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Cryogenic Deformation Behavior of TiAl and Insights Into Embrittlement After High-Temperature Exposure Combined With Secondary Ion Mass Spectroscopy of Near Surface Chemistry

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ABSTRACT

This study investigates the embrittlement of TiAl after high-temperature air exposure. The loss of room-temperature tensile ductility persists even when tested under liquid nitrogen (−196 °C), with brittle fracture occurring at higher stress levels than typical room-temperature fracture. Existing embrittlement mechanisms in TiAl literature fail to explain this phenomenon under liquid nitrogen. Using secondary ion mass spectrometry (SIMS), surface chemistry analysis of binary TiAl alloys exposed at 700 °C for 4 h in an artificial air-like environment (containing heavy water, ¹⁵N₂, and ¹⁸O₂) revealed dissociation of water vapor at the TiAl surface and absorption of deuterium into the material. This marks the first report of water vapor dissociation and deuterium (or hydrogen under natural conditions) ingress into heated TiAl specimens. A localized enrichment of hydrogen and deuterium was observed beneath the surface. Given that traditional embrittlement mechanisms do not account for the increased fracture stress under liquid nitrogen, it is proposed that hydrogen absorption during exposure and its near-surface enrichment contribute to embrittlement under these conditions.

1 | Introduction

Titanium aluminide-based alloys, which contain γ -TiAl as the majority phase and α_2 -Ti₃Al as a minority phase, sometimes together with other phases, are being increasingly used in aero-engine turbine applications [1]. Despite this, one area that is still not well understood is the significant room-temperature embrittlement of this already rather brittle material after exposure to high temperature [2–7]. According to Dowling and Donlon [2], even exposure under nominal vacuum conditions leads to embrittlement. From the literature, it is apparent that lower-strength alloys generally retain some room-temperature ductility after exposure, whereas high-strength alloys generally lose

practically all room-temperature ductility. Embrittlement is common to all TiAl-based alloys, although, according to Wu et al. [7], an increase in the fracture toughness is believed to reduce the effect of embrittlement. This could potentially be achieved, for example, by increasing the lamellar volume fraction and reducing the colony size.

Various hypotheses have been proposed to explain this embrittlement phenomenon, including hydrogen embrittlement [3] resulting from the room-temperature dissociation of water vapor at prematurely formed loading-induced cracks, the formation of which may also be promoted by a brittle surface layer [2, 3]. In [3], it was reported that testing under argon or oxygen did not

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lead to any embrittlement after exposure despite the formation of numerous surface cracks during testing; such cracks were also apparent after testing in air, where embrittlement was observed.

For intermetallic materials, it is generally accepted that moisture in the air plays a significant role in room-temperature embrittlement [8]. It is believed that water molecules dissociate into atomic hydrogen and oxygen on contact with the freshly created metallic surfaces that become exposed when surface cracks nucleate during room-temperature loading. The hydrogen can then quickly diffuse into the bulk material, which leads to embrittlement. This is the most widely recognized theory to explain embrittlement after exposure. In respect to TiAl alloys, it is believed that surface cracks nucleate prematurely after exposure due to the changed nature of the near-surface material. Water vapor is thought to dissociate at these cracks at an earlier stage of testing than for unexposed material, leading to premature failure via hydrogen embrittlement. Alternative explanations for the embrittlement of TiAl after exposure include the development of tensile stress on the outer surface of the specimen [7] and diffusion of oxygen into the near-surface layer, particularly into the α_2 -Ti₃Al phase [4, 5]. The development of near-surface tensile residual stress was confirmed in [9]. It is thought that different mechanisms play a role after short- or long-term exposure [6]. The present study was performed assuming that embrittlement results from the dissociation of water at newly formed surface cracks that develop during testing. Lowering the deformation temperature after exposure and performing the tests under liquid nitrogen are expected to have a significant effect on the dissociation of water vapor as well as hydrogen mobility. It has been shown that deformation under liquid nitrogen has mitigated the deleterious effect of water vapor in the air on the properties of a Ni₃(Si, Ti) intermetallic [10]. Performing tensile tests on exposed TiAl specimens under liquid nitrogen is assumed to exclude the influence of water vapor in the air and thus be able to give further insight into the origin of embrittlement after high-temperature exposure. There are two other possible sources of hydrogen in the material. One is residual hydrogen already present in the material, and the other is hydrogen resulting from the dissociation of water vapor during the exposure treatment. The effect of the atmosphere during high-temperature exposure on the near-surface chemistry has thus been investigated using secondary ion mass spectrometry (SIMS) to see if hydrogen from water vapor is absorbed into TiAl during the high-temperature exposure treatment.

2 | Materials and Methods

2.1 | Mechanical Testing

For this investigation, a vacuum arc remelted ingot of nominal composition Ti–46.5Al–5.5Nb–0.3Mo–0.2C–0.2B (at%) was extruded at 1250 °C to a 7:1 reduction ratio and then annealed at 1030 °C for 10 h. This alloy was chosen as it showed tensile plastic elongation both under liquid nitrogen and in air. Tensile test specimens, with a nominal gauge length of 24.5 and 3.5 mm diameter, were machined from the annealed extruded bar. After machining, the specimens were ground with silicon carbide paper and silicon oil to a p1200 surface finish. Tensile testing was done

using the displacement-controlled mode on a Zwick 1860 testing machine at a deformation rate of 0.03356 mm min^{−1}. This is equivalent to an initial strain rate of approximately 2.38×10^{-5} s^{−1} and was chosen to minimize strain rate effects and enable meaningful comparisons between different testing temperatures and environments. Such slow strain rates are often used in the hydrogen embrittlement research area [11]. Prior to testing, some tensile specimens were exposed to air at 700 °C for 1 h, followed by air cooling. Tensile tests were performed on unexposed and exposed specimens either in air at room temperature or under liquid nitrogen at a temperature of −196 °C. A summary of the tensile test conditions investigated is given in Table 1. A detailed description of the testing methodology can be found in the Supporting Information.

2.2 | Secondary Ion Mass Spectrometry

To study the influence of microstructure on water vapor dissociation and subsequent hydrogen absorption, different microstructures were established in binary TiAl alloys with compositions Ti–45Al and Ti–48.9Al (at%). These binary compositions were chosen to reduce the complexity and number of *m/z* signals during the SIMS analysis and because different representative microstructures could be established. Both alloys were prepared from gas-atomized powder that had been encapsulated in cylindrical titanium cans that were subsequently evacuated, sealed, and then hot isostatically pressed (HIPed) under argon gas at a pressure of 200 MPa at 1200 °C for 4 h. Disc-shaped TiAl specimens with a thickness of between 2.5 and 5.5 mm and a diameter of around 12 mm were prepared from the HIPed cylinders. The heat treatments applied to obtain the different microstructures are given in Table 2. After heat treatment, one of the flat round-shaped surfaces of each disc was ground using SiC paper down to p2500 and then polished using vibration polishing with colloidal silica solution. The various microstructures that were developed after heat treatment, which represent typical TiAl microstructures, have been imaged using back-scattered scanning electron microscopy (Zeiss Gemini scanning electron microscopy (SEM) operated at 20 keV) and are shown in Figure 1. A detailed description of how

TABLE 1 | Tensile tests were performed on a Ti–46.5Al–5.5Nb–0.3Mo–0.2C–0.2B (at%) alloy that had been extruded at 1250 °C to a 7:1 reduction ratio and then annealed at 1030 °C for 10 h. Specimens were tested either at room temperature in air or under liquid nitrogen. Unexposed and exposed (700 °C/1 h/air cool) specimens were tested. The number of tests performed for each condition and environment is indicated in the table.

Test environment	Exposed	
	Unexposed	(700 °C/1 h/air cool)
In air at room temperature	3 ⁺	2
Under liquid nitrogen (−196 °C)	5 ⁺⁺	5

⁺Indicates that one specimen underwent stress relaxation (SR: Figure 2a) during tensile testing. ⁺⁺Indicates that one sample underwent stress relaxation (SR1: Figure 2a) during tensile testing; a second specimen (SR2) was unloaded after the stress relaxation and then retested at room temperature.

TABLE 2 | Binary alloy composition and heat treatment used to establish the different microstructures for the SIMS high-temperature exposure investigations (FC = furnace cool). After the microstructures were established, the specimens were heat-treated in the isotopic gas and heavy water-containing atmosphere at 700 °C for 4 h, prior to SIMS analysis.

Alloy composition, at%	Microstructure	Heat treatment to establish microstructure
Ti-48.9Al	Near gamma	1200 °C/24 h/FC + 800 °C/8 h/FC
Ti-45Al	Duplex	1250 °C/24 h/FC + 800 °C/8 h/FC
Ti-45Al	Fully lamellar	1250 °C/24 h/FC + 800 °C/8 h/FC + 1325 °C/30 min/FC + 800 °C/8 h/FC

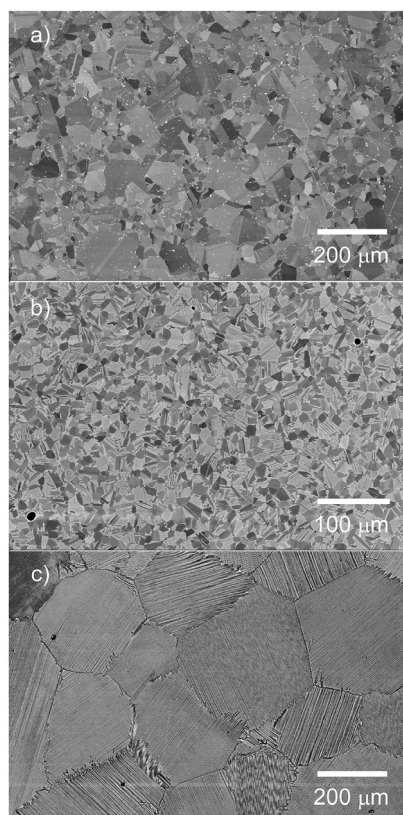


FIGURE 1 | Microstructures after the different heat treatments, which are indicated in Table 2, taken in the backscattered electron (BSE) mode, (a) Ti-48.9Al: Near gamma, (b) Ti-45Al: Duplex, and (c) Ti-45Al: fully lamellar. These microstructures were subsequently exposed at 700 °C for 4 h in an artificial isotopic air atmosphere composed of 80% ($^{15}\text{N}_2$), 20% ($^{18}\text{O}_2$) and D_2^{16}O prior to SIMS analysis.

the samples were exposed at 700 °C for 4 h in isotopic air with heavy water vapor is given in the Supporting Information.

After the exposure treatment was completed and the tube had cooled to room temperature, the tube was broken to remove the specimens, which were then investigated using a TOF. SIMS5 instrument (ION-TOF GmbH, Münster, Germany). In addition to using a 25 keV Bi_1^+ ion beam (HC bunched, 1.2–1.3 pA target current (100 μs cycle time)), a second beam of 2 keV Cs^+ ions was used to erode the samples while continuously taking spectra and images. Using electropositive Cs ions increases the ionization yield of negatively charged secondary ions. For the positive polarity mode, where 1 keV O_2^+ ions were used to erode the sample, the ionization of positively charged secondary ions was

improved. As the erosion speed depends on the local chemistry and the crater depth is not measured continuously, the fluence (number of sputter ions per unit area) is used as an arbitrary scale for depth. The results for hydrogen (^1H), isotopic oxygen (^{18}O), and deuterium (D (^2H)) are of most interest. Deuterium will be used to represent the behavior of hydrogen from water vapor in a normal atmosphere. The final crater depth after SIMS depth profiling was determined using a Bruker Dektak XT profilometer. A linear correlation between fluence (or sputtering time) and depth cannot be made due to the erosion not necessarily being constant, as the rate of erosion depends on local chemistry. For example, a hard alumina oxide layer may need more ions to erode to a certain (shallower) depth than softer base material. Thus, measuring the final depth and then making a linear relationship between depth and sputtering time or fluence is not appropriate. Table 3 shows various conditions and parameters used in the SIMS analyses.

3 | Results

3.1 | Mechanical Behavior

The room-temperature tensile properties of unexposed specimens show typical behavior for an annealed extruded bar, with a yield stress of around 520 MPa and just over 1% plastic strain to failure, Figure 2a. As shown, the tensile test curves do not start at 0 MPa because the specimens were loaded to a few 100 N before testing was started. For one of the three room-temperature tests, the specimen was held at a constant displacement for a period after undergoing plastic deformation (arrowed SR for stress relaxation). The drop in load was monitored as a function of time before the deformation was continued to failure. From the relaxation kinetics, the activation volume (V) could be determined.

The tensile curves obtained for unexposed specimens tested under liquid nitrogen, also shown in Figure 2a, exhibit significantly higher yield and fracture stresses, combined with a higher work hardening rate compared to the tests performed at room temperature in air. The apparent elastic modulus determined under liquid nitrogen from the load/displacement curves is about 30% higher than the value determined from the tests performed at room temperature. This difference is significantly larger than would be expected from the temperature dependence of the elastic modulus calculated using the software presented in [12] and the single-crystal elastic constants determined by Tanaka and Koiwa [13]. According to these calculations, the elastic modulus at -196 °C should be around 4.5% greater than at room temperature. It is well known that Young's moduli determined from tests where the strain is measured by displacement are somewhat

TABLE 3 | Conditions and parameters used in the SIMS investigation.

	Positive SI polarity	Negative SI polarity
Analysis beam, energy, target current	Bi^+ , 25 keV, 1.2–1.3 pA	
Analysis beam, field of view, resolution	$300 \times 300 \mu\text{m}^2$, 128×128 pixel	$100 \times 100 \mu\text{m}^2$, 64×64 pixel
Mass scale calibration points	^1H , ^7Li , ^{28}Si , ^{39}K , ^{46}Ti , ^{50}Ti	^1H , ^{12}C , Al^{16}O , Al^{18}O , Al^{16}O_2 , $^{46}\text{Ti}^{16}\text{O}$
Erosion beam, energy, target current, crater size	O_2^+ , 1 keV, 250 nA, $500 \times 500 \mu\text{m}^2$	Cs^+ , 2 keV, 150 nA, $250 \times 250 \mu\text{m}^2$

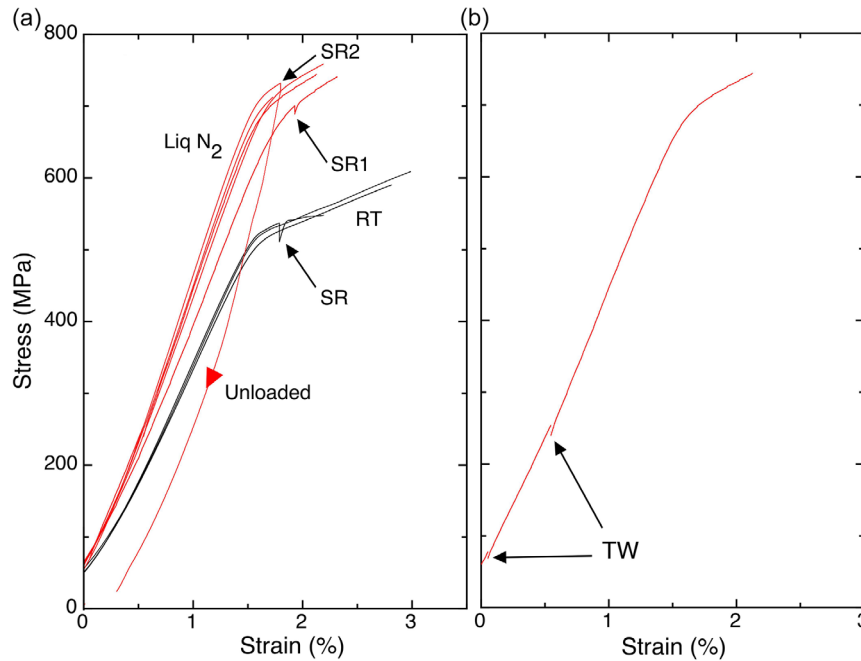


FIGURE 2 | (a) Tensile test curves for unexposed specimens (Ti-46.5Al-5.5Nb-0.3Mo-0.2C-0.2B) obtained under liquid nitrogen at -196°C (red curves) and in air at room temperature (black curves). The arrows labeled SR, SR1 and SR2 indicate where stress relaxations were made during the tests; the evolution of stress was continuously recorded, and the data used to calculate the reciprocal activation volume ($1/V$). One of the specimens loaded under liquid nitrogen was unloaded immediately after a stress relaxation (SR2) and then retested at room temperature in air (see Figure 11 for the complete test including the room temperature reloading). (b) Shows the test curve for one of the tests performed under liquid nitrogen, indicating positions where sharp drops in stress occurred that were also accompanied by a loud audible cracking sound (indicated by the arrows TW). It is believed that these drops in stress were caused by twinning deformation, but this is irrelevant for the discussion of the findings.

lower than the values that are determined with an extensometer fixed to the gauge length. Considering the relatively good thermal stability of the loading train before testing under liquid nitrogen, it is somewhat surprising that the difference in apparent modulus for tests performed at room and cryogenic temperatures is over 25% higher than that expected from the calculations.

In the present study, five tests on unexposed specimens were performed under liquid nitrogen, including one specimen that was allowed to relax at constant displacement (indicated by SR1 in Figure 2a), with loading then being continued until fracture. A second specimen was loaded under liquid nitrogen into the plastic regime, and a stress relaxation test was performed (arrowed SR2). This specimen was then unloaded and retested after being allowed to warm up to room temperature. One of the unexposed specimens that was loaded to fracture under liquid nitrogen (no stress relaxation test being performed) experienced a sudden load drop with an audible cracking-like sound; see Figure 2b.

Deformation is a thermally activated process, with the flow stress being determined from thermal and athermal stress contributions. As the thermal energy available to aid dislocation motion is reduced at cryogenic testing temperatures, a higher critical shear stress is necessary for moving the dislocations through the lattice in order to maintain the imposed strain rate. In unfavorably oriented regions, where dislocation motion is difficult, there can be a high build-up of stress that could be relieved via mechanical twinning. This is possibly the cause of the sudden drop in stress that was associated with the audible cracking-like sound (indicated by twinning (TW) in Figure 2b). Given the low fracture toughness of TiAl combined with the large drop in stress and the loudness of the cracking-like sound, we believe that twinning rather than crack initiation/growth was responsible for the sudden drop in stress. Crack initiation or propagation causing such a loud event would more than likely have led to complete specimen failure. Indeed, it is generally accepted that mechanical twinning is aided by testing at low temperatures or fast strain

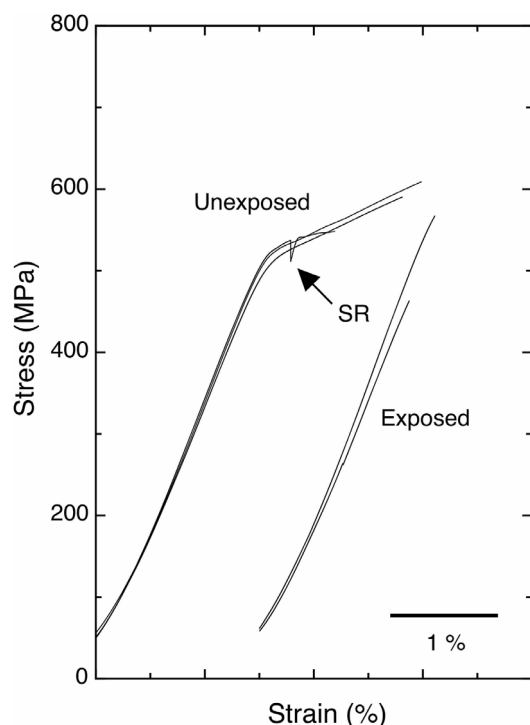


FIGURE 3 | Room temperature tensile test curves obtained for three unexposed and two exposed tensile test specimens. The unexposed material shows plastic deformation, whereas the two exposed specimens fractured in the elastic regime. SR indicates where a room-temperature stress relaxation test was performed on an unexposed tensile test specimen. Specimen composition Ti–46.5Al–5.5Nb–0.3Mo–0.2C–0.2B.

rates [14]—both testing conditions where thermal energy for the activation of dislocation motion is limited.

The room-temperature tensile test curves of unexposed and exposed specimens are shown in Figure 3. The exposure treatment of 1 h at 700 °C in air leads to a complete loss of plastic ductility on testing at room temperature. This is typical behavior for high-strength TiAl alloys. One of the exposed specimens fractured at a stress close to the yield stress of unexposed material, while the second fractured at a stress slightly above the yield stress. Literature observations indicate that on room-temperature loading, exposed TiAl specimens generally fail at different stages of deformation, depending on the strength level of the alloy being tested: (i) just before reaching the nominal yield stress in the elastic regime, (ii) just above the nominal yield stress, with very limited plastic elongation if any, or (iii) fracture after undergoing some plastic elongation, but significantly less than for unexposed material. High-strength alloys usually fracture in stages (i) and (ii), whereas lower-strength alloys usually fracture in stage (iii).

The tensile test curves for unexposed and exposed specimens tested at –196 °C under liquid nitrogen are shown in Figure 4. All the exposed samples fractured within the elastic regime. It is apparent that the elastic slopes of the unexposed samples are similar to each other, with little scatter. With regard to the exposed samples tested under liquid nitrogen, three specimens exhibited a similar elastic slope to the unexposed samples, while two specimens showed somewhat steeper slopes. This variation is possibly associated with (non) thermal equilibrium of the loading train,

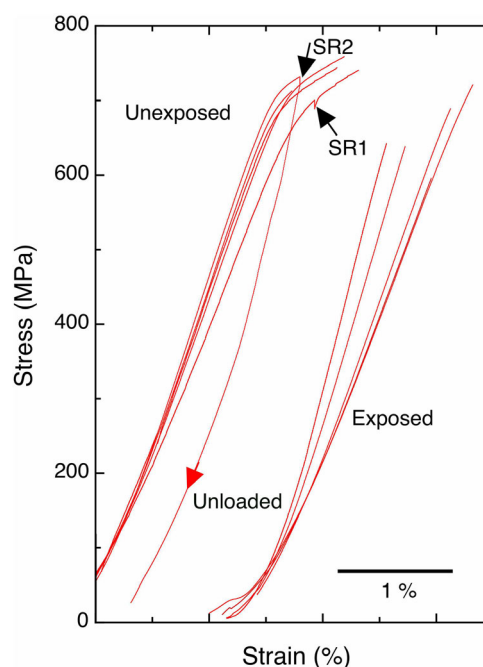


FIGURE 4 | Tensile tests performed on unexposed and exposed specimens under liquid nitrogen (–196 °C). All the unexposed specimens showed some limited degree of plastic deformation whereas the exposed specimens all fractured in the elastic regime. SR1 and SR2 denote where stress relaxation tests were performed on two of the unexposed specimens. One of these specimens (SR1), was then further loaded to fracture, while the other specimen (SR2) was immediately unloaded after the stress relaxation and then retested in air at room temperature (see Figure 11). Specimen composition Ti–46.5Al–5.5Nb–0.3Mo–0.2C–0.2B.

which is discussed in the Supporting Information. The points where stress relaxation tests were made are indicated by the arrows SR1 and SR2, as described earlier in Figure 2a.

3.2 | Surface Chemistry after Exposure

The signal intensity of Ti⁺ and Al⁺ ions against fluence for three types of microstructure is shown in Figure 5, with the final crater depths indicated within the figure key. As can be seen, all the Al⁺ signals are above the detector saturation level, as indicated by the gray shaded area. Normally, only isotopes with intensities below the saturation level are analyzed/considered, but Al has only one isotope (²⁷Al); thus, the results for Al should only be treated qualitatively. Titanium has five isotopes ranging from ⁴⁶Ti to ⁵⁰Ti, with the ⁴⁸Ti isotope accounting for almost 74% of all Ti found in nature. As for ²⁷Al⁺, the intensity of ⁴⁸Ti⁺ ions (not shown in the figure) was above the saturation level of the detector. However, the variation in the sum of the intensities of the other Ti isotopes is within the detection range and can be used to obtain the concentration profile of Ti in the three specimens. From Figure 5, it is clear that Ti is depleted close to the surface and continues to be enriched with distance away from the surface. Qualitatively, the intensity of Al⁺ ions is less for the near-gamma microstructure than the other microstructures, despite the Ti–48.9Al alloy containing more Al. The reliability of this observation is questionable due to the saturated detector intensity.

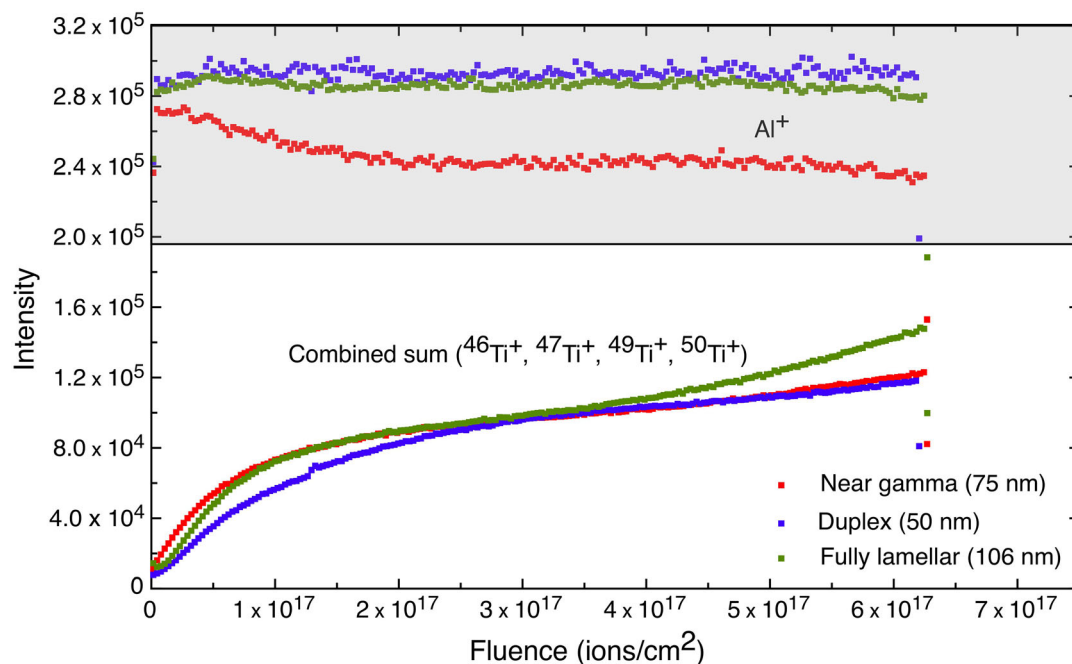


FIGURE 5 | Intensity variation of Al and the sum of the four minor isotopes of titanium as a function of fluence. The shaded area at the top of the graph indicates that the number of counts is above the saturation level of the detector. The titanium becomes enriched away from the surface. The depth of the craters at the end of depth profiling is indicated in the brackets. Near gamma microstructure: Ti–48.9Al, Duplex and fully lamellar microstructures: Ti–45Al.

A graph of depth-integrated signal intensities (positive polarity mode) against mass-to-charge ratio (m/z) is shown for the different microstructures in Figure 6a for the m/z range covering values for single-charged deuterium ions (D^+ ($^2H^+$), $m/z_{theo} = 2.0136$) and single-charged hydrogen molecules ($^1H_2^+$, $m/z_{theo} = 2.0151$). The mass resolution of the spectrometer (3400–3900 $M/\Delta M$ for this signal, width <1 ns) is sufficient to separate these signals. Due to the mass calibration points selected to cover a wide mass range of the spectrum, a systematic mass deviation for very low m/z signals—with very short flight times to the detector—cannot be avoided. H_2 signals are almost absent in the depth-integrated data shown in Figure 6a, only showing briefly in the depth profiles directly at the surface of the samples and disappearing right after the onset of erosion. It is apparent that the deuterium taken up by the duplex and fully lamellar microstructures is similar for the (different) volumes of material analyzed. The take-up for the near-gamma microstructure is slightly higher. In the negative polarity analyses, different positions on the samples were investigated; see Figure 6b. The depth-integrated intensity values were similar for each type of microstructure. In this polarity mode, the volumes of material probed were larger as the craters were deeper (the crater depths are indicated in the figure), and thus, the results are probably more reliable due to higher statistics.

Intensity signals for the common hydrogen isotope (1H) and deuterium (D) in positive and negative secondary ion polarity are shown as a function of fluence in Figure 7 for each type of microstructure. The figure shows that there is a significant surface enrichment of both 1H and D and that all microstructures contain significant levels of deuterium, which has been taken up from the heavy water vapor during the exposure treatment. The data obtained in the negative polarity mode, which probed deeper under the surface, shows a peak in both hydrogen isotopes

at a fluence of around $3\text{--}4 \times 10^{17}$ ions/cm². This indicates a local enrichment just under the surface. Such enrichment would have also been observed in the positive-polarity mode if deeper regions had been probed.

Figure 8a shows a graph of the ratio of the D^+ to $^1H^+$ signal intensities against fluence (positive-polarity mode). The natural abundance ratio for D to H is 1.5×10^{-4} (natural abundances of 0.015 and 99.985, respectively), as indicated in Figure 8a, assuming that the ionization and detection probabilities of the isotopes are the same during SIMS analysis. As can be seen, the levels of deuterium at the end of the SIMS measurements are at least 500 times higher than expected from its natural abundance and around 2470 times higher for the near-gamma microstructure. Similar results were obtained for the negative polarity mode, as shown in Figure 8b, where positively charged Cs^+ ions are used in the erosion process. It should be noted that the fluence values at the end of the erosion process are higher for the negative polarity mode, which is reflected by the much deeper crater depths of up to 619 nm compared to no deeper than 119 nm for the positive polarity mode.

In Figure 8b, where the deeper regions under the surface were probed, it can be seen that the deuterium-to-hydrogen ratio is not significantly reduced at the end of depth profiling compared to the surface, implying that deuterium atoms have diffused much deeper into the surface of the specimens. With the limited depth (fluence) probed, it is not possible to extrapolate to which depth deuterium penetrated into the samples during exposure. This would be indicated when the D to 1H ratio reaches a value approaching the natural abundance ratio.

The results clearly show that for all microstructures, the heavy water dissociated during the high-temperature exposure

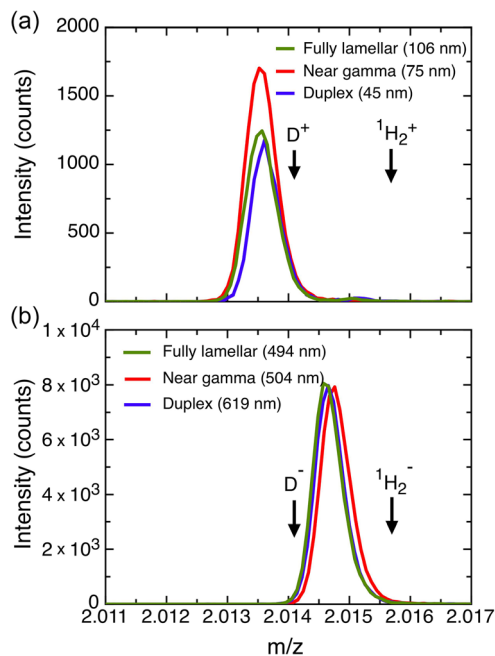


FIGURE 6 | Depth integrated signal intensity over the 2.011–2.017 m/z range for the (a) positive and (b) negative polarity modes. For the positive polarity mode (a), although slightly shifted to the left, the peaks correspond to single positively charged deuterium ions rather than singularly charged molecular hydrogen ions, the theoretical positions of which are indicated by the arrows. The area under the peaks are related to the total number of deuterium ions detected during depth profiling. The integral areas under the peaks (in kcts) are Near gamma 12.7, Duplex 7.8 and Fully lamellar 9.2. Near gamma microstructure: Ti–48.9Al, Duplex and fully lamellar microstructures: Ti–45Al. For the negative polarity mode (b), the peaks, although slightly shifted to the right, correspond to deuterium ions rather than molecular dihydrogen ions (which would have a very low ionization probability). The expected positions are again indicated by the arrows and the area under the peaks is related to the total number of deuterium ions detected during depth profiling. The results indicate that microstructure has no significant role in the amount of deuterium taken up during the exposure treatment.

treatment and that significant levels of deuterium entered the TiAl surface and diffused into the subsurface. This implies that normal water vapor in the air (or even that present in vacuum) would also dissociate on the surface of heated TiAl specimens and deeply penetrate into the subsurface.

As oxygen is weakly ionized in the positive-polarity mode, only results obtained using the negative-polarity mode will be presented. Unfortunately, up to a fluence of around 3.5×10^{17} ions/cm², the intensity of the $^{18}O^-$ ions was just slightly above the saturation level of the detector for all microstructures, Figure 9, which leads to an underestimation of the count rate in the fully oxidized surface region. The intensity signals for the $^{16}O^-$ ions are saturated to fluences of up to 4.5 – 5.5×10^{17} ions/cm². Thus, a graph of the intensity ratio of $^{18}O^-$ to $^{16}O^-$ ions against fluence would only show valid data for fluences above 5.5×10^{17} ions/cm². For fluence values above 7×10^{17} ions/cm², where the data is valid until the bottom of the craters, the $^{18}O^-/^{16}O^-$ intensity ratio remains constant and is around 40 times higher than expected from natural abundance (2.04×10^{-3}), indicating significant

ingress of ^{18}O , as has already been observed in the literature [5]. The $^{18}O^-$ to $^{16}O^-$ ratio is similar for all microstructures and does not seem to depend on the volume fraction of the different phases. This seems a little surprising, as the α_2 phase has been shown to take up more oxygen than the gamma phase [5], and the lamellar and duplex microstructures contain more α_2 phase compared to the gamma microstructure. With this knowledge, it would be expected that the gamma microstructure would have a lower $^{18}O^-/^{16}O^-$ ratio compared to the other microstructures. However, the level of ^{16}O from processing, etc., against which the level of ^{18}O uptake is compared, is also likely to be higher in the α_2 -containing microstructures on account of the higher affinity of the α_2 phase for oxygen. Thus, a potentially higher uptake of ^{18}O during exposure could be compensated for by an initially higher level of ^{16}O so that the values of the $^{18}O^-/^{16}O^-$ ratios are similar. This view is seemingly contradicted by the fact that the intensity of $^{18}O^-$ ions (Figure 9) for the near-gamma microstructure is intermediate between the values for the other two types of microstructures for fluences between 3.5×10^{17} and 6.0×10^{17} ions/cm².

It is not possible to detect nitrogen using positive polarity mode, and in the negative polarity mode, the ionization yield was very low, which resulted in no single secondary nitrogen ions being detected. It was possible to detect ^{15}N only in combination with ^{12}C , namely, the $^{12}C^{15}N$ species. A peak was also detected at an m/z value associated with $^{48}Ti^{15}N$, but this cannot be resolved from $^{47}Ti^{16}O$, and there was no peak observed for $^{46}Ti^{15}N$. The uptake of nitrogen during the exposure certainly takes place, but the findings are rather unclear and will not be discussed.

4 | Discussion

4.1 | Mechanical Properties and Activation Parameters

To the authors' knowledge, this investigation is only the second paper that has reported the tensile properties of TiAl under liquid nitrogen at $-196^\circ C$, with Huang and Hall [15] publishing a tensile test curve in 1991. Extensive investigations have been reported on compression under liquid nitrogen at $-196^\circ C$ [16, 17], a deformation mode where significantly larger strains are achievable than in tension and the brittle nature of the material poses less of a problem.

The activation volume (V) for thermally activated deformation processes can be determined from stress relaxations [16], where a specimen is held at constant strain (or in the current study, constant displacement) during a tensile or compression test, and the decrease in stress is recorded with time. The slope of a line through data encompassing the initial reduction in stress on a graph of $\ln(-\dot{\sigma})$ against σ is equivalent to V/MkT , where $M = 3.06$ is the Taylor factor, k is the Boltzmann constant, and T is the absolute temperature.

As described earlier, stress relaxations were performed during three of the tensile tests performed on unexposed material, one during a test at room temperature and two during tests at $-196^\circ C$. The reciprocal activation volume ($1/V$) determined from these stress

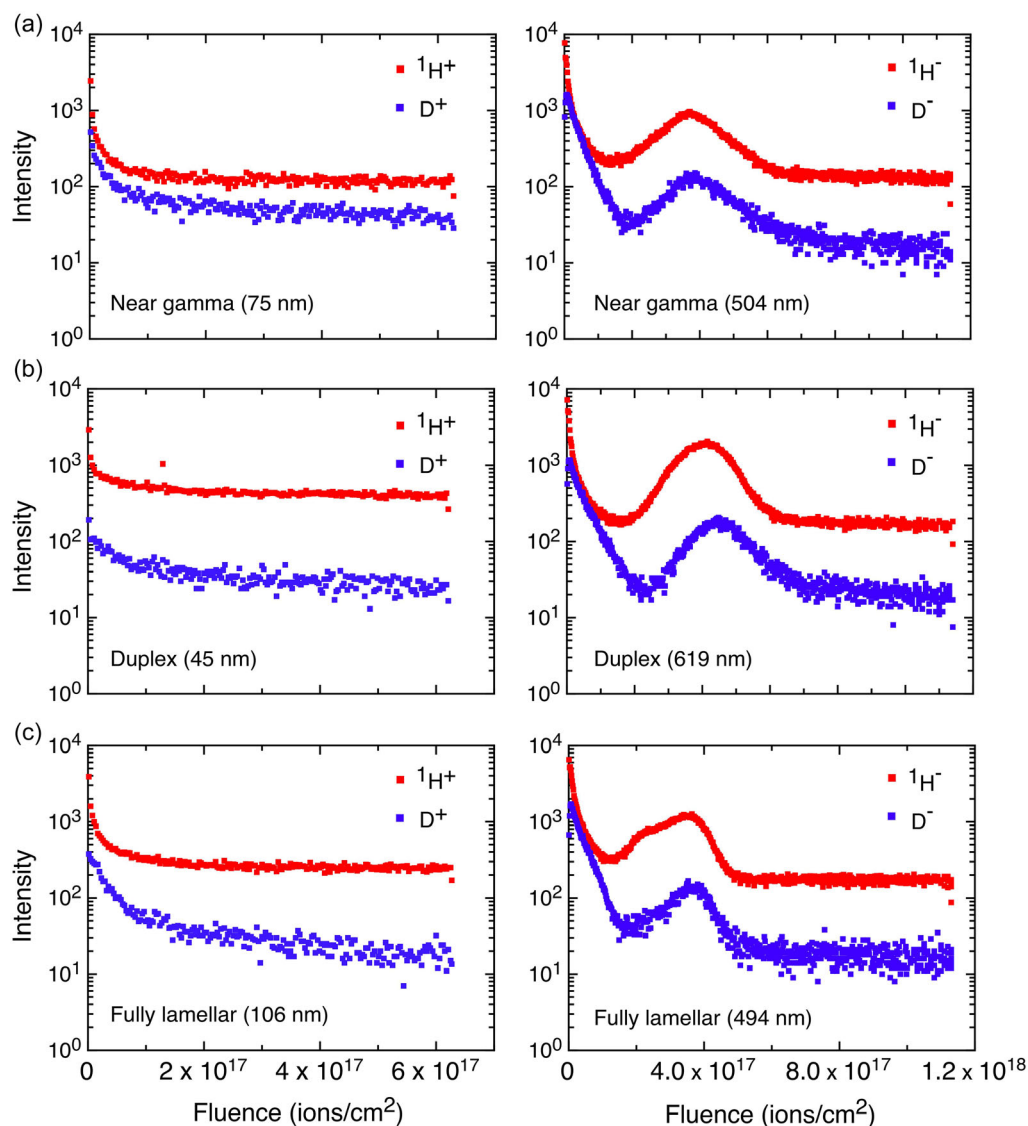


FIGURE 7 | Intensity variation of hydrogen and deuterium ions as a function of fluence for positive (left hand side graphs) and negative secondary ion polarities (right hand side graphs). It should be recognized that identical values of fluence for the different sputter ions do not relate to similar depths under the surface. For both modes the level of both hydrogen and deuterium are enhanced at the surface and then reduces. For the negative polarity mode, a peak in intensity for both hydrogen and deuterium is apparent under the surface with a peak maximum at a fluence of around $3\text{--}4 \times 10^{17}$ ions/cm². This roughly corresponds to the fluence value where the outer oxide—base metal interface is located, see Figure 9. The depth of the craters at the end of depth profiling are given in brackets. Near gamma microstructure: Ti-48.9Al, Duplex and fully lamellar microstructures: Ti-45Al.

relaxation experiments is plotted against plastic strain in Figure 10. This graph also shows lines for data obtained from compression tests performed at room temperature and under liquid nitrogen that were published in [17], which includes data from [18]. Figure 10 shows that the value of $1/V$ determined at room temperature is a little lower than those presented in [17] for Ti-45Al-5Nb-0.2C-0.2B and Ti-45Al-8Nb-0.2C but is similar to the values presented in [17, 18] for a variety of other TiAl alloys. All values of $1/V$ presented in [17, 18] were determined from strain rate cycling tests performed in compression. It is clear from Figure 10 that the reciprocal activation volumes for the stress relaxation tests performed at -196°C in tension are lower than the values determined at -196°C from compression tests presented in [17].

For the stress relaxation tests performed under liquid nitrogen, the stress reduction due to specimen relaxation at constant

displacement was $3\text{--}4.5$ MPa over a time period of $5\text{--}8$ s (this includes the influence of the loading train). The question arises as to whether the loading train is at thermal equilibrium or not during the stress relaxations, and if it was not, could this explain differences when comparing the present tensile test relaxation results from those performed under compression. If the loading train continues to become shorter at the maximum rate of 5.4 MPa min⁻¹ during the stress relaxation tests due to cooling, a value that was determined just before starting the test, then the measured relaxation in stress will be less than for the specimen alone. The maximum possible difference in stress due to the loading train not being in thermal equilibrium would be 0.72 MPa after a relaxation of 8 s. Thus, the reduction of stress observed during the stress relaxation tests could potentially be a little larger than indicated by the experimental measurements, which could slightly influence the values of $1/V$ determined from the

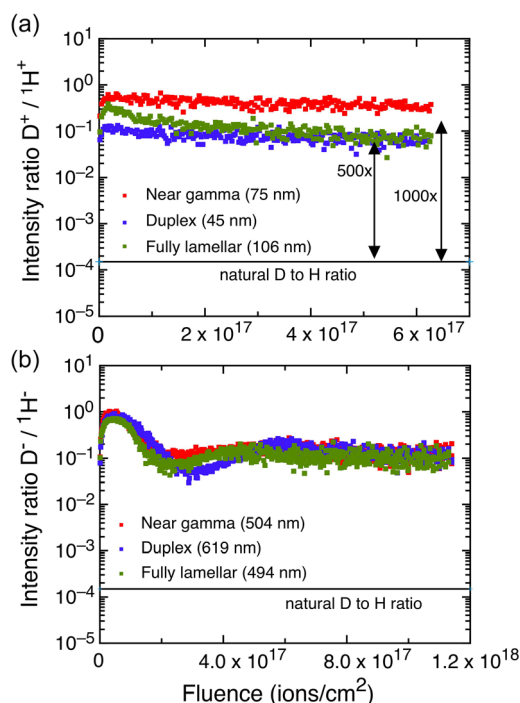


FIGURE 8 | Variation of the deuterium to hydrogen ion ratio as a function of fluence for the (a) positive and (b) negative polarity modes. For the positive polarity mode (a), the deuterium levels are at least 500 times higher than expected from natural occurrence. This demonstrates a significant absorption of deuterium from the heavy water vapor during the high temperature exposure treatment. Near gamma microstructure: Ti-48.9Al, Duplex and fully lamellar microstructures: Ti-45Al. A similar near surface absorption of deuterium is shown in (b). Even at the end of depth profiling the deuterium to hydrogen ratio is only slightly lower than at the surface. The depth of the craters at the end of profiling are given in brackets.

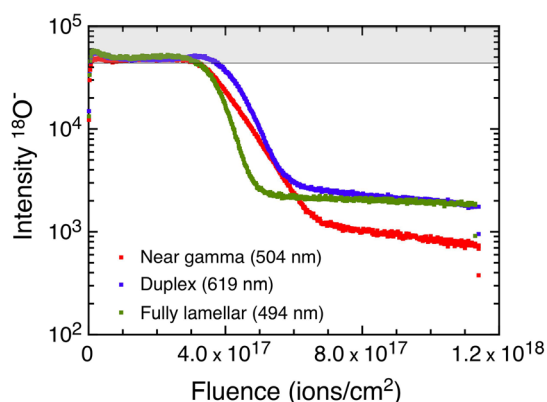


FIGURE 9 | Profile of the $^{18}\text{O}^-$ intensity as a function of fluence for the different microstructures. The outer oxide layers are indicated by a plateau at low values of fluence with the oxide to base metal interface being attained at fluence values of around 5×10^{17} ions/cm 2 . The ratio of the $^{18}\text{O}^-$ to $^{16}\text{O}^-$ ion intensities from fluence values where both ionic species are at levels under the saturation level of the detector to the bottom of the crater is above 40 times the value expected from natural occurrence. Near gamma microstructure: Ti-48.9Al, Duplex and fully lamellar microstructures: Ti-45Al.

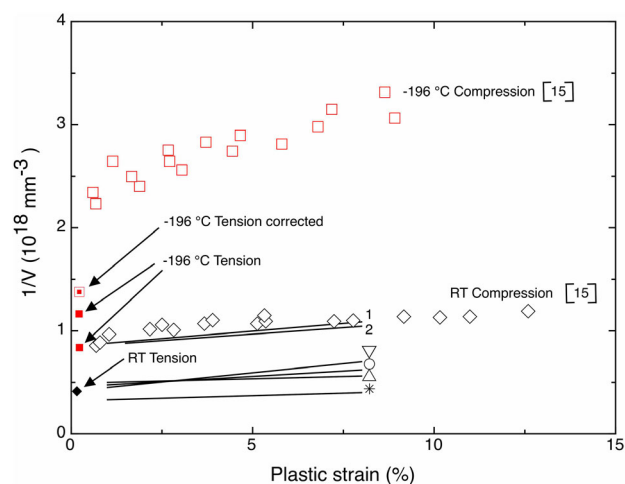


FIGURE 10 | Values of reciprocal activation volume ($1/V$) determined from stress relaxation tests performed on unexposed tensile test specimens at room temperature ($\blacklozenge$) or under liquid nitrogen ($\blacksquare$). As explained in the text, the stress relaxation tests performed under liquid nitrogen were re-evaluated considering the potential nonthermal equilibrium of the loading train, and the values of $1/V$ recalculated. These values are roughly identical and are plotted as a single symbol ($\blacksquare$). For comparison, the variation of the reciprocal activation volume for Ti-45Al-10Nb determined in compression via strain rate cycling tests at room temperature ($\diamond$) and under liquid nitrogen ($\square$), presented in [17] are shown as a function of plastic strain. The room temperature variation of $1/V$ with plastic strain for other alloys presented in [17] are also indicated (1 = Ti-45Al-5Nb-0.2C-0.2B, 2 = Ti-45Al-8Nb-0.2C, ∇ = Ti-47Al-2Cr-0.2Si, nearly lamellar, $\circ$ = Ti-47Al-2Cr-0.2Si, equiaxed, $\triangle$ = Ti-54Al, equiaxed, $*$ = Ti-48Al-2Cr, nearly lamellar).

experimental stress relaxations. If the stress relaxation tests were performed using compression specimens rather than tensile test specimens, the situation regarding thermal nonequilibrium would be opposite, with the measured stress relaxation being slightly larger than that from the specimen alone. The values of $1/V$ obtained under liquid nitrogen presented in the literature were determined from compression strain rate cycling tests. These results could be less influenced by thermal nonequilibrium of the loading train compared to stress relaxations because the time to establish the flow behavior with a constant work hardening rate is established very soon after the change in strain rate.

The influence of the potential thermal nonequilibrium of the loading train on the values of $1/V$ determined from the stress relaxation data has been analyzed to determine its possible influence on the values of $1/V$. To do this, the stress relaxation data, i.e., values of stress and time recorded during a relaxation test were reassessed. When the stress relaxation was initiated, the stress at this time zero is considered valid. The stress values thereafter were recalculated assuming a constant stress contribution of 5.4 MPa min^{-1} (0.09 MPa s^{-1}), which was the maximum rate of change of stress measured prior to testing due to thermal contraction of the loading train. Thus, the values of stress recorded for every point in time (Δt seconds) during the relaxation test were increased by a term that is given by $0.09 \times \Delta t \text{ MPa}$. This term is a stress contribution at each measured stress relaxation data point that arises from loading train contraction counteracting the stress

relaxation and should be added to the measured stress drop values so that the magnitude of the stress reduction is increased. The values of $1/V$ determined for the two relaxation tests performed under liquid nitrogen are very close and indicated by a single point in Figure 10 (indicated as -196°C tension corrected). With this stress correction, the values of $1/V$ for the stress relaxation tests performed in tension under liquid nitrogen are closer, but still lower, to those determined by strain rate cycling tests in compression.

Nevertheless, the trend of the results of the present investigation is in general agreement with the compression test results [17], the value of $1/V$ being higher for deformation at -196°C compared to deformation at room temperature. The higher value of $1/V$ indicates an increased contribution to flow stress from thermally activated processes that significantly raises the flow stress.

These findings are consistent with the established view in the TiAl literature that deformation is determined by several mechanisms [19]. These mechanisms include the elastic interaction of the dislocations with numerous internal boundaries. In addition, deformation is increasingly hindered by the development of constraint stresses due to the elasto-plastic codeformation of the various constituents. The resulting stress components are long-range and therefore only weakly dependent on temperature. These components are referred to as the athermal stress contribution σ_μ [19].

The dislocation velocity, on the other hand, is determined by the interaction with glide obstacles, which are characterized by a short-range stress field. Mechanisms identified are jog dragging, kink bulging, lattice friction (Peierls stress), impurity-related defects, and antisite defects [19]. Such glide obstacles can be overcome with the assistance of thermal activation, and therefore, the resulting thermal stress contributions depend on the deformation rate and strongly on temperature. The sum of the thermal contributions is denoted σ^* . The magnitude of the athermal and thermal stress contributions was determined in a recent study using dip tests for a series of TiAl alloys at room temperature [20]. According to the study, $\sigma_\mu = 0.8 \sigma$ is valid, where σ is the critical yield stress. Therefore, $\sigma_\mu = 416 \text{ MPa}$ and $\sigma^* = 104 \text{ MPa}$ can be expected for the alloy studied here at room temperature (critical yield stress $\approx 520 \text{ MPa}$). Deformation at -196°C increased the critical yield stress by about 200 MPa , which mainly results from an increase in σ^* (the thermal contribution), i.e., the thermal stress component almost tripled compared to the value at room temperature.

The activation volume V associated with the thermal stress contribution is usually related to the Burgers vector of unit dislocations, which primarily contribute to deformation. For the values measured in this study, $V = 50 b^3$ for deformation under liquid nitrogen and $V = 104 b^3$ at room temperature. As shown in [19], these activation volumes deviate considerably from the ideal values expected for the individual thermally activated processes listed above and most probably correspond to an average value of these quantities. Regardless, V is expected to decrease (i.e., $1/V$ increases) with decreasing temperature. According to this model, lowering the deformation temperature mainly increases the glide resistance of the dislocations.

The compression tests combined with strain rate cycling at -196°C indicate a strong increase in $1/V$ with increased plastic

strain, indicating the formation of deformation-induced obstacles [17]. It is not possible to achieve such large strains under tension. However, a similar mechanism can be expected to take place during tensile deformation, as is indicated by the higher value of $1/V$ at -196°C (Figure 10) and the strong increase of the work hardening rate with strain when compared to the tests performed at room temperature (Figure 2a). The frequency and extent of cross-slip events, which result in higher point defect and debris formation, could be enhanced during low-temperature deformation [17], as is indicated by the higher value of $1/V$ in Figure 10. On retesting at room temperature after deformation at -196°C , see Figure 11, it can be seen that the flow stress is relatively unaffected by the prior low-temperature deformation. High internal stresses and the high density of defects may lead to the defects recombining or agglomerating, which results in recovery of both the work hardening rate and the reciprocal activation volume, as described in [17]. Dislocations generated during the subsequent room-temperature deformation are proposed to act as sinks or recombination centers for point defects [17]. For compression tests, this resulted in a reduction in work hardening rate of about 10% at room temperature after low-temperature deformation, compared to specimens only tested at room temperature. For the room-temperature tensile tests, a linear work hardening rate (normalized by the temperature-dependent shear modulus) of around 0.09 was established after about 0.25% plastic strain and remained more or less constant up to fracture at around 1.1% plastic strain. For room-temperature testing after predeformation at -196°C to 0.2% strain, a slightly lower linear work hardening rate of 0.055 was established after 0.55% elongation at room temperature. Thus, a similar mechanism of dynamic recovery of defects and debris is thought to be taking place in tension (the current investigation), as reported to be the case in compression.

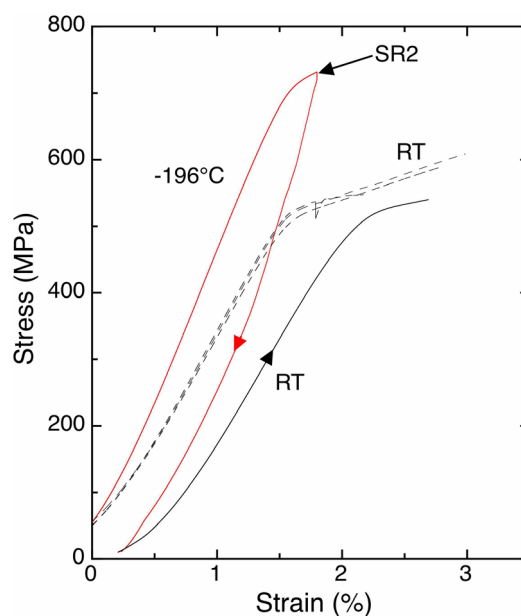


FIGURE 11 | Diagram showing the room-temperature stress-strain behavior of an unexposed specimen (solid black line) after predeformation (and stress relaxation, SR2) under liquid nitrogen (solid red line). The stress-strain curves for unexposed specimens tested at room temperature are also plotted (dotted lines), with one test also undergoing a stress relaxation (SR). Specimen composition Ti-46.5Al-5.5Nb-0.3Mo-0.2C-0.2B.

4.2 | Mechanical Properties, Surface Chemistry, and Embrittlement Mechanisms

The main goal of this work was to gain a better understanding of the mechanism/s that lead to the reduction or even total loss of room-temperature plastic ductility of TiAl after exposure at high temperature. The approach used was to determine mechanical properties under liquid nitrogen and then discuss the results obtained with regard to the various embrittlement mechanisms proposed. In addition, the near-surface chemistry after exposure has been investigated using SIMS to see how the high-temperature environment interacted with heated TiAl.

According to Ma et al. [10], the deleterious embrittling effect of water vapor on Ni₃(Si, Ti) could be suppressed by processing under liquid nitrogen. Such processing uses liquid nitrogen as a barrier to exclude the direct exposure of the specimen to water vapor and thus excludes the effect of hydrogen being released from atmospheric moisture. Additionally, it was stated that any moisture in contact with the surface would be frozen and thus unavailable for decomposition into atomic species. Importantly, during deformation at such cryogenic temperatures, if any dissociated hydrogen were present, then its diffusivity would be extremely low [10]. The present investigation, with tensile tests being performed under liquid nitrogen, was based on this presumption. Thus, the effect of atmospheric moisture on the fracture process during tensile testing is assumed to have been eliminated by testing under liquid nitrogen.

Many aspects of the embrittlement of TiAl after high-temperature exposure are similar to observations concerning hydrogen embrittlement of steels and superalloys. For example, in the hydrogen embrittlement literature of conventional materials, embrittlement is highly dependent on the strength level. High-strength materials are susceptible to hydrogen embrittlement, whereas the same alloy composition but heat-treated to a lower strength level is largely unaffected [21]. Similarly, after high-temperature exposure, high-strength TiAl alloys lose all plastic ductility at room temperature, whereas lower-strength alloys generally retain some ductility.

Work on unexposed TiAl has shown that performing tests in a moisture-rich environment leads to premature failure [22], albeit the strains to failure obtained seem rather high for room-temperature tensile tests. Early investigations concerning the effect of the test environment on the tensile properties of TiAl polysynthetically twinned (PST) crystals indicated that TiAl is susceptible to the test environment [23]. Interestingly, testing in hydrogen was even more detrimental to ductility than testing in humid air. These observations indicate that hydrogen from a hydrogen atmosphere or water vapor can enter the material during room-temperature testing, leading to embrittlement via a hydrogen embrittlement mechanism. However, in the present case, where embrittlement is observed under liquid nitrogen, hydrogen from such sources is excluded, so another embrittlement mechanism is believed to operate.

In order to conduct the study, it was necessary to choose an alloy that showed acceptable room-temperature ductility and, most importantly, some ductility when tested under liquid nitrogen. The tensile test curves shown in Figure 2a show an acceptable

level of room-temperature ductility and some plasticity when tensile testing was performed under liquid nitrogen. The observation that plastic ductility is not present when testing at -196°C after high-temperature exposure (Figure 4) and that the fracture stress of exposed specimens is significantly higher than that observed at room temperature is extremely significant and will be discussed with respect to the currently proposed embrittlement mechanisms.

One of the main embrittlement theories is that atmospheric moisture dissociates at newly/prematurely formed surface cracks during testing [2, 3, 8], the cracking possibly being promoted by a brittle surface layer formed during elevated-temperature exposure [2, 3]. This is believed to result in hydrogen diffusing into the bulk material during testing, leading to hydrogen embrittlement. If the assumptions and findings of Ma et al. [10] are correct and can be transferred to TiAl, then this mechanism can be disregarded for tests performed under liquid nitrogen, as little, if any, hydrogen should be able to enter the material; and even if it did, then it would not be able to diffuse due to the low temperature. Another proposed mechanism, sometimes discussed in combination with the above theory, concerns the premature formation of surface cracks due to either the formation of a brittle surface layer or embrittlement of the α_2 phase due to oxygen enrichment. Löffl et al. [24] have shown that the cracks leading to failure of unexposed specimens initiate within the interior of a specimen, whereas they preferentially initiate at the surface of specimens that have been exposed. Such surface cracks could certainly arise from surface embrittlement due to a brittle surface layer or embrittled α_2 phase, especially after long-term exposure. A third possible reason for premature surface cracking and fracture, reported by Wu et al. [7], is the formation of a tensile surface stress that replaces the surface compressive stress present prior to exposure. The proposed development of tensile stress in the near-surface material was confirmed by Paul et al. [9], who also recognized a reduction of the compressive residual stress deeper within the material. Wu et al. [7] reported that the oxygen-enriched surface region formed after exposure at 700°C was extremely thin, with an estimated thickness of 10–100 nm.

None of the above theories can explain why the fracture stress of exposed material (brittle in nature), when tested under liquid nitrogen, is higher than the fracture stress of both unexposed and exposed specimens at room temperature. For ductile materials, a higher flow stress is expected as deformation is a thermally activated process, but this is not the case for exposed TiAl tested under liquid nitrogen. For tests performed on a brittle material such as TiAl, the range of fracture stresses can be analyzed in terms of Weibull statistics [25, 26]. This has been done for the tests performed in the current study as shown in Figure 12. This clearly shows that the fracture stress after exposure is significantly higher at -196°C than that for both the exposed and unexposed specimens at room temperature. The fracture toughness K_{1c} is very unlikely to be higher at a temperature of -196°C than at room temperature, as it is determined by plasticity mechanisms that are limited at cryogenic temperatures. As discussed above, the relaxation tests have shown that the glide resistance of dislocations is significantly higher at liquid nitrogen temperature compared to that at room temperature. From literature, it is known that K_{1c} is constant or increases with temperature in metallic materials [27], as is also the case in TiAl alloys [19].

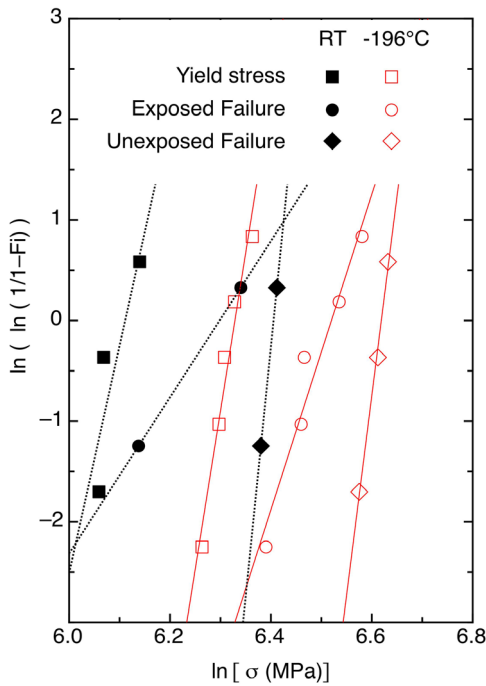


FIGURE 12 | Weibull plots for tests performed under liquid nitrogen or in air at room temperature. The plots indicate the range of yield and fracture stresses of unexposed specimens, as well as the range of fracture stresses of exposed specimens. It is clear for both room temperature tests and tests under liquid nitrogen that the fracture stress after exposure lies in between the yield stress and the fracture stress of unexposed specimens. It is interesting that the fracture stress of exposed specimens under liquid nitrogen is higher than the fracture stress of unexposed specimens at room temperature. Specimen composition Ti-46.5Al-5.5Nb-0.3Mo-0.2C-0.2B.

The fracture stress (σ_f) of a brittle material is given by the formula $\sigma_f = K_{Ic}/(\pi a_c)^{1/2}$, where K_{Ic} is the fracture toughness and a_c is the critical crack length to cause fracture. Thus, the fracture strength under liquid nitrogen, after exposure, could be expected to be similar to that at room temperature from a pure fracture mechanics point of view for a brittle material. This is not the case. A detailed characterization of the fracture surfaces, although potentially informative, was not performed because the primary aim of the work was to characterize the mechanical properties and investigate deuterium ingress during environmental exposure. Similarly, postfracture crack observations and quantitative crack density measurements would be valuable for further elucidating the fracture mechanisms.

Seemingly, none of the mechanisms proposed in the literature for the environmental embrittlement of TiAl can adequately explain the experimental finding with regard to the higher fracture stress of exposed specimens at -196°C . It is thus necessary to discuss what other mechanism/s could be causing the embrittlement.

It is well known that hydrogen can lead to embrittlement in a number of materials. The main TiAl environmental embrittlement theory assumes that hydrogen dissociates from moisture in the environment at newly/prematurely formed surface cracks in TiAl, as outlined earlier. In the general hydrogen embrittlement literature, there are a number of embrittlement mechanisms proposed,

including (i) hydrogen-induced blistering, (ii) cracking from precipitation of internal hydrogen, (iii) cracking from hydride formation, (iv) hydrogen attack, and (v) “hydrogen embrittlement” [28]. Mechanisms (i–iii) rely on hydrogen/hydrides forming cracks that lead to failure. These mechanisms are highly unlikely to cause embrittlement of TiAl, as embrittlement is reported to take place even when exposure of the specimen takes place in a good vacuum.

Of the various mechanisms mentioned above, “hydrogen embrittlement” seems to be the most likely. As described by Robertson et al. [29], there are various embrittlement mechanisms that come under the description of “hydrogen embrittlement.” The two most widely accepted mechanisms of the widely contested debate are “hydrogen-enhanced local plasticity” (HELP) and “hydrogen-enhanced decohesion” (HEDE). The HEDE mechanism involves the reduction of cohesive strength via hydrogen, which reduces fracture toughness and thus the critical crack length and, therefore, the fracture stress. With this mechanism, it is difficult to explain the higher fracture stress of exposed specimens under liquid nitrogen compared to room temperature. According to Robertson et al. [29], in its purest form, the “hydrogen-enhanced local plasticity” mechanism (HELP) enhances the production and mobility of dislocations in the presence of hydrogen. Birnbaum and Sofronis [30, 31] proposed a hydrogen-shielding concept to explain the enhanced mobility of dislocations in the presence of hydrogen. The mechanism considers hydrogen atoms segregating into and modifying the stress field of dislocations and other features. Robertson [29] explains that for dislocations, this makes the stress field in some directions increase while in other directions it decreases. It is indeed interesting that the fracture stress of exposed specimens (exhibiting zero plastic strain) when tested under liquid nitrogen is just above the stress at which yield in unexposed specimens starts to occur under liquid nitrogen. This is also the case for one of the tests at room temperature, the fracture stress of the exposed material (again with zero plastic strain) being similar to the yield stress of unexposed material. Thus, for this alloy in its processed condition, independent of testing temperature, it seems that fracture of exposed specimens takes place at stress levels around those where plasticity would normally start to occur. Such an observation seems to indicate that embrittlement is associated with the onset of plastic deformation, possibly via a hydrogen-enhanced local plasticity embrittlement mechanism.

In the hydrogen embrittlement literature of conventional materials, testing at cryogenic temperatures usually results in restoration or at least partial restoration of the ductility that is absent at higher testing temperatures [32]. The question then arises as to why at least some ductility is not restored when testing the exposed TiAl specimens at -196°C .

It is interesting to postulate if there is any influence of hydrogen already within the material on the fracture behavior of unexposed material. Hino et al. [33] performed tensile tests under ultra high vacuum (UHV) of specimens made from a cast + HIPed Ti-48Al alloy containing 76 mass ppm hydrogen. It was observed that hydrogen was released immediately after fracture, and it was speculated that hydrogen played some role in the fracture process. Unfortunately, this experiment is the only such

experiment described in the literature; repeat experiments would certainly be very useful to confirm the findings.

To summarize, it is concluded that none of the earlier proposed mechanisms for the environmental embrittlement of TiAl can fully explain the observed high brittle-fracture stress of exposed TiAl specimens when tested under liquid nitrogen. It is speculated that hydrogen, which has entered the tensile specimens either during manufacture or the high-temperature exposure treatment, could lead to embrittlement through a hydrogen embrittlement mechanism.

To clarify if hydrogen ingress into TiAl from atmospheric moisture took place during high-temperature exposure, secondary ion mass spectrometry (SIMS) was performed on three different types of TiAl microstructure, as outlined in Section 3.2. From the SIMS results, it has been clearly established that water vapor in the environment dissociates on the surface of TiAl at elevated temperatures and diffuses into the surface. As the depths probed by sample erosion for both positive and negative polarity modes were limited, with a maximum depth of approximately 619 nm, the actual depth of deuterium ingress into the material is uncertain. However, the excess level of deuterium at the end of the SIMS erosion process resulted in a much higher D to H ratio than that given by the natural deuterium to hydrogen isotopic ratio, as shown in Figure 8. Thus, it can be expected that the deuterium from the dissociated heavy water vapor has reached much deeper regions within the material. Quantitative determination of deuterium ingress to greater depth would be valuable for a more detailed understanding of uptake behavior; however, this would require specialized techniques such as NRA (nuclear reaction analysis) or ERDA (elastic recoil detection analysis), which were not available to the authors.

Takasaki et al. [34] investigated the take-up of gaseous hydrogen at elevated temperatures by thermal desorption spectroscopy for binary Ti–45Al and Ti–50Al alloys, the results suggesting higher hydrogen solubility in the alpha-2 phase than in the gamma. Connétable [35], who used density functional theory (DFT) calculations, states that the hydrogen solubility is higher in the alpha-2 phase compared to gamma. This work [35] also found that the diffusion of hydrogen is anisotropic in both the gamma and alpha-2 phases and that diffusion is slower in the gamma phase. If hydrogen solubility is higher in the alpha-2 phase, then its concentration could be expected to be higher than in the gamma phase. However, hydrogen could dissipate further away from the surface on account of its higher diffusivity in the alpha-2 phase, although depth-integrated deuterium images indicate no sign of local deuterium enrichment in the alpha-2 phase. The most important finding is that the heavy water dissociated during high-temperature exposure, and significant levels of deuterium entered the surface and subsurface regions.

One aspect that has been addressed in the general hydrogen embrittlement literature is where hydrogen tends to segregate in a material. After entering an alloy, either from the surrounding environment or during manufacture, hydrogen diffuses to, and is concentrated at, so-called traps. According to Louthan [28], absorbed hydrogen is present at either of two locations in the microstructure: at interstitial sites or at extraordinary sites, typically associated with crystalline defects. The absorption of

hydrogen leads to lattice expansion, which has the consequence that hydrogen prefers sites where the lattice is already expanded. Such sites include grain boundaries, vacancies, dislocations, regions under tensile stress, and any other regions where interstitial sites are expanded [28].

In the TiAl literature, it has been shown that the surface of polished samples is under a compressive stress, which reduces in magnitude away from the surface [9]. To balance stress, there must be a balancing tensile stress deeper within the material. It is interesting to speculate how mobile hydrogen would be distributed in such specimens with an inhomogeneous (near-surface tensile) residual stress distribution. The near-surface compressive residual stress of polished specimens should result in a reduced local hydrogen level compared to regions deeper within the specimen that would be under a balancing tensile residual stress and that would attract hydrogen. After exposure, the situation is reversed, with a high near-surface residual tensile stress and a reduced residual compressive stress deeper under the surface. Hydrogen that was already within the material, as well as that which has been incorporated from moisture in the environment, will be redistributed/distributed in the material, with regions under tensile stress having a higher hydrogen concentration compared to regions under compressive stress. Thus, the change in residual stress state, combined with hydrogen incorporated from atmospheric moisture, would lead to an increased level of near-surface hydrogen that could result in embrittlement. This phenomenon seems to be illustrated in Figure 7 for all three types of microstructure by the peak in hydrogen and deuterium intensity that is present under the surface. In this context, it is very interesting that a recent paper by Stangl et al. [36] highlights that the origin of embrittlement after exposure lies in the region close to the surface at a maximum depth of 2 μm .

As proposed earlier, none of the current mechanisms proposed in the literature can adequately explain the cryogenic tensile test findings. After exposure, it is plausible that hydrogen is concentrated in the near-surface regions due to high residual tensile stress and that, on a very localized atomic level, its concentration is rather high. The critical crack length in TiAl is determined by the fracture toughness and is low compared to that of conventional materials. Thus, when dislocations are shielded by hydrogen and their movement restricted (as postulated by Robertson [29] for the HELP mechanism), the stress quickly exceeds levels where the low fracture toughness results in defects within the material acting as critical cracks, leading to premature fracture. This is especially true for high-strength alloys where a high stress is required to initiate deformation. The behavior of low-strength alloys is different, as flow is initiated at lower stresses before the critical flow stress is reached. Nevertheless, once flow has been initiated, hydrogen could lead to premature fracture via the HELP mechanism.

5 | Concluding Remarks

This study has shown that the thermally activated deformation mechanisms of TiAl in tension under liquid nitrogen are similar to those previously reported for compression. It has been revealed that embrittlement after high-temperature exposure persists even when tensile testing is performed under liquid

nitrogen. When tensile testing of exposed specimens is performed under liquid nitrogen, we argue that surface cracks formed during testing cannot lead to hydrogen embrittlement via the mechanisms proposed in the literature due to the lack of available water for dissociation into hydrogen and the slow kinetics. The investigation has shown that hydrogen can enter TiAl from water vapor during the exposure treatment and that it penetrates deep into the subsurface. Earlier literature has shown the development of significant tensile residual stress at the TiAl surface after exposure and a change of the residual stress state deeper in the material. In the hydrogen embrittlement literature, it is well documented that hydrogen is concentrated in such regions under tensile stress. It is proposed that hydrogen within the material, originating from moisture dissociation during exposure and/or from prior processing, is concentrated at the surface, where it leads to hydrogen embrittlement. As highlighted in the literature, the origin of the embrittlement lies within 2 μm from the surface.

Author Contributions

Jonathan D.H. Paul: conceptualization (lead), data curation (lead), formal analysis (lead), investigation (equal), project administration (lead), resources (equal), validation (equal), visualization (lead), writing – original draft preparation (lead). **Alexander Welle:** investigation SIMS (lead), formal analysis SIMS (lead), resources (equal), validation SIMS (lead), writing – review and editing (equal). **Dirk Matthiessen:** investigation (equal), resources (equal), writing – review and editing (supporting). **Michael Oehring:** validation (equal), writing – review and editing (equal). **Fritz Appel:** validation (equal), writing – original draft preparation, writing – review and editing (equal). **Florian Pyczak:** resources (equal), validation (equal), writing – review and editing (equal).

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data presented in this study is available from the corresponding author upon reasonable request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.