SOLIDIFICATION BEHAVIOR DURING DIFFUSION BRAZING OF A NICKEL BASED superalloy

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Abstract
Solidification behavior during diffusion brazing of nickel base superalloy GTD-111 using a Ni-Si-B amorphous interlayer, MBF30, is investigated. Bonding was carried out at 1100°C with different holding time under vacuum. The effect of bonding time on solidification type (isothermal solidification vs. athermal solidification) is investigated. Solidification sequence in athermal solidification and the time required to obtain a joint free from centerline eutectic are determined.

1. INTRODUCTION
Gamma prime strengthened nickel-base superalloys are extensively used in hot sections of aero-engine and power generation turbines. They offer excellent high temperature tensile strength, stress rupture and creep properties, fatigue strength, oxidation and corrosion resistance, and microstructural stability at elevated temperatures.

Two important key microstructural requirements in γ′ strengthened nickel base superalloys joints are the avoidance of undesired intermetallic phase in the middle of the joint and development of a desired γ/γ′ microstructure in the joint region (POURANVARI et al., 2008). Production of joints which fulfill the microstructural requirements for high stresses and temperatures can be achieved via transient liquid phase (TLP) bonding or so called diffusion brazing process. In general, it is considered that there are three distinct stages during TLP bonding, namely: base metal dissolution, isothermal solidification and solid-state homogenization. Combining isothermal solidification with a subsequent solid state homogenization treatment, offers the possibility of producing ideal joints (GALE and BUTTS, 2004).

In this paper, solidification behavior during diffusion brazing of GTD-111 superalloy, using Ni-Si-B interlayer, is investigated.

2. EXPERIMENTAL PROCEDURE
The chemical composition of the base metal, GTD-111 superalloy, was Ni-13.5Cr-9.5Co-4.75Ti-3.3Al-3.8W-1.53Mo-2.7Ta-0.23Fe-0.09C-0.01B. A commercial Ni-4.5Si-3.2B alloy (MBF30), in the form of an amorphous foil with 25.4 µm thickness was used as the interlayer. The surfaces to be bonded were ground by using 600 grade SiC paper and cleaned in acetone before bonding. Bonding was carried out at 1100°C for various bonding times under a vacuum of approximately 10⁻⁴ torr in a vacuum furnace. Microstructures of joints were examined by optical microscopy and scanning electron microscopy (SEM) equipped with a beryllium window energy dispersive spectrometer (EDS) system using INCA software. For microstructural examinations, specimens were etched using two etchants. The Murakami etchant (10g KOH, 10g K₃[Fe(CN)₆], 100 ml H₂O) preferentially etches Cr-rich phases and can therefore be used to reveal precipitates adjacent to the joint/base metal interface. Molybdenum-acid etchant (0.5g MoO₃, 50ml HCl, 50ml HNO₃, 200ml H₂O), which preferentially etches γ′ phase, was used to indicate γ-γ′ microstructure of the joints, in addition to joint centerline microstructure.
3. RESULTS AND DISCUSSIONS

3-1- Microstructure of the joint

Fig. 1 shows SEM image of a bond made at 1100°C with a holding time of 30 min. As can be seen, bond region consists of three distinct zones which are named as follows:

1- Athermally Solidified Zone (ASZ)
2- Isothermally Solidified Zone (ISZ)
3- Diffusion Affected Zone (DAZ)

Since the melting point of interlayer is less than the bonding temperature, the interlayer melts and significant interdiffusion occurs between interlayer and base metal. According to Ni-Si-B ternary phase diagram (VILLARS et al., 1995), Si and B diffusion from molten interlayer into the base metal cause significant compositional changes in the liquid phase and increase liquidus temperature of liquid phase. Once the liquidus temperature increased to the bonding temperature (1100°C), isothermal solidification starts.

Microstructure of ISZ contains proeutectic γ-solid solution. A typical EDS chemical analysis of ISZ is given in table 2. Presence of elements such as Cr, Co, Al and Ti which were not present in initial interlayer composition (Ni-4.5Si-3.2B) indicates dissolution of the base metal.

Fig. 1 a) Microstructure and b) hardness profile of bonds made at 1100°C for 30 min

3-2- Solidification behavior of ASZ

SEM image of ASZ microstructure showed two distinct phases (Fig. 1). EDS spectra of intermetallic phase in the ASZ is shown in Fig. 2. Boron was detected in this phase. However, its concentration could not be determined with sufficient accuracy due to the X-ray absorption by EDS analyzer window. EDS compositional analysis of other elements (Table 1) suggests that the intermetallic phase is a nickel-rich boride and the second phase is identified as a γ-solid solution. Morphology of ASZ structure suggests that it is a binary eutectic of divorced morphology which is formed by eutectic transformation. Because of high interfacial energy between γ-solid solution and nickel boride, a high driving force is required for cooperative nucleation of two phases during transformation of liquid phase to normal eutectic structure. TUNG et al. (1995) in their work on microstructural evolution of brazed nickel 270 with BNi-4 filler metal, found that for slow cooled joint solidification (e.g. furnace cooled), formation of divorced eutectic was promoted due to the low driving force.

Like other usual solidification processes which cooling is the main driving force of crystallization, microstructural development in the ASZ is largely controlled by two interrelated solidification phenomena (OJO et al., 2004): dendrite formation and solute partitioning. ASZ microstructure can be explained by considering solidification sequence of remained liquid on cooling: general direction of solidification is from the base metal towards...
the centerline region of the melt. The initial formed phase in the centerline of the joint on cooling is $\gamma$-nickel phase in the form of dendrites growing from liquid/solid interface. During their continuous formation, solute elements with partition coefficient $k<1$ were rejected into liquid. Continuous solute enrichment of liquid could cause solute concentration exceeds over the solubility limit of solute in the $\gamma$ phase; therefore, secondary solidification constituents are formed between dendrites. Solubility of B in Ni (0.3% at, according to binary Ni-B equilibrium phase diagram) is much smaller than solubility of Si in Ni (15% at). Also, partition coefficient of B in Ni (~0.008 according to Ni-B binary phase diagram) is considerably smaller than partition coefficient of Si in Ni (~0.8 according to Ni-Si binary phase diagram). Therefore, B is rejected into adjacent melt, shifting composition of the melt towards eutectic composition; thus, binary eutectic of $\gamma$-solid solution and nickel boride is formed as solidification progressed.

Since boride contains no Si, the latter element becomes more concentrated in the remaining liquid. The melt, which is further enriched in silicon, is then transformed into ternary eutectic of $\gamma$ solid solution, nickel boride and nickel silicide (TUNG et al., 1996). However, in this work, according to microstructural investigations and EDS analyses, no silicide phase was observed. It seems that boron content is the controlling factor for microstructural development in ASZ. Interlayer thickness affects boron content of the joint. According to (JOHNSON, 1981) if boron level is limited, the ternary eutectic will not form. This is because volume fraction of borides is not sufficient to increase silicon content in the remaining liquid phase above the solid solubility limit in nickel phase solid solution. Therefore, only two phases are formed in ASZ on cooling: $\gamma$-solid solution and nickel boride.

In addition to brittleness of this eutectic-type structure, it can be prone to selective corrosion and oxidation. Presence of ASZ in the bond region can also reduce service temperature of bonded superalloy due to segregation of B into the centerline eutectic. Any subsequent attempt to diffuse B away and eliminate detrimental intermetallic phases would have to be conducted at a relatively low temperature (where diffusion rates are less efficient) if remelting of the joint was to be avoided. These difficulties can be eliminated by achieving isothermal solidification initially (DUVALL, 1974).

![Fig. 2. Typical EDS spectrum of nickel-rich boride in ASZ](image-url)
Table 1 Chemical composition (%at) of different metallic constituents of various phases observed in bonds made at 1100°C for 30 min.

<table>
<thead>
<tr>
<th>Element</th>
<th>ISZ</th>
<th>ASZ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Proeutectic γ-solid solution</td>
<td>Nickel rich boride phase</td>
</tr>
<tr>
<td>Ni</td>
<td>74.03</td>
<td>76.32</td>
</tr>
<tr>
<td>Cr</td>
<td>15.43</td>
<td>8.91</td>
</tr>
<tr>
<td>W</td>
<td>0.82</td>
<td>0.50</td>
</tr>
<tr>
<td>Co</td>
<td>1.60</td>
<td>2.04</td>
</tr>
<tr>
<td>Ti</td>
<td>1.23</td>
<td>2.01</td>
</tr>
<tr>
<td>Al</td>
<td>1.31</td>
<td>1.22</td>
</tr>
<tr>
<td>Mo</td>
<td>0.23</td>
<td>0.19</td>
</tr>
<tr>
<td>Si</td>
<td>5.35</td>
<td>8.81</td>
</tr>
</tbody>
</table>

3-3-Effect of bonding time on isothermal solidification progress

Joint microstructure which affects significantly the joint performance is depends on elemental interdiffusion between base metal and interlayer, which in turn is governed by bonding time. In the case of TLP bonding of GTD-111/MBF30/GTD-111, isothermal solidification process is controlled by formation and growth of γ-solid solution which is governed by MPD element diffusion in base metal. Fig.3 shows plot of ASZ size (or eutectic width) vs. square root of bonding time. The eutectic width decreases linearly with square root of bonding time. As can be seen in Fig.4, when bonding time increased to 75 min, no eutectic structure was observed in the bond region. Therefore, it is concluded that holding time of 75 min at 1100°C is sufficient for isothermal solidification completion.

Fig.3 Eutectic structure width (ASZ size) versus square root of bonding time

Fig.4 Microstructure of bond made for 75 min. Isothermal solidification is completed and no eutectic microconstituent is observed in the centerline of the joint.
4. Conclusions
Transient liquid phase bonding (TLP) bonding of GTD-111 nickel based superalloy has successfully been performed using Ni-Si-B. Effect of bonding time on microstructure development was investigated. According to the solidification behavior and ASZ microstructure, B is main controlling MPD element of isothermal solidification and Si play no important role in microstructure development during diffusion brazing using Ni-Si-B interlayer. The eutectic width decreases linearly with square root of bonding time.

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