

CHAPTER 1 - LITERATURE SURVEY

THE APPLICATION OF BRAZING, WIDE GAP BRAZING AND LIQUID PHASE SINTERING IN THE REPAIR OF NICKEL-BASE SUPERALLOY COMPONENTS FOR GAS TURBINE ENGINES

1.1) Introduction

A gas turbine engine, be it for an aircraft application or for power generation, typically ingests air from the atmosphere. The air is then compressed by the compressor and mixed with fuel. The mixture is combusted in a combustion chamber, usually referred to as the combustor can or the burner can, following which the hot gas is expanded through the turbine section, producing thrust. In essence, thermal energy is converted to mechanical energy.

Components within the turbine section of a gas turbine engine are generally identified as 'blades' and 'vanes', with 'blades' referring to rotating components and 'vanes' to stationary components. Some original engine manufacturers (OEM's), such as General Electric, refer to blades as 'buckets' and vanes as 'nozzles', while a number of European OEM's, such as ABB and Alstom, further confuse matters by referring to vanes as 'stator blades'.

Blades and vanes are not only exposed to high service temperatures (typically 1000°C to 1200°C), but also experience severe stresses and strains, oxidation and corrosive attack during service. As a result of the high temperatures that the turbine section is exposed to during service, the blades and vanes are usually manufactured from materials referred to as superalloys. By definition a superalloy is a material that can operate at 75% and higher of its melting point, while maintaining adequate mechanical strength. Steels have little mechanical strength within the temperature range mentioned above and are therefore not used in the manufacture of turbine components.

Materials used in the production of turbine components include iron-base superalloys, cobalt-base superalloys and nickel-base superalloys. In the early days of engine manufacture, iron-base alloys were widely utilized, but nowadays the majority of blades and vanes are produced from nickel- and cobalt-base superalloys. These alloys exhibit outstanding mechanical strength over the entire operating temperature range in a gas turbine engine and maintain good mechanical integrity, including high creep rupture strength, over long periods of time (up to 20000 hours). The nickel- and cobalt-base superalloys have close packed face centred cubic (FCC) austenitic crystal structures. Of significance in determining the properties of superalloys is the solubility of alloying elements in the austenite matrix and the precipitation of intermetallic compounds (such as gamma prime, γ') and various carbide phases. The cobalt-base superalloys are generally solid solution strengthened, whereas the nickel-base alloys used in engines today are typically γ' strengthened. Gamma prime, γ' , is a face centred cubic intermetallic compound of composition $\text{Ni}_3(\text{Al,Ti})$. Primary γ' exhibits a cuboidal structure, whereas secondary γ' has a more spheroidal morphology (as demonstrated in **Figure 1**). Although the γ' particle size varies depending on the heat treatment that the alloy receives, the typical size of the primary γ' particles is 0.5 μm to 0.8 μm , and that of the secondary γ' phase is between 0.1 μm and 0.2 μm . The two main heat treatments performed in industry are the solution heat treatment, which is performed above the γ' solvus temperature, and the aging heat treatment, which induces the precipitation of the cuboidal and

spheroidal γ' precipitates shown in **Figure 1**. Carbide phases may form intergranularly or intragranularly, as shown in **Figure 2**. Intergranular carbides prevent grain boundary sliding.

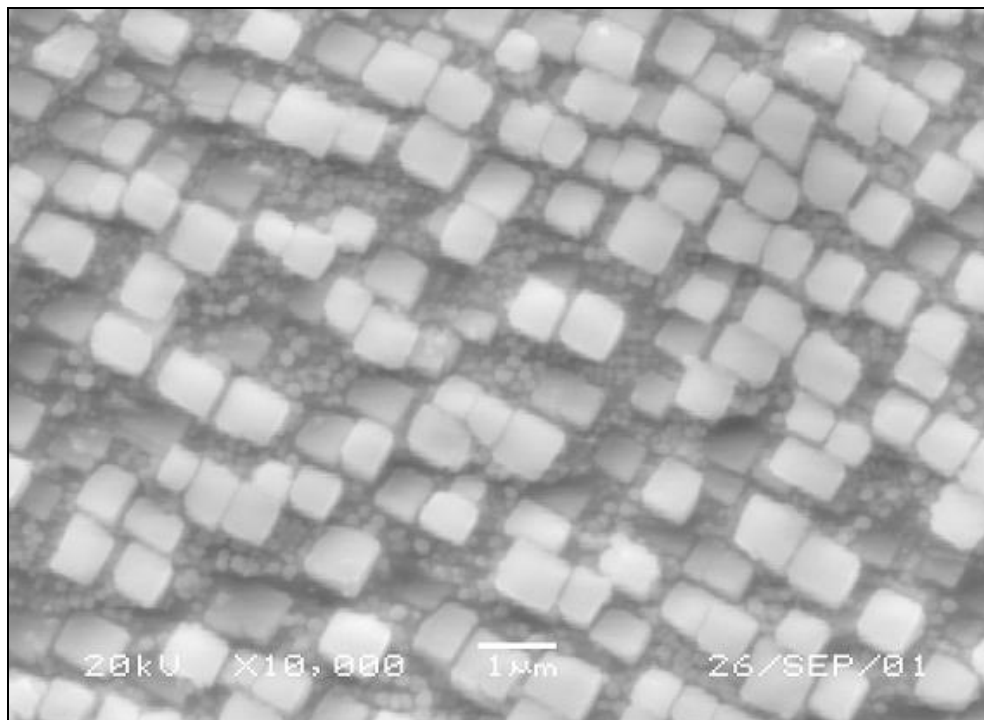


Figure 1 – The cuboidal and spheroidal structure of primary and secondary γ' precipitates (10% oxalic acid etch, magnification: 10000X).

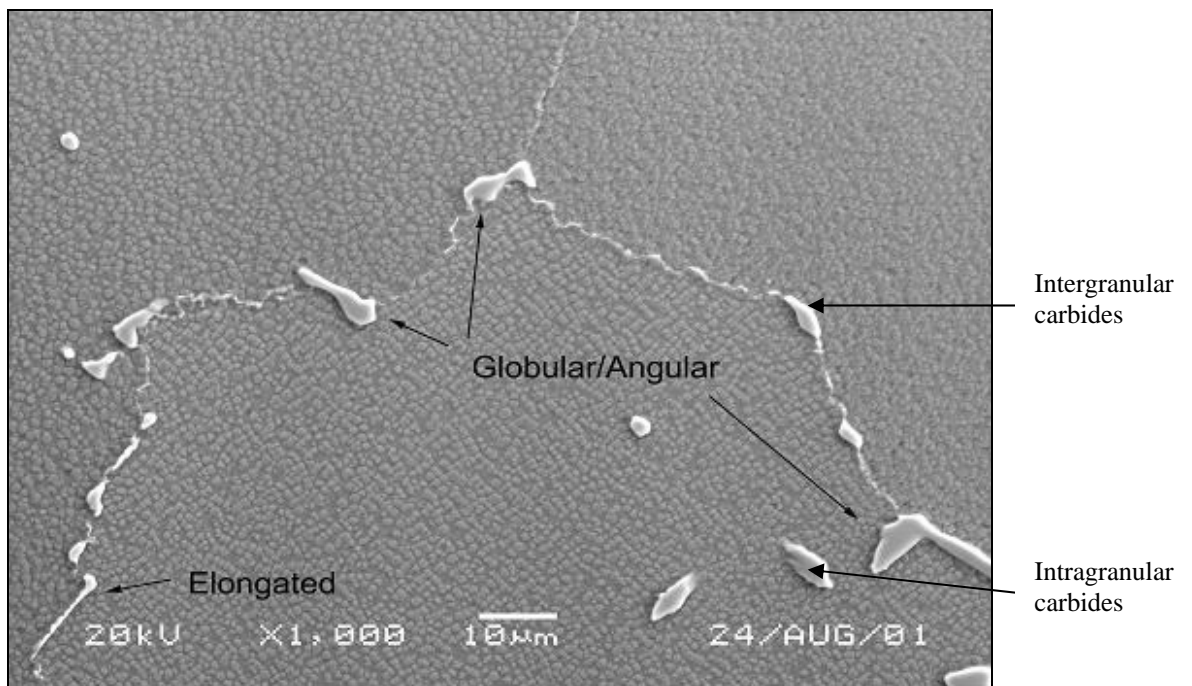


Figure 2 - Intergranular and intragranular carbide phases (10% oxalic acid etch, magnification: 1000X).

Table 1 displays the typical chemical compositions and commercial trade names of superalloys used in the casting of blades and vanes. These alloys usually consist of at least fourteen major alloying elements, in addition to some minor trace elements. Aluminium and titanium are added to form the γ' phase, while chromium is added for corrosion resistance and to promote the formation of carbides. Other carbide formers include molybdenum, tungsten, vanadium, niobium, tantalum and titanium. Nickel, cobalt, iron, molybdenum, tungsten and chromium may be found in the austenite (γ) matrix of the alloy.

Table 1 - Nominal chemical compositions (wt.%, balance Ni) of some Ni-base superalloys.

Alloy	C	Co	Cr	Mo	Al	W	Ta	Nb	Ti	Zr	Fe	Hf	B
In738	0.17	8.5	16.0	1.7	3.4	2.6	1.7	2.0	3.4	0.1	0	0	0.001
In939	0.15	19.0	22.5	0	1.9	2.0	1.4	0	3.7	0.1	0	0	0.001
Rene 80	0.17	9.5	14.0	4.0	3.0	4.0	0	0	5.0	0.03	0	0	0.001
MarM247	0.15	10.0	8.25	0.7	5.5	10.0	3.0	0	1.0	0.05	0.5	1.5	0.001

1.2) The brazing of superalloys and the influence of brazing parameters on joint quality

Fusion welding served as the main fabrication technique for joining these materials for many years. The solid solution family of nickel-base superalloys has been extensively welded using arc welding processes (mainly gas tungsten arc welding and plasma arc welding) and high energy density welding processes (such as electron beam welding). The solid solution alloys, however, do not contain significant amounts of Al and Ti, hence welding problems are seldom encountered. With the addition of Al and Ti (see **Table 1** above), the γ' strengthened alloys become unweldable due to heat-affected zone (HAZ) microfissuring and fusion zone (FZ) cracking (including liquation cracking, ductility dip cracking and strain age cracking).

As a result of these welding-related problems, designers and welding engineers examined brazing as an alternative method of joining these “difficult-to-weld” superalloys. Brazing is defined as a process that produces bonding of materials at the brazing temperature in the presence of a filler metal with a liquidus above 450°C and below the solidus of the parent metal. Unlike welding, the parent metal does not melt. The filler metal is distributed between the closely fitted mating surfaces of the joint through capillary action.

The brazing parameters have been shown to have a significant influence on the properties of the brazed joint. Five main factors, listed below and considered in more detail in the remainder of this chapter, affect the quality of a brazed joint. These factors are:

- the braze gap and joint design,
- the braze filler metal and its flow characteristics,
- the braze temperature and the holding time at temperature,
- the surface preparation and cleanliness of the joint, and
- the rate and source of heating (for example, induction brazing versus furnace brazing).

In the late 1960's, OEM's mainly used gold-base braze filler metals to join airfoils to stator rings to form nozzles. Au/Ni and Au/Cu alloys were used because Au flows well into joints at elevated temperatures. The braze temperatures for these filler metals varied from 900°C to 1100°C, depending on the alloying elements present. The Au-based filler metals resulted in

very ductile joints, but with the price of Au increasing, OEM's started replacing Au with less expensive precious metals such as palladium.

Regardless of the type of precious metal used, however, the high prices on the world market prompted inventors to develop Ni-base braze filler metals with alternative melt point depressants. In the early 1970's, three main melt point depressants were introduced, namely boron, silicon and phosphorus. It should be noted that the melting point of pure Ni is 1455°C. In 1976, Sheward and Bell [1] evaluated several braze filler metals doped with P for joining nuclear parts and components. Boron was considered undesirable in this application because of its high neutron capture cross section and the fact that it transmutes to He. During long term exposure this results in voids and possibly swelling within the joints. Shear test results, corrosion test results and oxidation test results revealed that acceptable braze joints can be achieved on using a braze filler metal with composition Ni-25Cr-10P. The liquidus temperature was in the range of 927°C to 950°C. According to Lee and Nash, quoted in the ASM Handbook [2], a eutectic point exists in the Ni-P system at 11% P and a temperature of 870°C. Many commercial manufacturers of braze filler metals have subsequently successfully produced braze filler metals with P contents ranging from 7% to 14%.

It is important to note that one of the most important factors in achieving a high strength joint is the **joint gap**. When brazing Ni-base superalloys, studies by Sulzer Metco (a popular supplier and manufacturer of Ni-base filler metals) have shown that the joint gap should be between 0.03 mm and 0.25 mm. Because of the difficulty in maintaining a joint gap of close tolerance, many manufacturers and fabricators intensely dislike the brazing process. If the recommended joint gap is exceeded, brittle centreline eutectic phases can form. In joints produced using Ni/P filler metal, wide gaps promote the formation of brittle Ni₃P and Ni₅P₂ phases. In joints with large clearances, soaking for long periods of time at elevated temperature promotes the diffusion of the melt point depressant, such as P, into the parent metal, preventing the formation of brittle phases. This has the distinct disadvantage that braze times on the order of several hours are required to achieve this, which may be uneconomical. Nevertheless, diffusing melt point depressants into the parent metal is often performed when high strength joints are required in turbine components. This process is referred to as diffusion brazing, and will be considered in more detail later.

Ni-base filler metals with Si as melt point depressant display a eutectic point at 30% Si according to Nash and Nash, quoted in the ASM Handbook [2]. Braze filler metals with 30% Si, however, result in brittle joints, as Si has a large atomic diameter and is not readily diffused into the parent metal. Hypoeutectic compositions containing between 8 and 12% Si are commercially manufactured and produce sound, reliable joints in the gas turbine industry. Ni₄Si and Ni₃Si silicide phases have, however, been found in joints with large clearances, resulting in severe embrittlement.

Similarly, for Ni-base filler metals with B as melt point depressant, Liao and Spear [2] reported a eutectic point in the Ni-B system at ±11% B, with a eutectic temperature of 1018°C. However, braze filler metals containing 11% B also result in brittle joints. Nevertheless, the small atomic diameter of B allows rapid diffusion into the parent metal, and joints with gaps as wide as 0.3 mm to 0.6 mm have been brazed successfully using filler metals with B as melt point depressant. A hypoeutectic composition of 3.6% B, corresponding to a melting temperature of 1100°C, is widely used, because it is easier to diffuse a small amount of B into the parent metal. Where filler metals containing 3.6% B are used, the joint is almost indistinguishable from the parent metal after brazing. Joints

produced with filler metals containing between 2% and 5% B are commercially manufactured and produce sound, reliable joints in the gas turbine industry. Nevertheless, if the joint gap is too wide, a variety of boride phases can form. Some of the brittle phases found to date include Ni_3B , Ni_2B and NiB .

In the majority of applications, braze filler metals do not contain a single melt point depressant, but a combination. The most popular Ni-base braze filler metals contain both B and Si. The Aerospace Materials Specification (AMS) introduced four Ni-base braze filler metals containing both B and Si. These are:

- a) AMS 4776, with a composition Ni-14Cr-3.3B-4.5Si-4Fe and a liquidus temperature of 1077°C ,
- b) AMS 4777, with a composition Ni-7Cr-3.2B-4.5Si-3Fe and a liquidus temperature of 1000°C ,
- c) AMS 4778, with a composition Ni-3.2B-4.5Si and a liquidus temperature of 1038°C , and
- d) AMS 4779, with a composition Ni-2B-3.5Si and a liquidus temperature of 1066°C .

These filler metals are the most popular braze filler metals used in the aircraft industry and are produced by many suppliers throughout the world.

During the course of an investigation into Ni-base braze filler metals containing Si and P as melt point depressants, Lugscheider and Kim [3] considered four braze filler metals with the following compositions:

- | | |
|-----------------------------|-----------------------------|
| 1) Ni-24Cr-15Fe-11.5Si-0.6P | 2) Ni-24Cr-15Fe-8.5Si-3.0P |
| 3) Ni-24Cr-15Fe-7.5Si-0.6P | 4) Ni-24Cr-15Fe-11.5Si-1.8P |

Brazing experiments were conducted to enable the brazing parameters (particularly temperature and time) to be optimized with regards to a suitable joint microstructure, and to determine the maximum allowable joint gap. Mechanical tests and corrosion tests revealed that the joints possessed high tensile strengths and excellent corrosion resistance.

Lugscheider and Partz [4] examined the effect of two filler metal compositions on the maximum allowable joint gap during the brazing of Ni-base superalloys. BNi-2 has a composition of Ni-7Cr-3.2B-4.5Si-3Fe and contains Si and B as melt point depressants, and BNi-5 has a composition of Ni-19Cr-10Si and contains only Si as melt point depressant. The authors reported that when BNi-2 was used as filler metal, the maximum allowable joint gap ranged between 0.03 mm and 0.04 mm for a brazing time of 10 minutes at a temperature of between 1010°C and 1120°C . Increasing the brazing time to 60 minutes, however, increased the maximum allowable joint gap to between 0.05 mm and 0.1 mm. When BNi-5 was used as filler metal, the maximum joint gap was between 0.018 mm and 0.022 mm for a brazing time of 10 minutes at a temperature of 1150°C to 1210°C . Increasing the brazing time to 60 minutes increased the maximum allowable joint gap to between 0.035 mm and 0.05 mm. The authors also reported that brazing for either 10 minutes or 60 minutes at temperatures between 980°C and 1100°C reduced the maximum joint gap to 0.01 mm. The narrow gap required for producing quality joints limits the wider application of braze filler metals containing P as melt point depressant. In this author's opinion, the most popular melt point depressants used for joining Ni-base superalloy turbine components are those containing B or Si, or a combination of these two elements, as melt point depressants.

In a similar study, Johnson [5] examined the hard, brittle centreline eutectic phases in a joint brazed with BNi-4 filler metal (with a composition of Ni-2B-3.5Si), shown in **Figure 3**. In **Figure 3A**, the wide centreline eutectic component contains multiple cracks. Even the narrow, but continuous, centreline eutectic phase evident in **Figure 3B** promotes crack propagation. The centreline phases are probably a combination of boride and silicide phases, although this was not stated in the document.

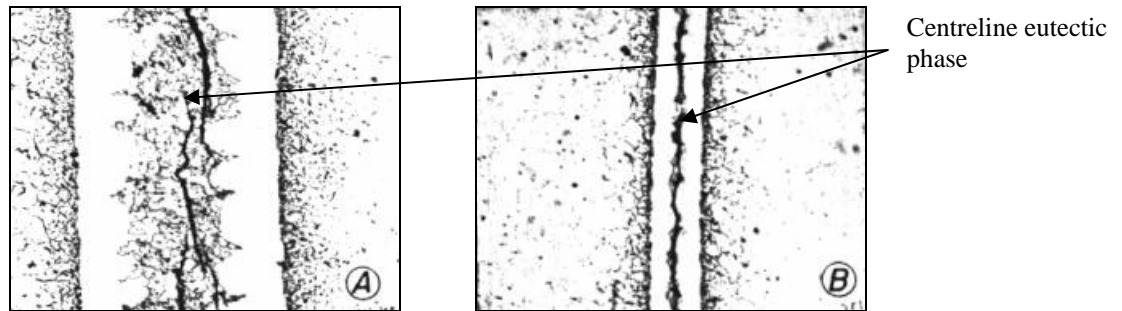


Figure 3 – Centreline cracking in a joint brazed with BNi-4 (with a composition of Ni-2B-3.5Si) [5].

Figure 4 shows the different microstructures that exist within braze joints produced using four braze filler metals with compositions shown below. The brittle centreline phases are clearly visible.

BNi-2: Ni-7Cr-3.2B-4.5Si-3Fe
BNi-4: Ni-2B-3.5Si

BNi-3: Ni-3.2B-4.5Si
NK10: Ni-15Cr-1.5Fe-3.6B

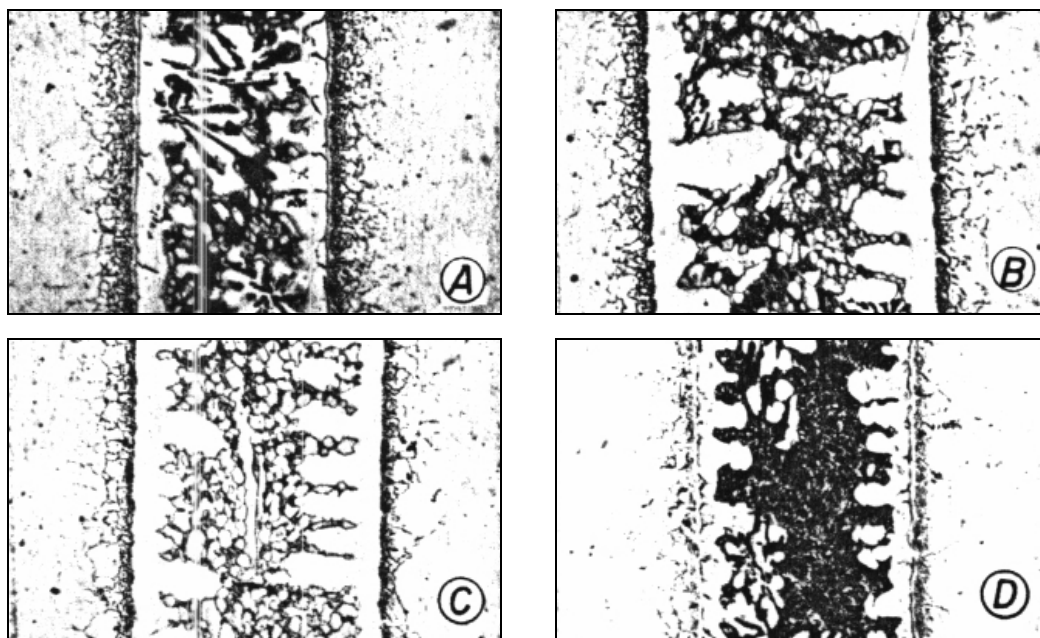


Figure 4 – Typical joint microstructures in four filler metals. A: BNi-2; B: BNi-3; C: BNi-4; and D: NK10. Magnification: 200X [5].

Figure 5 depicts the manner in which the joint microstructures vary as a function of the joint gap. In **Figure 5E**, the joint gap is wide and a continuous eutectic centreline phase is evident.

When the joint gap is narrow, however, as shown in **Figure 5H**, only isolated eutectic phases are present. Continuous centreline eutectic phases facilitate crack propagation.

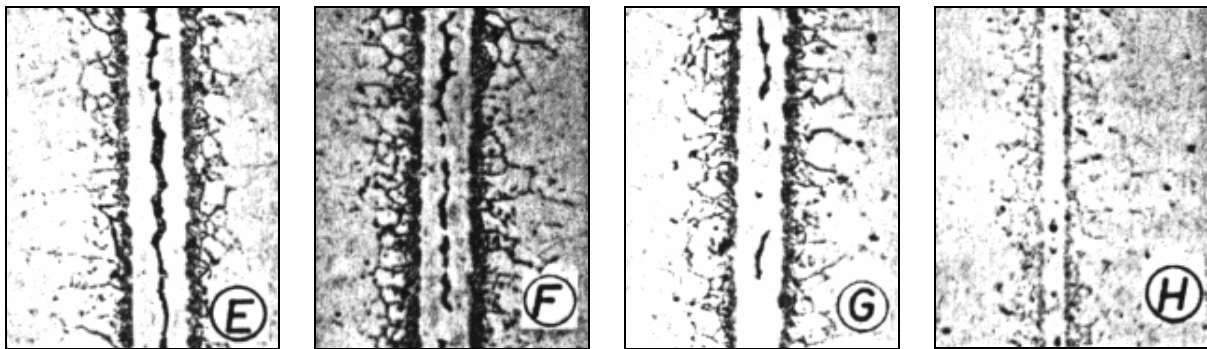


Figure 5 – Variation in microstructure with decreasing gap width. Magnification: 200X [5].

As shown in **Figure 5**, the joint gap needs to be controlled in order to ensure brazed joints with good mechanical properties. It is, however, often difficult to control the joint gap in practice. In the event of a wide gap, a longer brazing time can be used to remove continuous centreline phases. This is illustrated in **Figure 6** for brazing times between 10 minutes and 640 minutes. As the brazing time increases, the centreline eutectic component shrinks, and would probably become discontinuous at holding times exceeding 640 minutes.

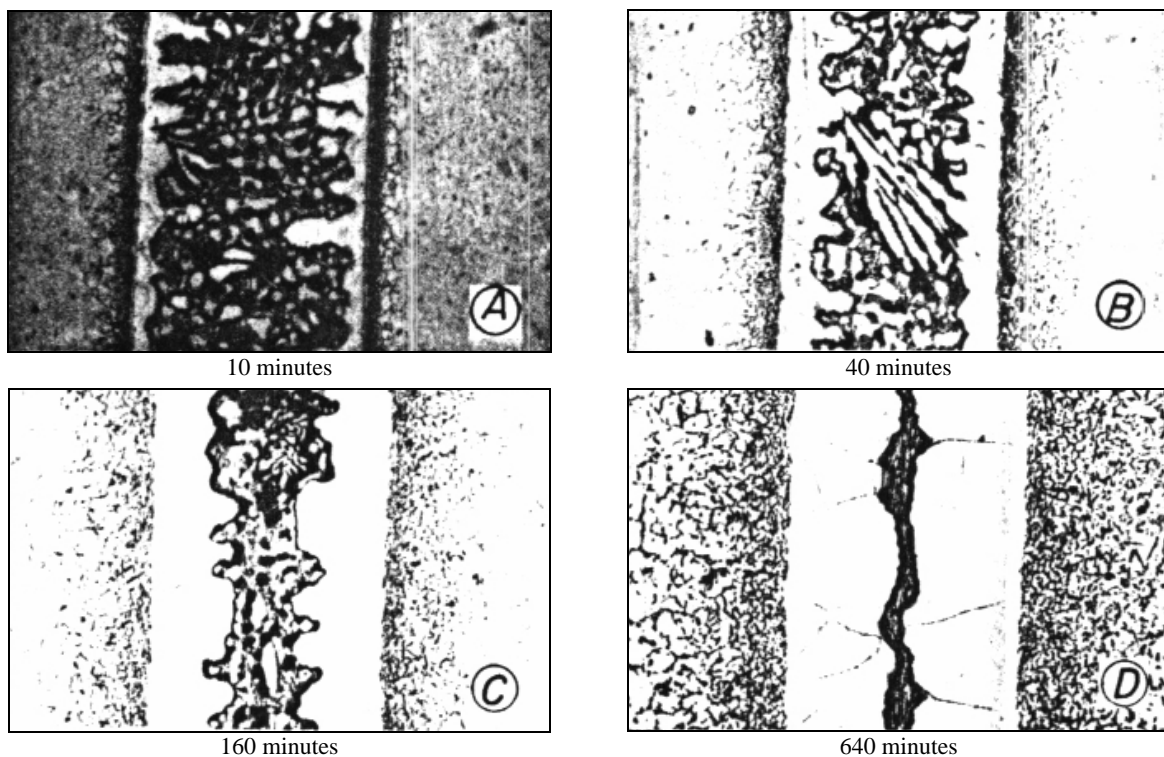


Figure 6 – Effect of holding time on the brazed joint microstructure. A: 10 minutes; B: 40 minutes; C: 160 minutes; and D: 640 minutes. Magnification: 200X [5].

In the event of a wide joint gap, **temperature** can also be used to render a braze joint free of continuous centreline phases. **Figure 7** shows the effect of increasing temperature on the joint microstructure. The microstructures shown in the first three micrographs (A, B and C in **Figure 7**) are comparable with those in **Figure 6** showing the effect of increasing braze time.

At 1250°C, however, the microstructure changes considerably. As a result of isothermal diffusion, elements from the parent metal also diffuse into the joint at the high braze temperature and a new type of eutectic forms in the joint. This new eutectic is believed to be less brittle than the more typical boride or silicide centreline phases.

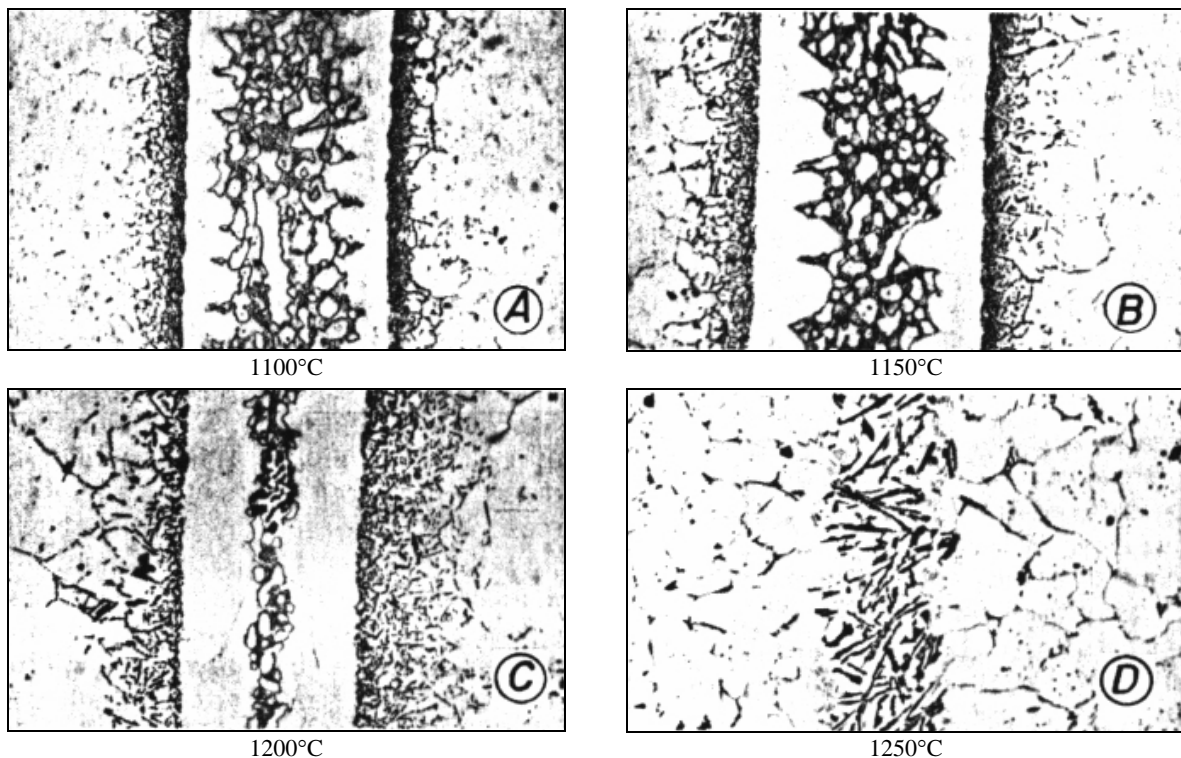


Figure 7 – Effect of brazing temperature on joint microstructure. A: 1100°C; B: 1150°C; C: 1200°C; and D: 1250°C. Magnification: A, B and C = 200X, and D = 100X [5].

Sakamoto *et al* [6] performed a similar investigation in 1989, and found that increasing the time at the brazing temperature or increasing the brazing temperature can result in joints without eutectic phases. **Figure 8A** displays the characteristic continuous brittle eutectic centreline component in a 0.05 mm wide joint, held for 10 minutes at 1075°C. On increasing the braze temperature to 1175°C, a braze joint free of eutectic phases was obtained, as seen in **Figure 8B**. Similarly, **Figure 8C** shows irregular centreline eutectic phases in a 0.05 mm wide joint, held for 30 minutes at 1075°C. On increasing the holding time to 90 minutes at 1075°C, a braze joint free of eutectic phases was obtained (**Figure 8D**).

It is evident from the published research described above that the type of braze filler metal, the joint gap, the time at the brazing temperature, and the brazing temperature are important variables associated with the braze process.

These variables also play a major role in determining the mechanical properties of the braze joint. Miyazawa and Ariga [7] reported the effect of brazing time and temperature on the shear strength of brazed joints produced using BNi-1 braze foil (Ni-14Cr-3.3B-4.5Si-3Fe). As demonstrated in **Figure 9**, the shear strength of the joint increased with an increase in braze time and temperature. After 60 minutes at 1275°C the brazed joint displayed the highest shear strength (320 MPa).

Similarly, when using BNi-2 braze foil (Ni-7Cr-3.2B-4.5Si-3Fe), the shear strength of the joint increased with an increase in braze time and temperature, as shown in **Figure 10**. After 60 minutes at 1275°C the brazed joint displayed the highest shear strength (320 MPa). When joining steel to nickel, it is therefore more desirable to use BNi-2, rather than BNi-1, because the same shear strength can be achieved at a lower brazing temperature (1150°C compared to 1275°C).

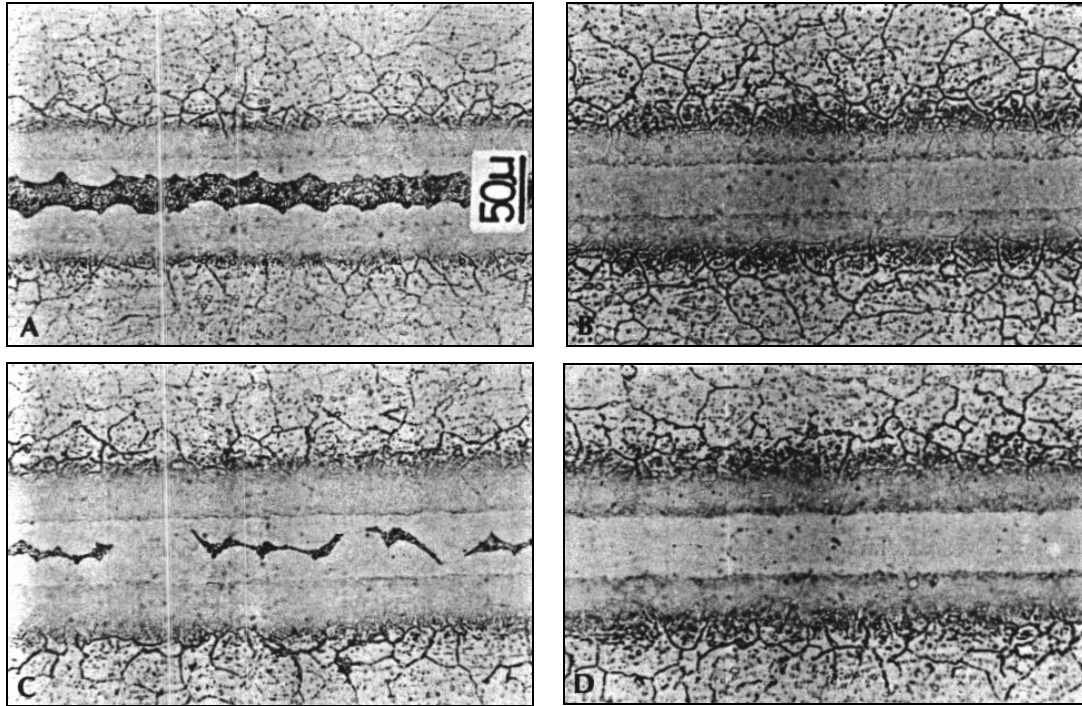


Figure 8 – Microstructure of brazed joints with a 0.05 mm gap. A: 1075°C for 10 minutes; B: 1175°C for 10 minutes; C: 1075°C for 30 minutes; and D: 1075°C for 90 minutes [6].

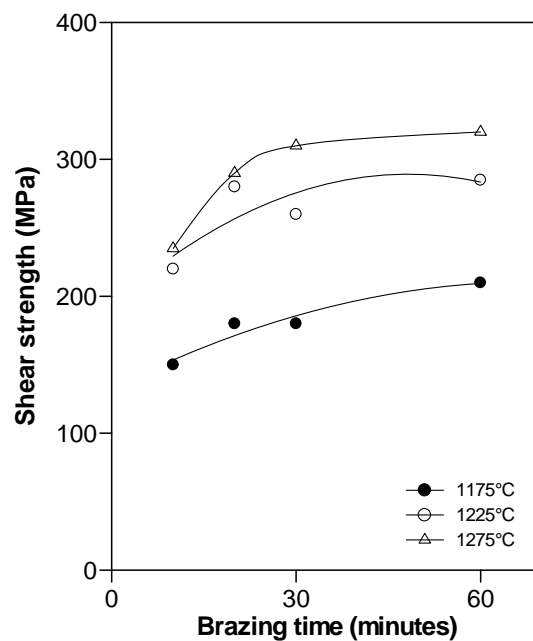


Figure 9 – The effect of brazing time and brazing temperature on joint shear strength (braze foil BNi-1) [7].

The same trend is evident on using BNi-3 braze foil (Ni-3.2B-4.5Si), **Figure 11**. After 60 minutes at 1190°C the brazed joint displayed the highest shear strength of 250 MPa, 70 MPa less than that achieved when using BNi-1 or BNi-2 braze filler metals. The lower shear strength can be attributed to the absence of Cr and Fe in the BNi-3 filler metal. The joint therefore relies on diffusion of Cr from the nickel-base parent metal for solid solution strengthening, and a brazing time of 60 minutes is too short to allow sufficient Cr diffusion from the parent metal into the joint.

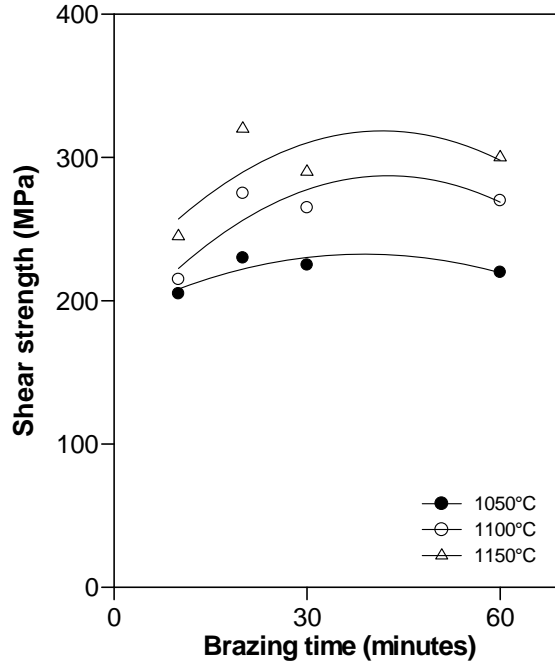


Figure 10 - Effect of brazing time and brazing temperature on the joint shear strength (braze foil BNi-2) [7].

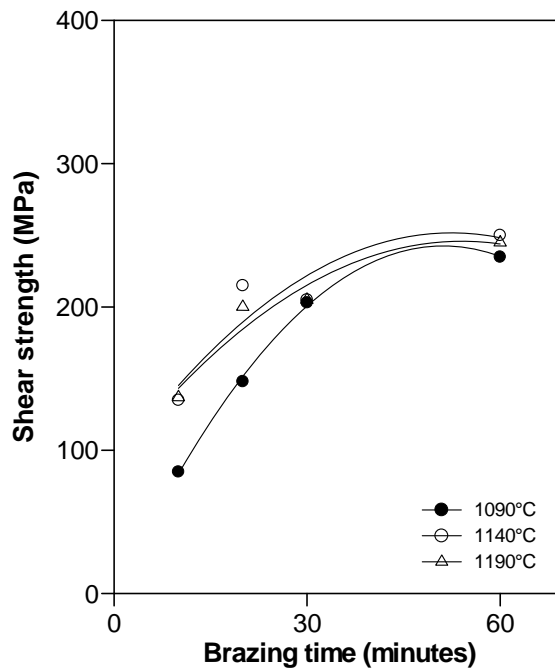


Figure 11 - Effect of brazing time and brazing temperature on the joint shear strength (braze foil BNi-3) [7].

In a similar study undertaken by Kavishe and Baker [8], an increase in tensile strength with decreasing gap width was reported for copper brazed alloy steel joints, as shown in **Figure 12(a)**. **Figure 12(b)** demonstrates a corresponding increase in the percentage elongation with an increase in gap width.

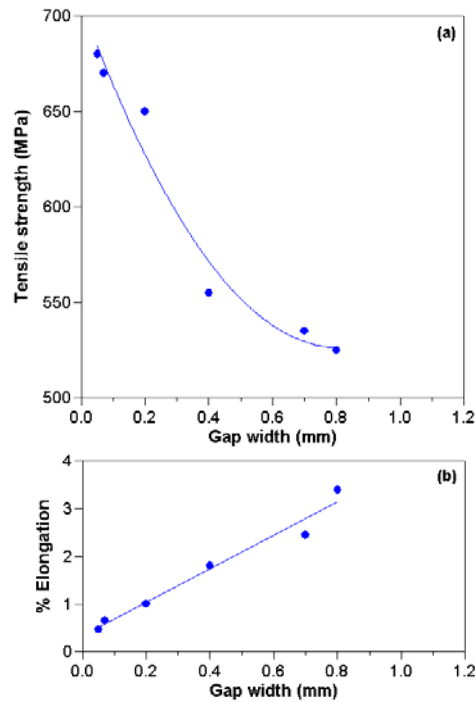


Figure 12 – Influence of joint gap on (a) tensile strength, and (b) percentage elongation of copper brazed alloy steel joints [8].

These authors also reported that the proof stress of the joints was slightly lower than the yield strength of mild steel for narrow gaps, but that the tensile strength was significantly greater than the yield strength of mild steel, as seen in **Figure 13**. The fracture toughness of the steel brazed joints decreased with a decrease in joint gap, as shown in **Figure 14**. This is associated with the increase in joint strength.

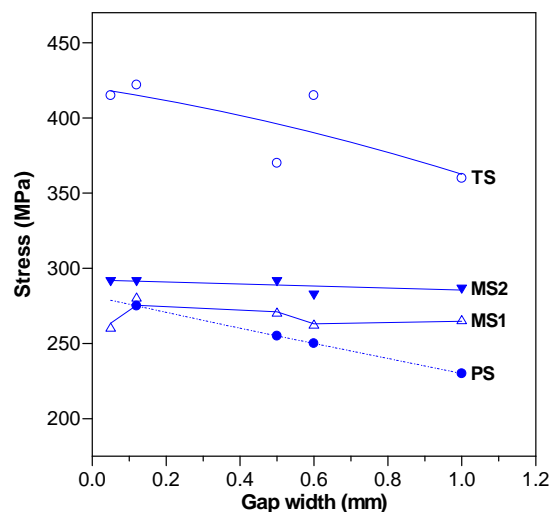


Figure 13 – Influence of gap width on the tensile strength (TS) and proof stress (PS) of copper brazed mild steel joints. MS1 and MS2 are the yield points of mild steel [8].

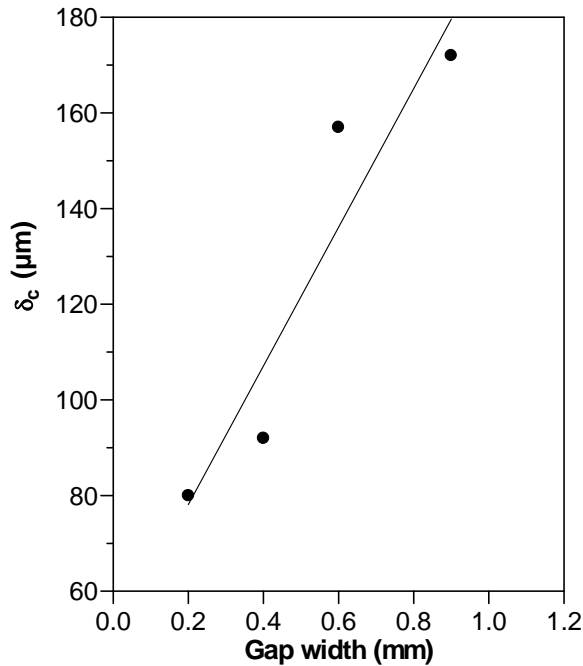


Figure 14 – The influence of gap width on the fracture toughness, as characterized by δ_c (the crack tip opening displacement), for copper brazed mild steel joints [8].

Lugscheider and Krappitz [9] studied the influence of gap width on the impact strength of Inconel 625 joints brazed with Au-6 filler metal. These authors reported a maximum notch impact energy at a joint gap of 12 μm , as illustrated in **Figure 15**.

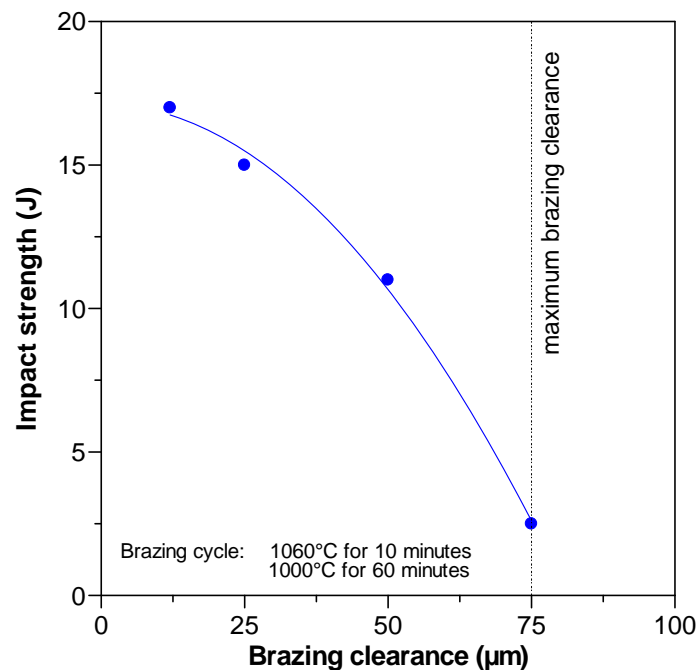


Figure 15 – Dependence of impact strength on joint clearance for Inconel 625 brazed with Au-6 (Ni-20.5Au-5.6Cr-2.3Fe-3.4Si-2.3B) filler metal [9].

Draugelates and Hartmann [10] studied the fatigue properties of a Nimonic 80 Ni-base superalloy, brazed with BNi-5 (Ni-19Cr-10Si-0.1C) filler metal. They found that the braze cycle, particularly braze temperature and time, had a significant influence on the fatigue properties of the joint. As seen in **Figure 16**, brazing at 1190° C for 5 minutes, followed by

soaking at 1100°C for 8 hours and aging at 710°C for 16 hours, resulted in a 40% increase in fatigue life, when compared to brazing at 1190°C for 5 minutes, followed by aging at 710°C for 16 hours. The increase in fatigue life was attributed to the removal of brittle Cr-silicide phases from the joint during the extended heat treatment. Since Si has a large atomic diameter, extended times at temperature are required to diffuse the silicon into the parent metal and to reduce the occurrence of brittle phases.

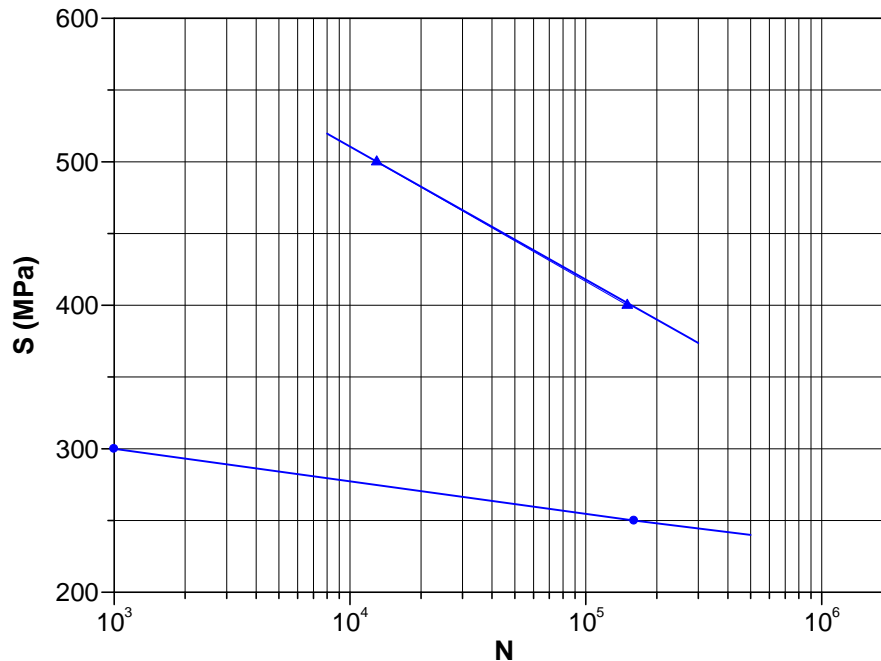


Figure 16 – Fatigue behavior of brazed joints (tested at room temperature, $R = 0.1$).

- brazing at 1190°C for 5 minutes, followed by aging at 710°C for 16 hours.
- ▲ brazing at 1190°C for 5 minutes and 1100°C for 10 hours, followed by aging at 710°C for 16 hours [10].

The preceding discussion illustrates that four important parameters need to be controlled in order to achieve high-strength joints free of brittle centreline eutectic phases. These parameters are:

- brazing time,
- brazing temperature,
- gap width/joint gap, and
- braze filler metal.

It is also apparent from the preceding discussion that metallurgical reactions which take place during the braze cycle affect the properties of the joints. During the braze cycle the melt point depressants in the nickel-base braze filler metal (such as P, B and/or Si) diffuse into the parent metal, thereby increasing the remelt temperature of the brazed joint and making the joint capable of higher temperature service. The diffusion of elements from the braze filler metal also affects the ductility of the completed joint. During the braze cycle a limited amount of parent metal may dissolve in the liquid braze filler metal, which increases the melt liquidus temperature. Diffusion of alloying elements from the parent metal into the joint has a similar effect.

As mentioned earlier, the main melt point depressants in use today are B, Si and P. Consideration of the alloy phase diagrams [2], however, suggests that Zn and Cd may also act as melt point depressants. Due to the high vapour pressures of these elements, however, they are unsuitable for use in vacuum brazing. Many Ag- and Cu-base braze filler metals are doped with Zn or Cd, but use of these fillers is restricted to flame brazing, induction brazing or inert atmosphere brazing.

1.3) Characterization of the eutectic phases that form in brazed joints

As stated earlier, Ni-base braze filler metals typically contain melt point depressants, such as B, Si and P. These elements tend to form hard, brittle structures in the joint. If the melt point depressants diffuse into the parent metal during the braze cycle, brittle phases may also form adjacent to the joint, depending on the composition of the parent metal. **Figure 17** displays hardness profiles across brazed joints in Inconel 625 (a Ni-base superalloy) for three different filler metals, BNi-2, BNi-5 and Au-6. The highest hardness was observed in the joint brazed with BNi-5, which contains Si as melt point depressant and forms brittle silicide phases even after an extended brazing cycle at 1150°C for 10 minutes, followed by holding at 1100°C for 60 minutes. As a result of this braze cycle, the hardness of the parent metal was increased to a level exceeding that of the brazed region. The joint with the next highest hardness was BNi-2, containing both Si and B as melt point depressants. Brittle silicide and boride phases formed even after brazing at 1065°C for 10 minutes, followed by holding at 1000°C for 60 minutes. The joint with the lowest hardness was Au-6, containing 20.55% Au, as well as B and Si. Au is known for its ductility and softness. The B and Si in Au-6 still resulted in the formation of some silicide and boride phases after brazing at 1060°C for 60 minutes, but the joint hardness was considerably lower.

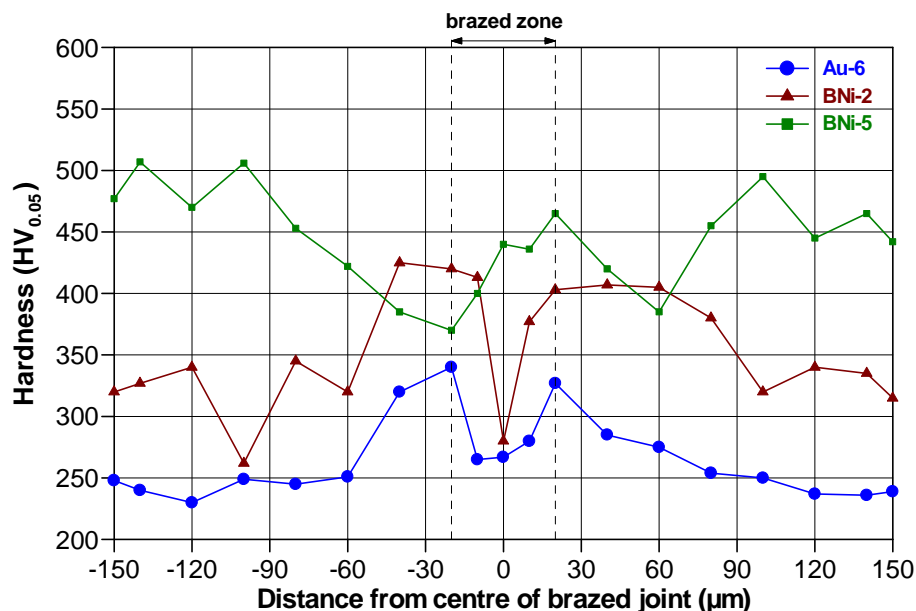


Figure 17 – Hardness profiles across brazed joints in Inconel 625 [7].

Tung, Lim and Lai [11] examined four braze filler metals, BNi-5 (Ni-19Cr-10.2Si), Microbraz 150 (Ni-15Cr-3.5B), BNi-4 (Ni-3.5Si-1.5B) and BNi-1 (Ni-14Cr-4.5Si-4.5Fe-3B), and concluded that the braze melt point depressants tend to form hard and brittle intermetallic compounds with nickel, and that the presence of these compounds is detrimental to the mechanical properties of the brazed joints. An incentive therefore exists to control the

microstructures that develop in brazed joints and to develop brazing alloys that are less sensitive to the formation of detrimental phases. **Figure 18** shows the typical microstructure of a 0.5 mm wide joint brazed with BNi-5. The only intermetallic compound observed in this braze was nickel silicide, which appears white in the micrograph. It solidified as a component phase of the binary eutectic with γ -nickel, the latter appearing as the dark phase in **Figure 18**. The microstructure of a joint brazed with Nicrobraz 150 is shown in **Figure 19(a)**. The phase marked G1 in this micrograph is nickel boride, while the phase marked G2 is the nickel-rich γ solid solution. In the centreline region of the joint a ternary eutectic of γ -nickel, nickel boride and chromium boride was present, as shown in **Figure 19(b)**.

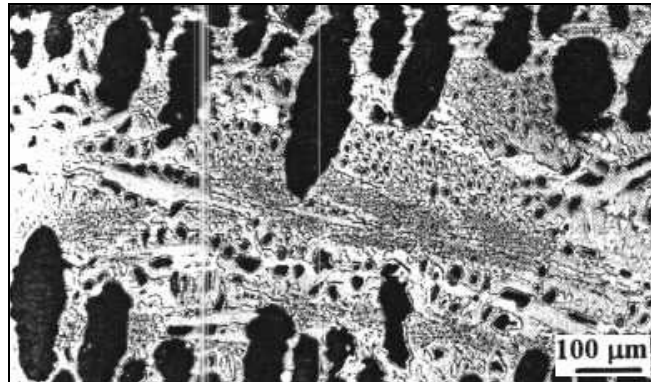


Figure 18 – Typical microstructure of a joint brazed with BNi-5 [11].

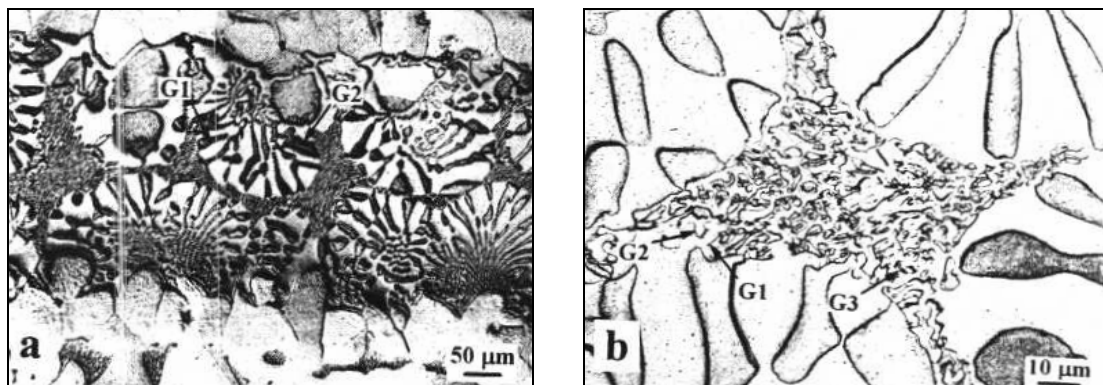


Figure 19 - (a) Microstructure of a joint brazed with Nicrobraz 150 at 1125°C; and (b) a magnified view showing the details of the ternary eutectic component [11].

Typical microstructures of joints brazed with BNi-4 filler metal are shown in **Figure 20**. The various phases formed in this joint, shown in **Figure 20(a)**, include γ -nickel solid solution layers (marked M*) found adjacent to the joint mating surfaces, γ -nickel nodules (marked M), bulky nickel borides (marked R), binary eutectics of γ -nickel and nickel boride, and ternary eutectics of γ -nickel, nickel boride and nickel silicide (marked X). The binary eutectic of normal morphology (marked N) formed adjacent to the layers of single-phase γ -nickel. **Figure 20(b)** shows details of the ternary eutectic (X). The phases designated X1, X2 and X3, are nickel silicide, γ -nickel and nickel boride, respectively. Nickel silicide (marked m), which precipitates in the solid state, was found in the outer regions of the γ -nickel nodules, especially those in the centreline region of the joint.

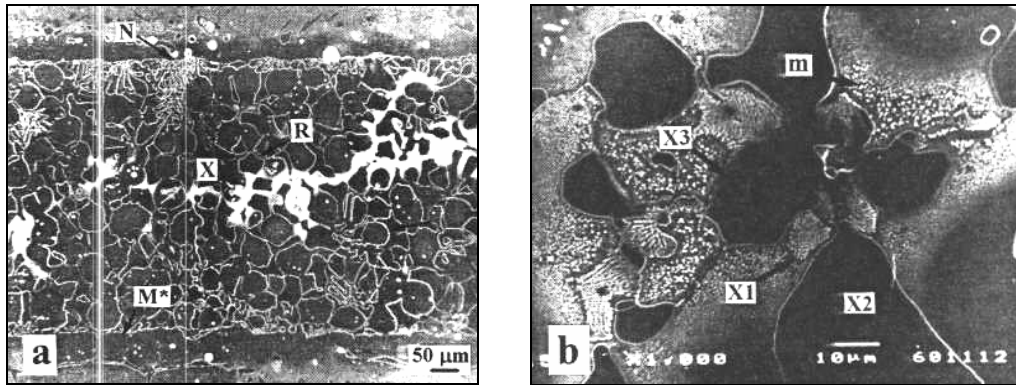


Figure 20 - (a) The constituents and component phases in a joint brazed with BNi-4; and (b) details of the ternary eutectic and nickel silicide precipitates in the joint centreline [11].

The microstructure resulting from the solidification of the molten filler metal in the joint brazed with BNi-1 was found to be extremely complex. Three intermetallic compounds formed in this braze, namely nickel boride, nickel silicide and chromium boride. The typical microstructure of a BNi-1 joint is shown in **Figure 21(a)**. The phases marked L1a, L1b and L1c are nickel borides, L2a and L2b are γ -nickel, L3 is nickel silicide, and L4 is chromium boride. Three eutectic constituents were identified: a binary eutectic of γ -nickel and nickel boride (L2a/L1a), a binary eutectic of γ -nickel and chromium boride (L2a/L4), and a ternary eutectic of γ -nickel, nickel boride and nickel silicide (L2a/L1c/L3). Details of the ternary eutectic are given in **Figure 21(b)**. It is interesting to note that in the presence of silicon, the formation of the ternary eutectic of γ -nickel, nickel boride and chromium boride was suppressed, in that chromium boride solidified with γ -nickel as a binary eutectic. The fine precipitates in γ -nickel (L2a) are nickel silicide particles, which formed in the solid state on cooling to room temperature.

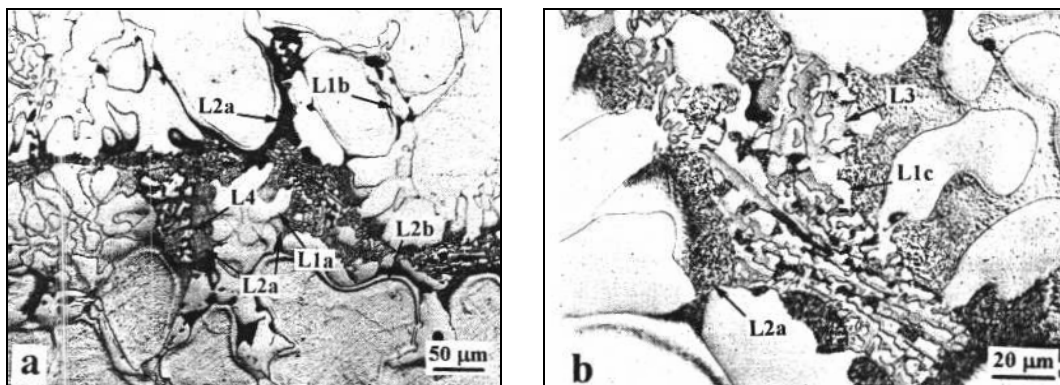


Figure 21 - (a) Microstructure of a joint brazed with BNi-1 at 1125°C; and (b) a magnified view showing the details of the eutectic phases [11].

It can therefore be concluded that the intermetallic compounds formed in brazed joints using nickel-base filler metals containing chromium, boron and silicon, are nickel boride, nickel silicide and chromium boride. These intermetallic compounds form as constituents of binary or ternary eutectics with γ -nickel. The binary eutectics are γ -nickel/nickel boride, γ -nickel/nickel silicide and γ -nickel/chromium boride, whereas the ternary eutectics are γ -nickel/nickel boride/chromium boride and γ -nickel/nickel boride/nickel silicide.

Johnson [12] performed microprobe analyses to identify the phases formed on brazing ferritic steel using various gap widths. The braze filler metals evaluated were the popular BNi-2 (Ni-7Cr-3.2B-4.5Si-3Fe) and BNi-4 (Ni-3.5Si-1.5B). The phases identified were α -nickel (containing Si, but no B), nickel boride, nickel silicide and chromium boride. As the joint gap narrowed, the number of phases was reduced, as shown in **Figures 22 to 25**. The first phase to disappear was nickel boride, followed by nickel silicide, and lastly chromium boride. Finally only α -nickel remained, as seen in **Figure 25**.

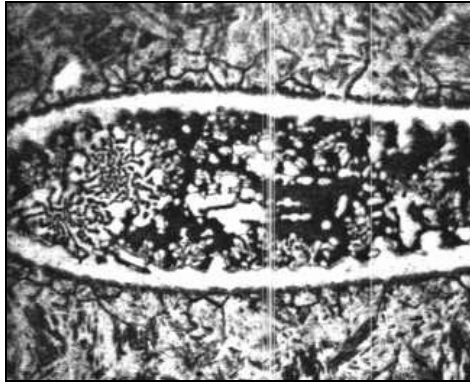


Figure 22 – Brazed joint of BNi-2 with 4 phases present. Magnification: 200X (reduced 50% on reproduction) [12].

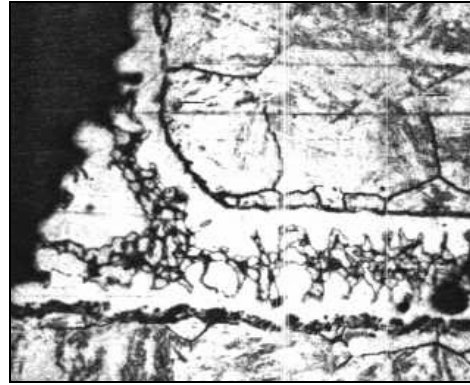


Figure 23 – Brazed joint of BNi-4 with 3 phases present. Magnification: 200X (reduced 50% on reproduction) [12].

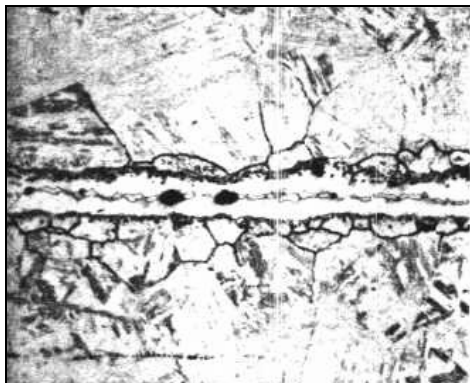


Figure 24 – Brazed joint of BNi-4 with 2 phases present. Magnification: 200X (reduced 50% on reproduction) [12].

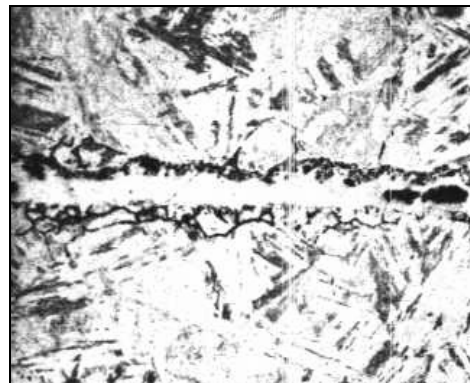


Figure 25 – Brazed joint of BNi-4 with 1 phase present. Magnification: 200X (reduced 50% on reproduction) [12].

While the braze filler metal was enriched in elements from the steel parent metal through erosion and diffusion, filler metal alloying elements were also entering the parent metal. In BNi-4, nickel and silicon entered by bulk diffusion into the parent metal to a distance of about 15 μm , but boron (which diffuses along the grain boundaries) migrated to a maximum distance of 140 μm . In BNi-2, the corresponding diffusion distances were 8 μm and 60 μm . It is evident in **Figures 26 and 27** that the B formed almost continuous stringers of iron boride along the grain boundaries.

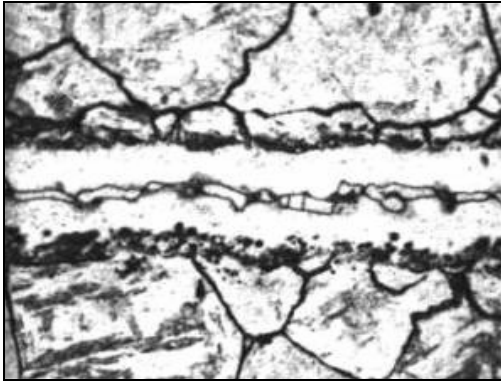


Figure 26 – Boride particles in the steel parent metal (BNi-4 braze).
Magnification: 500X (reduced 50% on reproduction) [12].

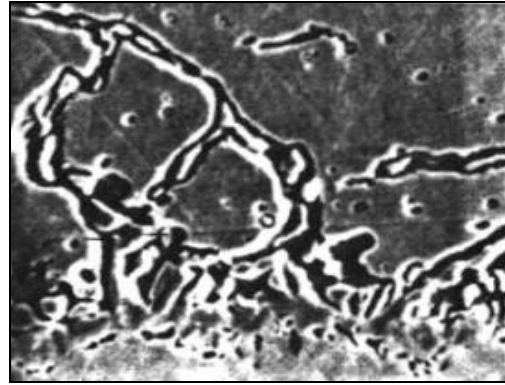


Figure 27 – Boride particles in the steel parent metal (BNi-4 braze).
Magnification: 2000X (reduced 50% on reproduction) [12].

The implication of Johnson's research is that in order to make serviceable brazed joints, the braze filler metal should be ductile and contain no regions of weakness or brittleness. With the nickel-base filler metals investigated, this ideal was realized in narrow joints less than 40 to 50 μm in width, containing only α -nickel. Wider joint gaps allowed the formation of boride and silicide eutectics along the centreline of the joint. As these phases have high hardness values, in the region of 900 HV (hardness on the Vickers scale), they possess only limited ductility and may crack if high tensile stresses are generated along or across the joint. These hard particles may also rupture to form fatigue crack nuclei. While a long brazing time facilitated the diffusion of B into the steel parent metal to some extent, such an extended high temperature soak is generally not a viable option if liquation of the grain boundaries is to be avoided.

Gale and Wallach [13] studied Ni-Cr joints brazed with BNi-3 (Ni-3.2B-4.5Si) and observed Ni_{23}B_6 within the joints. This phase formed intragranularly in the proeutectic nickel phase immediately adjacent to the eutectic mixture. These boride phases generally formed as platelets along $\langle 001 \rangle_{\text{Ni}}$ directions, although cuboidal morphologies were also observed. The origin of Ni_{23}B_6 precipitation remains uncertain, especially as this phase does not appear on the available phase diagrams for the Ni-Si-B system. Nevertheless, Ni_{23}B_6 formation occurred reproducibly in samples held for 3 minutes at 1065°C, but not in those subjected to longer soaking times. The Ni_3Si phase formed throughout the joint within the nickel component of the filler metal eutectic, and had a cuboidal structure aligned along the $\langle 100 \rangle$ directions. The most pronounced precipitation in the eutectic phase occurred in samples not subjected to long holding times.

Gale and Wallach concluded that:

- for Ni and Ni-5Cr substrates, Ni_3B formed at the original substrate/filler interface and M_{23}B_6 formed in the bulk substrate,
- for Ni-10Cr substrates, M_{23}B_6 formed throughout the substrate,
- for Ni-15Cr substrates, M_{23}B_6 and Cr_5B_3 formed throughout the substrate, and
- for Ni-20Cr substrates, M_{23}B_6 , Cr_5B_3 and Ni_3Si formed at the original substrate/filler interface, while M_{23}B_6 and Cr_5B_3 formed throughout the substrate.

Similarly, Lasalmonie [14] examined the phases precipitated during the brazing of DS 247 (Ni-9.5Co-8Cr-3.3Ta-0.5Mo-9.5W-5.5Al-0.6Ti-0.07C) and ATGP 3 (Ni-15Co-15Cr-5.2Mo-4.4Al-3.5Ti-0.06C) using 120 μm thick BNi-3 (Ni-4.5Si-3.2B) braze filler metal. Brazing was performed at 1040°C for 3 hours. The phases present in the structure (shown in **Figure 28**) were reported as:

- M_{23}B_6 with a hardness in the region of 1000 HV (with M consisting of Ni, Cr, Co, Al and Ti),
- Cr_5B_3 , with a hardness of 3000 HV,
- W_2B ,
- Ta-Hf carbides, and
- MB_{12} (with M consisting of Cr, Mo and W).

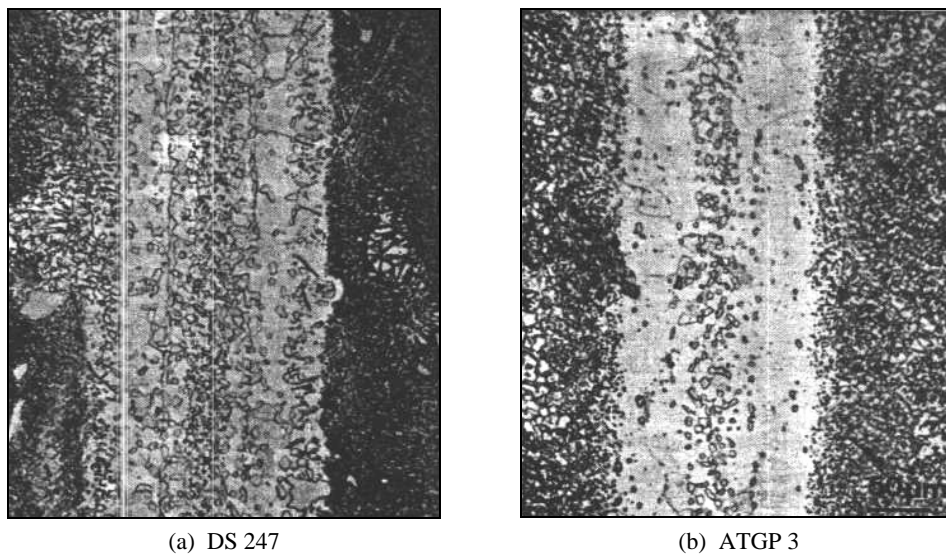


Figure 28 - Brazed joints in two nickel-base superalloys produced with BNi-3 filler metal at 1040°C for 3 hours [14].

Savage and Kane [15] attributed a number of field failures observed during the joining of Nickel 201 tubing to Nickel 201 plate stock using BNi-3 filler metal to the formation of nickel silicide and nickel boride phases in the joint. The braze cycle of 1093°C for 30 minutes resulted in rapid grain boundary diffusion of B from the braze joint into the base metal. This sensitized the grain boundaries, causing the tubing to undergo intergranular corrosion. The authors reported that quenching, as opposed to slow cooling from the braze temperature, changed the boride morphology in the joint. After quenching the boride phase displayed a needle-like morphology and no intergranular corrosion attack was observed. Failure was primarily as a result of crevice corrosion involving attack of this needle-like boride phase, with the corrosion rate determined by the joint gap. The quench rate from the brazing temperature is therefore also an important parameter that needs to be controlled, since a different boride or silicide morphology can affect the mechanical and corrosion properties of the brazed joints.

Tung, Lim and Lai [16] evaluated the intermetallic phases that form in Ni-base brazed joints, and reported the presence of bulky nickel boride and nickel silicide phases in a solid solution area referred to as γ -nickel. The compositions and hardness values of the phases observed are as follows:

- γ -nickel, consisting of Ni and 3.0 to 4.8% Si, with a hardness between 108 and 188 HV,
- nickel boride, consisting of Ni and 0.2 to 0.3% Si, with a hardness between 776 and 906 HV, and
- nickel silicide, consisting of Ni and 8.0 to 13.1% Si (the hardness was not measured).

The relative nickel and silicon weight percentages listed above were obtained by means of standardless EDS analysis. Since the EDS system employed could not measure B contents accurately, the B concentrations were not reported. Despite this deficiency, the information given above was sufficient to distinguish the different phases. The general direction of solidification was from the base metal towards the centreline of the joint. The first phase to form was primary γ -nickel, solidifying in the form of solid solution layers next to the joint faying surfaces. This caused the melt to become enriched in B. As solidification proceeded, eutectics of nickel boride solidified. Higher brazing temperatures and faster cooling rates facilitated the formation of binary γ -nickel/nickel boride eutectics. Higher cooling rates also promoted the formation of ternary eutectics of γ -nickel, nickel boride and nickel silicide in the last remaining liquid. On further cooling to room temperature, solid state precipitation of nickel silicide occurred within the γ -nickel nodules, especially those formed in the latter stages of solidification near the centreline of the joint. Bands of nickel boride precipitates were observed in the base metal adjacent to the joint interface in joints brazed at 1090°C, below the eutectic temperature of the binary Ni-B system.

1.4) Repair of turbine components using brazing

Degradation of engine components during service may result from thermal cracking and distortion, oxidation, sulphidation, corrosion, erosion, fretting, wear, foreign object damage (FOD, i.e. objects ingested into the engine) and creep. Degraded components are replaced not only because of their loss of structural integrity, but because there is a loss of operating efficiency in the engine. In many instances, especially in the land-based industry (turbines used to generate electrical power) it is more cost effective to carry out repairs to return the components to serviceable condition for a fraction of the cost of a new component. Typically, repair costs are approximately 10 to 50% of the cost of a new component. This is a very lucrative business and there are numerous companies throughout the world whose primary business is to repair turbine components.

As shown in §1.2 and §1.3, the major variables which need to be controlled in order to achieve a high quality brazed joint are gap width, braze alloy/filler metal, braze temperature and time, cooling rate and cleanliness. When it comes to braze repair of turbine components, however, controlling the joint gap is near impossible. This is because components have predefined and precise crack widths after service exposure. In the early era of crack repair using brazing, only cracks with widths between 0.025 mm and 0.254 mm were repaired. Once the combustion products were removed by processes such as fluoride ion cleaning (a process that uses a combination of H₂ gas and HF gas to reduce the aluminum oxide and titanium oxide present in the crack), capillary action would draw the molten braze filler metal into the crack. Braze filler metals containing B and/or Si as melt point depressants were initially evaluated for crack repair, but as a result of the brittle silicide and boride phases that form in the repaired joint, the braze joint would re-crack when returned to service. Since Si has a large atomic diameter and do not readily diffuse into the parent metal, investigators concluded that only braze filler metals with B as melt point depressant could be used for crack repair. This encouraged the introduction of a number of new filler metals into the market. Some of these braze alloys are listed below:

- DF3 - (Ni-20Cr-20Co-3Ta-3B-0.05La)
- DF4B – (Ni-14Cr-10Co-2.5Ta-3.5Al-2.7B-0.02Y)
- DF5 – (Ni-13Cr-3Ta-4Al-2.7B-0.02Y)
- DF6 – (Ni-20Cr-3Ta-2.8B-0.04Y)
- BRB – (Ni-14Cr-9.5Co-4Al-2.5B)
- 775 – (Ni-15Cr-3.5B)
- S57B – (Co-10Ni-21Cr-5Ta-2.5Al-3B-3Si-0.02Y)

Lecomte-Martens [17] from the repair company C.R.M in Belgium investigated the use of DF4B (with the composition shown above) in the braze repair of In792 nickel-base superalloy vanes, as well as the use of S57B in the braze repair of H188 cobalt-base superalloy vanes. In792 has a composition of Ni-12.7Cr-9Co-2Mo-4.2W-4.1Ti-3.4Al-4.2Ta-1.0Hf-0.05Zr-0.015B-0.14C, and H188 consists of Co-22Cr-22Ni-14W-1.5Fe-0.08La-0.08C. The brazing temperature for the DF4B filler metal was 1200°C and the brazing time 15 minutes, followed by a 3 hour diffusion cycle at 1057°C (to diffuse the B away from the joint). The brazing temperature for the S57B filler metal was 1220°C and the brazing time 15 minutes, followed by a 3 hour diffusion cycle at 1040°C (to diffuse the B and Si away from the joint). For both joints, 18 hour and 30 hour diffusion cycles were also investigated. The joints produced with S57B filler metal displayed evidence of a Co-Ni-Cr solid solution, Cr carbides, W carbides, Ta carbides, Cr borides and Cr-Co-W silicide phases. The joints produced with DF4B filler metal contained a Ni-Co-Cr solid solution, Ta-Ti-Hf carbides, Cr carbides and Cr borides. Fatigue tests were performed on actual braze repaired vanes, as opposed to test specimens. The first engine test showed that new vanes cracked after 441200 cycles, whereas the braze repaired vanes cracked after 324200 cycles. The second engine test showed that new vanes cracked after 409200 cycles, whereas the braze repaired vanes cracked after 270300 cycles. In the third and fourth engine tests, new vanes cracked after 397600 and 417325 cycles, respectively, whereas the braze repaired vanes cracked after 240100 and 280250 cycles. It was concluded that, on average, the number of cycles required to fracture a braze repaired vane is about 2/3 of that required for a new vane. This was acceptable since the price of a repaired vane is typically 10 to 50% of that of a new vane, and hence the braze repair was still economical. The total number of cracks found on the new vanes was 40, the total crack length was 287 mm and the average crack length was 7.2 mm. For the braze repaired vane, 39 cracks were found in total, the total crack length was 218 mm and the average crack length was 5.6 mm. These results suggest that, although cracks initiated earlier in a braze repaired vane, the average crack length was less than in a new vane. The crack propagation rate therefore appeared to be slower in the brazed joint than in the parent metal. **Figure 29** compares cracks detected in a new vane and in a repaired vane after engine testing. An important conclusion reached by the author was that cracks wider than 0.5 mm were not completely filled by the molten braze filler metal and should be repaired using wide gap brazing. The topic of wide gap diffusion brazing is considered in §1.5.

Elder, Thamburaj and Patnaik [18] investigated the repair of narrow cracks in MA 754 (Ni-19.7Cr-0.35Al-0.45Ti-0.37Fe-0.05C-0.57Y₂O₃-0.39O₂) using vacuum brazing with fourteen different braze alloys. The braze filler metals contained either B, or B and Si, as melt point depressants. Microprobe analyses revealed the presence of Cr boride and Ni silicide in brazed joints containing both B and Si as melt point depressants. Joints containing only B as melt point depressant contained Cr-W boride phases. Narrow cracks (0.038 mm in this investigation) resulted in joints free of brittle phases. As the crack width approached 0.762 mm, brittle intermetallic phases formed, reducing joint ductility to 1.3% (compared with the parent metal ductility of 4%). The authors also concluded that these brittle intermetallic

phases act as preferential crack initiation sites, and recommended the use of B as the sole melt point depressant in repair brazing. For joints approaching 0.762 mm in width, wide gap brazing was recommended.

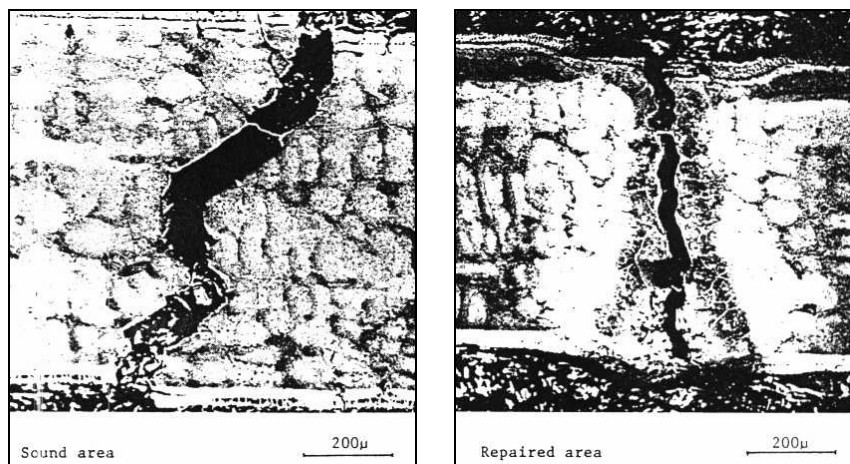


Figure 29 – Cracks in new and repaired vanes after engine testing [17].

It is important to note that when cracks form during engine operation, combustion products are often entrapped within the cracks. The crack surfaces also tend to be covered in Al and Ti oxides. These must be removed before cracks are repaired. As mentioned earlier, cleanliness is important in achieving high quality brazed joints. If the crack is dirty and filled with contaminants, capillary action will not draw the molten braze filler metal into the joint. In order to clean a crack prior to vacuum brazing, a process called FIC (fluoride ion cleaning) was developed to reduce the oxide layers in the crack and to remove dirt and other contaminants. The process is performed at elevated temperature and uses a mixture of HF and H₂ gas. Rose, Price and Thyssen [19], employed by Chromalloy, developed a braze repair process using FIC and a braze filler metal with a composition of Ni-12Cr-4.5Mo-6Al-4Ta-0.6Ti-0.1Zr-0.05C-2.5B. Without the boron alloying addition, the composition of the braze filler metal matches that of In713 nickel-base superalloy. This publication contained the first mention in open literature of a new braze filler metal composition developed by a repair company. The braze temperature and time were not documented and are considered proprietary. An interesting observation reported was that the joints contained a certain percentage of porosity, and that the authors relied on the use of a process referred to as HIP'ing to close the pores. HIP'ing is a process performed at elevated temperature under high isostatic pressure, applied using Ar gas, to plastically close the pores. This repair process using FIC, a proprietary braze filler metal and HIP'ing, was used to repair cracks in the saddle and blade areas of a Garrett GTCP 85 APU component that provides electrical power and compressed air for commercial aircraft such as Boeing 727 and 737 and McDonnell-Douglas DC-9 and MD-80. To qualify the braze repair, tensile tests and fatigue tests were performed at room temperature. After achieving acceptable mechanical test results, the authors performed thermal fatigue tests, and reported satisfactory results.

Lee, McMurray and Miller [20] patented a novel technique, referred to as M-Fill, to repair cracks in stationary components. This process does not rely on capillary action to draw the molten metal into the joint area. The crack is mechanically removed as per a welding process, then the surface of the routed out area is Ni-plated. A braze paste is placed in the groove and the component is processed in a vacuum furnace at 954°C for 1 hour, followed by soaking at 1065°C for 15 minutes and 982°C for 3 hours to diffuse the B and Si into the parent metal.

The braze filler metal contained Ni, 8-10% Cr, 7-9% W, 2.5-4% Fe, 3-4.5% Si, 2-3% B and 0.06% C. Although boride and silicide phases formed, they were inconsequential because the cracks were in low stress areas and hence the braze repair was considered non-structural. The authors showed that the braze joint could be readily coated with an aluminide coating for corrosion and oxidation protection. The joint remained intact during engine testing. This repair is still applied in the TF40 and T55 Allied Signal engines used in helicopters.

1.5) Wide Gap Diffusion Brazing

As mentioned earlier, controlling the joint gap is very important in producing good quality, high-strength joints free of brittle eutectic and intermetallic phases. It is fairly easy to control joint gaps in manufacturing assemblies, but when it comes to repair, the size of the crack cannot be controlled. In the author's experience, cracks in aircraft turbine vanes range from 0.05 mm to 1 mm in width, whereas cracks in industrial turbine engines can range from 1 mm to 6 mm in width. To repair these types of defects, the wide gap diffusion brazing process was invented.

GE, an OEM, invented and patented a process called activated diffusion brazing (ADB). It is also referred to as activated diffusion bonding or activated diffusion healing (ADH). Hoppin and Berry [21] defined this process as a joining method for high strength nickel-base superalloys, involving a combination of the best current knowledge of conventional brazing and solid state diffusion bonding technology. The process combines the manufacturing ease of brazing with the high joint strengths achievable during solid state diffusion bonding. ADB involves vacuum furnace brazing with an ultra high-strength bonding alloy, nearly identical in chemical composition to the base metal being joined. Diffusion and aging heat treatments enable the joint to achieve maximum mechanical strength at the operating temperature of the engine component. The ultra high-strength bonding alloy is a mixture of braze powder and superalloy powder in a 60/40 ratio.

Figure 30 shows the tensile strength properties of 0.25 mm wide ADB joints in Rene 80 base metal at 650°C and 870°C, and indicates that the tensile properties of the joints are equivalent to those of the base metal. Results of creep rupture tests on Rene 80 brazed with AMS 4782 (Ni-19Cr-10Si), AMS 4786 (Au-22Ni-8Pd) and the ultra high-strength bonding alloy can be seen in **Figure 31**. Typical creep rupture strengths of 80 to 90% of the parent metal's creep rupture properties are attained, and the creep rupture properties of the ADB joints are two orders of magnitude greater than those achievable with conventional braze filler metals such as AMS 4782. Fatigue tests were performed at 760°C for the ADB joints and the resultant high cycle fatigue curve is shown in **Figure 32**. The high cycle fatigue properties are approximately 70% of those of the Rene 80 base metal. The elevated temperature tensile, creep rupture and high cycle fatigue tests therefore demonstrated that ADB joint strengths of 70 to 90% of those of the base metal can be achieved, and the authors concluded that the ADB process is suitable for replacing fusion welding in the crack repair of aircraft gas turbine components (Rene 80 base metal displays a tendency towards cracking during fusion welding).

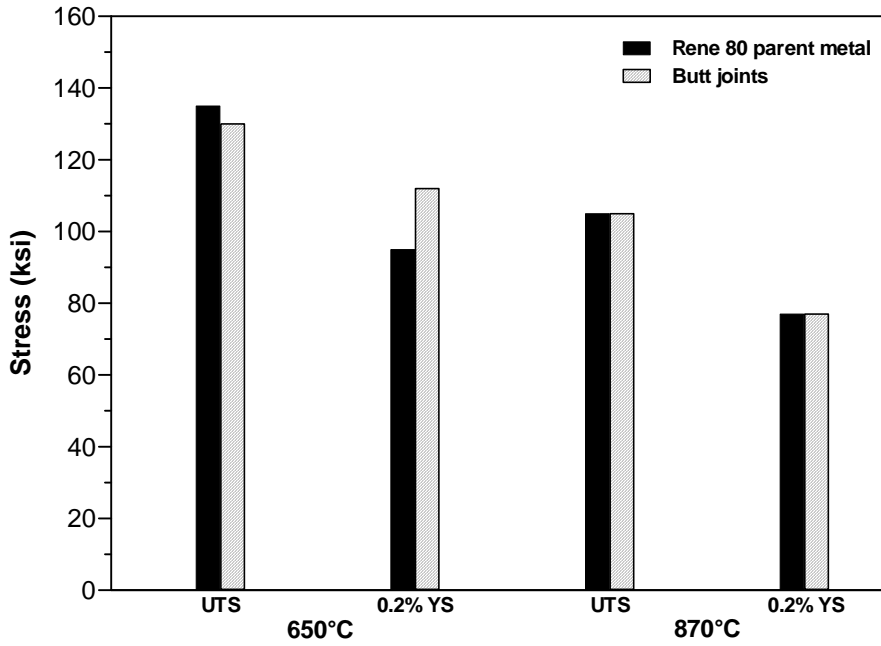


Figure 30 - Tensile properties (UTS: ultimate tensile strength, and 0.2% YS: 0.2% proof stress) of activated diffusion bonded butt joints in Rene 80, compared with those of the base metal [21].

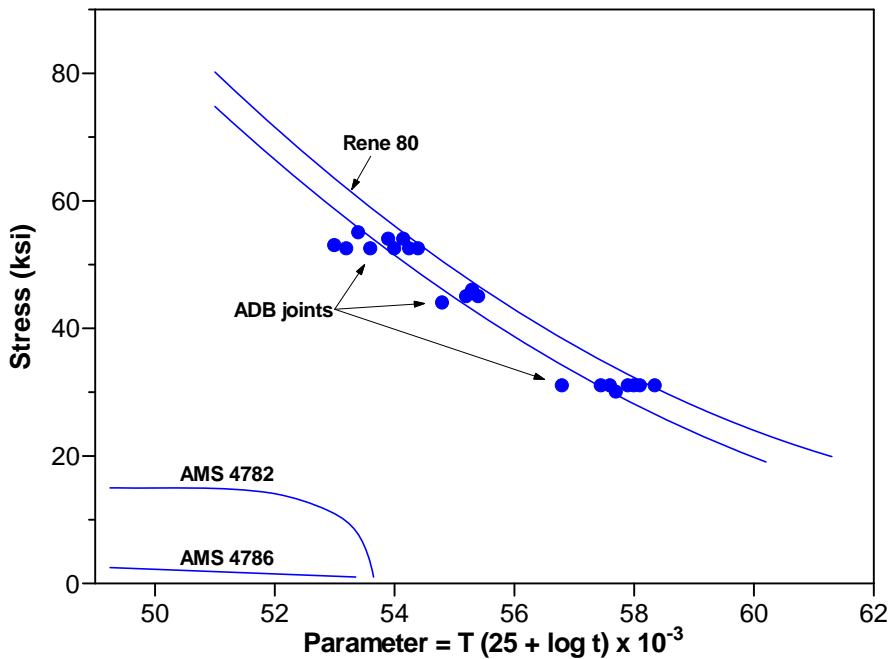


Figure 31 - Creep rupture properties of activated diffusion bonded joints in Rene 80, compared with those of the base metal and conventional brazed joints [21].

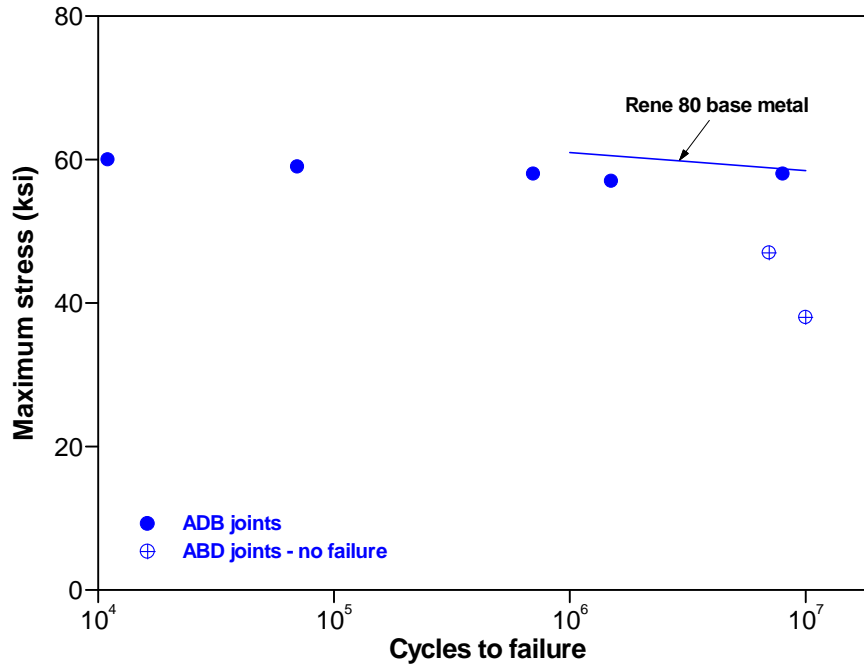


Figure 32 - High cycle fatigue strengths of activated diffusion bonded butt joints in Rene 80 at 760°C [21].

The ADB (or ADH) process was also described by Demo and Ferrigno [22]. As shown in **Figure 33**, the ADH process uses a mixture of superalloy powder and braze powder called a low-melting matrix. The superalloy powder in this low-melting matrix has the same composition as the substrate material. The low-melting braze powder used by Demo and Ferrigno consisted of the elements Ni-Cr-Co-Al-Ta-B, but the relative percentages of the elements were not documented. Brazing was performed at 1205°C for 30 minutes, followed by an undisclosed diffusion cycle and aging treatment. **Figure 34** shows the tensile properties measured at 870°C for various joint gaps ranging from 0.075 mm to 1 mm. The joint tensile strength was approximately 80% of the parent metal tensile strength, and the tensile strength did not appear to vary significantly over the range of joint gaps tested. The creep rupture properties, however, varied significantly with joint gap, as shown in **Figure 35**. Joints with gaps of 0.075 mm achieved approximately 90% of the creep rupture properties of the parent metal, whereas joint gaps of 0.5 mm and 1.0 mm resulted in only 60% and 50% of the parent metal creep rupture properties, respectively.

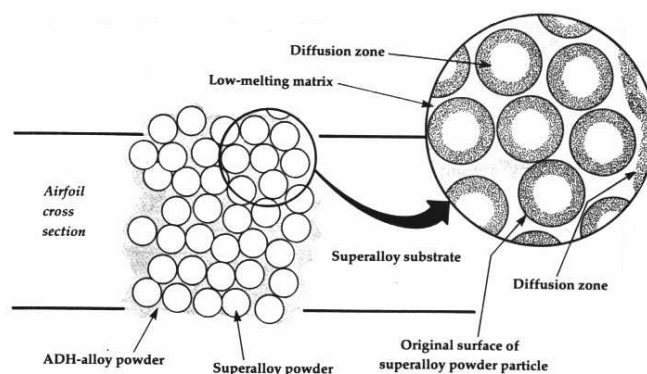


Figure 33 - In the ADH repair process, a superalloy is “cast” into the crack using a lower melting point bonding alloy [22].

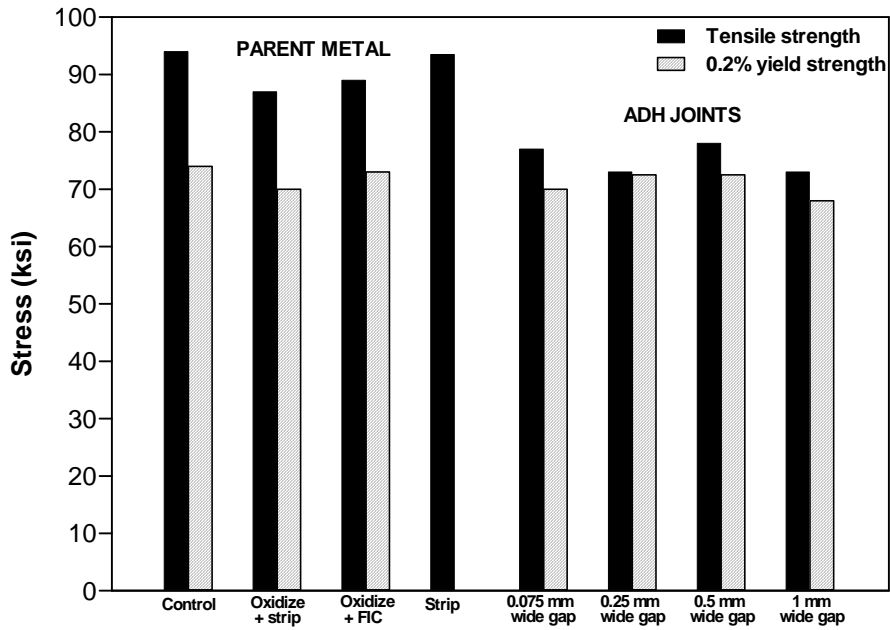


Figure 34 - Tensile strength data at 870°C (1600°F) for the parent metal and brazed joints in Rene 80 base metal. ('Oxidised' refers to a simulated engine run; 'Strip' refers to chemical stripping simulating the removal of the aluminide coating; and 'FIC' refers to fluoride ion cleaning) [22].

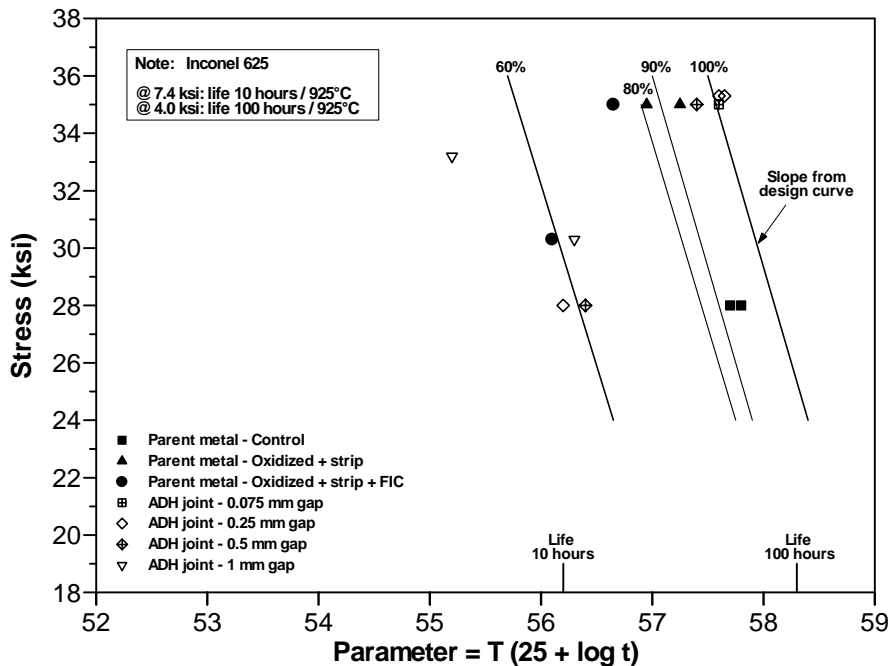


Figure 35 - Creep rupture curves for different width ADH joints in Rene 80 base metal [22].

Young [23] evaluated the ADH process by determining the nil strength temperature, defined as the temperature at which the bonded joint is incapable of sustaining a constant load of 0.86 MPa (125 psi), for two ADH alloys. An ADH joint consisting of 50% D-15 braze alloy and 50% X-40 cobalt-base superalloy powder attained a room temperature tensile strength of 82.4 ksi (569 MPa) and a nil strength temperature of 1260°C, whereas an ADH mixture consisting of 80% H-33 braze alloy and 20% X-40 cobalt-base superalloy powder had a room temperature tensile strength of 658 MPa (95.4 ksi) and a nil strength temperature of 1232°C. This compares well with the X-40 parent metal, which has a room temperature tensile strength

of 794 MPa (115 ksi) and a nil strength temperature of 1329°C. For ADH processing of nickel-base superalloys such as Rene 80, a 50% D-15 braze alloy and 50% Rene 80 powder mixture was evaluated. The braze cycle consisted of holding at 1204°C for 30 minutes, followed by a boron diffusion cycle at 1093°C for 2 hours, 1149°C for 2 hours, and 1190°C for 2 hours. The first aging cycle was performed at 1093°C for 4 hours, followed by a second aging cycle at 843°C for 24 hours. The 1 mm wide joints attained 80% of the Rene 80 parent metal tensile strength measured at 870°C. Creep rupture testing at 925°C demonstrated a 10% reduction in rupture life for a joint gap of 0.025 mm, a 20% reduction in rupture life for a 0.075 mm gap, and a 30% reduction in rupture life for a 0.25 mm gap. A 1 mm gap resulted in a 40% reduction in creep rupture life. It is evident that a wider joint gap results in a reduction in mechanical properties. Despite this, the ADH process has been used successfully for the past two decades to repair cracks in aircraft turbine blades, and the FAA (Federal Aviation Authority) has never reported an engine failure as a result of an inappropriate ADH braze application. This shows that, although the mechanical properties are not equivalent to the base metal properties, ADH braze joints can perform reliably in an engine. For this reason, the process has replaced conventional gas tungsten arc welding (GTAW) with In625 filler metal in this application.

Knotek and Lugscheider [24] mixed stainless steel powder and Ni-base braze filler metal of composition Ni-10Cr-4.2Si-6.3Fe-3B in three different ratios: 45:55, 50:50 and 55:45, and performed brazing at a temperature of 1000°C with a joint gap of 0.1 mm. The results of tensile tests carried out at 20°C, 800°C, 1000°C and 1200°C are shown in **Figure 36**. The last two test temperatures are higher than the solidus temperature of the braze alloy in the mixture. As shown in **Figure 36**, all three mixtures had similar tensile strengths at elevated temperature. At room temperature the tensile strengths ranged from 480 MPa to 540 MPa, and at 1000°C the tensile strengths were in the region of 70 MPa. These tensile strengths are higher than those of the popular Ni-Cr-B-Si braze filler metals such as AMS 4777 and AMS 4776. No significant change in the tensile strength values at 1000°C was observed after a 1 hour diffusion heat treatment, as shown in **Table 2**.

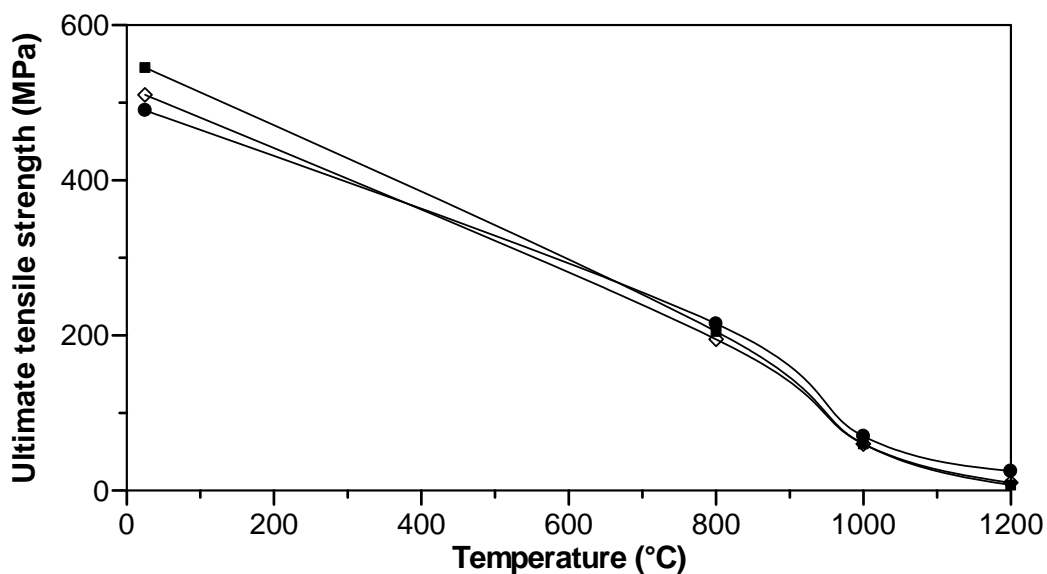


Figure 36 - Tensile strength at elevated temperature for various ratios of superalloy powder to braze powder [24].

Table 2 – Influence of heat treatment on the tensile strength (1000°C) of reacting brazed joints [24].

Component (wt.%)		Composition after reaction (wt.%, balance Ni)				Tensile strength at 1000°C			
						As-brazed		Brazed + 1 hr @ 800°C	
A	B	Cr	B	Si	Fe	MPa	ksi	MPa	ksi
55	45	8.25	1.65	2.30	2.00	74.6	10.8	66.7	9.7
50	50	7.50	1.50	2.10	1.85	68.7	10.0	68.6	10.0
45	55	6.75	1.35	1.90	1.70	64.8	9.4	67.6	9.8

Van Esch [25] from Elbar, a repair vendor in Holland, developed a proprietary wide gap braze process to repair blades from the Industrial Gas Turbine engine referred to as GE Frame 5. The compositions of the two alloys used, the mix ratio and the braze temperature and time were not documented. Since the wide gap braze process was used to repair blades, not vanes, the butt joints were not tested. Instead, samples with gauge diameters consisting of 20% braze build-up and 80% parent metal were tested. Creep rupture tests were performed using In738 nickel-base superalloy parent material. **Figure 37** shows the creep rupture properties of the joints. The joints displayed creep rupture lives ranging from 62% to 100% of that of the In738 alloy. Because of the comparatively low amount of boron in the wide gap braze joint, the borides could be rounded and distributed more evenly by an annealing heat treatment, as seen in **Figures 38 and 39**. This improved the joint ductility.

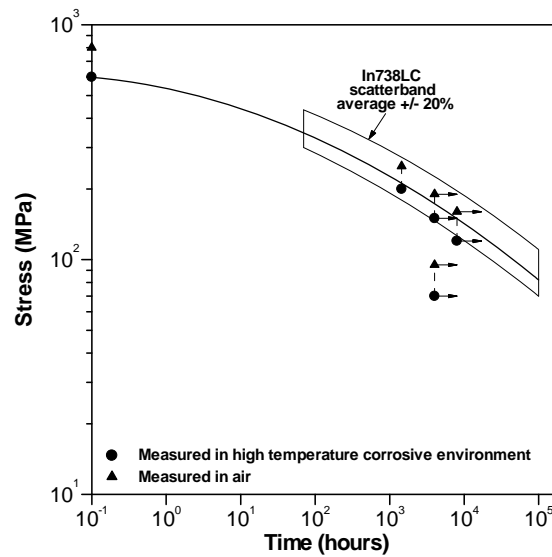


Figure 37 - Creep rupture tests performed at 850°C (base material is In738 and the wide gap braze is a proprietary material referred to as Elniment 100) [25].

Su, Chou, Wu and Lih [26] evaluated the phases that formed in ADB joints in In738 base metal. Three braze alloys, namely Nicrobraz 150, BRB and DF4B, were evaluated. The chemical compositions of these alloys are given in **Table 3**.

Table 3 - Nominal compositions of powders and base metal (wt.%, balance Ni).

Alloy	Cr	Co	Al	Ti	W	Mo	Ta	Nb	B	C	Zr	Y
In738	16.0	8.4	3.4	3.4	2.7	1.7	1.7	0.8	0.01	0.1	0.03	-
Nicrobraz 150	15.0	-	-	-	-	-	-	-	3.50	0.1	-	-
BRB	13.5	9.5	4.0	-	-	-	-	-	2.50	N/A	-	-
DF4B	14.0	10.0	3.5	-	-	-	2.5	-	2.70	N/A	-	0.02

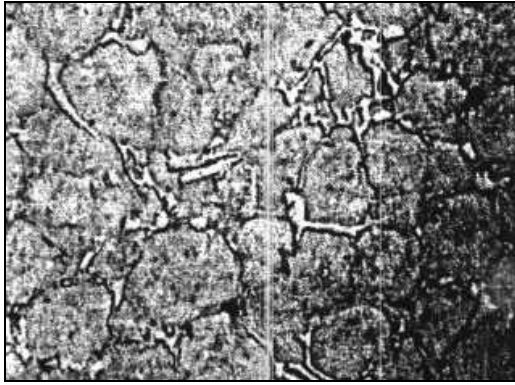


Figure 38 - Elniment 10 wide gap braze, as-brazed without subsequent heat treatment. The borides have an oblong shape [25].



Figure 39 - Elniment 10 wide gap braze, as-brazed with annealing heat treatment. The borides appear more rounded [25].

Brazing mixtures, consisting of brazing alloy and In738 superalloy powder, were prepared in weight percentage ratios of 30:70, 40:60 and 50:50. Microstructural observations were made using optical microscopy, scanning electron microscopy (SEM) and electron probe x-ray microanalysis (EPMA). The percentage porosity detected in the ADB joints is shown in **Figure 40** as a function of the filler metal ratio for the BRB and DF4B braze alloys. It is evident that joints containing 30% BRB or 30% DF4B mixed with In738 powder exhibited very high porosity levels after brazing at temperatures of 1180°C and 1190°C. Powder mixes containing 40% or 50% DF4B brazing alloy exhibited no porosity. The interstitial voids were small and randomly distributed in the 40% and 50% joints containing BRB as braze alloy.

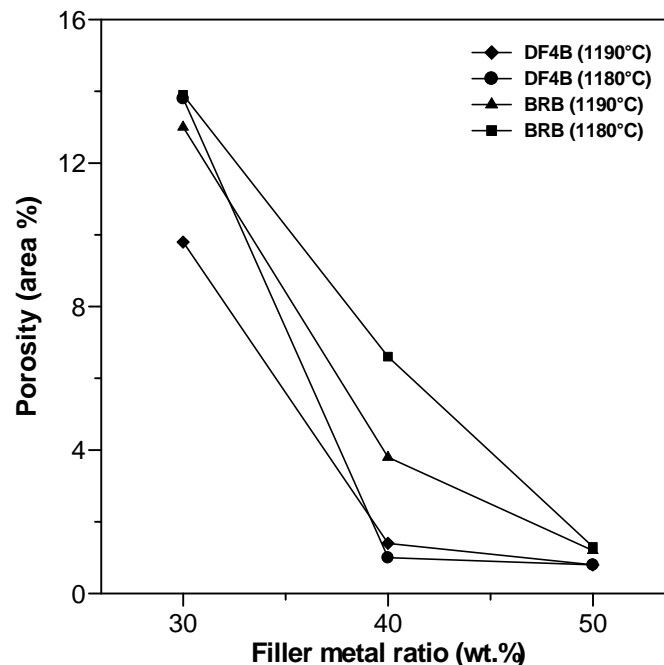


Figure 40 - Percentage porosity as a function of braze alloy content [26].

Figure 41(a) shows the microstructure of a 40% Nicrobraz 150 specimen after ADB processing. No pores are evident. The microstructure at high magnification is shown in **Figure 41(b)**. The matrix and secondary (blocky) phases are more evident, and island-like blocky boride phases are present in the In738 powder particles. **Table 4** shows the chemical

compositions of the two phases observed. Quantitatively, the blocky phase has a higher concentration of light elements (boron and carbon) than the matrix. The results of the quantitative analysis indicate that the blocky phase is Cr(B,C) with low levels of Co, Al, Ni, Ta and Ti in solution, while comparatively rich in Mo and W. The matrix of the Nicrobraz 150 braze alloy is predominantly Ni₃B with reduced amounts of B and C, but with high concentrations of Co, Ti and Ta. Cr boride is thermodynamically stable at all the temperatures evaluated, and its chemistry does not change once it has nucleated. The compound present probably has the stoichiometry CrB. **Figure 41(b)** also shows a Ni-Ni₃B eutectic precipitated in the braze alloy matrix (designated 'N'). This phase contains higher amounts of Co and Ti, derived from the superalloy powder by diffusion. The chain-like structure of the CrB, Ni₃B and Ni-Ni₃B eutectic reduces the ductility and the strength of the joint.

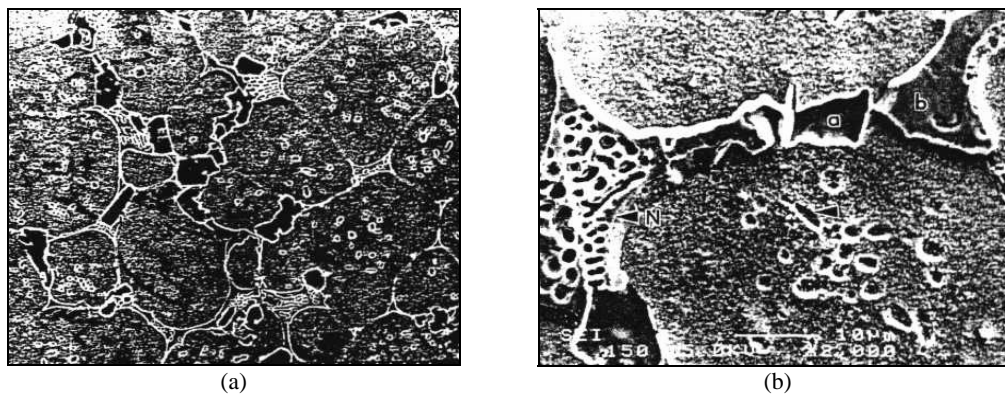


Figure 41 – SEM micrographs of a brazed joint produced from a mixture containing 40 wt.% Nicrobraz 150: (a) blocky boride phase (magnification: approximately 270X), and (b) Ni-Ni₃B eutectic (N). The arrow highlights the blocky boride phase precipitated within the metal powder particles (magnification: approximately 1800X) [26].

Table 4 – Chemical compositions of phases in specimens containing 40 wt.% Nicrobraz 150 braze filler metal [26].

Element	Matrix		Blocky phase	
	wt.%	at.%	wt.%	at.%
Ni	76.248	67.473	4.753	2.957
Cr	4.789	4.783	68.858	48.349
Co	5.833	5.140	1.917	1.188
Al	0.594	1.144	0.006	0.008
Ti	5.117	5.548	0.257	0.196
Ta	2.276	0.654	0	0
Mo	0.248	0.134	5.978	2.275
Nb	1.394	0.779	0.038	0.015
W	0.366	0.103	4.467	0.887
B	1.447	6.946	7.135	24.083
C	1.687	7.295	6.591	20.041

Figure 42(a) shows the microstructure of a joint containing 40% DF4B and 60% In738 processed at 1190°C. The initial spherical shape of the superalloy powder has disappeared and the blocky phase is still present. However, the matrix is not clearly identifiable, in contrast to **Figure 41(a)**. As seen in **Figure 42(b)**, the blocky boride phase is present within the superalloy powder particles. Darker matrix phases are also present alongside the blocky phase. The results of compositional analyses are shown in **Table 5**. The blocky boride phase

contains higher concentrations of Mo and W, compared to the Nicrobraz 150 joints. The composition of the irregular lathy dark-etching phase alongside the blocky boride phase revealed it to be γ' phase, containing Al and Ti, which had diffused from the superalloy powder. The results shown in **Figure 42** and **Table 5** indicate that within the superalloy powder particles, the gamma prime (γ') phase had coarsened to form a lathy structure in the boron diffusion direction. Within the DF4B powder, a dark matrix structure and blocky boride phase formed.

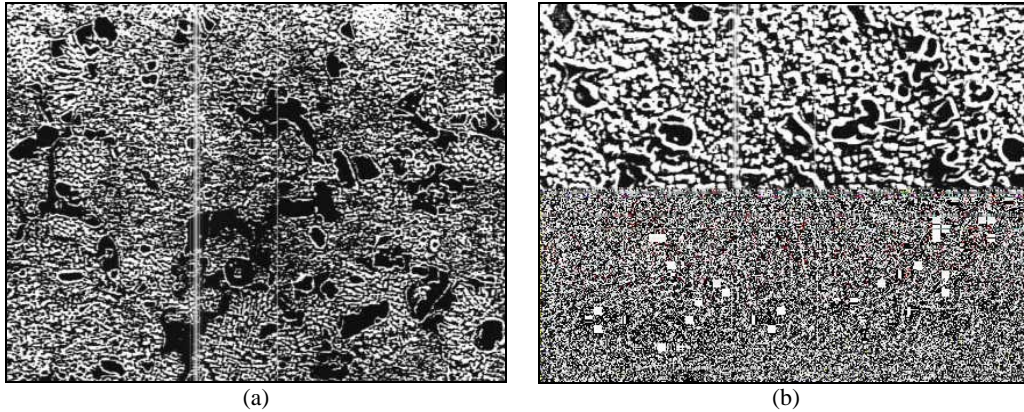


Figure 42 – SEM micrographs of a brazed joint produced from a mixture containing 40 wt.% DF4B: (a) blocky boride phase (magnification: approximately 350X), and (b) darker γ' phase. The arrow highlights the blocky boride phase precipitated within the metal powder particles (magnification: approximately 1750X) [26].

Table 5 – Chemical compositions of phases in specimens containing 40 wt.% DF4B braze filler metal [26].

Element	Matrix		Blocky phase	
	wt.%	at.%	wt.%	at.%
Ni	73.337	67.269	4.673	3.373
Cr	3.474	3.596	70.230	57.209
Co	6.064	5.539	3.725	2.678
Al	6.844	13.656	0.018	0.028
Ti	4.548	5.111	0.528	0.467
Ta	3.899	1.160	0.684	0.160
Mo	0.256	0.144	5.816	2.568
Nb	0.545	0.316	0.108	0.049
W	0.339	0.099	5.777	1.331
B	0.008	0.040	6.081	23.811
C	0.685	3.070	2.360	8.325

Figure 43 shows the microstructure of a joint consisting of 40% BRB filler metal and 60% In738 powder processed at 1190°C. The blocky boride phase and the darker lathy phase are similar to those observed within the DF4B joint. The compositions of the darker phase and the blocky phase can be found in **Table 6**.

Subsequent tensile investigations of these ADB butt joints showed that the ultimate tensile strength (UTS) of the DF4B/In738 joints attained 85% of the room temperature UTS of the In738 base metal, and 100% of the UTS of the In738 base metal at 980°C. For the Nicrobraz 150/In738 joints, the UTS was 40% of the room temperature UTS of the In738 base metal. The reduction in mechanical strength was attributed to the presence of the Ni-Ni₃B eutectic phase within the joint. This eutectic not observed in the DF4B/In738 or BRB/In738 joints.

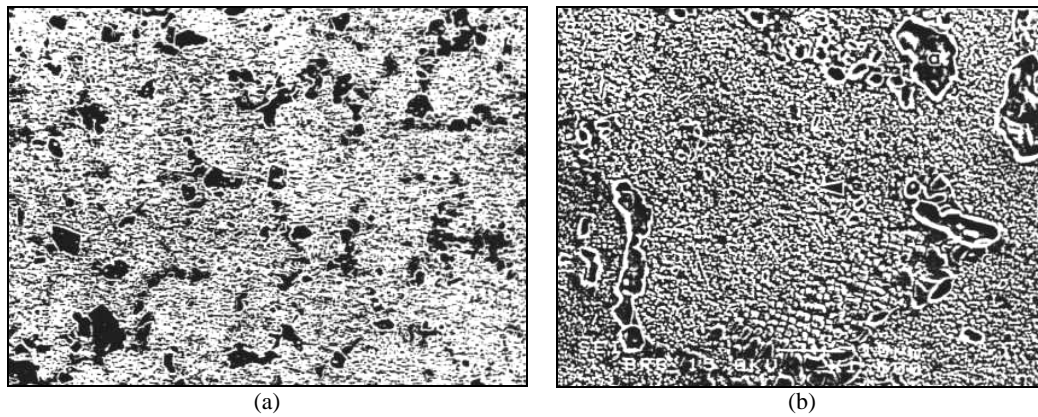


Figure 43 – SEM micrographs of a brazed joint produced from a mixture containing 40 wt.% BRB: (a) blocky boride phase (magnification: approximately 225X), and (b) darker γ' phase. The arrow highlights the blocky boride phase precipitated within the metal powder particles (magnification: approximately 1325X) [26].

Table 6 – Chemical compositions of phases in specimens containing 40 wt.% BRB braze filler metal [26].

Element	Matrix		Blocky phase	
	wt. %	at. %	wt. %	at. %
Ni	6.724	5.500	73.889	68.778
Cr	67.700	62.494	4.724	4.962
Co	3.028	2.467	6.183	5.731
Al	0.185	0.329	6.511	13.184
Ti	0.445	0.446	4.352	4.964
Ta	0.113	0.030	2.372	0.716
Mo	6.373	3.189	0.308	0.175
Nb	0.073	0.338	0.825	0.485
W	9.893	2.583	0.657	0.195
B	3.099	13.751	0	0
C	2.283	9.126	0.178	0.810

1.6) Sintering of Ni-base superalloys using braze filler metals

As illustrated in §1.5, mixing of braze filler metal powder and base metal powder does not result in adequate joint strength when the joint gap approaches 1 mm in width. The results considered above also indicate a significant loss in creep rupture life when the ADB process is used for joints gaps approaching 1 mm in width. In an aircraft engine, stationary components such as vanes seldom contain cracks approaching 1 mm in width, and the ADB process has therefore been used successfully during the last two decades to repair aircraft engine components. There are many profitable companies throughout the world which offer a service repairing aircraft engine components. South African Airways spent \$50 million dollars per annum in the 1990's on the repair of aircraft engine components at repair companies located in Europe and the USA.

With the tremendous growth in global energy consumption, however, the repair of land-based power generation gas turbines has become a lucrative business. A typical land-based turbine blade is ten times the length of an aircraft turbine blade and a land-based vane weighs more than 20 kg as opposed to an aircraft vane that weighs approximately 5 kg. Thermal fatigue

cracks in land-based turbine vanes can be up to 20 cm long, 5 mm wide and 6 mm deep. The ADB process and conventional narrow gap brazing processes cannot be used to repair these large defects successfully. An incentive therefore exists for the development of new joining technologies suitable for repairing wide cracks in land-based turbine components.

In 1979, Chasteen and Metzger [27] developed a sintering process during which a large gap is filled with a metal powder. The powder is then sintered in the gap. Simply stated, sintering is a process involving the compacting and agglomeration of loose powder particles, usually at elevated temperature. The authors sintered gaps varying from 0.025 mm to 2 mm in width in Hastelloy X base metal using four different powders: Hastelloy C (fine and coarse particle size), Rene 80 and a 79%Ni-20%Cr-1%Si powder. The compositions of the powders are given in **Table 7**.

Table 7 – Chemical compositions of the base metal and sinter powders (S1-S4) used in the Chasteen and Metzger investigation [27].

Alloy	Common designation	Nominal chemical composition (wt.%, balance Ni)									Melting temperature (°F)		Mesh size
		Cr	Fe	Co	Mo	W	Si	B	Al	Ti	Solidus	Liquidus	
Base metal	Hastelloy X	22	18	2	9	1	-	-	-	-	2350	2470	-
Sinter filler													
S1	-	20	-	-	-	-	1	-	-	-	2500	2575	-325
S2	Hastelloy C	16	6	2	16	4	-	-	-	-	2320	2380	-150/+325
S3	Hastelloy C	16	6	2	16	4	-	-	-	-	2320	2380	-325
S4	Rene 80	14	-	10	4	4	-	-	3	5	-	-	-100
Braze filler													
B1	-	7	3	-	-	6	4.5	3	-	-	1790	1900	-

The powders were sintered at a temperature of 1129°C for 30 minutes. After sintering, the joints displayed an average of 33% porosity by volume. By adding a braze filler metal, referred to as B1 (see **Table 7**), the porosity could be minimized. The sintering and subsequent brazing process resulted in the joint microstructure shown in **Figure 44**. A few voids are evident in the micrograph and this is believed to be due to the low temperature used during the brazing cycle (1129°C for 2 hours).

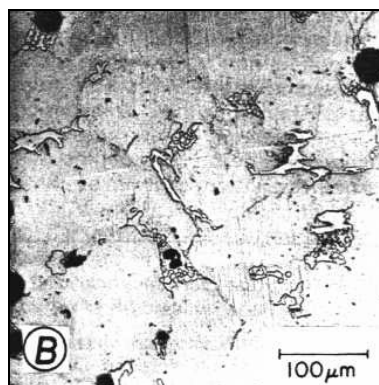


Figure 44 - Braze joint of 1.25 mm clearance using sinter filler metal S1 and braze filler metal B1 (as shown in Table 7) [28].

Figure 45 shows the tensile strength variation as a function of temperature for 0.5 mm joints with sinter powder, joints with no sinter powder, and the base metal. The joints with sinter

powder displayed tensile strengths corresponding to approximately 70% of the base metal strength at temperatures below 650°C, but more than 90% of the base metal strength at temperatures greater than 760°C. The brazed joints without sinter powder displayed very low tensile strength values (about 20% of the base metal tensile strength).

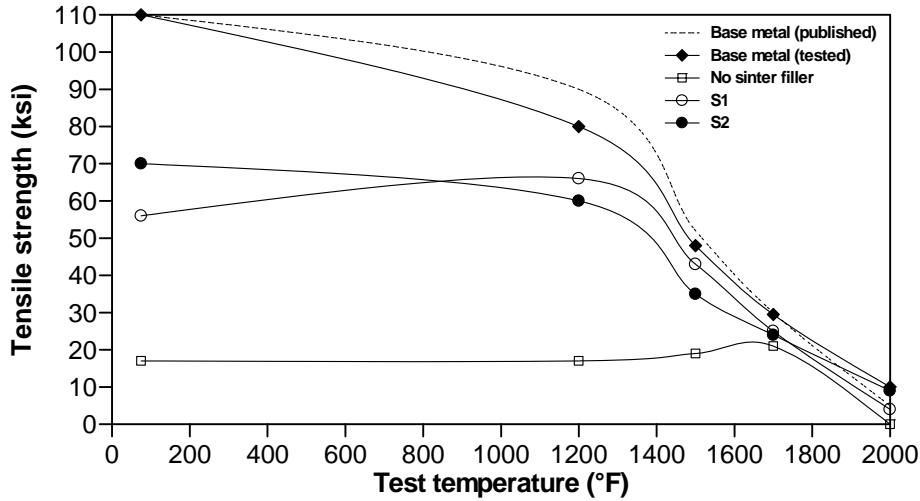


Figure 45 - Tensile strength as a function of temperature for the base metal, and for sintered and brazed joints with 0.5 mm clearance [27].

Figure 46 shows the variation in tensile strength with joint clearance. The results indicate that at low joint clearances, joints brazed without sinter powder had joints strengths comparable with those of joints containing sinter powder and braze powder. At joint clearances greater than 0.15 mm, the joint strength (with no sinter powder) decreased rapidly. Joints containing S2 powder displayed higher strength values at all joint clearances tested than joints with S1 sinter powder. The strength of joints brazed with S1 sinter powder remained fairly constant at about 60 ksi (414 MPa) (54% of the base metal strength), while the curve for the S2 joints displayed a slight decrease in strength with increasing clearance.

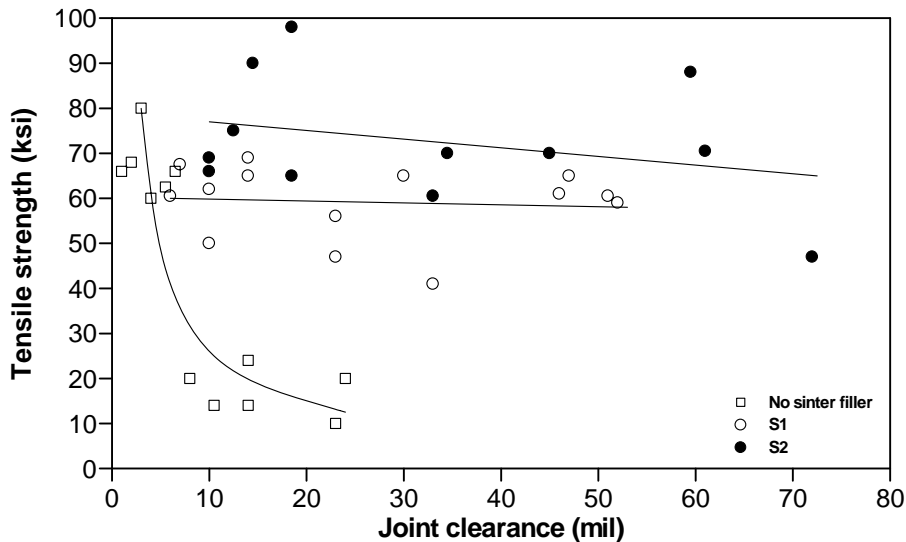


Figure 46 – Room temperature tensile strength as a function of joint clearance for sintered and brazed joints and for the joints containing no sinter powder [27].

The method developed by Chasteen and Metzger for filling wide gaps therefore consists of two steps. The first step involves sintering a nickel-base alloy of high melting point (called the sinter filler metal) in powder form in the joint. Light sintering results in a porous, but not friable, metallic mass in the joint. The second step involves filling the powder interstices by brazing with a nickel-base filler metal (called the braze filler metal) to complete the joint. The results of this investigation encouraged researchers to optimize the process for use in repairing wide cracks in gas turbine components.

In 1992, Liburdi *et al* [28] patented a similar two step process. The first step involved sintering in the solid state at elevated temperatures and for extended times (e.g. 1200°C for 4 hours), resulting in a dense structure. The braze filler metal was therefore only required to close a small number of pores, leading to superior mechanical properties (as shown in **Figure 47**). On average, the creep rupture properties were at least 75% of the base metal properties for a 1.5 mm wide gap (such as those typically found in gas turbine components). Whereas Chasteen and Metzger used conventional, commercially available braze filler metals, Liburdi *et al* used braze filler metal especially designed to match the composition of the base metal being repaired, except for the addition of both B and Si as melt point depressants.

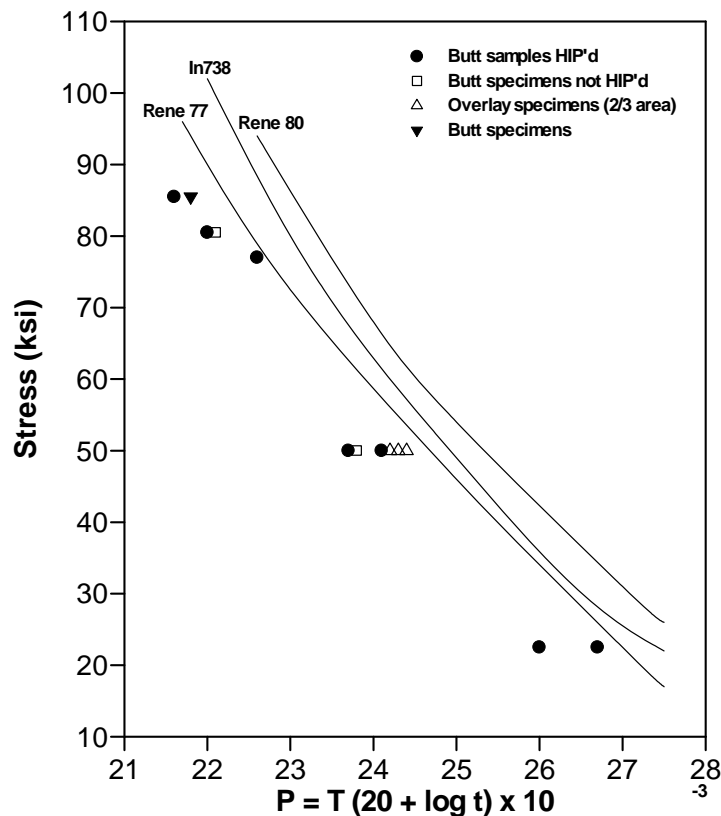


Figure 47 - Larson Miller plot for wide gap joints produced by the Liburdi solid state sintering process [28].

In 1983, Jahnke and Demny [29] developed a process referred to as liquid phase diffusion sintering. They claimed it had potential for closing wide gaps, and for developing improved mechanical strength compared to conventional wide gap brazed joints, such as those produced through the ADH process. The joints produced with this method generally have high thermal fatigue resistance and good hot corrosion properties. The steps involved in this process are listed below, and schematically illustrated in **Figure 48**.

- 1) Melting of the filler metal on heating above the solidus temperature.
- 2) Rearrangement of solid grains by sliding on the liquid films separating them.
- 3) Densification.
- 4) Melting of the parent metal (powder particles) and dilution until the concentration of the liquid reaches C_L (see **Figure 48**).
- 5) Diffusion of the melt point depressants (boron and silicon) into the solid, resulting in isothermal solidification.
- 6) Recession of the solid-liquid interface and a reduction in the liquid zone until the solubility limit in the base metal powder particles is reached.

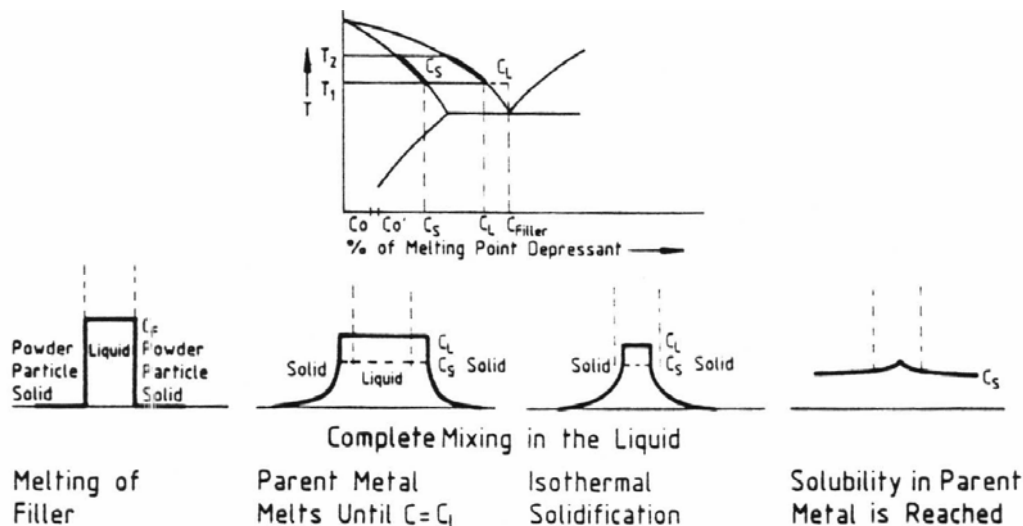


Figure 48 - Liquid phase diffusion sintering: general description of diffusion solidification [29].

In a subsequent development, Miglietti (US patent number US6520401(B1)) developed a liquid phase diffusion bonding process, described in more detail in four technical papers [30-33] supplied in Appendices A to D. During this bonding process, a crack is filled with MarM247 nickel-base superalloy powder. This powder has a solidus temperature in excess of 1315°C, well above the recommended brazing temperature range. The MarM247 powder is then covered with a Ni-base superalloy braze powder or paste. The braze powder or paste is doped with either B, Zr or Hf, or a mixture of all three elements, to lower its melting point. Adding Zr or Hf as melt point depressant to braze filler metals for joining Ni-base superalloys is novel and the results are considered in more detail in subsequent chapters. The braze filler metal is then heated to the brazing temperature of between 1220°C to 1280°C. The braze powder melts to form a liquid, which is carried into the spaces between the MarM247 powder particles to form a solid diffusion bond that joins the powder particles. Thermal processing consists of heating to a brazing temperature between 1220°C to 1280°C and holding at this temperature for a maximum of 30 to 45 minutes. The temperature is then lowered to approximately 1200°C to diffuse the melt point depressants into the parent metal.

The remaining chapters of this document describe the results of a series of experiments aimed at evaluating the potential of novel Ni-Hf and Ni-Zr braze filler metals for joining Ni-base superalloys using the liquid phase diffusion bonding process.