THE EFFECT OF OXYGEN PARTIAL PRESSURE DURING HIGH TEMPERATURE EXPOSURE ON SENSITIVITY TO EMBRITTLEMENT OF DIFFUSION BONDED INCONEL 625

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ABSTRACT

It has been shown in previous work that the ductility of nickel and nickel base superalloys may be severely reduced after high temperature exposure to oxygen. This study has explored the embrittling effects of oxygen on Inconel 625 and diffusion bonded Inconel 625.

Tensile specimens of bonded and unbonded Inconel 625 were exposed to three partial pressures of oxygen in the range from 0.2 to 1×10^{-27}atm at temperatures of 1000°C and 1100°C for 24 hours. After this initial exposure, intended to simulate the parameters which the material would see during the diffusion bonding process, the extent of embrittlement was determined through tensile testing in air at both room temperature and 650°C. Embrittlement due to oxygen penetration was related to the maximum radial amount of intergranular fracture observed on the tensile specimen fracture surfaces. Specimens exposed to the lowest partial pressure of oxygen showed no intergranular fracture.

Flat tensile specimens 1mm thick were given similar exposures at 1100°C and internal penetration of oxygen was observed along grain boundaries in the form of gas bubbles near the material surface which led to the conclusion that CO_2 bubbles were being formed and were contributing to the loss in ductility of the material.

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INTRODUCTION

When fabricating thin sections of materials into actual designs, the diffusion bonding process may be employed in order to obtain complex structures without appreciable distortion of the material. By using suitable interlayers, interdiffusion between two substrates is enhanced during bonding at high temperatures under pressure in an industrial vacuum, and acceptable mechanical properties are obtained.

This joining process is advantageous in that it has many engineering applications, especially in the formation of parts where little or no material distortion is imperative and post bond machining impractical due to material thinness or geometrical considerations[1,2]. This process is superior when used on parts which are hard to access by normal welding methods. Hollow components, because they have multiple joints, may be diffusion bonded in one operation. The major drawback, though, is the long thermal cycle needed to produce the bond. Because of this, diffusion bonding has not been a popular mass production process.

During the bonding cycle, the material is exposed in a commercial vacuum or argon inert atmosphere at an elevated temperature for a relatively long period of time. Any oxygen present in the furnace could potentially render the material brittle. Oxygen embrittles nickel and nickel base superalloys in a number of ways, depending on the alloy constituents, temperature conditions, and amount of oxygen present in the environment.

Woodford and Bricknell[3] doped Ni270 with sulfur in order to promote intergranular fracture at room temperature. These doped samples were given various high temperature heat treatments in both air and evacuated environments. After breaking the samples intergranularly, it was noted that the faces of the grains after vacuum exposure were clean and featureless, yet those in the air exposure revealed fine precipitates identified as complex oxides containing the trace elements found in Ni 270. This indicated oxygen penetration down the grain boundaries and reacting with the surrounding material.

As oxygen diffuses along grain boundaries, it may also react with carbon, in either elemental or carbide form, and produce either CO or CO_2 gas bubbles[4]. It has been shown [5] that, although CO gas bubbles, as well as CO_2 bubbles, are thermodynamically producable in pure nickel, it is unlikely that CO will form in the more complex nickel base superalloys. Once the bubbles form, they link together, acting as stress raisers and crack nucleation sites. The removal of carbon prevents the formation of such voids in pure nickel. These voids may also act as creep cavity nuclei, or they may reduce grain boundary mobility, thus rendering the material brittle.

Oxygen may also diffuse down the grain boundaries of the material and cause chemical reactions to occur which would in turn release deleterious elements and embrittle these areas. Bricknell and Woodford[6] studied the release of embrittling sulfur onto the grain boundaries of a Ni-Mn-S alloy after oxygen had diffused down and reacted with the sulfides to form oxides.

Oxygen may also penetrate into a material and react with hydrogen, forming embrittling steam bubbles along grain boundaries.

This research sought to determine whether the diffusion bonding of Inconel 625 would be affected by high temperature exposure to a low oxygen partial pressure environment present during the hot isostatic press (HIP) bonding process and subsequent vacuum annealing. Typically, Inconel 625 would be HIP bonded in a commercial argon furnace for approximately 4 hours at 1100°C followed by vacuum anneling. The question arises, how good an environment must be used for the material to be unaffected by the oxygen at the elevated temperature and is the material affected by even a low partial pressure of oxygen? To what extent would Inconel 625 be embrittled due to oxygen? O. Ohashi and K. Sasabe[7] have reported on the effect and importance of the bonding atmosphere on the mechanical properties of diffusion bonded joints. Using such bonding environments as vacuums of $3.8x10^{-8}$atm and $3.8x10^{-5}$atm, Argon gas, Hydrogen gas, and air at 0.2 atm, the integrity of diffusion bonded alloys was investigated and it was found that all of the environments, except the vacuum at $3.8x10^{-8}$atm, resulted in damaged material. Even the bond created in the "vacuum" of $3.8x10^{-5}$atm perfomed substantially poorer than that bond formed in the "vacuum" of $3.8x10^{-8}$atm.

In addition to the initial diffusion bond applied to the material, subsequent bonds could be applied to a particular part in the vicinity of the first in order to achieve the desired design configuration. In this case, each bond would be exposed to multiple bonding cycles. This implies that if bonded Inconel 625 specimens show a degradation of material properties after only one bonding heat treatment cycle, they will probably degrade further after subsequent heat treatments.

Not only is the diffusion bonding process of interest with respect to high temperature embrittlement of Inconel 625 by oxygen, but also the effects of oxygen on thin sheets of the nickel alloy. Because the diffusion bonding process is often used in conjunction with thin sections of material so as to keep part distortions at a minimum, the embrittlement of thin sheets of Inconel 625 in a diffusion bonding environment due to oxygen was also of interest.

EXPERIMENTAL PROCEDURES

The experimental procedures followed were similar to those used by Iacocca and Woodford [8], and Beckman [9] in their investigations into the embrittling effects of gaseous species at high temperatures on nickel and nickel base alloys. This involved heat treatment of Inconel 625 diffusion bonded and unbonded specimens at elevated temperatures in different partial pressures of oxygen and then subsequent mechanical testing of the material at both room temperature and elevated temperature, and then metallographic characterization to observe and record the embrittling effects of oxygen.

All specimens used in this work were machined and formed from Inconel 625. This nickel base superalloy has a nominal chemical composition given in Table I.

The work may be divided into two sets of experiments. The first case involved the diffusion bonding of two hot rolled plates of Inconel 625 with a 0.012 mm thick pure nickel interlayer. The surfaces of the two plates were ground to produce a clean, uniform finish prior to bonding. Plating of the nickel interlayer was accomplished using a sulfamate bath. Care was taken to ensure the deposition of a clean, uniform, and adherent nickel interlayer, which are the determining factors in the integrity of the bond. Hydrogen, which may have been incorporated into the deposits, was removed by baking the plates in a vacuum. The two plates were then placed on top of one another with the electrodeposited surfaces in contact and then sealed off using an electron beam weld applied to the outer perimeter of the workpiece. The actual bonding process was accomplished in a hot isostatic pressing (HIP) unit. The process involved applying a gas pressure of 103.4 MPa for four hours at a temperature of 1093°C. As was noted by Dini[10], sufficient pressure must be applied to the plate surfaces to maximize metal-to-metal contact and allow diffusion across the bondline to occur. After sufficient contact was achieved, the pressure was removed and the diffusion process was allowed to run its course in a vacuum.

Buttonhead tensile specimens with bonded joints with 2.54 mm diameter reduced sections were electro discharge machined (EDM'd) from the diffusion bonded block such that the bond was perpendicular to the tensile axis and was located in the center of the gage length. As Figure 1 shows, the specimens were machined from the center bulk of the block of material to eliminate the possibility of any pre-existing oxygen damage in the bonded region.

TABLE I
NOMINAL COMPOSITION OF INCONEL 625 [W/O]

Ni	Fe	Cr	Mo	Ti	Al	Nb	C	Si	Mn
bal	4	21.5	8	0.2	0.2	3.5	.04	0.1	0.1

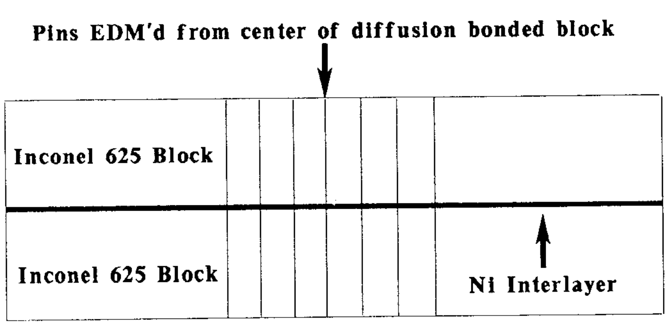

Figure 1 - Schematic diagram of diffusion bonded Inconel 625 plates with Ni interlayer. Vertical lines denote area from which tensile specimens were EDM'd. Material in center of block unaffected by diffusion bonding environment.

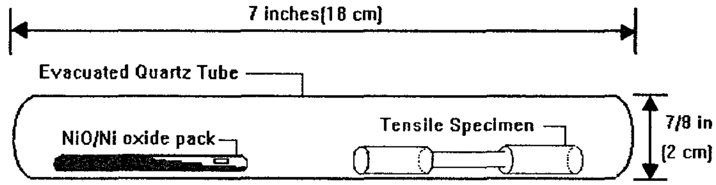

Figure 2 - Diagram of encapsulation showing tensile specimen and metal/oxide mixture in evacuated quartz tube.

The specimens were then exposed to partial pressures and temperatures which were representative of those used during the diffusion bonding process in a manufacturing situation. The controlled partial pressures of oxygen were achieved by sealing the samples along with specific metal oxides in an evacuated quartz tube, as seen in Figure 2. The samples were exposed at 1000°C and 1100°C for 24 hours in partial pressures of oxygen of 0.2, 1.4×10^{-10}, and 5.5×10^{-27} atm (at 1000°C) and 0.2, 3.5×10^{-9}, and 1.8×10^{-24} atm (at 1100°C). Table II outlines the full test matrix. The partial pressure of 0.2 atm corresponds to exposure in air, where no encapsulation was used. The four other lower partial pressures of oxygen are associated with the dissociation of nickel oxide and silica at the specified exposure temperatures. When no oxide pack was included in the quartz tube encapsulation, it was assumed that any residual oxygen which might have been present in the capsule was rapidly absorbed to establish the equilibrium dissociation pressure of the silica glass at the exposure temperature. This environment, which had no oxide pack included in the quartz capsule, is subsequently referred to as inert.

After exposure, specimens were tensile tested at both an elevated temperature (650°C) and at room temperature. The initial testing temperature of 650°C corresponded with the ductility minimum usually associated with nickel base superalloys in the range of this elevated temperature. If any embrittlement had occured during exposures at 1000°C or 1100°C, the damage would be particularly pronounced during testing at 650°C. After it was noted that diffusion bonded Inconel 625 was sufficiently embrittled after exposure to oxygen to cause a loss in ductility after tensile testing at room temperature, all subsequent tests were confined to this convenient temperature. The crosshead speed used was 1.27cm/minute.

After tensile testing, the specimens were metallographically prepared for observation on an optical metallograph. Fracture surfaces were examined on an SEM for evidence of intergranular fracture which may have occured due to oxygen embrittlement and to quantify the depth of penetration into the alloy.

These procedures and testing were repeated for control specimens of unbonded Inconel 625. All tensile testing of the base material was confined to 650°C because tests conducted at room temperature were not sensitive enough to reveal any damage.

A second series of tests was performed on 1mm thick flat tensile specimens of unbonded Inconel 625. The thickness of these samples was more representative of the dimensions of parts which might be diffusion bonded. These samples were expected to be more sensitive to the oxygen environment in terms of tensile properties. These flat tensiles were given the oxygen exposures associated with the heat treatment temperature of 1100°C as outlined in Table II. They were tensile tested to failure at room temperature using a crosshead speed of 2.5mm/minute.

The flat tensile specimens were metallographically mounted at an angle in epoxy so as to produce a taper magnification of 5.7 times of the surface damage. This process allowed for higher resolution of the nature of the oxygen damage, as well as semi-quantitative measurement of the observable oxygen penetration into the sample using the optical metallograph.

TABLE II TEST MATRIX

Heat Treatment Temperature [°C]	Exposure Time [Hours]	Partial Pressure of Oxygen [Atm]
1000	24	0.2
1000	24	1.4X10(-10)
1000	24	5.5X10(-27)
1100	24	0.2
1100	24	3.5X10(-9)
1100	24	1.8X10(-24)

RESULTS AND DISCUSSION

BUTTONHEAD SPECIMEN TENSILE RESULTS

Figures 3 and 4 are comparative graphs of the strengths and ductilities of the diffusion bonded and unbonded Inconel 625 tensile tested at both room temperature and 650°C. The results shown in both graphs are for the specimens which were exposed at 1100°C for 24 hours. Exposures at the lower temperature of 1000°C revealed no appreciable differences in mechanical properties among the three different oxygen partial pressures. This was probably due to the fact that at this temperature, the activity of oxygen was not great enough to enable penetration down the grain boundaries and the formation of CO_2 bubbles to occur. This was especially true for the unbonded Inconel 625. The bonded Inconel 625 samples did show evidence of embrittlement after exposures at 1000°C, but the more striking differences were revealed after the 1100°C exposure.

Diffusion Bonded Specimen Tensile Results. The diffusion bonded Inconel 625 proved to be most sensitive to an oxygen environment at elevated exposure temperatures. Whether tensile tested at 650°C or room temperature, the diffusion bonded samples showed a decrease in ductility, as indicated by a drop in the elongations to fracture of Figure 3, and a decrease in strength, as indicated by a drop in the ultimate tensile stress/fracture resistance of Figure 4, after exposure to oxygen at elevated temperatures. It should be noted that the ultimate tensile strengths and fracture stresses of the diffusion bonded specimens were the same, due to the fact that no necking was observed during tensile testing. The stress-strain curves closely followed those of the parent Inconel 625, yet the ductility of the unbonded material was never achieved because the bonds failed so abruptly.

All diffusion bonded specimens tensile tested at 650°C failed at maximum load in the bondline. No necking was noted before fracture and no surface cracking was seen after test completion. The best mechanical properties were seen in those specimens exposed in an inert environment, but even then, as Figures 3 and 4 show, the properties of the base material were not attained. The worst mechanical behavior was noted in the specimens exposed in the intermediate partial pressure of oxygen. This phenomenon may be attributed to the fact that no protective Cr_2O_3 scale was able to form on the pure nickel interlayer material. When the samples exposed at these partial pressures of oxygen were removed from the furnace, a relatively shiny band around the circumference of the specimen in known area of the diffusion bond was noted, indicating no Cr_2O_3 oxide formation. This was due to lack of Cr diffusion across the bondline. If no scale is formed, the oxygen will penetrate down the grain boundaries in this region and cause a severe degradation in the integrity of the bond, thus causing the material to display inferior mechanical properties when compared to those of the parent alloy. It has also been shown that insufficient Cr diffusion across the bondline in In625 during the bonding process leads to rapid stress corrosion cracking in the Ni-rich bonded area[11]. Those samples exposed in an inert environment were the only ones which even approached 50% of the total ductility of the unbonded alloy and almost 50% of the base material's ultimate tensile strength.

Tensile tests were conducted at room temperature on diffusion bonded Inconel 625 after it was discovered that embrittlement due to oxygen was evident at this test temperature, as well as at 650°C. Diffusion bonded Inconel 625 tensile tested at room temperature after exposure at both 1000°C and 1100°C showed a sensitivity to oxygen. As Figures 3 and 4 indicate, the fracture stresses and elongations to fracture of the intermediate and high partial pressure exposures at 1100°C were noticeably lower than those of the inert environment exposure. Most interesting to note is the fact that of all the diffusion bonded Inconel 625 examined in this research, those specimens exposed in an inert environment at both 1000°C and 1100°C and subsequently tensile tested at room temperature were the only to fail away from the bondline in the base material.

Diffusion Bonded Specimen Fractography Results. Figures 5 and 6 are SEM micrographs taken of the fracture surfaces of the diffusion bonded Inconel 625 which was tensile tested at 650°C. Figure 5 was taken of the specimen exposed in 3.5×10^{-9} atm at 1100°C for 24 hours. A ring of intergranular fracture at the outer circumference of the specimen is evident. The lower portion of the fractograph shows the transgranular fracture and a sharp transition which occurs at approximately 1/3 of the way up from the bottom of the photo. In the upper embrittled region, the fracture surface is flat and faceted. If closely examined, many grain boundaries and triple points are evident, as well as carbon dioxide gas bubbles on the faces of the flat grains. Smaller voids along grain boundaries were apparent in higher magnification fractographs. These small CO_2 gas bubbles eventually grow and join to form the larger bubbles, thus rendering the material brittle.

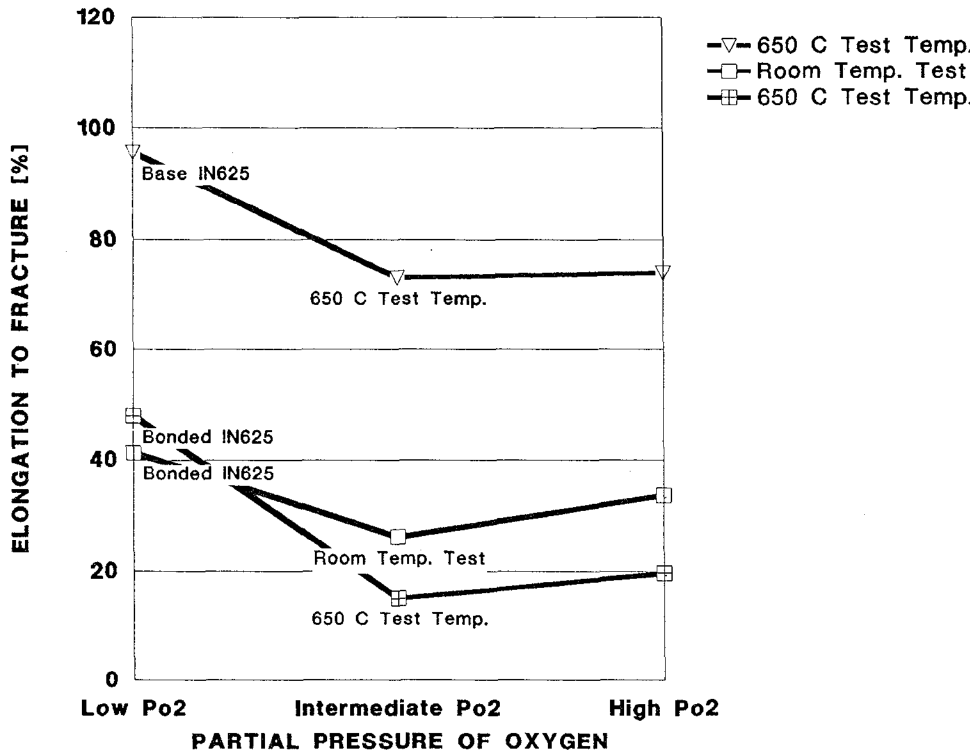

Figure 3 - Comparison of elongations to fracture of diffusion bonded Inconel 625 tensile tested at 650°C and room temperature and unbonded Inconel 625 tensile tested at 650°C. Specimens exposed in three different partial pressures of oxygen at 1100°C.

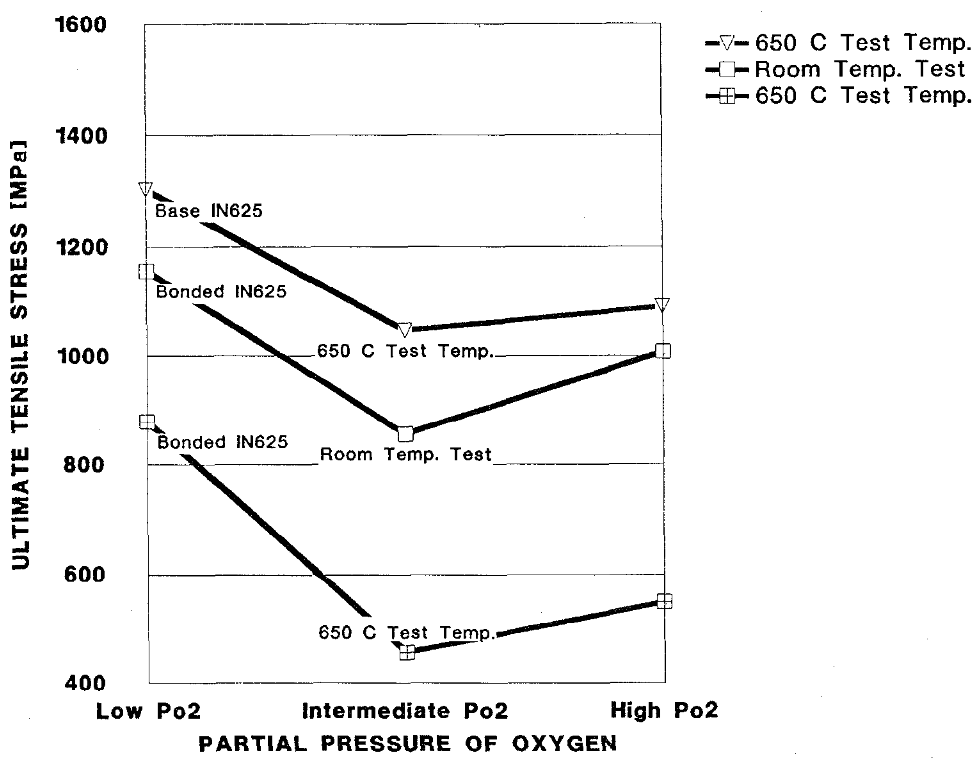

Figure 4 - Comparison of ultimate tensile stress/fracture resistance of diffusion bonded Inconel 625 tensile tested at 650°C and room temperature and unbonded Inconel 625 tensile tested at 650°C. Specimens exposed in three different partial pressures of oxygen at 1100°C.

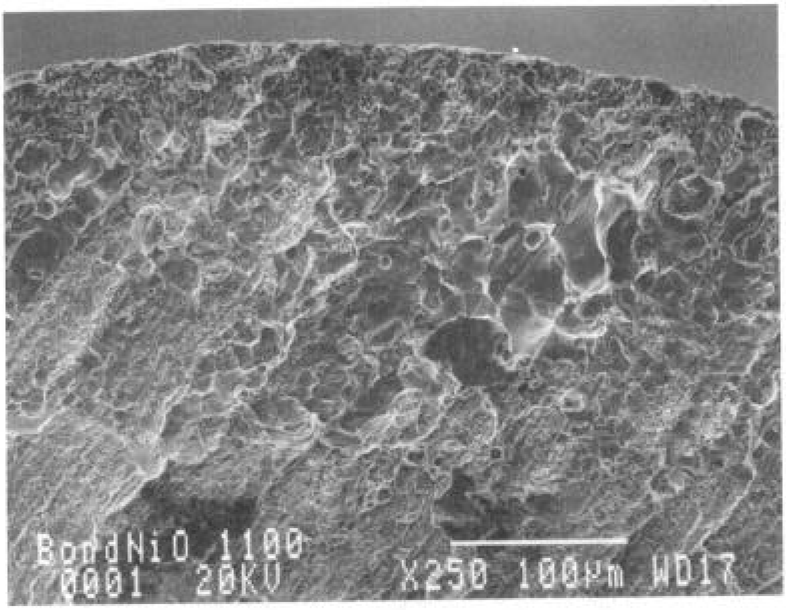

Figure 5 - Diffusion bonded Inconel 625 exposed in 3.5×10^{-9} atm oxygen at 1100°C for 24 hours and tensile tested at 650°C.

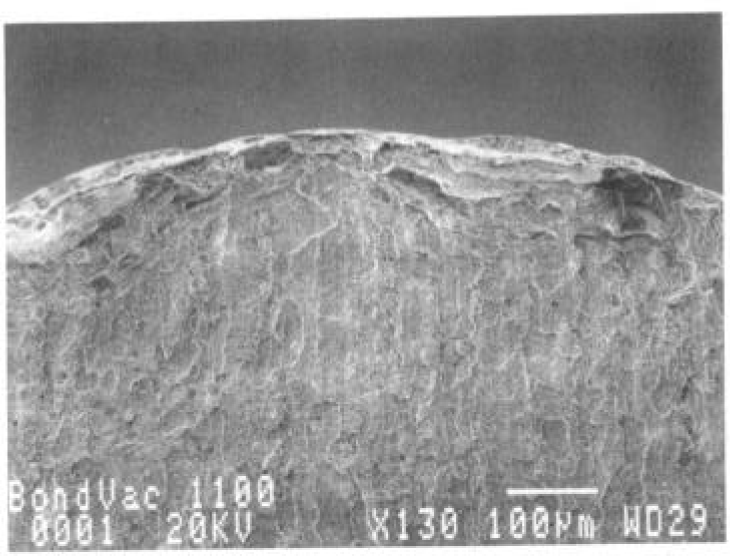

Figure 6 - Diffusion bonded Inconel 625 exposed in an inert environment at 1100°C for 24 hours and tensile tested at 650°C.

In contrast, Figure 6 shows the fracture surface of the diffusion bonded Inconel 625 specimen tensile tested at 650°C after exposure in an inert environment for 24 hours at 1100°C. This sample displayed none of the intergranular, brittle fracture features seen in the oxygen exposed specimens. The fracture was ductile across the full fracture surface and is similar in appearance to the area just below the embrittled ring seen in Figure 5. Similar results were obtained after observation of the diffusion bonded tensile specimens tested at room temperature.

Table III summarizes the apparent oxygen damage penetration in the diffusion bonded Inconel 625 specimens tensile tested at both 650°C and room temperature. At 1100°C exposure temperature, the intermediate partial pressure of oxygen produced the greatest depth of damage, measured at 160-220 μm. The air exposure produced between 120 and 150 μm of oxygen penetration. The inert environment exposure gave no apparent damage measurement. Similarly, of those specimens tested at room temperature after exposure at 1100°C for 24 hours, the specimen exposed in the intermediate partial pressure of oxygen showed the greatest amount of damage, specifically, between 50-90μm. The sample exposed in air had 20-40μm and the inert environment exposure produced no perceptible damage. These results support the relative amount of degradation in mechanical properties seen in these tensile samples.

As is concluded from Table III, embrittlement by the gaseous species occurred after elevated temperature exposure in an oxygenated environment. The intermediate partial pressure exposures revealed the greatest depth of damage due to the inability of the bonded region to form a protective oxide scale.

Inconel 625 Control Specimen Tensile Test Results. As seen in Figures 3 and 4, the control specimens of unbonded Inconel 625 were also embrittled by pre-exposure in an oxygen environment. After heat treatment at 1100°C, a marked decrease in ductility in terms of total elongation was seen in samples exposed in the higher partial pressures of oxygen. Both the air and intermediate partial pressure exposures were approximately 74%, yet both were less than the inert environment exposure which failed after 95.5% elongation. The elongation data correlated well with the fracture stresses. The inert environment exposed sample proved to be the strongest with the greatest applied fracture stress.

FLAT TENSILE SPECIMEN RESULTS

The 1mm thick flat tensile specimens of unbonded Inconel 625 were tested at room temperature after exposure at 1100°C for 24 hours to various partial pressures of oxygen ranging from 0.2atm (air exposure) to 1.8×10^{-24}atm (inert exposure). These specimens also showed increased loss in mechanical properties with increased partial pressure of oxygen. These flat specimens were metallographically mounted longitudinally at a 10° taper to give a taper magnification of 5.7. The intergranular surface damage was revealed as gas bubbles in both the undeformed specimen head and deformed gage section. Figure 7 shows the unbonded Inconel 625 specimen which was exposed at 1100°C for 24 hours in 3.5×10^{-9}atm of oxygen. The damage resulting from oxygen attack is clear. The three separate parts of the tensile specimen are shown. Figure 7a is the undeformed region, Figure 7b is in the transition region, and Figure 7c is taken from the deformed gage section of the sample. All three micrographs illustrate the embrittling effects of oxygen and the extensive surface damage which resulted. The intergranular bubbles shown become more pronounced with increased deformation and eventually form cracks along the grain boundaries in the heavily deformed region.

TABLE III OXYGEN DAMAGE PENETRATION IN BONDED IN625

Partial Pressure of Oxygen	**Oxygen Damage Penetration**
TENSILE TESTED AT 650°C	
Low Partial Pressure	None Apparent
Intermediate Partial Pressure	160-220 um
High Partial Pressure	120-150 um
TENSILE TESTED AT ROOM TEMPERATURE	
Partial Pressure of Oxygen	**Oxygen Damage Penetration**
Low Partial Pressure	None Apparent
Intermediate Partial Pressure	50-90 um
High Partial Pressure	20-40 um

Note: All exposures done at 1100°C for 24 hours.

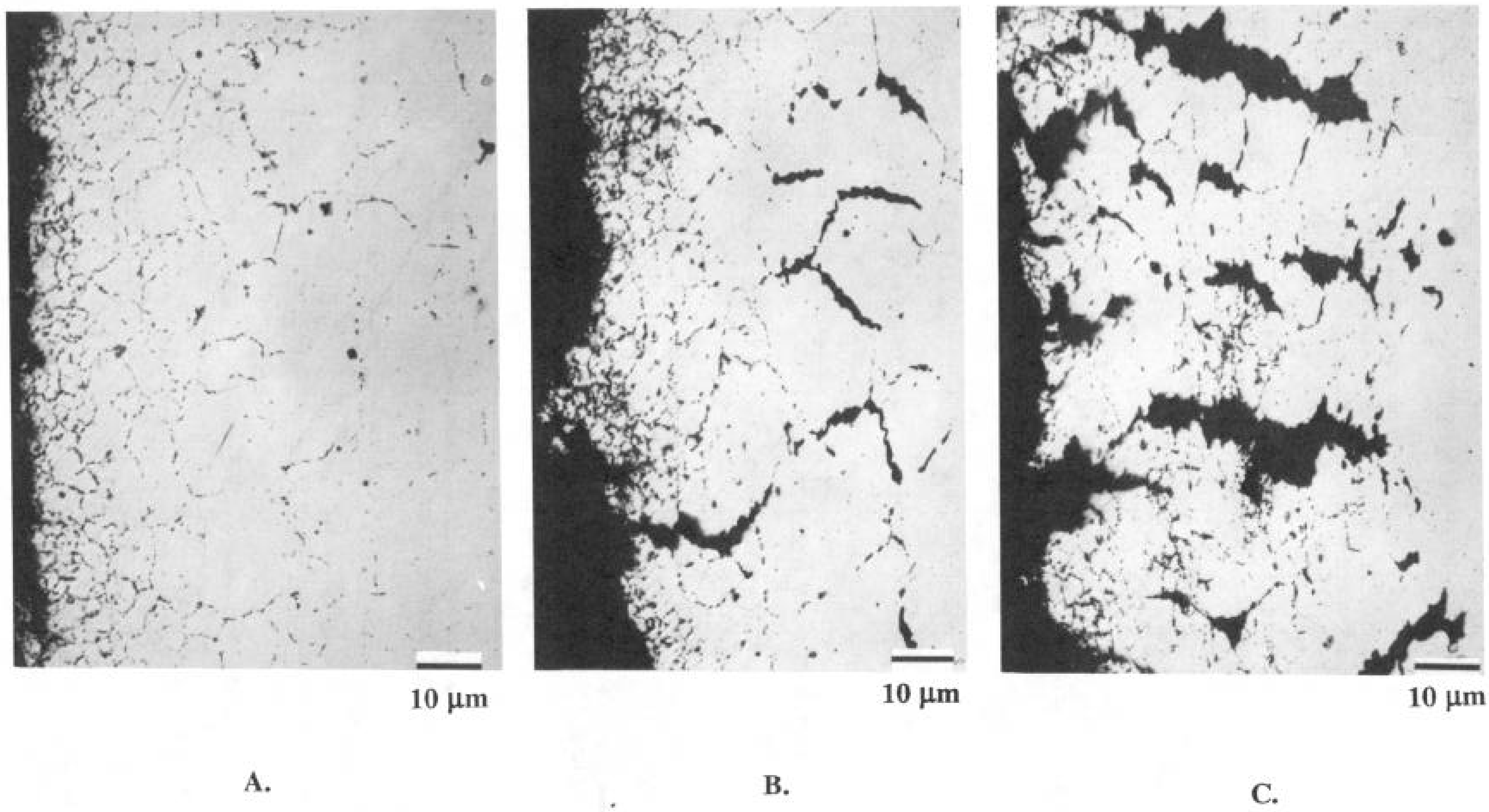

Figure 7 - Unbonded Inconel 625 flat tensile specimen exposed in 3.5×10^{-9} atm oxygen at 1100°C for 24-hours and tensile tested at room temperature. 7A shows the undeformed region of the sample. 7B is in the transition region and 7C is taken from the fully deformed gage section.

CONCLUSIONS

1) Both ductility and strength of diffusion bonded Inconel 625 show a sensitivity to oxygen during simulated diffusion bonding cycles at 1100°C and 1000°C after exposure for 24 hours, with the higher of the two temperatures producing the most embrittled material. The intermediate low partial pressure of oxygen showed the most dramatic effect on loss of mechanical properties at both heat treatment temperatures.

2) The only diffusion bonded specimens which failed outside the bond were those tested at room temperature following the inert environment exposure at both 1000°C and 1100°C.

3) For tensile tests conducted at 650°C, the diffusion bond proved always to be the weak link, even after exposure in an inert environment.

4) Thin sections of the base alloy show significant damage due to oxygen exposure at 1100°C after 24 hours. Carbon dioxide gas bubble formation in subsurface region was noted. Inert environment exposures showed no such embrittling effects of oxygen.

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