Effect of Exposure on the Mechanical Properties of Gamma MET PX

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Abstract

The effect of a service environment exposure on the mechanical properties of a high Nb content TiAl alloy, Gamma MET PX[1], was assessed. Gamma MET PX, like other TiAl alloys, experiences a reduction of ductility following high temperature exposure. Exposure in Ar, air, and high-purity oxygen all resulted in a loss of ductility with the ductility reduction increasing with oxygen content in the exposure atmosphere. Embrittling mechanisms, including bulk microstructural changes, moisture induced environmental embrittlement, and near surface effects were investigated. The embrittlement has been shown to be a near-surface effect, most likely due to the diffusion of oxygen into the alloy.

Keywords

A. titanium aluminides, B. brittleness and ductility, B. environmental embrittlement, B. fracture toughness, B. oxidation

Introduction

Gamma MET PX, a high Nb-content TiAl alloy, has been under evaluation for several NASA programs including the turbine based combine cycle program (TBCC) for

[1] Gamma MET PX is a trademark of PLANSEE AG, Austria. Alloy composition is based on TNB alloys developed by GKSS Research Center, Germany.

the next generation launch vehicle. Gamma MET PX has excellent mechanical properties including improved oxidation resistance and high tensile, creep, and fatigue strength[1]. During the evaluation, the tensile and fatigue properties after a simulated service exposure of 800 °C for 200 h in air was assessed and a significant reduction in room temperature ductility was observed due to the high temperature exposure[1]. A more comprehensive investigation of the mechanical properties following a high temperature exposure is reported in this paper.

Materials and Procedures

Triple vacuum arc remelted Ti-45Al-5Nb-B-C (at. %) gamma TiAl ingots were extruded in two steps at a nominal billet preheat temperature of 1280 °C to a final extrusion ratio 100:1 for 12.7 mm diameter bars and 14:1 for 38 mm diameter bars. Three separate batches of material were utilized in the investigation. The as-extruded bars had a duplex microstructure with a high volume fraction of lamellar grains, which varied slightly from batch to batch. The lamellar grain size was approximately 20 μm and small (~ 4 μm) gamma grains were located in between lamellar colonies for all batches. A fully lamellar microstructure, with a lamellar colony size of 325 ± 45 μm, was formed by heat treating the 12.7 mm bars at 1340°C for 40 min in vacuum followed by furnace cooling. The threads on tensile specimens were not machined until after the high temperature exposure to avoid failures in the threads. Tensile specimens were exposed at 700 and 800 °C for 200 h in air. Additional tests included exposing unprotected samples to 800 °C for 200 h in dry, ultra-high purity O_2, and exposing samples wrapped in Ta foil to Ar with a purity of 99.999%. Only the results of gage failures are reported, and all error bands represent 95% confidence intervals. Tensile specimens were tested at 23 and 650 °C using a constant strain rate of 1×10^{-4} s^{-1}.

High cycle fatigue specimens were tested at 23 and 650 °C with a frequency of 100 Hz and a load ratio, R, of 0.05 ($R=\sigma_{min}/\sigma_{max}$). Due to the flat nature of γ-TiAl's stress vs. cycles to failure curve, step fatigue tests were used to determine the maximum fatigue strength[2-4]. If the sample survived 10^6 cycles, the stress was increased by 13.8 MPa and run to failure or an additional 10^6 cycles. Fatigue strength was taken as the stress at the next-to-last step, i.e., the stress representing the fatigue threshold. Three samples were machined for every condition but if the sample failed in the first step, the test was considered invalid and the data were not used. Dynamic fracture toughness testing was performed on both as-extruded material and as-extruded material exposed to 700 °C for 100, 200, and 300 h using a notched, 3 –point bend specimen in a modified Split Hopkinson pressure bar configuration [5]. A 3.0 mm notch with a 1 mm pre-crack extension was wire electro-discharge machined into a 50 x 10 mm sample.

Results

The room temperature plastic elongation to failure was significantly affected by the high temperature exposure of both as-extruded and lamellar heat treated Gamma MET PX, Table I. At room temperature, the plastic elongation of as-extruded samples from all three batches of material, 16 samples, averaged of 1.54 ± 0.29%. The room temperature plastic elongation decreased to 0.37 and 0.10% after exposure at 700 and 800 °C for 200 h, respectively. While the room temperature ultimate tensile strength (UTS) of Gamma MET PX decreased with high temperature exposure, the reduction was relatively small and was a result of reduced strain hardening. The samples which were wrapped in Ta foil and exposed to high purity Ar at 800 °C for 200 h had a shiny gold tint to their surface upon removal from the furnace. Exposure to Ar was less detrimental to room temperature ductility but still resulted in a 57% decrease in ductility.

The ductility of the lamellar heat treated material was low, averaging only 0.32% in the as-heat treated condition, and decreased to below 0.1% after exposure in air to 800 °C for 200 h. At the elevated test temperature of 650 °C, the as-extruded and lamellar material retained 64 - 69% of its ductility after exposure in air to 800 °C for 200 h, Table I. Fracture took place in a macroscopically brittle manner for both unexposed and exposed samples and at both 23 and 650 °C. The fracture morphology was similar for both exposed and unexposed samples with no evidence of intergranular fracture near the sample surface. Initiation sites were only visible on a few of the as-extruded tensile samples in which microstructural inhomogeneities such as a larger than normal lamellar colony[1] initiated failure. Scanning electron microscopy (SEM) examination of longitudinally polished samples revealed a variety of crack propagation paths including translamellar, interlamellar, and intergranular.

As-extruded and lamellar high cycle fatigue specimens, both as-received and after 800 °C for 200 h exposures, were step fatigue tested at room temperature and 650 °C, Figure 1. The as-extruded fatigue strength was not affected by the high temperature exposure at either room temperature or 650 °C. The fatigue strength of the lamellar microstructure was significantly lower than as-extruded, averaging 522 and 562 MPa at 23 and 650 °C, respectively. As with the as-extruded microstructure, the lamellar fatigue strength was not diminished by the high temperature exposures at either room temperature or 650 °C.

As-extruded material was machined into fracture toughness samples and then exposed to 700 °C for 0, 100, 200, and 300 h. Dynamic fracture toughness, already being performed on as-extruded Gamma MET PX under another program, was measured on the exposed material using a modified Split Hopkinson pressure bar . The

as-extruded material had a fracture toughness averaging 22 MPa $m^{1/2}$, Figure 2a. After just 100 h exposure, the K_{IC}^{d} decreased to 13.2 MPa $m^{1/2}$ and was 11.4 MPa $m^{1/2}$ after 300 h at 700 °C. Both the exposed and unexposed fracture toughness samples had brittle fracture morphology, Figure 2b.

In order to investigate the embrittlement problem, metallographic samples were polished and the near surface region was analyzed using a microprobe. The oxide layers, a mixture of TiO_2 and Al_2O_3, were only 4-5 μm in total thickness after exposure at 800 °C for 200 h in air, Figure 3a. Oxygen was detected only in the oxide layer. The oxygen detectability limit is approximately 0.1 weight percent using wavelength dispersive spectroscopy. At the oxide-alloy interface, a layer of Ti/Al-N was observed, similar to that observed in other TiAl alloys[6-8]. A higher level of C was also detected in this Ti/Al-N layer. The near-surface microstructure was nearly 100 % γ-TiAl, enriched in Al and Nb and depleted of Ti, within ~8 μm of the surface. A very fine Nb-enriched phase was also present at the grain boundaries. Beyond 8 – 10 μm, the microstructure and chemical composition was unchanged from the as-extruded microstructure. Exposure in Ar resulted in a very thin Ti-Al/N layer, less than 1 μm in thickness, which also contained O and C on the surface, Figure 3b. Beneath this layer was a region of α_2 depletion, enriched in Al and Nb and depleted of Ti. The α_2 depleted zone was approximately 6 μm deep.

Vickers microhardness measurements were made on a variety of samples using both 50 and 100 gm loads. The indent diagonals were approximately 17 and 24 μm for the 50 and 100 gm loads, respectively, and therefore the ability to place indents close to the edge was limited. However, there was no trend indicating a change in hardness from the edge inward, Figure 4. The as-extruded material had a higher hardness close

to the edge due to high levels of strain which accumulate near the extrusion surface. However, all the tensile samples were machined away from the extrusion edge.

Various mechanisms were investigated as possible sources of embrittlement including: 1) bulk microstructural changes, 2) hydrogen embrittlement, and 3) near-surface effects. Bulk microstructural changes, such as carbide coarsening, could be occurring during the exposure. Extruded bars were exposed in air to 800 °C for 200 h and then machined into tensile samples, thus eliminating any surface effect. The tensile properties of the exposed and then machined samples were equivalent to as-extruded properties, Table I. Additionally, SEM and transmission electron microscopy (TEM) analysis did not reveal any changes in bulk microstructure after exposure. Therefore, as with other TiAl alloys[7, 9-11], bulk microstructural changes were not responsible for the embrittlement of Gamma MET PX.

Moisture-induced hydrogen embrittlement has been determined to be the cause of ambient temperature ductility reduction in other TiAl alloys [7,9,11,12]. Therefore, a series of tests were undertaken to determine if such embrittlement, occurring either during the room temperature tests following exposure or during the high temperature exposure, was the cause of Gamma MET PX's embrittlement. Tensile samples exposed at both 700 and 800 °C for 200 h in air were then tested under 99.995% pure Ar. No difference in tensile ductility was found between testing in Ar compared to testing in air, Figure 5. The amount of water vapor in the Ar atmosphere was substantially less than in air and therefore some improvement in ductility should have been observed if water-induced environmental embrittlement was the mechanism. Testing of other TiAl alloys in Ar or oxygen, above 200 °C, or at high strain rates after high temperature exposures all resulted in normal ductility[9, 11]. Exposed Gamma

MET PX had lower than normal ductility at elevated temperature, even as high as 650 °C, Table I. Therefore, a different embrittlement mechanism appears to be operative although moisture-induced environmental embrittlement may also be occurring. To determine the effect of hydrogen during the exposure, samples were exposed to Ar and dry, ultra-high purity oxygen for 800 °C for 200 h and tensile tested. The results are included in Table I. The Ar exposed samples had a very thin layer of Ti-Al/N, which also contained a small amount of O, on the sample surface. While it is unlikely that moisture induced environmental degradation could be occurring at these temperatures in this environment, the environment was not completely protective. The presence of hydrogen during the elevated temperature exposure was eliminated by exposing tensile samples to dry, ultra-high purity oxygen at 800 °C for 200 h. The samples exposed to ultra-high purity oxygen failed to reach 0.2% offset yield and plastic elongations were minimal, less than 0.05%. Hydrogen would not have been present during the exposures in dry, ultra-high purity oxygen and therefore, moisture-induced environmental embrittlement did not occur in these samples. Yet, their ductility was the lowest measured.

SEM and energy dispersive spectroscopy (EDS) analysis of the samples exposed to ultra-high purity oxygen revealed internal oxidation and a different near surface microstructure compared to samples exposed in air or Ar, Figure 6. The oxide scale thickness was not as uniform and varied from less than 1 μm up to 15 μm. The Ti/Al-N phase was not detected near the oxide/alloy interface. Instead of having an α_2 depleted zone, α_2 formed in the near surface region. Two different types of internal oxidation were observed. TiO_2 sporadically grew in from the surface, up to 20 μm in depth, and was surrounded by Al_2O_3. Secondary cracking occurred at these areas.

Additionally, internal Al_2O_3 formed in the near surface region, Figure 6b. The Al_2O_3 did not appear to be associated with secondary cracking. While external oxidation is reduced for high Nb content alloys, TiAl alloys with Nb contents greater than 2% have been shown to promote internal oxidation [6,12]. The presence of nitrogen in the exposure atmosphere has been shown to affect the overall oxidation resistance of Ti-50Al but the oxidation rates of Nb modified TiAl alloys has been shown to be less dependent on the composition of the gas [13]. However, it appears as though the Ti/Al-N phase which formed during the exposure of Gamma MET PX in air may have acted as a diffusion barrier, as the samples exposed to air did not have internal oxidation.

In order to determine the effect of the oxide layer and/or near surface microstructure changes on RT tensile ductility, flat, dog-bone shaped samples were exposed to 800 °C for 200 h in air and then polished using 600 grit SiC paper to remove 25, 50, and 75 μm from the surface, Table II. The ductility was fully restored after removal of between 25 – 50 μm from the surface and therefore, it is clear that the embrittlement is a near-surface effect. However, the microstructural variations were only observed within ~10 μm of the surface by SEM for samples exposed at 800 °C for 200 h, while it took removal of more than 25 μm to completely restore the ductility.

Compressive residual stresses possibly beneficial to tensile ductility could be induced during the machining process, and subsequently relieved during the high temperature exposure to contribute to the loss of ductility. While residual stresses were not measured, the hardness profiles of machined samples do not suggest the presence of work hardening indicative of compressive residual stresses. Additionally, removal of the surface layer by polishing is not likely to induce substrantial residual stress, and yet

the ductility was restored after 50 μm were removed from the surface. Surface removal by electropolishing was not possible with the oxide present.

Discussion

Gamma MET PX suffers from a loss of ductility following high temperature exposure which has been shown to be a near surface effect as polishing 50 μm from the surface restored the ductility. Three different exposure atmospheres were utilized and the near surface microstructure varied with the exposure atmosphere. The remnant ductility inversely correlated with the oxygen content of the exposure atmosphere, with the greatest ductility following exposure in Ar and the least following exposure in ultra-high purity oxygen. Oxygen was not detected within the resolution limit in the sub-surface microstructure by microprobe analysis for samples exposed in Ar and air. However, sufficient oxygen may have diffused into the near-surface microstructure to embrittle the alloy and still be below the detectability limit of the microprobe. Internal oxidation was observed in the samples exposed to oxygen and this internal oxidation was associated with secondary cracking.

The loss of room temperature ductility following high temperature exposure has been observed for other TiAl alloys previously [7, 9-12]. Kelly et al [9] observed the ductility of Ti-48Al-2Cr-2Nb drops in half after exposure to 649 °C for 16 h. For a direct comparison, cast Ti-48Al-2Cr-2Nb was exposed to 800 °C for 200 h and the ductility dropped from an average of 1.0% for unexposed to 0.23% after exposure. Data was gathered from the literature[7], in-house work, and a NASA contract [14] and a trend was observed toward increasing embrittlement due to exposure for higher Nb content alloys, Figure 7. However, this trend needs to be verified with a higher than 6 at.%Nb alloy.

While it has been known for quite some time that TiAl alloys suffer from loss of room temperature ductility following high temperature exposure, the embrittlement issue has not been of great concern. This was because it has typically only been observed below 200 °C, a temperature regime of little concern in service [9]. However, Gamma MET PX has a more substantial room temperature ductility reduction than previous alloys, and also exhibits reductions in fracture toughness and ductility at temperatures as high as 650 °C. Increased care had to be taken to only machine the sample threads after exposure to prevent failure in the grips with Gamma MET PX, indicating an increased notched sensitivity for Gamma MET PX after exposure.

Conclusions

Gamma MET PX suffers from a loss of ductility following high temperature exposure that has been shown to be a result of near-surface microstructural changes, most likely diffusion of oxygen into the near surface region. While all TiAl alloys suffer from a loss of ductility following high temperature exposure, the embrittlement is the most severe in high Nb content alloys. In general, other TiAl alloys' loss of ductility following high temperature exposure has been at least partially attributed to moisture induced environmental embrittlement, but this was not shown to predominate for Gamma MET PX. While the fatigue strength was unaffected by the exposure, the low tensile ductility and reduced fracture toughness would be of concern for aerospace applications, and future work is needed to thoroughly understand and address the problem.

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Figure Captions

1. Effect of 800 °C exposure on fatigue strength of extruded and lamellar microstructures at both 23 and 650 °C.

2. (a) Dynamic fracture toughness decreased with increasing time at 700 °C. (b) A brittle fracture morphology was observed on both unexposed and exposed samples tested at room temperature.

3. Near surface microstructure of an as-extruded sample exposed to 800 °C for 200 h in (a) air and (b) Ar.

4. Hardness profiles do not indicate an increase in hardness due to the high temperature exposures.

5. Tensile test environment had no effect on tensile ductility after high temperature exposure.

6. Internal oxidation in the form of (a) TiO_2 growing in from the surface and (b) Al_2O_3 forming internally were observed in as-extruded samples exposed to 800 °C for 200 h in dry, ultra-high purity oxygen.

7. With data obtained from in-house work, a contract [14], and the literature [7,9], a trend of increasing embrittlement with increasing Nb content in TiAl alloys was observed.

Table I. Tensile ductility of Gamma MET PX under various exposure conditions

Material	Exposure Temp. (°C) /Time (h)	Exposure Atmosphere	Test Temp. (°C)	UTS (MPa)	Plastic Elongation (%)
As-extruded	none		23	1070 ± 43	1.54 ± 0.29
As-extruded	700/200 h	Air	23	989 ± 110	0.37 ± 0.35
As-extruded	800/200 h	Air	23	875 ± 69	0.10 ± 0.15
As-extruded	800/200 h	Ar	23	948 ± 41	0.67 ± 0.16
As-extruded	none		650	1015 ± 134	1.39 ± 0.38
As-extruded	800/200 h	Air	650	965 ± 45	0.89 ± 0.24
As-extruded	800/200 h	Dry Oxygen	23	854 ± 9	0.04 ± 0.03
As-extruded, machined from center following exposure	800/200 h	Air	23	1091 ± 84	2.4, 1.75
Lamellar	none		23	806 ± 31	0.32 ± 0.04
Lamellar	800/200 h	Air	23	722 ± 42	0.09 ± 0.03
Lamellar	None		650	793 ± 25	1.38 ± 0.55
Lamellar	800/200 h	Air	650	749 ± 47	0.95 ± 0.36

Table II. Tensile ductility after exposure and subsequent surface removal by polishing

Specimen Preparation	**Exposure**	**RT Plastic Elong., %**
As-machined	None	1.14, 1.35
0 μm polished	800 °C/ 200 h/ air	0 – 0.24
25 μm polished	800 °C/ 200 h/ air	0.70, 0.87
50 μm polished	800 °C/ 200 h/ air	1.11, 1.28
75 μm polished	800 °C/ 200 h/ air	1.03, 1.60

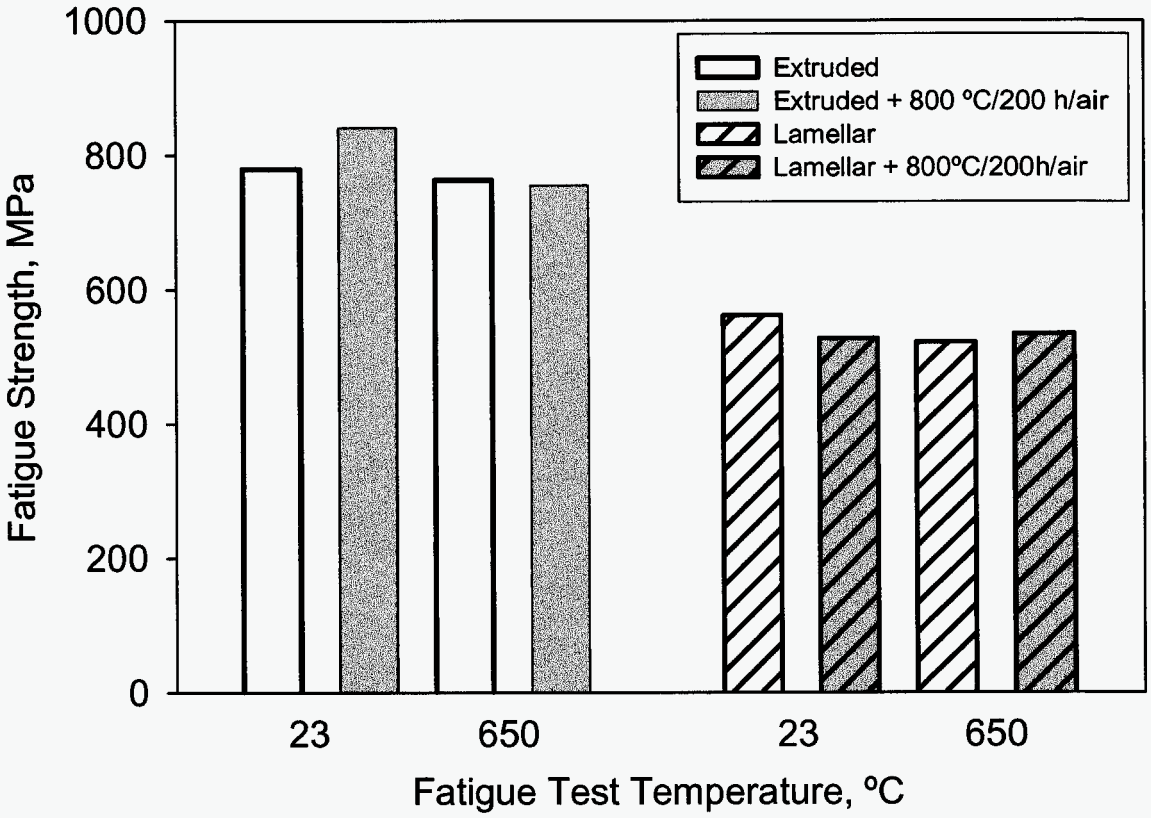
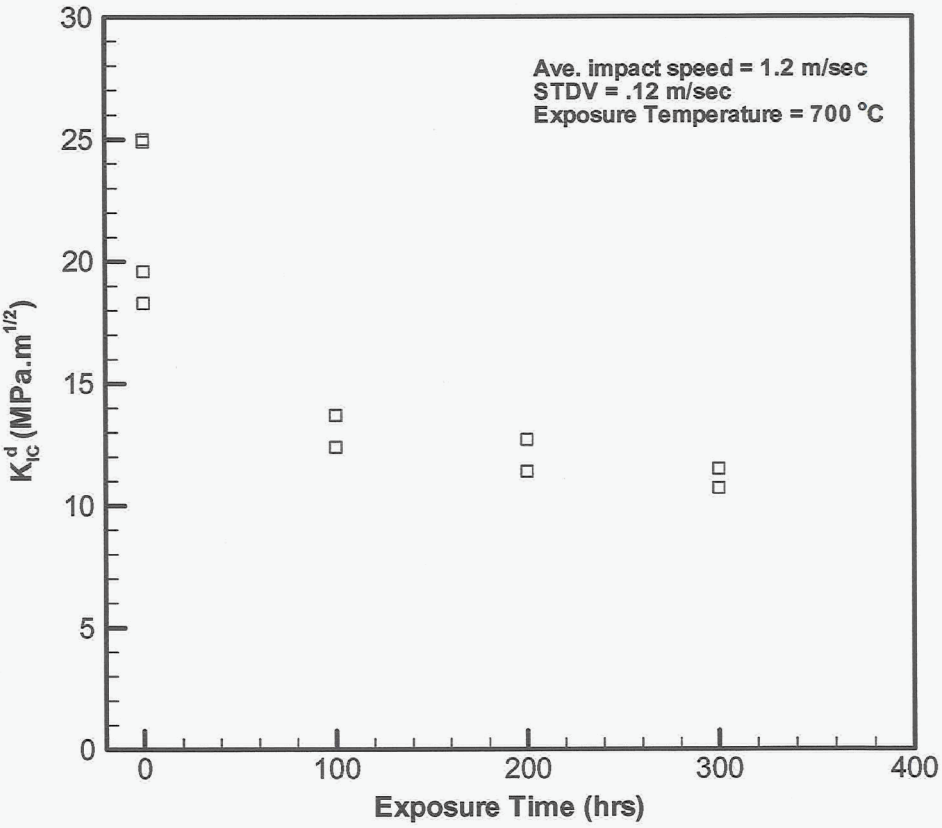
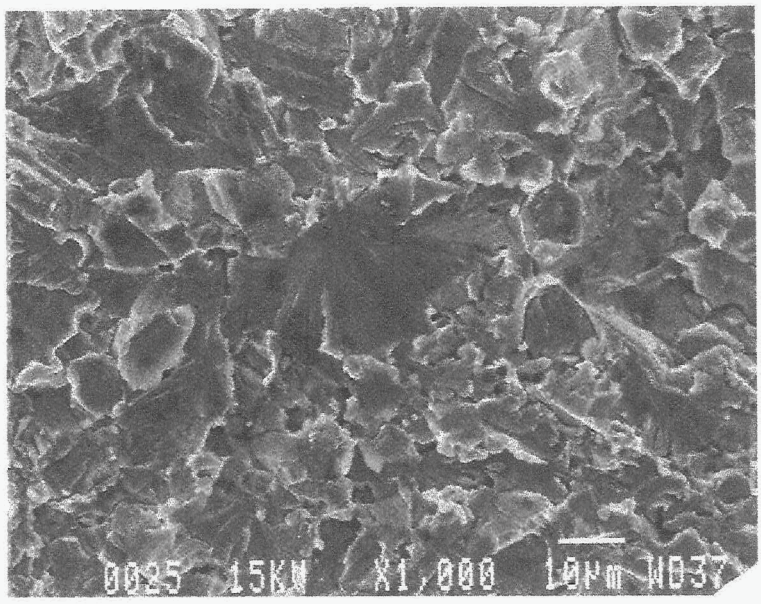


Figure 1. Effect of 800 °C exposure on fatigue strength of extruded and lamellar microstructures at both 23 and 650 °C.

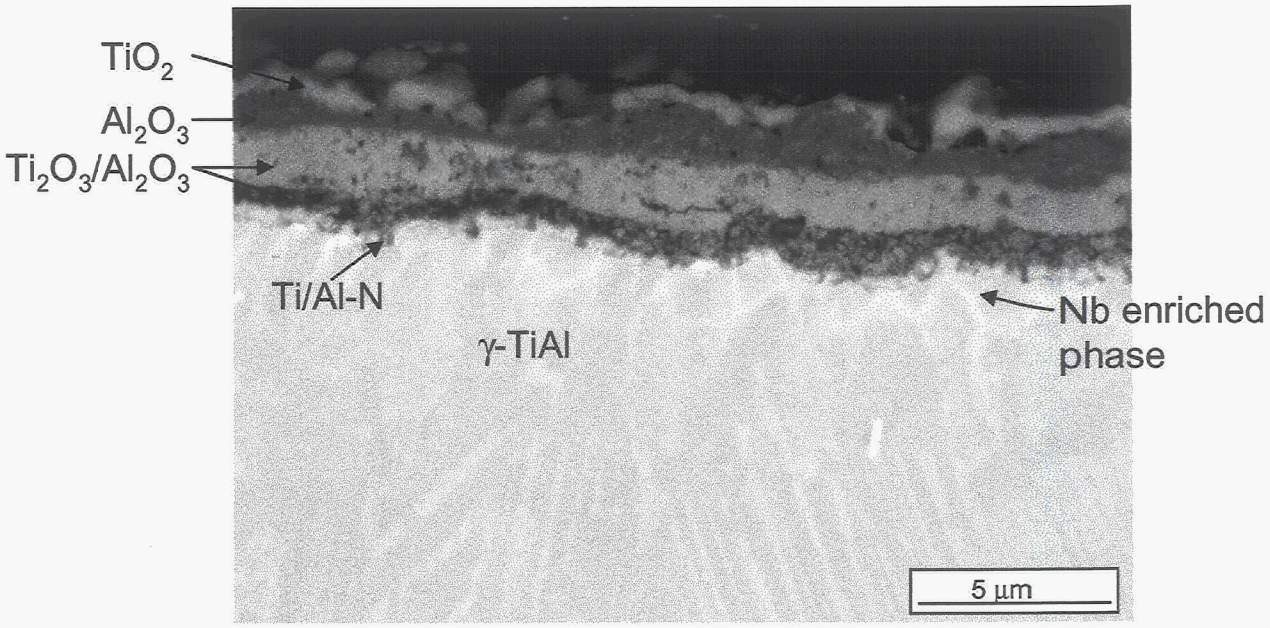


(a)



(b)

Figure 2. (a) Dynamic fracture toughness decreased with increasing time at 700 °C. (b) A brittle fracture morphology was observed on both unexposed and exposed samples tested at room temperature.



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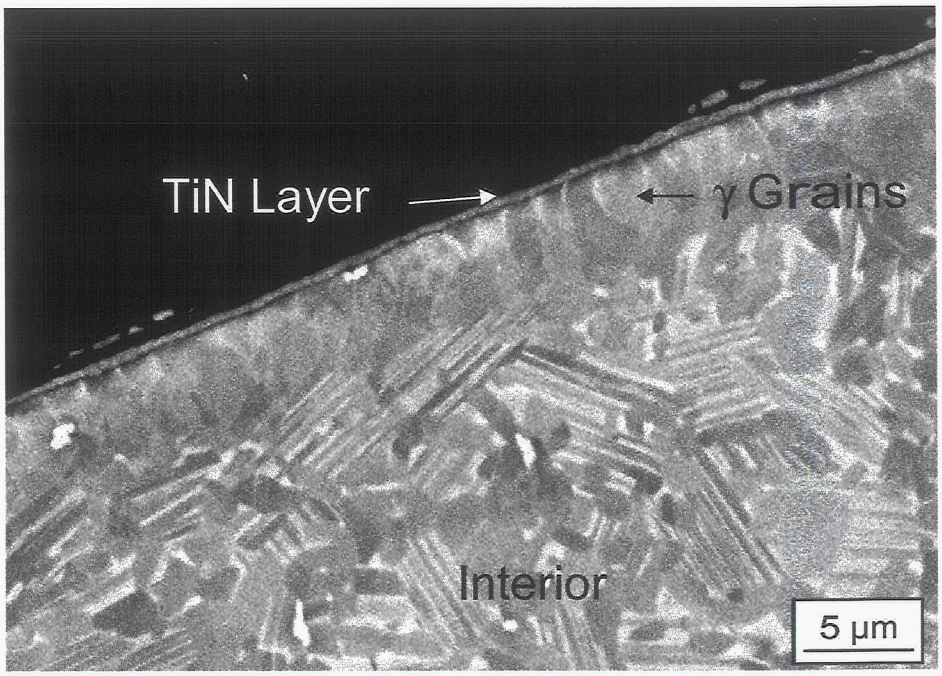


(b)

Figure 3. Near surface microstructure of an as-extruded sample exposed to 800 °C for 200 h in (a) air and (b) Ar.

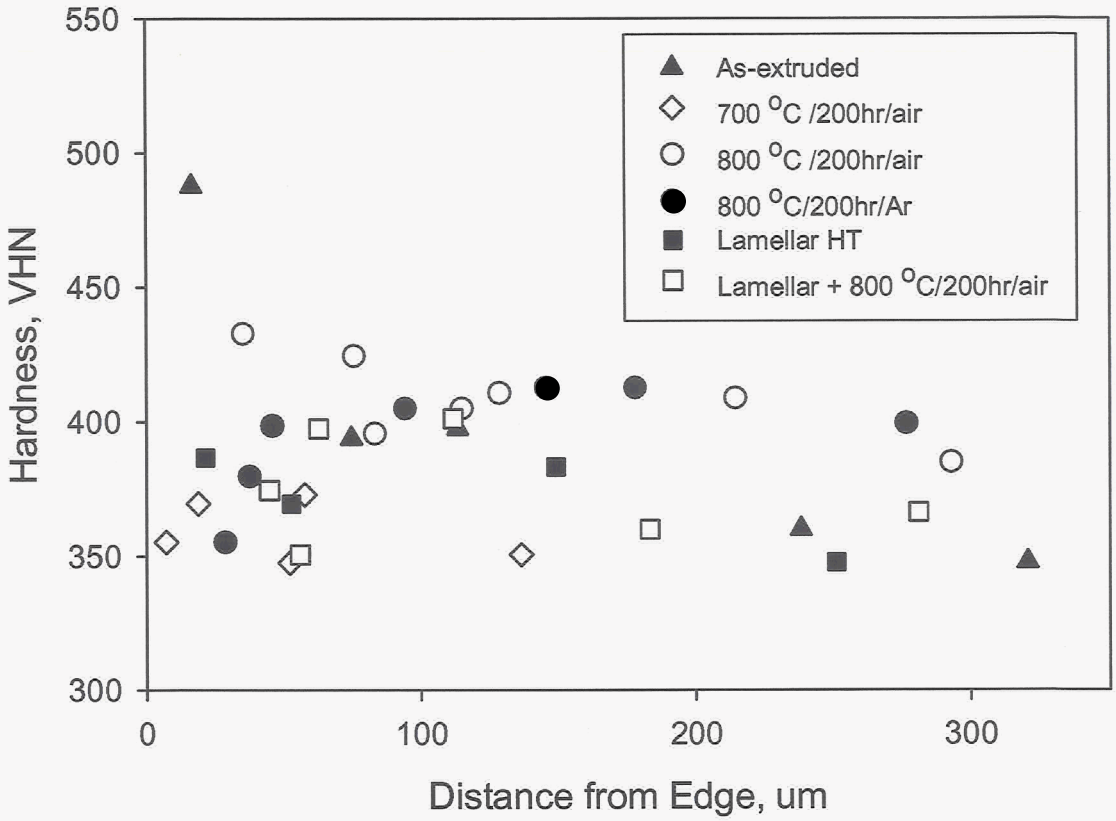


Figure 4. Hardness profiles do not indicate an increase in hardness due to the high temperature exposures.

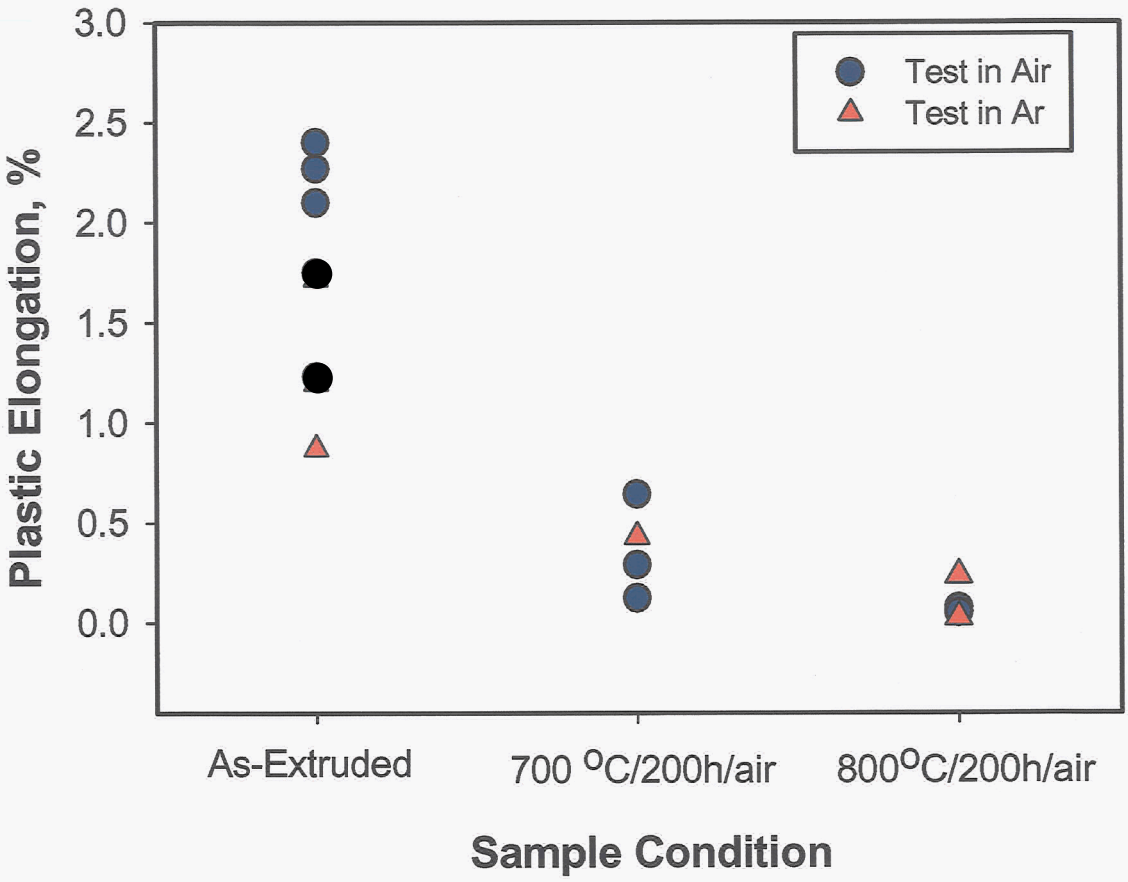
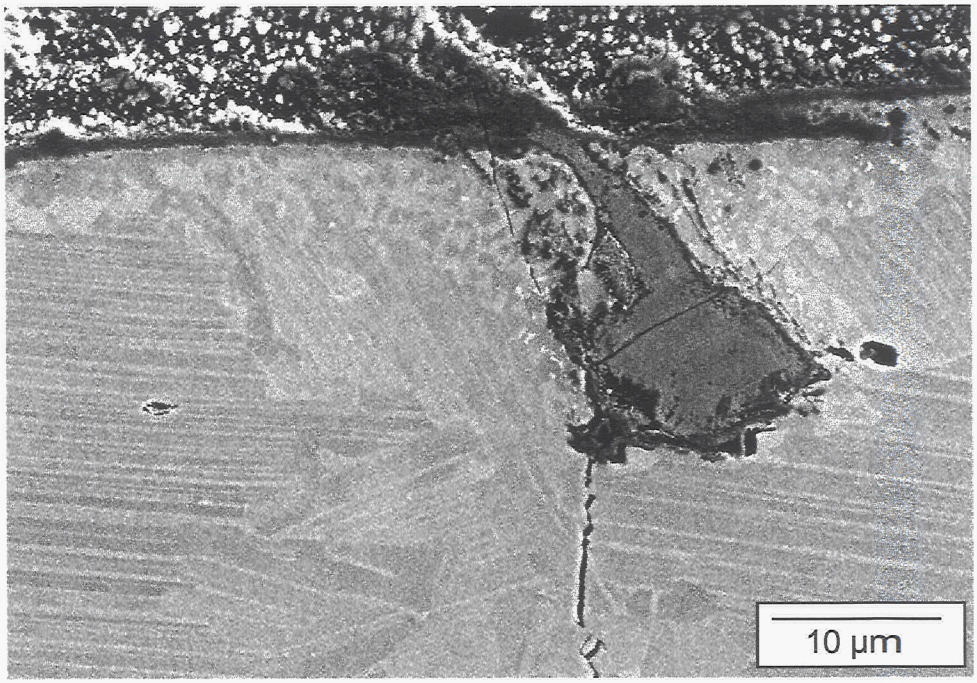
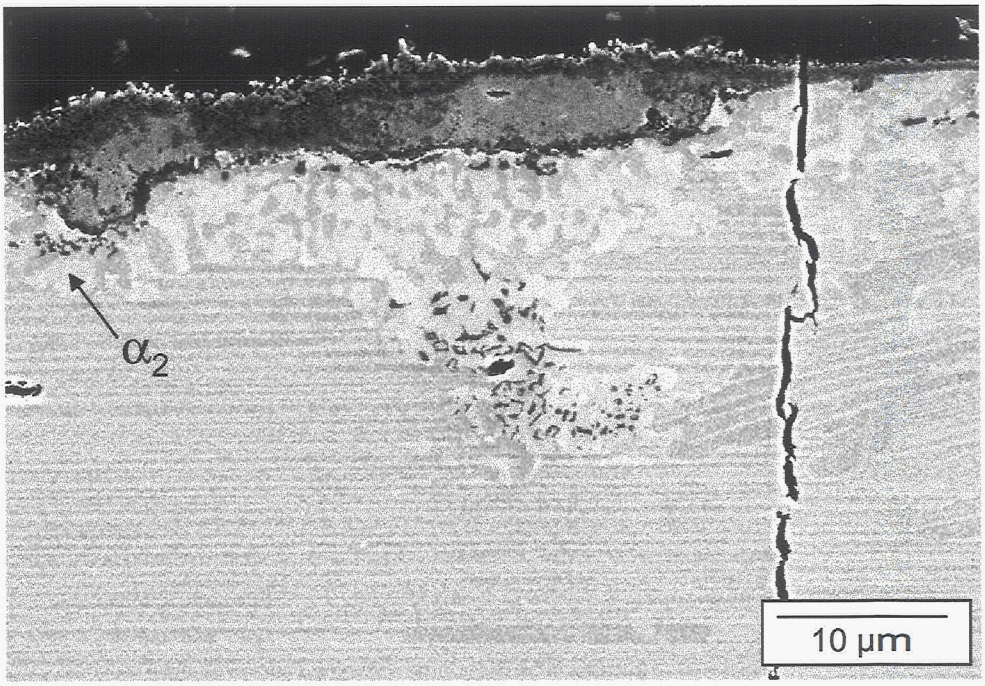


Figure 5. Tensile test environment had no effect on tensile ductility after high temperature exposure.



(a)



(b)

Figure 6. Internal oxidation in the form of (a) TiO_2 growing in from the surface and (b) Al_2O_3 forming internally were observed in as-extruded samples exposed to 800 °C for 200 h in dry, ultra-high purity oxygen.

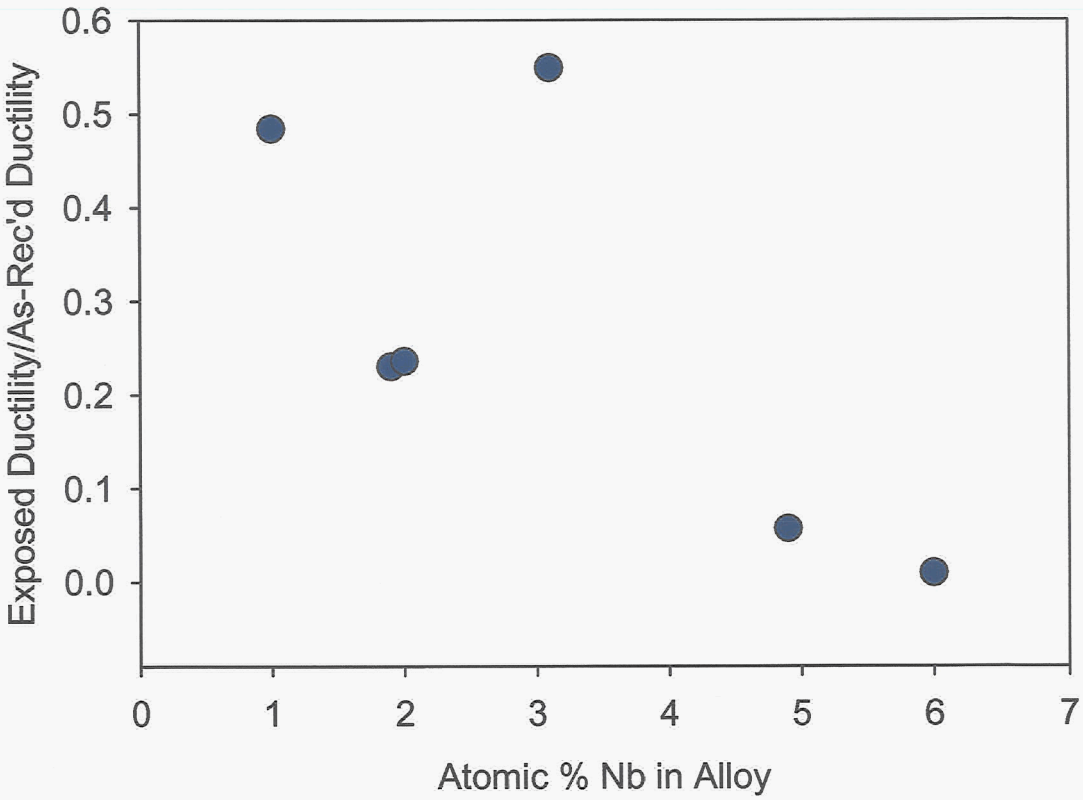


Figure 7. With data obtained from in-house work, a contract [14], and the literature [7,9], a trend of increasing embrittlement with increasing Nb content in TiAl alloys was observed.