

# Mechanical Properties of Haynes Alloy 188 after 22,500 Hours of Exposure to LiF-22CaF<sub>2</sub> and Vacuum at 1093 K

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As a continuation of a study of a space-based thermal energy storage system centered on a LiF-CaF<sub>2</sub> eutectic salt contained by Haynes alloy 188, this Co-base superalloy was subjected to molten salt, its vapor, and vacuum for 22,500 h at 1093 K. Samples from all three exposure conditions were tensile tested between 77 to 1200 K; in addition, vacuum and molten-salt exposed specimens were vacuum creep rupture tested at 1050 K. Comparison of these mechanical properties with those measured for the as-received alloy reveals no evidence for degradation beyond that ascribed to simple thermal aging of Haynes alloy 188. This behavior is identical to the 10,000 h results (Ref 3); hence, Haynes alloy 188 is a suitable containment material for an eutectic LiF-CaF<sub>2</sub> thermal energy storage salt.

## Keywords

Haynes alloy 188, heat treatment, long term exposure, mechanical properties, superalloy, thermal energy storage

## 1. Introduction

A SOLAR dynamic system (Ref 1) was proposed as a means to supply heat and electrical power to earth orbiting space stations. A critical concern for successful application of this concept was efficient energy storage. The use of the latent heat of fusion of fluoride salts was forwarded because of their high energy density on either a volume or weight basis. Energy storage by this means, however, leads to a question of long term viability because molten fluorides tend to be very corrosive. Thus the conventional Co-base superalloy Haynes\* alloy 188 (alloy 188) was exposed to the near eutectic salt LiF-22CaF<sub>2</sub>\*\* at 1093 K, which is 50 K higher than the melting temperature of the eutectic. Test samples were exposed to the molten salt, its vapor, and vacuum with this latter environment utilized as a control. To date, alloy 188 has been given exposures of 400 to 10,000 h, examined for signs of degradation, and subjected to mechanical property testing (Ref 2, 3). To provide a more conventional frame of reference, a similar effort involving long-term exposures of alloy 188 to air at 1093 K also was conducted (Ref 3-5).

The originally planned 22,500 h exposure of alloy 188 to the molten LiF-CaF<sub>2</sub> eutectic, its vapor, and vacuum at 1093 K has been completed, and the post-exposure mechanical properties have been measured. This paper presents the results of salt and/or vacuum exposure on the structure of this containment material, the 77 to 1200 K tensile properties from specimens exposed to all three environments, and the 1050 K creep rupture characteristics of vacuum and molten-salt exposed samples.

\*Haynes is a registered trade name of Haynes International, Inc., Kokomo, IN.

\*\*All compositions are in mole percent unless noted.

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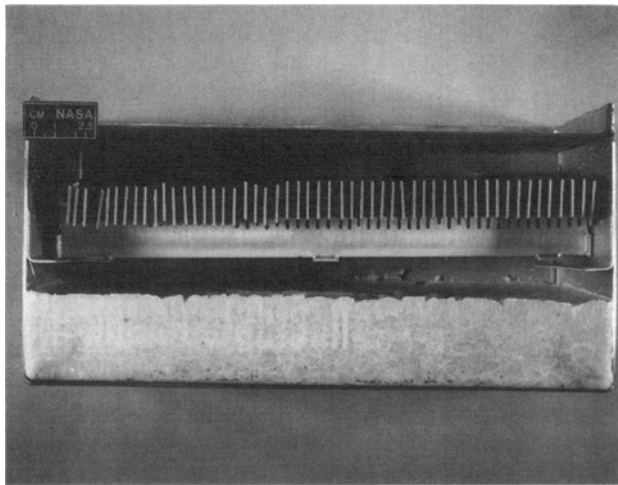
## 2. Experimental Procedures

Details of the as-received state of alloy 188, the tensile specimen fabrication, methodology of salt and vacuum exposures, and the mechanical property testing were completely described in Ref 2 and 3. However to provide a general frame of reference, a brief outline of the experiments is provided below.

Pin and clevis tensile type specimens (31.8 mm by 9.8 mm gage section) were directly punched from approximately 1.27-mm-thick by 0.6-m by 1.2-m sheets of alloy 188 (Cabot Corp., Heat 188061773 with the following chemistry in weight percent: 0.005B-0.11C-21.69Cr-1.95Fe-0.048La-0.72Mn-23.03Ni-0.013P-<0.002S-0.38Si-14.02W-Co). This material was supplied in a solution treated condition with silver metallic sheen. Polished and etched metallurgical sections revealed that the microstructure of the sheet consisted of uniform, equiaxed grains with an average diameter of approximately 20 μm (Ref 2-4). This same alloy sheet also was utilized for fabrication of the approximately 280-mm-long by 140-mm-high by 115-mm-wide bread pan capsules through a combination of bending and welding without foreign metal as filler.

After cleaning, weighing, and measuring, each tensile specimen was placed onto racks. One rack then was placed in a bread pan capsule and covered with about 2.6 kg of salt (Cerac Inc., Heat 23590-A-5-12 with the following chemistry in weight percent: <0.001Al-<0.001Cu-0.005Fe-14.6Li-0.005Mg-0.001Si, which converts to LiF-21.7 mole percent CaF<sub>2</sub>). A second rack was set on tabs within the capsule, and a lid was gas-tungsten-arc welded to the main body in an argon atmosphere. The capsule was then put into a furnace and slowly heated to 1093 K under vacuum (4 h from room temperature to 993 K, 2 h to 1093 K, 1 h hold at temperature, and a furnace cool) to allow dissolved gases and water in the salt to escape through small holes in the lid. These holes were immediately closed by electron beam welding in vacuum following this heat treatment.

The bread pan capsule with a third rack of specimens on top was exposed for 22,500 h at 1093 K in a cryogenically pumped vacuum of approximately  $1.3 \times 10^{-4}$  Pa or better. This exposure was not continuous; shut downs due to loss of electrical power or cooling water, vacuum leaks, regeneration of the cryopumps



**Fig. 1** Photograph of the opened Haynes alloy 188 bread pan capsule after heat treating in vacuum at 1093 K for 22,500 h

(approximately every 400 h), etc. were experienced. Upon completion of the planned corrosion experiment, the capsule was cut open and photographed, and several samples of frozen salt were taken for chemical analysis. Prior to measuring and weighing, the molten salt exposed specimens were wiped with a clean lint-free cloth. With a single exception, neither the salt-vapor nor the vacuum-annealed samples were cleaned prior to postexposure measurements. Occasionally, splashed salt droplets were found on the vapor-exposed specimens. As many as possible of these drops were removed by scratching with a gloved finger before weighing.

Triplicate tensile tests at 77, 298, 750, 900, 1050, and 1200 K were conducted under contract at the Cortest Laboratories, Inc. (NAS3-25759) on LiF-CaF<sub>2</sub> eutectic salt-exposed and vacuum-annealed specimens. All 77 K tensile tests were conducted in liquid N<sub>2</sub>, whereas the 298 K tests were undertaken in air. At and above 750 K, the salt and/or vacuum exposed samples were tested in vacuum (<10<sup>-3</sup> Pa). Test data included 0.02 and 0.2 percent offset yield strengths, ultimate tensile strength (UTS), and elongation at failure. Vacuum (<10<sup>-3</sup> Pa) creep rupture experiments at 1050 K were also undertaken via this contract where testing was limited to samples exposed either in vacuum or liquid LiF-22CaF<sub>2</sub>. Whereas nine vacuum-exposed samples were tested at engineering stress levels designed to produce failure in 10 to 1500 h, only three molten-salt exposed specimens were creep rupture tested. The limited creep testing of the molten-salt exposed samples was a result of a redirection of the overall space station program. The creep data gathered included time to 0.1, 0.2, 0.5, 1, 2, 5, and 10 percent strain; steady-state creep rate; and failure time and elongation. All mechanical properties were calculated on the basis of the original (preexposure) dimensions.

Standard metallographic procedures and chemical analysis were employed for characterization. When required, the exposed alloy 188 was electrolytically etched at 4 V and 0.5 amp in 95 ml H<sub>2</sub>O plus 5 ml HCl or 95 ml H<sub>2</sub>O plus 5 ml HF.

**Table 1** Statistical summary of weight changes found in Haynes alloy 188 tensile type specimens after 22,500 h exposure to molten LiF-22CaF<sub>2</sub>, salt vapor, or vacuum at 1093 K

Statistical parameters	Weight change (exposed – as received), mg		
	Molten salt	Salt vapor	Vacuum
Average	-7.7	0.5	-17.2
Standard deviation	1.9	0.9	0.9
Maximum	-1.8	2.8	-15.5
Minimum	-11.4	-0.8	-19.8

**Note:** Data represent results from at least 50 tensile-type specimens where each sample weighed ~17 g and had ~33 cm<sup>2</sup> of surface area. Vacuum exposed results do not include the end samples, which lost considerably more weight due to free evaporation from the unshielded side (Ref 4).

### 3. Results

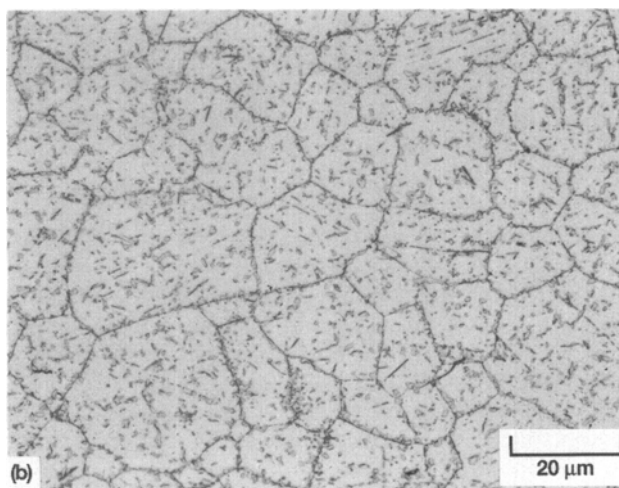
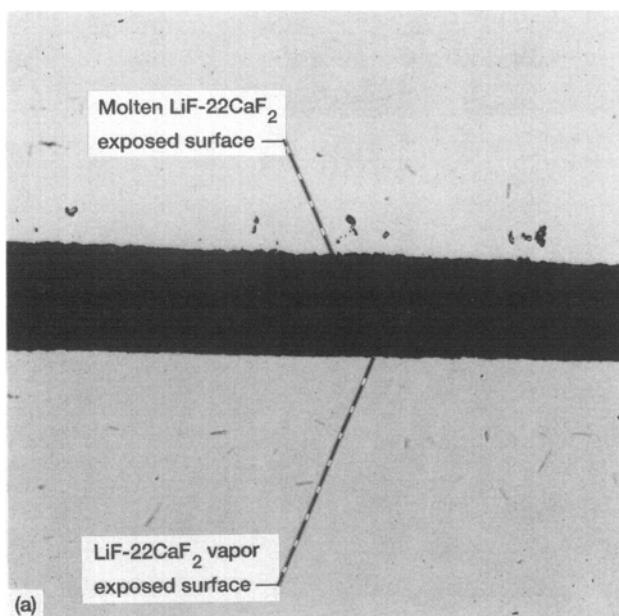
#### 3.1 Salt and/or Vacuum Exposures

The LiF-22CaF<sub>2</sub> filled alloy 188 capsule was successfully vacuum heat treated for 22,500 h at 1093 K where the exterior surfaces of the capsule and the rack of vacuum-exposed tensile specimens were basically unblemished and possessed a dull matte metallic finish. Figure 1 illustrates the inside of this heat treated alloy 188 bread pan after one side wall was cut away. The lower rack of specimens was completely immersed in frozen salt while the upper rack was maintained above the molten LiF-22CaF<sub>2</sub> in the salt vapor. The visible inner surfaces of the bread pan (Fig. 1) and the vapor-exposed alloy 188 specimens were dull matte gray without any visible sign of corrosion. A few vapor-exposed specimens, however, had small droplets of frozen salt on the surface.

The frozen block of LiF-22CaF<sub>2</sub> visible in Fig. 1 did not adhere to the capsule walls and had a dull gray appearance. Samples of the salt for chemical analysis taken from the side and bottom of the block and from regions between the tensile specimen did not show any evidence of contamination. The tensile samples encapsulated in the solidified salt were broken free by careful hammering and mechanical manipulation. Once freed, the molten-salt exposed alloy 188 specimens were found to have a mottled gray metallic appearance with patches of a yellow-brown scum.

The weight change results after 22,500 h of exposure at 1093 K are summarized in Table 1. As opposed to the LiF-22CaF<sub>2</sub> vapor-exposed samples, which slightly gained in weight, the molten and vacuum samples lost some weight. Compared to the original surface area (~33 cm<sup>2</sup>) for each specimen, the relative change after 22,500 h is negligible (<1 mg/cm<sup>2</sup>) even in the worst case (Table 1). Such meager weight changes combined with metallic surface finishes after long-term exposure indicate that neither LiF-22CaF<sub>2</sub> nor vacuum seriously attack alloy 188. This behavior agrees with the results from alloy 188 bread pans heat treated for 400 to 10,000 h (Ref 2, 3).

Metallurgical specimens to evaluate possible microstructural damage were cut from the bread pan. The alloy 188 contacted by the molten LiF-22CaF<sub>2</sub> exhibited occasional pits and a slightly roughened surface (Fig. 2a); the salt-vapor exposed



**Fig. 2** Photomicrographs of Haynes alloy 188 after heat treating for 22,500 h at 1093 K. (a) Molten LiF-22CaF<sub>2</sub> and salt-vapor exposed surfaces. Unetched. (b) Microstructure beneath sheet surface. Etched

surface (Fig. 2a), on the other hand, remained as smooth as the original alloy with little sign of pitting. Examination of the vacuum exposure material also indicated a slight surface roughening (Ref 4) similar in scope to that shown after immersion in molten salt (Fig. 2a). Inspection of salt and/or vacuum exposed gas-tungsten welds did not reveal any unusual behavior either in the weld itself or in the heat affected zone. After etching the thin sheet, M<sub>6</sub>C and Laves phases (Ref 2, 4) both within the grains and on the boundaries were clearly visible (Fig. 2b), and

measurements of the average grain size gave a diameter of 28.2 μm with a 5 μm standard deviation. Although this value is greater than approximately 20 μm for the as-received alloy 188, it is nearly the same size found after 4900 or 10,000 h heat treatments at 1093 K (Ref 3, 4).

### 3.2 Tensile Testing

Bar diagrams comparing the tensile properties of exposed alloy 188 to those measured for as-received material are presented in Fig. 3, and statistical summaries (average value and standard deviation) of the tensile test results are given in Table 2. As was the case with shorter term exposures (Ref 2, 3), the greatest degradations in mechanical properties are seen at 77 K. Exposure of 22,500 h to any of the three environments resulted in some loss in the 0.02% (Fig. 3a) and 0.2% (Fig. 3b) yield strengths and UTS (Fig. 3c). However such reductions in mechanical strength are minor (30% at most) compared to greater than 60% decrease in tensile ductility at 77 K (Fig. 3d) where the as-received elongation of over 30% is reduced to about 12%. Based on the current results, degradation of the 77 K UTS and ductility are independent of the environment; however, the 77 K yield strength data (Fig. 3a, b) suggest that vacuum might be more benign than either molten LiF-22CaF<sub>2</sub> salt or its vapor.

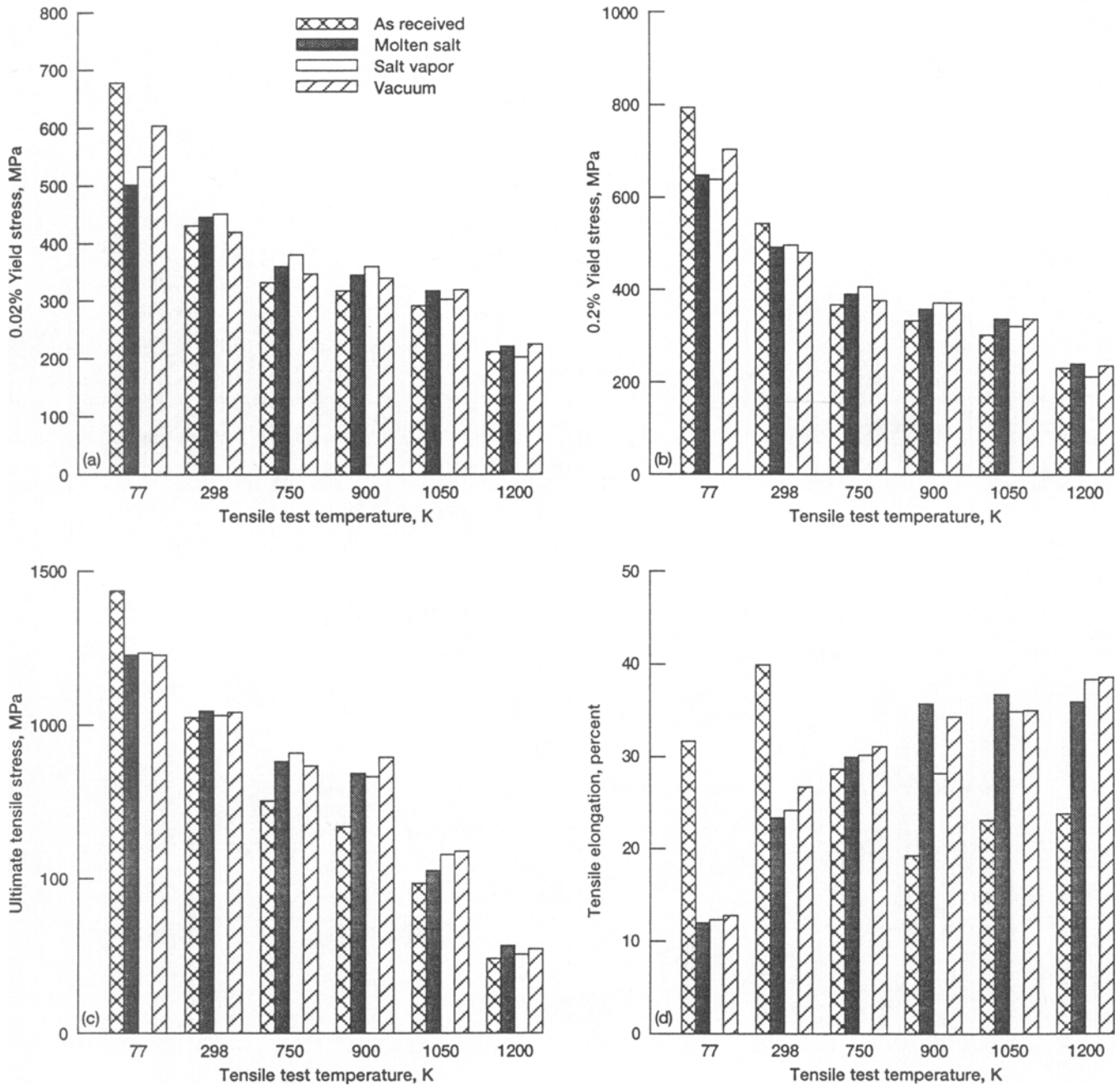
Tensile elongation at room temperature (Fig. 3d) is also reduced by prior exposure, but approximately 25% is more than half the measured ductility of 40% for the as-received material. As opposed to the mechanical strengths at 77 K, postexposure testing at 298 K did not show consistent degradation. While the 0.2% yield strengths of molten LiF-22CaF<sub>2</sub>, salt vapor, and vacuum-exposed alloy were less than the as-received value (Fig. 3b), this behavior was not observed in either the 0.02% yield strength (Fig. 3a) or UTS (Fig. 3c). In fact, prior exposure appears to improve these latter two measures of strength.

Postexposure testing at 750, 900, 1050, and 1200 K indicates that 22,500 h heat treatments at 1093 K basically improve all the tensile properties at elevated temperatures. The yield strengths (Fig. 3a, b) are better than, or essentially equal to, those measured for the as-received condition. In addition, the UTS values (Fig. 3c) and the tensile elongations (Fig. 3d) exceed the as-received values. Furthermore, examination of the measured elevated-temperature tensile properties in terms of the three different exposure conditions does not reveal any significant bias for any one environment over another.

In summary, no convincing evidence can be found in the tensile test results for alloy 188 given 22,500 h of exposure at 1093 K in molten LiF-22CaF<sub>2</sub>, salt vapor, or vacuum, which suggests additional degradation due to a specific environment. In actuality, regardless of the environment, long-term exposures improved the elevated-temperature ( $\geq 750$  K) tensile behavior. While exposure did affect the lower temperature (77 and 298 K) properties, particularly the tensile ductility (Fig. 3d), such degradations were not dependent on the environment.

### 3.3 1050 K Creep Rupture Testing

A summary of the 1050 K vacuum creep rupture data generated for alloy 188 after 22,500 h of exposure at 1093 K to vacuum or molten LiF-22CaF<sub>2</sub> is presented in Table 3, and examples of the creep rupture curves are illustrated in Fig. 4 as



**Fig. 3** Tensile properties of Haynes alloy 188 after 22,500 h of exposure to molten LiF-22CaF<sub>2</sub>, its vapor, and vacuum at 1093 K. (a) 0.02% yield strength. (b) 0.2% yield strength. (c) Ultimate tensile strength. (d) Tensile elongation

a function of engineering stress. These curves are typical for short (Fig. 4a), intermediate (Fig. 4b), and long (Fig. 4c) lives, and they illustrate that normal, three-stage creep occurs. The results of creep rupture testing in terms of the time-to-failure,  $t_r$ , (Fig. 5a) and the engineering steady-state creep rate,  $\dot{\epsilon}$ , (Fig. 5b) indicate typical behavior where the rupture life increased and the creep rate decreased with decreasing stress. Although only three data points were available for the molten-salt exposure condition, little visible difference in properties between the salt- and vacuum-exposed alloy 188 can be seen in Fig. 5. This hypothesis was statistically tested via linear regression

techniques and a dummy variable in combination with two power law equations, which describe  $t_r$  and  $\dot{\epsilon}$  in terms of engineering stress ( $\sigma$ ):

$$t_r = A\sigma^p \quad (\text{Eq 1})$$

$$\dot{\epsilon} = B\sigma^n \quad (\text{Eq 2})$$

where  $A$  and  $B$  are constants and  $p$  and  $n$  are stress exponents.

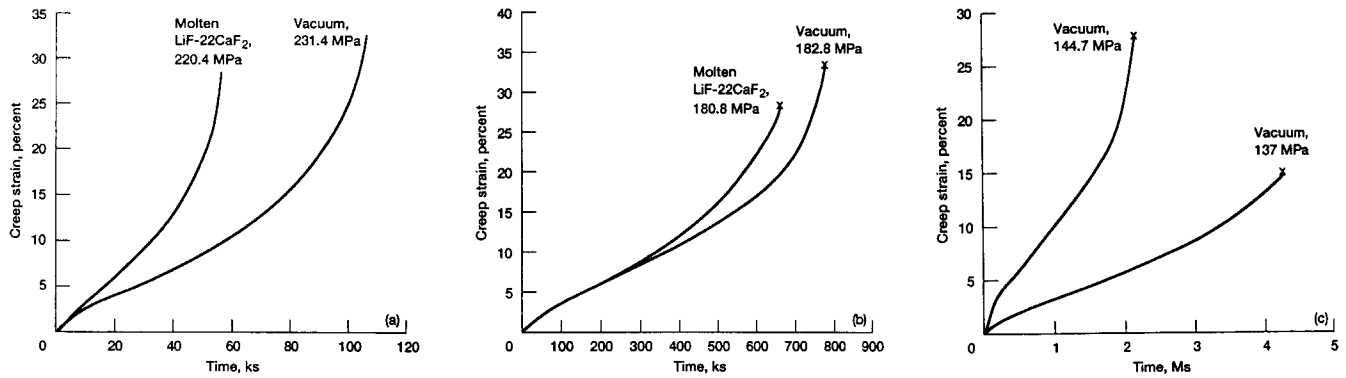


Fig. 4 Representative engineering 1050 K vacuum creep rupture curves for Haynes alloy 188 after exposure to molten LiF-22CaF<sub>2</sub> and vacuum for 22,500 h at 1093 K. (a) Short, (b) intermediate, and (c) long life times

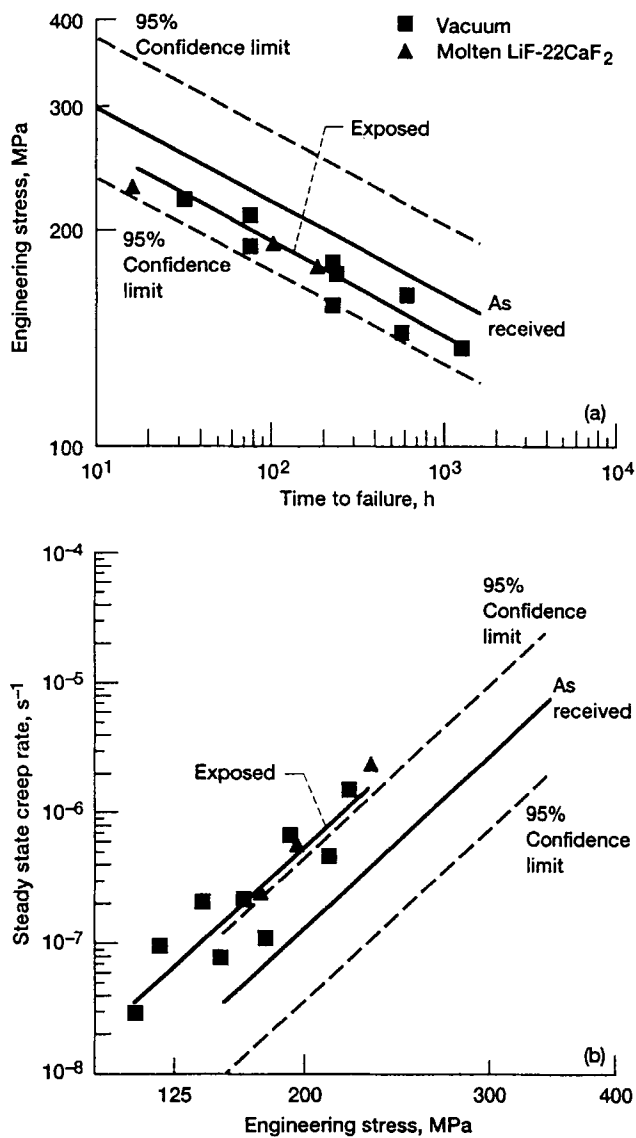
Table 2 Tensile properties of Haynes alloy 188 after various 22,500 h exposures at 1093 K

Test temperature, K	0.02 % Yield stress		0.2 % Yield stress		UTS		Elongation	
	Average, MPa	Standard deviation, MPa	Average, MPa	Standard deviation, MPa	Average, MPa	Standard deviation, MPa	Average, %	Standard deviation, %
<b>22,500 h in liquid LiF-22CaF<sub>2</sub></b>								
77	499.2	123.7	643.8	112.9	1227.8	84.4	11.9	1.8
298	442.8	13.9	493.7	11.4	1046.1	32.0	23.3	2.8
750	358.0	25.8	388.7	17.5	882.8	44.8	30.2	2.5
900	341.9	7.3	361.8	12.0	846.7	10.8	35.9	5.0
1050	311.5	5.4	341.9	6.8	533.5	14.9	36.7	2.9
1200	218.0	13.5	244.3	7.4	279.5	5.3	36.1	2.1
<b>22,500 h in LiF-22CaF<sub>2</sub> vapor</b>								
77	532.0	168.7	632.7	135.5	1236.5	8.9	12.2	1.6
298	447.8	11.9	495.3	11.2	1035.1	40.9	24.1	3.0
750	377.9	26.1	408.5	20.1	914.9	38.2	30.3	1.0
900	356.4	24.8	369.2	21.9	839.8	62.7	28.2	7.8
1050	299.4	3.7	325.4	3.7	577.9	12.3	34.9	0.8
1200	201.3	21.7	217.7	18.7	249.4	18.7	38.3	0.9
<b>22,500 h in vacuum</b>								
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

No statistical difference in 1050 K creep rupture properties could be found between alloy 188 samples exposed to molten salt or vacuum; therefore, both sets of data were joined and fitted to Eq 1 and 2. The calculated stress exponents, coefficient of determination ( $R_d^2$ ), and standard deviations for  $p$  and  $n$  ( $\delta_p$  and  $\delta_n$ ) are given in Table 4, and linear regression curves representing the data are plotted in Fig. 5. These curves allow a direct comparison with the predicted behavior for as-received alloy 188 (Ref 3), which is also shown in Fig. 5. The time-to-failure results (Fig. 5a) reveal that 22,500 h exposures at 1093 K bias the rupture strength toward the weaker 95% confidence limit for as-received alloy 188. On the other hand, the steady-state creep-rate data (Fig. 5b) indicate that the very long-term exposure reduces the creep properties to slightly less than the weaker 95% confidence limit for as-received alloy 188. While

the postexposure results indicate some weakening, the stress exponents (Table 4) for both the time-to-failure (Eq 1) and steady-state creep-rate (Eq 2) fits are identical to the  $p$  and  $n$  values obtained for the as-received alloy 188. This finding is strong evidence that the creep deformation mechanism for alloy 188 is not affected by prior exposure to molten LiF-22CaF<sub>2</sub> or vacuum at 1093 K.

Summarizing the 1050 K vacuum creep rupture testing of exposed alloy 188, with the caveat that only a few samples in contact with molten LiF-22CaF<sub>2</sub> were tested, no difference in properties based on the specific environmental exposure were found. However both vacuum and liquid salt samples exposed for 22,500 h at 1093 K possessed a decreased time-to-failure and an increased steady-state creep rate compared to the properties of as-received material. Although the changes are quite

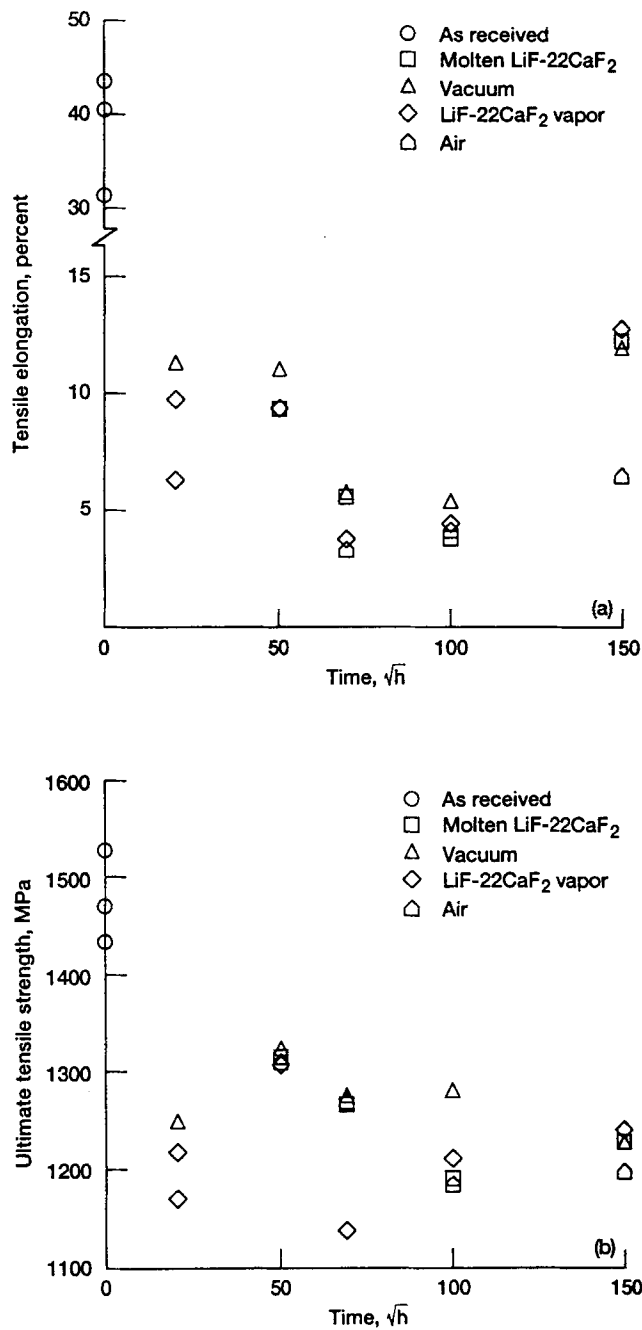


**Fig. 5** Time-to-failure (a) and steady-state creep rate (b) as a function of engineering stress from 1050 K vacuum creep rupture testing of Haynes alloy 188 after exposure to molten LiF-22CaF<sub>2</sub> and vacuum for 22,500 h at 1093 K

evident, they basically lie within or very close to the weaker 95% confidence limit for as-received alloy 188.

#### 4. Discussion

This paper completes the NASA-sponsored study in support of a space-based solar dynamic heat receiver utilizing Haynes alloy 188 to contain an eutectic LiF-CaF<sub>2</sub> energy storage media. To this end, the structure and mechanical properties of alloy 188 were examined after 400 to 22,500 h exposures to molten LiF-22CaF<sub>2</sub>, its vapor, vacuum, and air at 1093 K. Differences between the as-received and exposed materials were, of course, seen. For example, in terms of the structure of alloy 188: (1) all exposures produced intergranular and intragranular



**Fig. 6** The 77 K tensile properties of Haynes alloy 188 after various periods of exposure to molten LiF-22CaF<sub>2</sub>, its vapor, vacuum, and air at 1093 K. (a) Tensile elongation. (b) Ultimate tensile strength

precipitation of carbides (Fig. 2b, Ref 2-4); (2) surface roughening was seen after molten salt and/or vacuum exposures but not after contact with LiF-22CaF<sub>2</sub> vapor (Fig. 2a, Ref 2, 3); and (3) while occasionally pitting was observed after molten-salt exposures (Fig. 2a, Ref 2, 3), heat treatment in air produced pits at surface connected grain boundaries in addition to the oxide scale (Ref 3, 4).

The most significant structural change is the precipitation of carbides, which is responsible for the large decrease in tensile

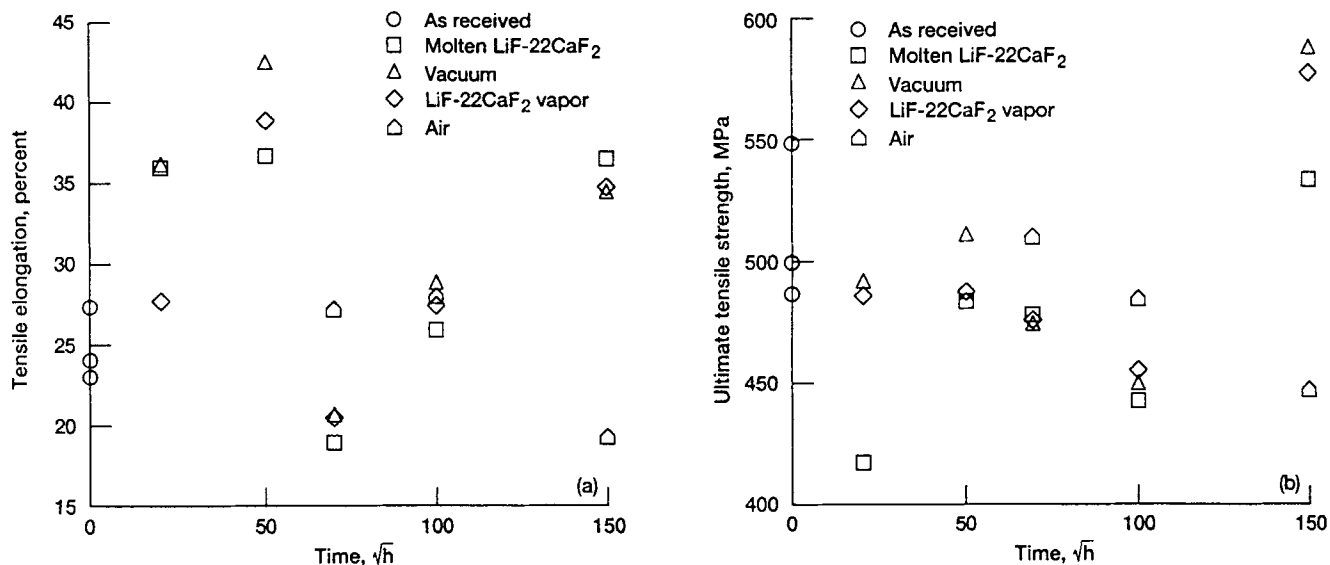


Fig. 7 The 1050 K tensile properties of Haynes alloy 188 after various periods of exposure to molten LiF-22CaF<sub>2</sub>, its vapor, vacuum, and air at 1093 K. (a) Tensile elongation. (b) Ultimate tensile strength

Table 3 1050 K vacuum creep rupture results of Haynes alloy 188 exposed to several environments for 22,500 h at 1093 K

Stress, MPa	Time to percent strain, h								Elongation at end test or rupture, %	Steady-state creep rate, s <sup>-1</sup>
	0.1	0.2	0.5	1.0	2.0	5.0	10.0	Rupture		
Exposed to molten LiF-22CaF <sub>2</sub>										
180.8	0.25	0.50	2.20	5.80	12.0	44.0	99.0	184.0	28.3	2.55E-07
195.5	0.25	0.45	1.33	2.75	6.6	28.0	49.0	103.0	27.8	5.73E-07
231.4	0.08	0.16	0.39	0.78	1.6	4.6	9.2	15.8	28.4	2.48E-06
Exposed to vacuum										
137.0	1.33	3.50	14.50	40.00	143.0	485.0	945.0	1203.0	15.4	2.71E-08
144.7	0.46	0.92	2.87	7.16	26.0	91.0	270.0	591.0	27.4	9.56E-08
159.3	0.08	0.16	0.44	2.95	16.0	60.0	125.0	220.0	31.7	1.98E-07
165.8	0.30	0.70	9.30	26.00	55.0	170.0	340.0	613.3	29.8	7.44E-08
174.8	0.10	0.20	1.10	2.75	13.0	54.0	118.0	223.5	30.8	2.08E-07
182.8	0.28	0.57	1.45	4.90	12.0	43.0	102.0	218.0	33.8	1.11E-07
192.1	0.20	0.38	0.94	2.42	4.8	16.6	36.0	73.5	36.4	6.60E-07
209.8	0.40	0.80	2.00	5.40	12.0	24.0	43.0	72.5	32.8	4.80E-07
220.4	0.08	0.16	0.41	0.82	2.2	7.6	16.4	29.5	32.7	1.50E-06

ductility at 77 and 298 K in comparison to the as-received alloy 188. The carbides promote intergranular fracture at the expense of the transgranular failure in the as-received, solution-treated material, and embrittlement after high-temperature heat treatments is a well-documented effect (Ref 5, 6). The 77 K tensile ductility of alloy 188 exposed for various periods at 1093 K in four different environments is presented in Fig. 6(a) where, for convenience, the square root of time is utilized as the abscissa. The results indicate that low-temperature embrittlement occurs throughout the time frame of this study; however, the greatest degradation takes place after intermediate anneals (4900 and 10,000 h). Lesser periods of time and, surprisingly except for the air exposure, longer periods result in greater levels of residual ductility. As opposed to minimum in the elongation-exposure behavior (Fig. 6a), the 77 K UTS does not indicate any real dependence on time (Fig. 6b). Essentially all the postexposure

values lie in a band from 1150 to 1300 MPa, irrespective of time at 1093 K.

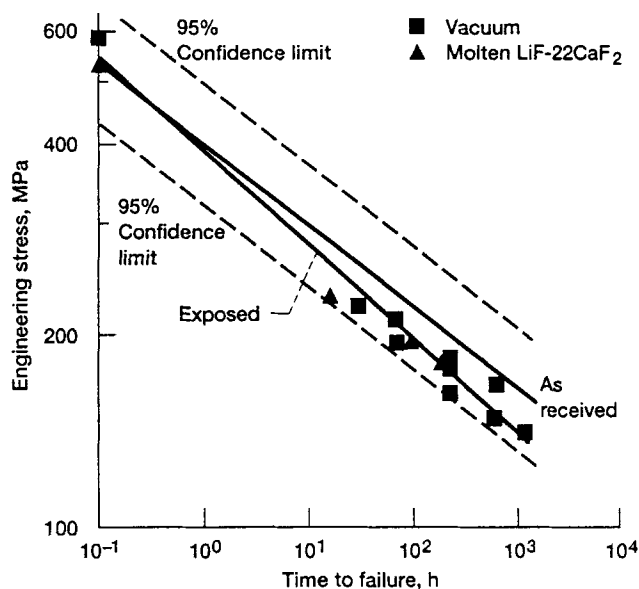
Examination of the postexposure, elevated-temperature tensile properties of alloy 188 also indicated that minimums in the high-temperature ductility can occur. Figure 7(a) presents the 1050 K tensile elongation data after being exposed to molten salt, its vapor, vacuum, or air for periods ranging from 400 to 22,500 h. These results show an increasing ductility through 2500 h and a sudden drop at 4900 h, which is followed by a continuous increase with time except for the air-exposed material. While the sharp drop in tensile elongation from approximately 40% at 2500 h to approximately 20% after 4900 h is clear, this decline really would not qualify as a degradation because it is nearly equal to the as-received value of about 25%.

Based on the 1050 K ultimate tensile strength data in Fig. 7(b), with one exception (400 h in liquid LiF-22CaF<sub>2</sub>), prior ex-

**Table 4 Power law and descriptive statistical parameters for 1050 K vacuum creep rupture testing of Haynes alloy 188 after exposure to molten LiF-22CaF<sub>2</sub> and vacuum for 22,500 h at 1093 K**

Testing condition	Time to rupture				Steady-state creep rate			
	Constant A, h	Stress exponent, <i>p</i>	Coefficient of determination, <i>R<sub>d</sub><sup>2</sup></i>	Standard deviation, $\delta_p$	Constant B, s <sup>-1</sup>	Stress exponent, <i>n</i>	Coefficient of determination, <i>R<sub>d</sub><sup>2</sup></i>	Standard deviation, $\delta_n$
As-received (Ref 3)	$7.80 \times 10^{19}$	-7.64	0.922	0.57	$5.55 \times 10^{-25}$	7.57	0.891	0.70
Exposed in molten salt and/or vacuum	$1.22 \times 10^{19}$	-7.48	0.904	0.77	$4.69 \times 10^{-24}$	7.43	0.843	1.01
Exposed in molten salt and/or vacuum and exposed UTS data(a)	$1.26 \times 10^{17}$	-6.60	0.981	0.27	...	...	...	...

(a) Fit includes the 1050 K UTS values from the 22,500 h exposed material



**Fig. 8** Time-to-failure as a function of engineering stress for 1050 K vacuum creep-rupture testing of Haynes alloy 188 after exposure to molten LiF-22CaF<sub>2</sub> and vacuum for 22,500 h at 1093 K. Ultimate tensile strengths utilized as a measure of the stress to produce failure in 0.1 h

posure through 10,000 h at 1093 K seems to be causing a progressive but minor weakening. Therefore, the sudden increase of the UTS by 10 to 20% over that of the as-received alloy after 22,500 h of salt or vacuum exposures was unexpected. Use of these data in the analysis of the vacuum creep rupture results significantly affected the interpretation. In order to extend the range of data for all material conditions in Ref 3, the average UTS values were utilized as a measure of the stress to produce failure at 0.1 h. As the UTS values demonstrated a gentle decline with exposure time through 10,000 h (Fig. 7b) in conjunction with generally weakening found by rupture testing (Ref 3), use of the UTS values in Eq 1 did not produce any anomalies. Specifically, the stress exponent for as-received and exposed materials has essentially the same values, ranging from -7.6 to -8.0 (Ref 3). However, if the 22,500 h vacuum and molten-salt exposed UTS data are used in Eq 1, a significant change in behavior seems to occur (Fig. 8, Table 4). The two UTS values force a change in the stress exponent of one unit (from -7.6 for as-received to -6.6 for 22,500 h exposure). This indicates a

change in deformation mechanism and, upon extrapolation, predicts a much weaker material.

However, the current 1050 K steady-state creep rate results (Fig. 5b) and those after 2500, 4900, and 10,000 h of prior exposure (Ref 3) do not indicate any change in deformation mechanism between the as-received and exposed materials. Thus it is hard to rationalize a major change in the time-to-rupture characteristics. Furthermore, analysis without the UTS values resulted in a stress exponent for rupture perfectly consistent with the as-received alloy (Fig. 5a, Table 4) and alloy 188 samples after 2500, 4900, and 10,000 h of prior exposure (Ref 3). Thus it is concluded that the valid interpretation of the postexposure 22,500 h time-to-rupture properties is that shown in Fig. 5(a), which discounts the postexposure 1050 K UTS data.

Although it has been stated several times (Ref 2, 3) that no evidence for additional degradation of mechanical properties beyond that due to simple thermal aging has been found in alloy 188 after exposures up to 10,000 h in molten LiF-22CaF<sub>2</sub>, its vapor, vacuum, or air, it now appears that this statement should be limited to the fluoride salt and vacuum exposures when longer periods at 1093 K are under consideration. Comparison of the UTS and elongation data for the 22,500 h exposed materials (Table 2 and Ref 5) indicates that heat treatment in air generally leads to lower properties than equivalent length exposures in molten LiF-22CaF<sub>2</sub>, salt vapor, or vacuum. Prime examples of this tendency are seen in the 77 K tensile ductility (Fig. 6a), the 1050 K elongations (Fig. 7a), and the 1050 K UTS values (Fig. 7b). The relative embrittlement and weakening of air-exposed alloy 188 in comparison to the other three environments is not surprising because heat treatment in air results in significant grain boundary pitting and growth of oxide scales (Ref 4). As oxidation will remove the alloying elements, which strengthen, and pitting reduces the local cross-section area, eventual degradation must occur.

## 5. Conclusion

The possible containment of a molten LiF-CaF<sub>2</sub> eutectic at 1093 K in Haynes alloy 188 was tested for periods ranging from 400 to 22,500 h. The current study examined the effects of 22,500 h exposures in vacuum, molten LiF-22CaF<sub>2</sub>, and its vapor on the structure. The 77 to 1200 K tensile properties and the 1050 K vacuum creep-rupture behavior does not give any evidence for additional degradation beyond that due to thermal ex-



posure, which can be ascribed to one of these three environments. Therefore, the conclusion that Haynes alloy 188 is a viable containment alloy for a space-based LiF-CaF<sub>2</sub> based thermal energy storage system is more valid today than when projected from 10,000 h exposures. Furthermore, it is concluded that very long-term 1093 K exposures to air are much more damaging than to either LiF-CaF<sub>2</sub> or vacuum environments.

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