (Fig. 4a) and air- (Fig. 3a) exposed results, both environments produce similar effects on the yield strength at all test temperatures. The 77 K ultimate tensile strength of HA 230 is also dramatically influenced by long-term exposure, where 25% reduction in UTS occurred (Fig. 3b and 4b). Slight decreases in tensile strength also take place at 298 and 1200 K with prolonged heat treatments, whereas prior exposure increases the 900 and 1050 UTS. Although little difference in 77 to 1200 K ultimate tensile strengths exist between 2500 and 10,000 h vacuum-exposed HA 230 (Fig. 4b), the UTS for 1093 K air-exposed alloy (Fig. 3b) at 77, 298, and possibly 750 K progressively decrease with time of exposure.

As was the case for HA 188, the greatest effect of 1093 K heat treatment lies in the residual tensile ductility (Fig. 3c and 4c). Concentrating on the 77 K results, these tensile elongation data suggest that both time of exposure and environment are important. The degradation progressively increases as the time at temperature in air is increased (Fig. 3c), where the ~30% elongation for as-received material is reduced to <5% after 22,500 h. Although the 10,000 vacuum-exposed samples have undergone a loss of tensile ductility to about 15% at 77 K (Fig. 4c), this value is at least twice that found in 10,000 h air-exposed specimens, tested at 77 K (Fig. 3c). The 298 K tensile ductility also decreases, with air exposure being more debilitating (~17% after 10,000 h, Fig. 3c) than an equivalent vacuum exposure (~27% after 10,000 h, Fig. 4c). In comparison to the as-received material, air exposures also decrease the elongations at 750 and 900 K, whereas the ductilities at 1050 and 1200 K increase (Fig. 3c). Prior exposure to vacuum, on the other hand, increases the tensile elongations over those measured in the as-received condition between 750 and 1200 K (Fig. 4c).

3.2.3 IN 617

With the exception of the ~15% decrease after the 22,500 h heat treatment condition, prior exposure of IN 617 in air has little influence on its 0.2% yield strength (Fig. 5a). Although the vacuum-exposed alloy samples (Fig. 6a) generally follow this trend, some degradation is evident at 77 K where an approximately 15% loss was found after only ~8000 h. At and above 298 K, the ultimate tensile strengths (Fig. 5b) are only slightly affected by air heat treatments. Comparison of the 298 to 1200 K tensile strengths after 22,500 h to the other conditions (as-received or 4900 or 10,000 h) suggests, however, that prolonged air exposure has a definite and consistent weakening effect. At 77 K, UTS is substantially lowered after 10,000 or 22,500 h in air, where strengths have been reduced at least 25% compared to the as-received value. Although prior vacuum exposure also decreases the 77 K ultimate tensile strength, the loss is only about 10% after ~8000 h.

Once again, ductility is the most significantly affected tensile property, and air appears to be more incapacitating than vacuum (Fig. 5c and 6c). Between 77 and 900 K, the degradation in tensile elongation for the air-exposed IN 617 increases

Table 6 Tensile properties of HA 230 after air exposure at 1093 K

Temperature, K	0.02% yield stress Avg MPa	0.02% yield stress Std dev MPa	0.2% yield stress Avg MPa	0.2% yield stress Std dev MPa	Ultimate tensile strength Avg MPa	Ultimate tensile strength Std dev MPa	Elongation, % Avg	Elongation, % Std dev
As-received								
77	642.2	69.5	710.8	47.4	1255.1	13.6	29.9	1.5
298	411.5	12.3	460.1	7.3	869.3	9.1	32.6	0.6
750	317.8	6.5	340.2	3.0	699.1	8.0	28.1	1.0
900	301.7	5.4	322.4	5.4	574.0	0.0	17.7	0.7
1050	281.0	3.8	303.5	5.5	420.0	9.6	8.6	0.4
1200	164.1	6.9	198.2	1.4	219.0	0.5	17.3	1.4
4900 h								
77	504.1	9.7	576.6	8.7	987.9	40.4	9.0	1.0
298	342.2	43.9	401.5	20.6	807.5	72.4	14.5	5.3
750	304.9	0.9	321.7	1.7	726.0	6.1	22.1	1.4
900	287.9	5.6	294.8	7.0	637.9	24.7	15.2	1.8
1050	266.0	3.5	272.9	4.6	417.2	4.9	26.7	0.3
1200	125.2	8.0	160.0	1.2	191.2	4.4	32.3	0.8
10,000 h								
77	486.5	20.8	518.9	16.8	899.5	5.2	6.6	1.0
298	319.5	8.3	361.0	5.9	763.1	25.0	17.6	1.1
750	245.5	17.8	273.2	4.8	682.6	11.7	20.1	1.3
900	261.2	9.9	274.9	13.8	618.4	15.5	16.4	1.0
1050	253.1	11.3	270.2	6.1	456.8	6.2	16.8	2.6
1200	171.5	15.6	191.6	12.6	221.8	10.8	22.6	0.5
22,500 h								
77	478.4	13.0	522.7	15.3	857.7	12.4	4.6	0.4
298	379.5	8.4	400.4	10.7	734.6	21.3	12.4	0.8
750	281.6	14.9	316.2	7.1	656.1	34.1	12.7	3.6
900	260.5	10.5	284.1	6.7	564.4	44.8	10.7	3.1
1050	265.5	6.8	285.3	9.4	466.7	4.6	16.8	2.2
1200	175.1	7.3	183.9	5.2	212.3	3.8	20.0	1.0

Table 7 Tensile properties of HA 230 after vacuum exposure at 1093 K

Temperature, K	0.02% yield stress Avg MPa	0.02% yield stress Std dev MPa	0.2% yield stress Avg MPa	0.2% yield stress Std dev MPa	Ultimate tensile strength Avg MPa	Ultimate tensile strength Std dev MPa	Elongation, % Avg	Elongation, % Std dev
As-received								
77	678.7	2.9	734.3	20.2	1264.3	29.2	36.3	3.1
298	452.0	22.0	475.0	23.0	889.7	4.5	36.7	1.7
750	325.5	13.5	347.0	4.0	696.0	4.3	24.7	0.5
900	312.7	14.7	342.7	3.4	572.7	18.7	18.7	4.5
1050	308.3	20.0	335.3	7.7	460.3	17.0	7.3	1.9
1200	120.0	7.8	139.7	6.2	209.0	8.3	16.7	3.1
2500 h, Small tensile specimen geometry								
77	601.7	109.4	640.0	92.8	963.7	89.2	16.7	2.1
298	360.0	19.8	412.7	9.7	839.7	7.6	23.3	1.2
750	309.7	9.0	332.3	6.8	734.0	3.7	30.7	1.2
900	301.0	1.6	325.7	2.5	663.3	15.1	21.7	2.1
1050	242.5	16.5	275.5	5.5	420.0	0.8	22.3	1.2
1200	107.0	11.0	135.0	6.5	198.0	6.2	24.7	1.7
10,000 h								
77	406.4	10.1	516.9	5.7	968.1	17.8	15.4	0.9
298	291.7	19.7	366.0	3.7	839.3	7.5	27.2	0.9
750	285.3	1.0	301.0	2.5	739.9	24.7	28.0	1.5
900	278.3	10.1	294.9	16.1	669.8	44.9	24.1	0.6
1050	254.8	3.8	259.4	4.4	414.2	27.4	22.6	0.2
1200	169.1	2.2	183.3	4.4	204.7	4.8	28.4	2.4

with time of exposure up to 10,000 h, where the loss is greatest at 77 K, with 18% for as-received specimens being reduced to ~3% after 10,000 h (Fig. 5c). This trend is not, however, continued with longer air heat treatments, and the 22,500 h air-exposed samples are considerably more ductile than either the 4900 or 10,000 h specimens at all tensile test temperatures.

Somewhat similar behavior is also noted in vacuum-exposed IN 617, where the shorter term (≤2500 h) vacuum-exposed samples (Fig. 6c) experienced some loss in ductility between 77 and 900 K. A longer term vacuum anneal (~8000 h), on the other hand, led to consistently higher elongation at all test temperatures.

Table 8 Tensile properties of IN 617 after air exposure at 1093 K

Temperature, K	0.02% yield stress Avg MPa	0.02% yield stress Std dev MPa	0.2% yield stress Avg MPa	0.2% yield stress Std dev MPa	Ultimate tensile strength Avg MPa	Ultimate tensile strength Std dev MPa	Elongation, % Avg	Elongation, % Std dev
As-received, tested in vacuum								
77	489.9	32.3	540.0	52.1	906.7	22.3	19.0	1.4
298	357.8	19.8	374.7	13.6	673.2	9.9	29.2	0.7
750	250.1	12.2	282.6	11.1	553.9	10.7	28.5	2.6
900	224.3	6.6	249.3	2.8	494.8	4.0	26.8	1.4
1050	215.1	3.9	239.8	3.1	417.3	5.6	25.6	0.2
1200	190.6	5.5	204.8	6.5	206.4	5.7	28.1	1.0
4900 h								
77	515.9	30.2	543.1	19.4	806.9	27.3	7.9	0.4
298	324.4	7.0	339.0	3.7	626.9	28.3	14.3	2.3
750	242.5	28.5	261.5	20.6	583.2	11.0	21.7	1.1
900	195.9	14.3	236.3	11.7	537.8	18.2	20.3	1.9
1050	199.0	16.1	229.5	1.0	397.6	27.1	19.6	4.8
1200	172.9	10.0	191.1	1.3	198.0	3.3	27.5	1.1
10,000 h								
77	478.1	13.3	513.2	11.9	681.1	20.0	3.5	1.4
298	336.6	11.1	369.8	11.5	623.3	9.5	9.8	0.2
750	265.0	5.7	283.7	12.7	589.9	12.3	17.9	1.9
900	241.0	3.3	267.3	8.9	560.8	19.0	19.2	0.9
1050	231.3	11.3	240.2	6.1	395.9	45.2	22.9	1.3
1200	196.2	4.4	198.9	4.1	212.0	3.8	30.4	4.1
22,500 h								
77	436.6	20.8	468.8	13.0	662.6	15.1	10.6	1.8
298	254.9	12.9	285.7	11.5	532.9	40.3	22.7	0.6
750	203.3	8.1	217.7	11.0	502.7	18.2	32.6	3.1
900	195.5	21.2	227.8	8.7	445.5	10.4	30.3	5.2
1050	190.8	11.6	207.0	11.4	348.0	9.8	37.0	1.3
1200	140.1	18.6	155.2	10.3	171.6	9.9	39.5	0.2

3.3 *Microstructure of Tensile Fractures*

3.3.1 HA 188

Typical examples of the microstructure of as-received and air-exposed alloys after tensile testing at room temperature are presented in Fig. 7. The transition from a ductile, shear failure for the as-received condition (Fig. 7a) to intergranular fracture after 1093 K heat treatment in air (Fig. 7b to d) is clear. A similar change in fracture mode was also observed after 77 K tensile testing and has been documented[3] for a 4900-h exposed specimen. Tensile fracture in air-exposed HA 188 occurred intergranularly up to at least 750 K. At and above 1050 K, previously air-exposed HA 188 is quite plastic, and samples fractured via transgranular shear and tearing.[3] Testing of air-exposed alloy at 900 K, on the other hand, yielded signs of both inter- and intragranular mechanisms at the failure sites, in most cases. Irrespective of the time of exposure, after tensile testing, the 1093 K vacuum heat treated HA 188 had microstructures similar to those found after air testing with (1) intergranular fracture at and below 750 K, (2) transgranular shear and tearing at 1050 K and higher temperatures, and (3) a mixed mode at 900 K. In comparison to the behavior of either the air- or vacuum-exposed alloy, testing of as-received HA 188 yielded ductile failure at all test temperatures.

3.3.2 HA 230

Typical examples of the microstructure of as-received and 1093 K air-exposed alloys after tensile testing at 77 K are presented in Fig. 8, where the exposed HA 230 (Fig. 8b to d) failed in an intergranular mode, whereas the as-received samples (Fig. 8a) underwent transgranular ductile shear fracture. Examination of the 22,500 h air-exposed samples revealed that (1) intergranular fracture also occurred after 298 K testing, (2) mixed inter- and intragranular failure was observed in 750 K tested HA 230, and (3) all of the higher tensile testing temperatures resulted in transgranular fracture. Spot checking of 4900 and 10,000 h air-exposure samples confirmed this fracture pattern as a function of tensile test temperature. Examination of the HA 230 exposed to vacuum at 1093 K for 10,000 h indicated that the fracture after 77 K tension was intergranular, but after 298 K testing, mixed mode failure was observed. At the higher test temperatures, all of the tensile fractures were by ductile transgranular mechanisms. The same pattern as a function of test temperature was followed by the 2500 and 400 h vacuum-exposed alloy.[2] As opposed to this behavior after exposure, as-received HA 230 failed by ductile transgranular mechanisms at all temperatures.

3.3.3 IN 617

Examples of typical microstructures of as-received and 1093 K air-exposed IN 617 are presented in Fig. 9 for 77 K tensile tested samples. The as-received alloy (Fig. 9a) failed in a ductile manner, whereas the various 1093 K exposures (Fig. 9b to d) led to intergranular fracture. Examination of 298 K tensile tested samples that were heat treated in air indicated that they failed intergranularly, whereas the as-received alloy exhibited ductile fracture. Air-exposed specimens revealed signs of both inter- and transgranular failure after either 750 or 900 K test-

Table 9 **Tensile properties of IN 617 after vacuum exposure at 1093 K**

Temperature, K	0.02% yield stress Avg MPa	0.02% yield stress Std dev MPa	0.2% yield stress Avg MPa	0.2% yield stress Std dev MPa	Ultimate tensile strength Avg MPa	Ultimate tensile strength Std dev MPa	Elongation, % Avg	Elongation, % Std dev
As-received								
77	489.9	32.3	540.0	52.1	906.7	22.3	19.0	1.4
298	357.8	19.8	374.7	13.6	673.2	9.9	29.2	0.7
750	250.1	12.2	282.6	11.1	553.9	10.7	28.5	2.6
900	224.3	6.6	249.3	2.8	494.8	4.0	26.8	1.4
1050	215.1	3.9	239.8	3.1	417.3	5.6	25.6	0.2
1200	190.6	5.5	204.8	6.5	206.4	5.7	28.1	1.0
400 h								
77	495.2	27.9	557.0	10.5	904.8	20.0	12.1	1.2
298	335.4	8.6	361.6	6.5	718.2	19.5	21.0	1.6
750	271.3	3.7	285.5	4.2	643.3	20.5	24.9	1.2
900	249.7	4.4	271.3	1.3	605.2	17.2	21.8	1.7
1050	233.5	9.6	251.6	3.7	441.0	3.2	29.2	0.6
1200	181.3	8.7	198.6	1.6	211.6	2.5	34.5	1.0
2500 h								
77	463.7	24.0	511.0	24.2	882.9	9.5	12.2	0.4
298	330.2	2.0	363.9	4.9	728.0	20.7	22.0	2.0
750	252.0	5.1	273.1	0.9	650.3	4.1	28.2	0.9
900	244.3	15.3	261.9	14.9	617.2	4.2	26.1	0.7
1050	230.6	2.6	238.8	0.8	431.6	10.7	30.6	0.9
1200	189.2	14.2	206.8	7.9	216.0	4.9	36.1	0.7
7913.8 h								
77	390.9	43.1	452.9	21.9	829.0	8.0	21.7	0.9
298	307.3	41.2	346.4	28.0	728.1	14.5	37.3	3.3
750	263.1	10.2	272.5	11.9	612.2	48.5	51.3	2.9
900	236.1	4.9	241.7	5.8	613.0	8.0	51.3	2.4
1050	223.5	2.9	236.4	12.6	467.0	11.9	47.6	2.7
1200	182.2	32.6	194.9	29.3	222.9	11.3	45.1	3.5

ing, but at the higher temperatures only ductile fractures were found. Tensile testing of 1093 K vacuum-exposed IN 617 yielded microstructures that, with the exception of surface-connected intergranular oxidation, are identical to those observed after air testing. Specifically for 400 to ~7914 h of vacuum exposure, intergranular fracture was observed after 77 and 298 K tension, mixed mode after 750 and 900 K testing, and transgranular shear at 1050 and 1200 K. In contrast, ductile failure occurred at all test temperatures for the as-received alloy.

4. Discussion

Based on the observed microstructural changes after long-term 1093 K exposures,[6] certain expectations regarding tensile properties were developed. For instance, all three alloys exhibited intergranular precipitation, which should decrease residual tensile ductility, particularly at the lower test temperatures.[2,3] Furthermore, this tendency could be enhanced in air-exposed alloys due to surface-connected grain boundary oxidation attack. This anticipation was met for HA 230, where the 77 K tensile elongation continuously decreased with time of exposure, and air was a more aggressive environment (Fig. 3c) than vacuum (Fig. 4c). In the case of HA 188, exposure to either air (Fig. 1c) or vacuum (Fig. 2c) for 4900 h reduces both the 77 and 298 K ductility compared to as-received values. However, additional time of exposure to either environment increased residual ductilities. IN 617 exhibits a similar ductility minimum after 400-h vacuum exposure (Fig. 6c), but with air exposure the lower temperature tensile elongations decrease with time through 10,000 h (Fig. 5c) and then exhibit a large increase after 22,500 h at 1093 K.

The possibility of surface-connected intergranular attack in air-exposed samples acting as sites for premature fracture was the second expectation. In the case of HA 188, intergranular oxidation at the surface[6] is clearly visible in Fig. 7(d) and to a lesser extent in Fig. 7(b) and (c). Similar degradation of the surface grains did not occur after vacuum exposure.[3,6] Because the tensile elongation values of air-exposed HA 188 (Fig. 1c) were consistently lower than those for identical periods of vacuum exposure (Fig. 2c) at all test temperatures, it is probable that the intergranular attack regions served as sites for premature failure. IN 617 also underwent intergranular oxidation (Fig. 9b to d), whereas the vacuum-exposed alloy did not.[6] However, direct comparison of the influence of atmosphere on ductility is not possible due to the different lengths of 1093 K exposures. Nevertheless, the 77 to 1200 K tensile elongations of the 2500 and 7914 h vacuum heat treated alloy (Fig. 6c) are greater than those after 4900 and 10,000 h in air. Hence, the crack-like nature of intergranular oxidation in IN 617 appears to act as fracture initiation sites. The situation for HA 230 is somewhat different, because the vacuum-exposed alloy did possess shallow pits (maximum 10 μm deep),[6] which were traceable to the original sheet processing. However, long-term exposure of this alloy to air significantly increased their depth; for example, to a maximum of 45 μm after 10,000 h.[6] Because the tensile elongations measured after 10,000 h heat treatment

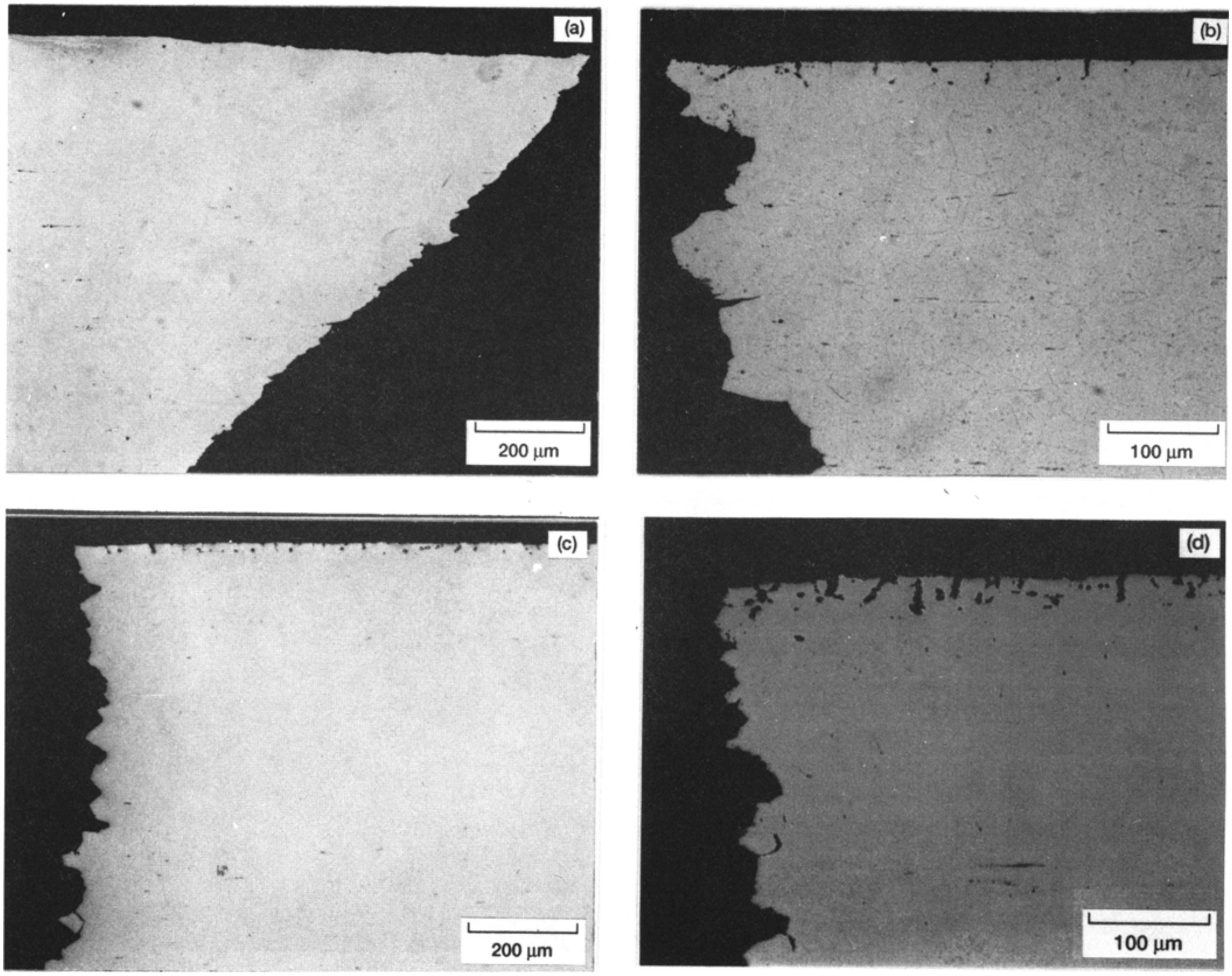

Fig. 7 Typical photomicrographs of unetched HA 188 tensile tested at 298 K after being heat treated in air at 1093 K for various periods of time. (a) as-received, 28.2% elongation. (b) 4900 h, 2.7% elongation. (c) 10,000 h, 8.6% elongation. (d) 22,500 h, 14.9% elongation.

in air (Fig. 3c) are less than those measured after 10,000 h in vacuum (Fig. 3d), the deeper cracks from oxidation could, once again, lead to early fracture.

In terms of overall tensile ductility for the three superalloys, it appears that air is a more damaging environment than vacuum. However, it should be emphasized that no instances were found where the air-exposed alloys were "brittle," whereas the vacuum-exposed materials were "ductile." The difference in these two environments was simply a bias in behavior, with 1093 K air exposure yielding less residual tensile elongation than a similar vacuum exposure.

The last expectation involved the residual strength properties, where air-exposed alloys should be weaker than the vacuum heat treated materials because of the relatively deep surface-connected grain boundary cracks from oxidation.

Examination of the yield strength (Fig. 1a and 2a) or ultimate tensile strength (Fig. 1b and 2b) data for HA 188 fail, however, to reveal any consistent pattern based on differences in environment. Examination of the results for HA 230 (Fig. 3a and b versus Fig. 4a and b) and IN 617 (Fig. 5a and b versus Fig. 6a and b) also indicates a neutrality to either air or vacuum exposure. Part of this indifference is traceable to the oxidation attack to sheet thickness ratio and the relatively small grain size. For example, after 22,500 h in air at 1093 K, surface-connected attack up to 80 μm deep was found in IN 617; such intergranular oxidation would reduce the local load-bearing area by about 6%. Because it is unlikely that all the grains across the ~10 mm gage width would have suffered similar attack, the actual loss of load-bearing area should be much less than this value. Therefore, for the nominally 1.3 mm superalloy sheet tested in this program, heat treatments as long as 22,500 h in air at 1093 K have little effect on the strength properties beyond that ascribed to simple thermal exposure.

Although the heat treatment undertaken in vacuum for the majority of the test samples were not true "vacuum" exposures because shadowing by neighboring specimens partially pre-

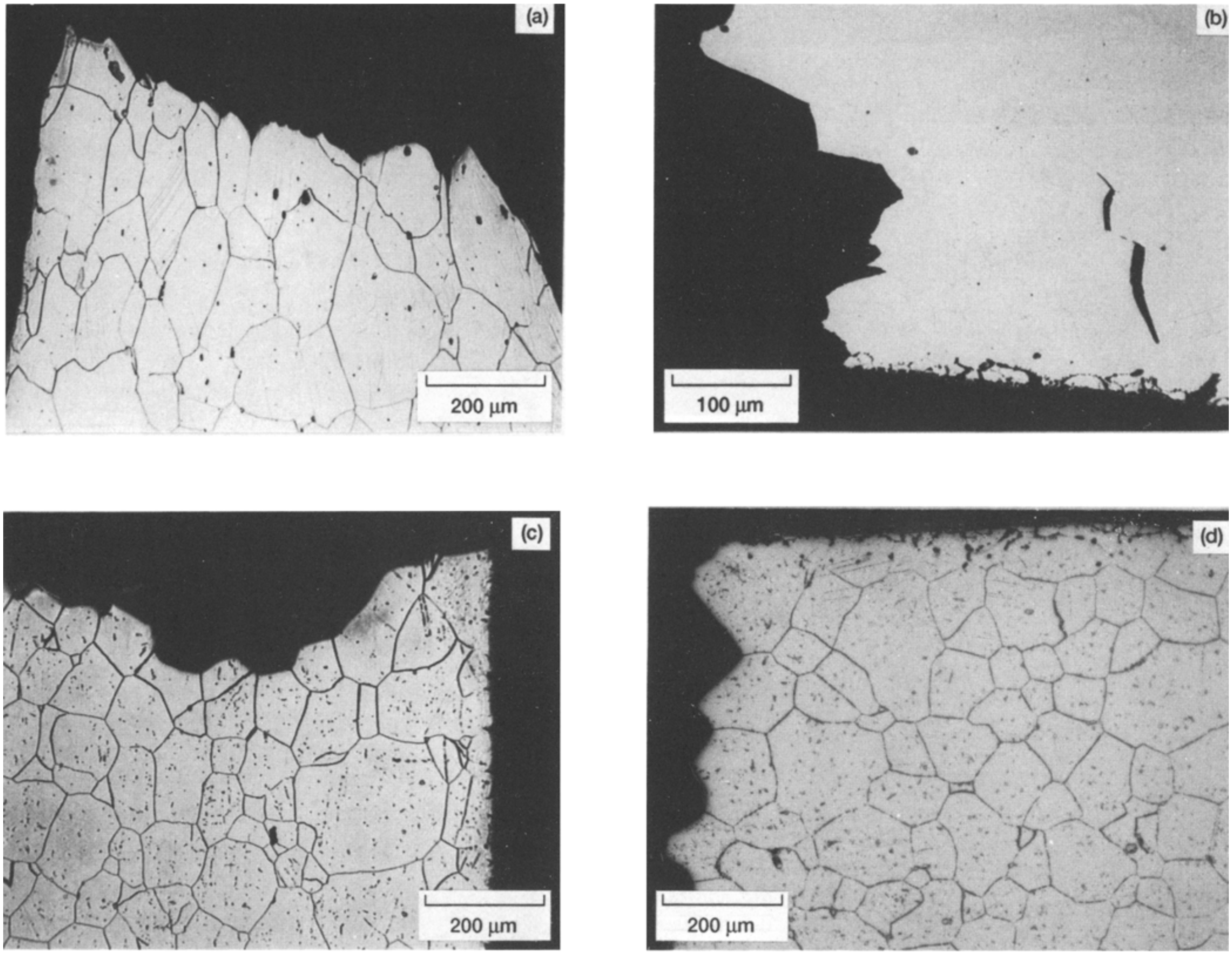

Fig. 8 Typical photomicrographs of etched HA 230 tensile tested at 77 K after being heat treated in air at 1093 K for various periods of time. (a) As-received, 28% elongation. (b) 4900 h, 7.8% elongation. (c) 10,000 h, 5.6% elongation. (d) 22,500 h, 4.1% elongation.

vented loss of volatilized elements,[6] some speculation on the effects of 1093 K vacuum annealing can be made. Based on the results for the end specimens,[6] uninhibited volatilization only yields a small weight loss (maximum of 2 mg/cm^2 after 22,500 h), and it is a diffusion-controlled process. These observations indicate that volatilization of the strengthening solutes (i.e., Cr and Mn) is no faster than that experienced during oxidation and that very little matter is really lost. Therefore, degradation of mechanical properties from unrestrained volatilization in vacuum is probably no worse than that experienced after oxidation. In fact, vacuum exposure might result in less damage, because surface-connected grain boundary cracks from oxidation would not be formed.[6]

5. Summary of Results

The 77 to 1200 K tensile properties of Haynes Alloy 188, Haynes Alloy 230, and Inconel 617 have been measured after long-term exposure to air or vacuum at 1093 K. Due to the geometry of the experiment, the vacuum-exposed samples were protected from loss of the volatile elements by evaporation. Hence, such specimens were simply given 1093 K heat treatments in an innocuous environment, which produced very little surface attack. Compared to the properties of the as-received alloys, prior exposure tends to reduce both the yield strength and ultimate tensile strength, with the greatest reductions at 77 and 298 K. The most dramatic effect of previous heat treatments was found in the low-temperature residual tensile elongations, where decreases from 40 to 5% at 77 K were found. Ductility is the only property that was found to have a consistent dependency on environment, with air exposure always yielding less tensile elongation than vacuum exposure.

6. Conclusion

Based on the results from studies of the structure[6] and the tensile properties of wrought Co-base Haynes Alloy 188 and Ni-base Haynes alloy 230 and Inconel 617 sheet after long-

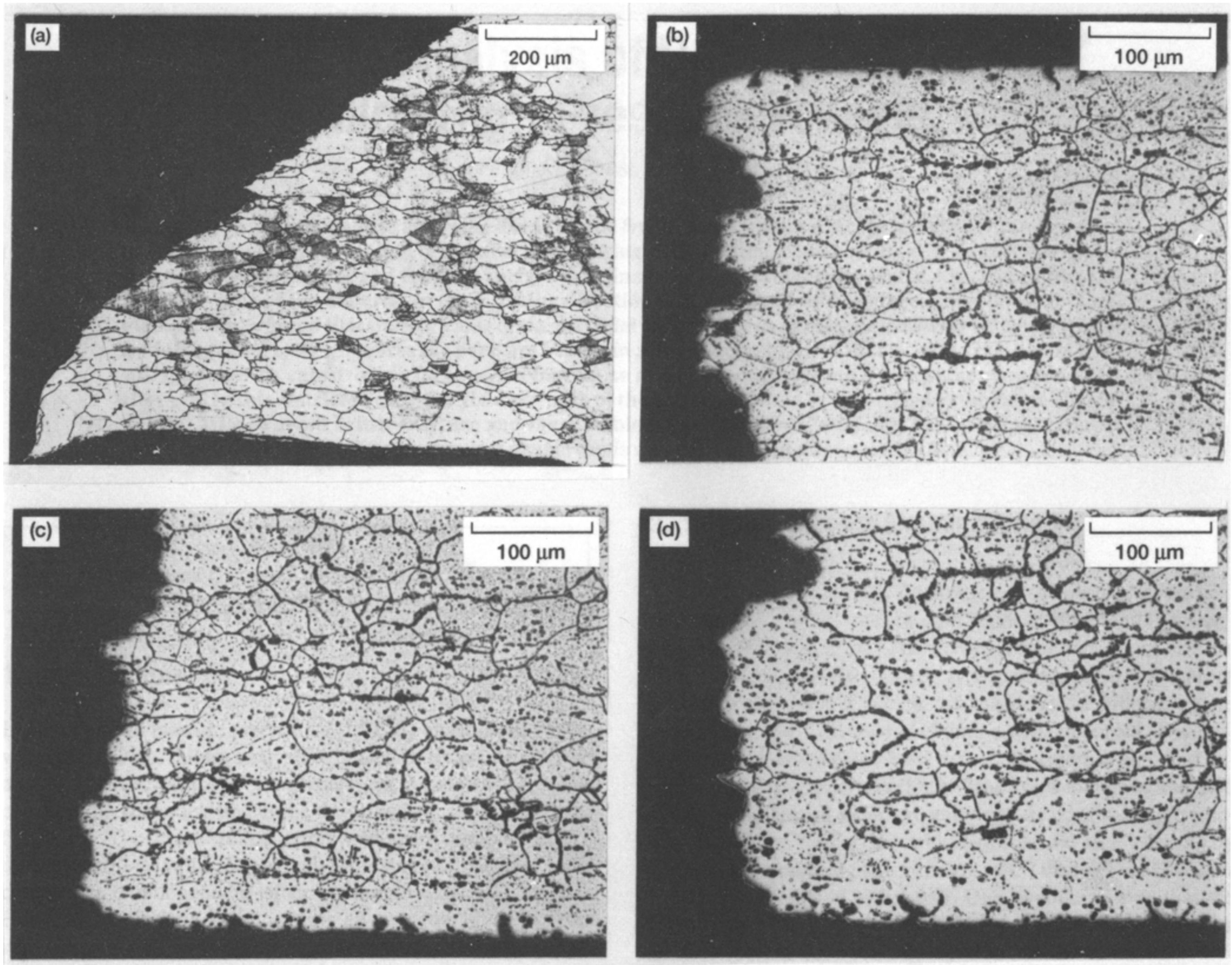

Fig. 9 Typical photomicrographs of IN 617 tensile tested at 77 K after being heat treated in air at 1093 K for various periods of time. (a) As-received, 17.2% elongation. (b) 4900 h, 7.5% elongation. (c) 10,000 h, 2% elongation. (d) 22,500 h, 8.5% elongation. (a), (c), and (d) are etched; (b) is unetched.

term heat treatments at 1093 K, the thermal stability of all three alloys is roughly equal in air or in an inert environment. Hence, it was concluded that any of these three superalloys would be successful thermal energy storage containment vessel materials, provided no adverse reaction(s) between the alloy and energy storage salt occur and exposure does not drastically decrease creep strength.

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