MICROSTRUCTURE AND BONDING BEHAVIOR OF A NEW ZR-BEARING

INTERLAYER ALLOY FOR SINGLE CRYSTAL NICKEL-BASE SUPERALLOY

Yunrong Zheng * † and Kris Tangri **

* Institute of Aeronautical Materials, Beijing 100095, China

** Department of Mechanical and Industrial Engineering, University of Manitoba,

Winnipeg, Manitoba, Canada R3T 2N2

Abstract

Based on the composition of the interdendritic Zr-rich melt in the later stages of solidification of Zr-containing superalloys, a Ni-10Co-8Cr-4W-13Zr (wt.%) alloy was selected as an interlayer alloy for brazing and transient-liquid-phase (TLP) bonding of single crystal superalloys. All the elements in the interlayer alloy are beneficial to the single crystal superalloys. Using the above alloy, bonds free of brittle phases in the single crystal superalloy have been obtained by isothermal solidification at 1270°C for 48 hours. In the present work, the microstructural characteristics of the interlayer alloy and the phase relationships in the bond during brazing and TLP processes are reported.

[†] Yunrong Zheng is currently a visiting research fellow in Metallurgical Science Laboraotry, University of Manitoba, Winnipeg, Manitoba, Canada, R3T 2N2

Introduction

Single crystal nickel-base superalloys have been widely used in the manufacture of aeroengine blades. Unfortunately, it is very difficult to fusion-weld this kind of alloy due to their high content of Al, Ti and the refractory elements. However, transient-liquid-phase (TLP) bonding has been successfully utilized in production (1). It is very important to design a suitable interlayer alloy which does not contain any deleterious phases and has a melting point lower than that of the base metal. In order to obtain suitable interlayer alloys, a great deal of research has been carried out since the 1960's. B, Si, Mn, Nb and Ti are added to Ni-Cr and Ni-Cr-Co alloys as melting point depressants. The effort has led to Ni-Cr-Si-B alloys to be used for brazing superalloys (2). However, B and Si addition should be avoided because these elements are harmful impurity elements in single crystal superalloys.

Zr is a potential melting point depressant in the interlayer alloys which has not been evaluated to date. It is known that the melting temperature range of Ni₅Zr which exists at the interdendrites in Zr-containing superalloys is 1140° - 1170° C (3) and the solid solubility of Zr in the eutectic γ' is 1.0 at % (4). Zr addition to superalloys is beneficial for improving the strength, ductility (5) and low cycle fatigue life of directionally solidified superalloys (4). Zr additions are also known to counteract the harmful effects of sulphur (6) and effectively strengthen the γ' phase (7). These factors make Zr a suitable addition element for brazing materials. The objectives of this investigation are to characterize the microstructure of a Zr-bearing interlayer alloy and to determine the effect of Zr on the solidification of bonds during brazing and TLP processes.

Experimental

The substrate material is a single crystal superalloys DD3 with [001] orientation and its composition is as follows: Ni-5.2Co-8.9 Cr-5.3W-3.1Mo-5.6Al-1.6Ti (wt%). This alloy is strengthened by γ' precipitation of about 60 vol %, but has no eutectic $\gamma + \gamma'$ due to the lower content of Ti. Thus the hot-tearing tendency of the alloy is very low. The directionally solidified superalloy DZ3 which is essentially the DD3 alloy containing 0.10Zr-0.14C-0.11B wt % was used for isothermal solidification tests in order to determine the composition of the melts in the later stages of solidification. For this purpose, the specimens were heated to 1370°C, soaked for 15 minutes, then cooled to 1220°C and held for 15 minutes of isothermal solidification at this temperature before quenching into water. The composition of Zr-rich melts formed at interdendrites during 1220°C isothermal solidification was determined using x-ray energy dispersive analysis (EDAX). The results of this analysis were used to design the Zr-bearing interlayer alloy as following: Ni-10Co-8Cr-4W-13Zr (wt %).

The bonding tests on single crystal superalloys were as follows: (a) a thin (about 50 μ m) interlayer alloy was inserted between two pieces of single crystal and held together, (b) the combination specimens were sealed in quartz ampoules evacuated to 1 x 10⁻³ Pa and backfilled with high purity Ar to 2 x 10⁴ Pa pressure, and (c) the ampoules with specimens were treated

Table I	Bonding	Schemes	for Single	Crystal	Superallovs	DD3
1 4010 1	Donume	OCHULIOS	IOI DINEIU	Crystar	Duberanovs	1212.7

Scheme	Temperature/Time	Cooling		
I	1250°C/25 min + 1230°C/8h, 48h, 96h	Air-cooling or water-quenching		
II	1250°C/25 min + 1140°C/48h	air-cooling		
III	1270°C/15 min, 2h, 8h, 24h, 48h	air-cooling or furnace cooling		

according to the schemes listed in Table I. The microstructures of both the interlayer alloy and the bonds were characterized by optical microscopy (OM), transmission electron microscopy (TEM), scanning electron microscopy (SEM), EDAX and X-ray diffraction (XD).

Results and Discussion

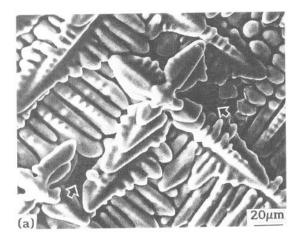
Composition of the Interlayer Alloy

Microstructure of DZ3 alloy after isothermal solidification at 1220°C for 15 minutes is shown in Fig. 1. The γ dendrites and the pores on the surface of specimen, as pointed out by arrows, are seen in Fig. 1a. The pores at the interdendrites form due to the flowing out of the low melting point melts. In the interior of the specimen, the residual liquid which fills the interdendritic capillaries, transforms into the eutectic γ + Ni₅Zr (Fig. 1b). The average composition of the eutectic zones was determined to be Ni-5.0Co-12.1Cr-1.5W-8.8Mo-2.2Al-3.0Ti-12.1Zr (wt %) by EDAX. It can be seen that Zr mainly segregates at interdendrites producing a low melting point melt. The γ dendrites formed in the early stage of solidification may be considered to be joined by the interdendritic Zr-rich melt, therefore, the composition of the melt may be utilized as a basic composition for the interlayer alloy.

Al and Ti diffuse easily into the bonds from the matrix alloy, hence, the interlayer alloy does not contain these elements. However, W which is an important strengthening element for both the γ and the γ' phase, diffuses very slowly and as such must be incorporated into the interlayer alloy. Mo, another strengthening element and a slow diffuser is excluded because it segregates at the interdendrites and is a stronger promoter of μ phase formation than W. Moreover, the strengthening role of Mo can be provided by adjusting the amount of W in the interlayer alloy. The content of Co and Cr in the interlayer alloy is maintained at the same level as in the cast nickel-base superalloy. The final composition which is based on the above considerations is as follows: Ni-10Co-8Cr-4W-13Zr.

Microstructure of the Interlayer Alloy

The microstructure of the as-cast interlayer alloy is hypoeutectic and consists of the primary γ and $\gamma + Ni_5Zr$ eutectic, as shown in Fig. 2a. At a higher magnification it is seen that this eutectic consists of γ bars surrounded by the phase Ni_5Zr (Fig. 2b). A TEM study was undertaken on the as-cast interlayer alloy, and the structure of the Ni_5Zr phase was determined to be FCC. Fig. 3a shows the γ phase in a matrix of Ni_5Zr phase. Fig. 3b is a diffraction pattern showing a [112] zone axis and Fig. 3c shows the [011] zone axis. The existence of the Ni_5Zr phase in the interlayer alloy was also confirmed by x-ray diffraction of powder



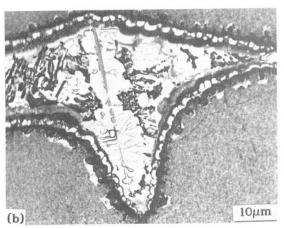


Figure 1 - Microstructure of DZ3 superalloy after isothermal solidification at 1220°C for 15 minutes and water quenching: (a) morphology of the γ dendrites, the arrows indicate the pores on the surface of a specimen; (b) the low melting interdendritic region in the interior of the same specimen.

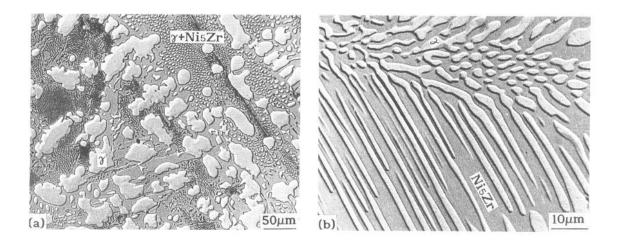


Figure 2 - Microstructure of as-cast interlayer alloy: (a) the primary γ dendrites and γ + Ni₅Zr eutectic; (b) Morphology of the γ + Ni₅Zr eutectic showing different orientations of the γ bars in neighbouring colonies.

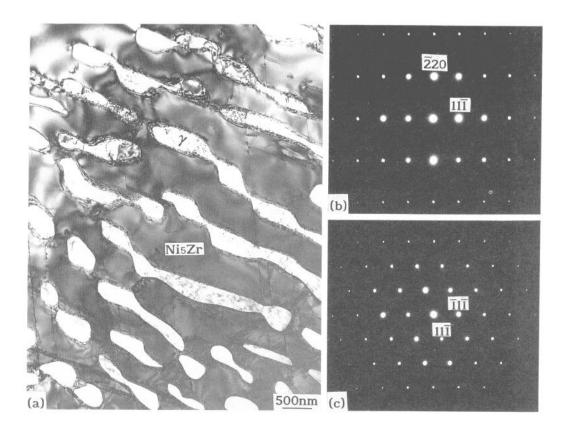


Figure 3 - Transmission electron micrograph and diffraction patterns of the γ + Ni₅Zr eutectic: (a) TEM view of the γ + Ni₅Zr eutectic region, (b) and (c) diffraction pattern of the Ni₅Zr phase showing the zone axis [112] and [011] respectively.

specimens. The composition of various phases in the interlayer alloy was determined by EDAX. The results are listed in Table II. It is seen that except for the higher solubility of Co, other elements have very low solubility in the Ni₅Zr phase. Microhardness measurement with a 50 gram load on Ni₅Zr phase in the interlayer alloy gave an average value of 4541 MPa. Despite this higher hardness of the Ni₅Zr phase, the interlayer alloy was rather ductile and was not fragmented during hammering.

Table II Composition of Phases in the Interlayer Alloy, wt %

Phase	Ni	Co	Cr	Zr	W
Primary γ	59.8	14.4	14.8	0.6	10.4
Eutectic γ	65.4	15.3	14.4	0.4	4.5
Eutectic Ni ₅ Zr	67.9	5.5	1.6	24.3	0.7

Bonding of Single Crystal Superalloy

The liquidus and solidus temperatures of the single crystal superalloy are 1380° and 1310°C respectively whereas the liquidus temperature of the interlayer alloy is 1220°C. There is a 90°C temperature gap between the solidus of the base alloy and the liquidus of the interlayer alloy, which provides some degree of freedom in the choice of the bonding temperature.

At the beginning, the bonding tests were performed by scheme I (Table I). The specimens were heated to 1250°C, soaked for 25 minutes, then furnace-cooled to 1230°C and held for different times of isothermal solidification at this temperature before air-cooling to room temperature.

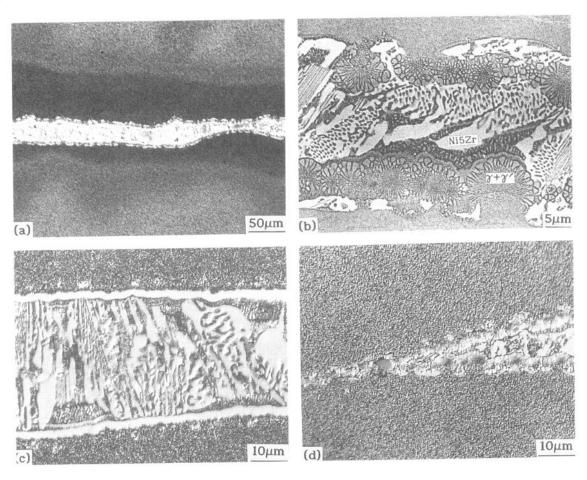


Figure 4 - Microstructure of the bond after 25 minutes at 1250°C furnace-cooling to the soaking temperature of 1230°C: (a) and (b) 8h soak, (c) 24h soak, (d) 96h soak; (a), (b) and (d) air cooling, (c) quenching in water.

The results showed that it was very difficult to remove the liquid phase in the bond by the isothermal solidification at 1250°C, as shown in Fig. 4.

In scheme II (Table I), specimens were heated to 1250°C, held for 25 minutes, then air-cooled to room temperature in order to obtain a brazing bond. Afterwards a 48 hour diffusion treatment at 1140°C, which is lower than the solidus of the interlayer alloy, was applied to homogenize the bond. However, a great deal of the low melting point Ni₅Zr phase still existed in the bond after the above treatment. Hence, the isothermal solidification at a higher temperature in scheme III was resorted to.

The bond in Fig. 5 was produced in 15 minutes at 1270° C. The light zone is the γ solid solution (Fig. 5a and 5b). The γ + Ni₅Zr eutectic exists in the centre of this band (Fig. 5b). The average thickness of this band is $140~\mu$ m which is larger than the original gap of about $60~\mu$ m width. Chemical reaction of the liquid and the adjacent base metal increases the Zr content at the base metal surface causing it to melt. The local melt back of the mating surfaces decreases the concentration of Zr in the liquid interlayer and enlarges the melted zone. The melt back increases the content of Al and Ti in the bond. Therefore, in the eutectic zone, a fine γ + γ ' eutectic (marked B in Fig. 5d), fine precipitates of γ ' (marked C in Fig. 5d) and the Ni₅Zr phase are formed after air-cooling. Analysis of the different areas was carried out by EDAX and the results are listed in Table III. It may be seen that the elements Al and Ti are easily replenished at the bond by diffusion from the base metal. The microsegregation in both

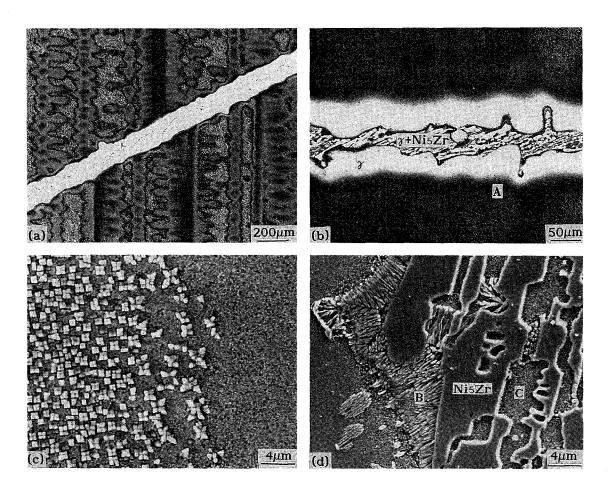


Figure 5 - Microstructure of the bond made at 1270° C for 15 minutes in DD3 single crystal superalloy: (a) dendrites in the base alloy and γ solid solution in the bond (light zone), (b) the γ phase and the γ + Ni₅Zr eutectic, (c) the A zone in (b), (d) the zone of γ + Ni₅Zr in (b) at higher magnification.

Table III Analysis of Different Areas in the Eutectic Zone of Fig. 5d, wt %

Area	Ni	Co	Cr	Zr	W	Мо	Ti	Al
В	75.5	5.9	5.5	1.4	2.2	0.8	2.3 1.5 0.6	6.4
C	72.5	7.3	8.5	0.9	3.3	1.5	1.5	4.5
C Ni ₅ Zr	69.8	4.0	1.0	23.2	0.7	0.3	0.6	0.4

the base metal and the bond is not removed due to the absence of sufficient time for diffusion. This is a typical brazing microstructure.

The microstructure of the bond after 2 hours at 1270°C and subsequent furnace cooling is presented in Fig. 6 where the melt zone (MZ), the isothermal solidification zone (ISZ) and the eutectic zone (EZ) are marked. The average width of the melt zone is similar to that found in the sample heated for only 15 minutes. This indicates that after about 15 minutes of heating at 1270°C , further melting of the base metal surface ceases and the isothermal solidification process begins because of the continuing diffusion of Zr and Co away from the joint and enrichment of the melt with base metal elements. From metallographic examination of specimens quenched from various temperatures, it was determined that the $L \to \gamma + \gamma'$ eutectic reaction occurs at 1220°C and the $L \to \gamma + \text{Ni}_5\text{Zr}$

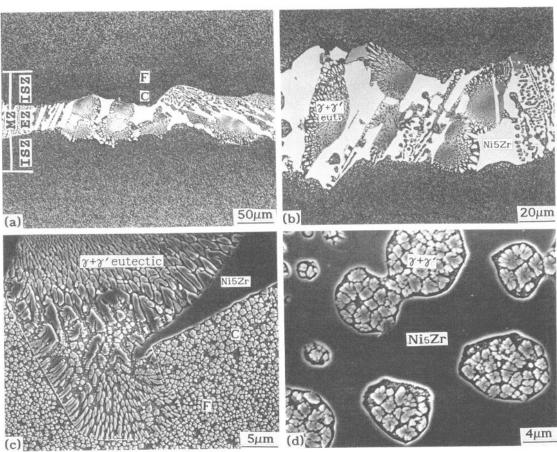


Figure 6 - Microstructure of the bond after 1270°C for 2 hours: (a) the melt zone (MZ), the isothermal solidification zone (ISZ) and the eutectic zone (EZ); (b) the γ + γ' eutectic and γ + Ni₅Zr eutectic formed in the EZ zone; (c) γ + γ' eutectic; (d) γ + Ni₅Zr eutectic showing the γ' precipitates in the γ phase of the cellular eutectic.

eutectic reaction takes place at 1150° C. These results are in agreement with DTA results for the Zr-bearing nickel-base superalloys (3). Thus, during cooling, a portion of the liquid left at the end of the isothermal solidification process transforms to the flower shaped eutectic $\gamma + \gamma'$ at 1220° C and the balance to a cellular eutectic of $\gamma + \text{Ni}_5\text{Zr}$ at 1150° C. On further cooling γ' is precipitated out in the γ phase of the cellular eutectic.

Zr promotes the formation of both the secondary γ' and the eutectic γ' (4). Our results show that the maximum solid solubility of Zr in the eutectic γ' is 2.9 wt (1.8 at %). Because Zr has a large solubility in the eutectic γ' and the volume percent of γ' in the eutectic γ' is much higher than that of γ , the eutectic reaction $L \to \gamma + \text{Ni}_5\text{Zr}$ is suppressed and the compound Ni $_5\text{Zr}$ in the bond is replaced by eutectic γ' . The concentration of Al and Zr in the bond plays an important role in determining the quantity, size and morphology of the secondary γ' phase. In the isothermal solidification zone, the size and shape of the γ' are very different and depend upon their location: the coarse cube-shaped γ' exists in a 20 μ m wide band starting from the edge of the eutectic zone (region C), and next to this band lies another band of 30 μ m width containing fine spherical γ' (region F), as shown in Figs. 6a and 6c.

As holding time at 1270°C is increased, the concentration of Zr in the eutectic zone decreases, as a consequence, there is a corresponding decrease in the width of eutectic zone in the bond (Table IV). After isothermal solidification at 1270°C for 24 hours, a part of the eutectic zone in the bond is filled with the $\gamma + \gamma'$ eutectic, and the $\gamma + Ni_5Zr$ eutectic becomes a narrow channel (Fig. 7). After 48 hours no Ni₅Zr or eutectic γ' is left and the secondary γ' containing 0.3 wt % Zr is uniformly distributed in the bond (Fig. 8). This structure is very similar to that of the base alloy after solid solution treatment (Fig. 9). Thus it is clear that TLP bonding of

Table IV Width and Composition of Eutectic Zone at 1270°C for Different Times

Time	Width	Composition (wt %)							
(h)	(µm)	Ni	Co	Cr	Zr	W	Mo	Ti	Al
0.25	73	71.2	5.6	4.1	13.5	1.6	0.7	1.0	2.3
2	67	72.6	6.1	4.2	9.3	2.4	0.7	1.3	3.4
8	57	74.0	4.9	4.8	5.3	3.0	1.5	2.0	4.5
24	26	73.5	5.0	5.7	3.6	4.1	1.7	1.8	4.6

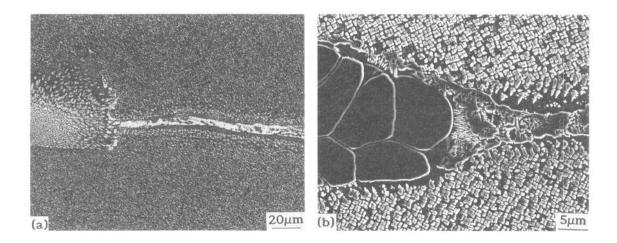
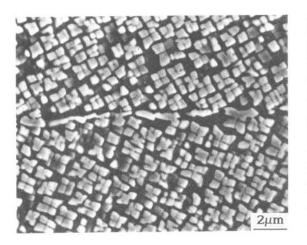


Figure 7 - Microstructure of bond after 1270°C for 24 hours.



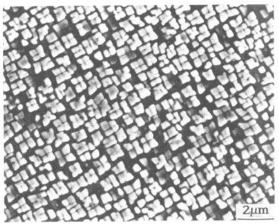


Figure 8 - Typical TLP microstructure of the bond after 1270°C for 48 hours. Secondary γ' is uniformly distributed in the γ phase.

Figure 9 - Morphology of the secondary γ' phase in the base alloy.

single crystal superalloy, without the use of Si and B can be achieved by incorporating Zr in the interlayer alloy.

Conclusions

- 1. Using a silicon and boron free interlayer alloy containing Ni-10Co-8Cr-4W-13Zr (wt %), ductile TLP bonds between single crystal nickel base superalloys have been produced by isothermal solidification at 1270°C for 48 hours.
- 2. This interlayer alloy is hypoeutectic and consists of the primary γ and γ + Ni₅Zr eutectic. Except for the higher solubility of Co, refractory elements Cr and W have very low solubility in the Ni₅Zr phase.
- 3. Using this interlayer alloy, brazing bonds can also be obtained by heating above 1250°C for different times. During heating, Zr promotes the formation of the γ' phase and the Ni₅Zr phase in the bond is replaced by the eutectic γ'

Acknowledgements

This research was supported by the Natural Sciences and Engineering Council Canada. The technical assistance from Mr. D. Mardis and J. Van Dorp is gratefully acknowledged.

References

- 1. D.S. Duvall, W.A. Owczarski, and D.F. Paulonis, "TLP Bonding: A New Method for Joining Heat Resistant Alloys," <u>Welding J.</u>, 53 (4) (1974). 203-214.
- 2. E.F. Bradley, <u>Superalloys A Technical Guide</u> (ASM International, Metals Park, OH 44073, 1988), 222.
- 3. S. Ma, Y. Zheng, and Y. Cai, "Solution and Transformation of Ni₅Zr in Cast Nickel-Base Superalloy," Acta Metall. Sinica, 17 (10) (1981), 522-528.
- 4. Y. Zheng, Y. Wang, J. Xie, P. Caron, and T. Khan, "Effect of Chemistry Modifications and Heat Treatments on the Mechanical Properties of DS Mar-M200 Superalloy", Superalloys 1988, ed. S. Reichman, D.N. Duhl, G. Maurer, S. Antolovich, and C. Lund (Warrendale, PA: The Metallurgical Society, 1988), 335-344.

- 5. D.N. Duhl, "Enhancement of Transverse Properties of Directionally Solidified Superalloys," <u>USPO 3,700,433</u>, (1972).
- 6. J.E. Doherty, A.F. Giamei, and B.H. Kear, "The Importance of Grain Boundary Morphology and Cohesion on Intergranular Strength," <u>Canadian Metallurgical Quarterly</u>, 13 (1) (1974), 229-236.
- 7. J.E. Doherty, B.H. Kear, and A.F. Giamei, "On the Origin of the Ductility Enhancement in Hf-Doped Mar-M 200," J. Metals, 23 (11) (1971), 59-62.