



Microstructural Aspects of Brazing a Ferritic Steel with Two Ni-S-B Braze Filler Metals

Boron diffuses into the steel to form borides along the grain boundaries, and on tempering at 750 C further diffusion to form $M_{23}(C,B)_6$ occurs

BY R. JOHNSON

For many years in the fabrication of structures utilizing metals, the welded joint has enjoyed unrivalled success. Indeed, in many applications there is unlikely to be any substitute joining process in the foreseeable future. In several applications, however, high temperature brazing has been shown to be not only a viable alternative in specific applications, but even to confer improved mechanical properties upon the joint.¹ The use of temperatures well below the fusion point of the metals used can obviously be of great value in the avoidance of extensive grain growth, the generation of relatively low melting point eutectics, and similar undesirable microstructures.

The selection of high temperature brazing for various applications has been the subject of continuing investigation in the Welding and Brazing Section at Springfields Nuclear Power Development Laboratories (SNL),^{2,3} and the results reported here were collected as part of a background survey into the brazing of transformable low alloy steels. The subsequent heat treatment of such joints after

Table 1—Analyses of Steel and Braze Filler Metals, Wt-%

	Steel	Braze filler metals	
		BNi2	BNi4
Ni	—	Bal.	Bal.
B	—	2.5	1.8
Si	0.5	4.2	3.6
Cr	9.0	6.8	0.02
Fe	Bal.	2.8	1.8
C	0.1	0.02	0.06
Mn	0.5	—	—
S	0.005	—	—
Mo	1.0	—	—
Trace elements	Co, Cu, Ni	Ca, Mn	Al, Ca, Mg, Mn, Mo

brazing and before they can be used in service is of great importance but is

Paper presented at the Ninth International AWS-WRC Brazing Conference in New Orleans, Louisiana, during April 4-6, 1978.

R. JOHNSON is with the Springfields Nuclear Power Development Laboratories, United Kingdom Atomic Energy Authority, Springfields, Salwick, Preston, England.

outside the scope of this paper. Instead, the paper concentrates on the identification of the phases formed during the brazing operation and their possible effects on the performance in service of joints brazed with these filler metals.

Experimental

The compositions of the steel and braze filler metals used are given in Table 1. The steel is under review for various applications in nuclear plant; after discussions with brazing experts, two nickel-silicon-boron braze filler metals were selected as being the most suitable of the commercially available alloys for brazing this steel. The two selected were BNi2 and BNi4, both of which have good flow properties. The nickel alloys generally have good corrosion resistance, which is necessary to match the corrosion properties of a medium-chrome steel such as this one.

The braze filler metals were obtained in powder form and later BNi4 was obtained as rolled strip. The parallel-joint specimens were assembled

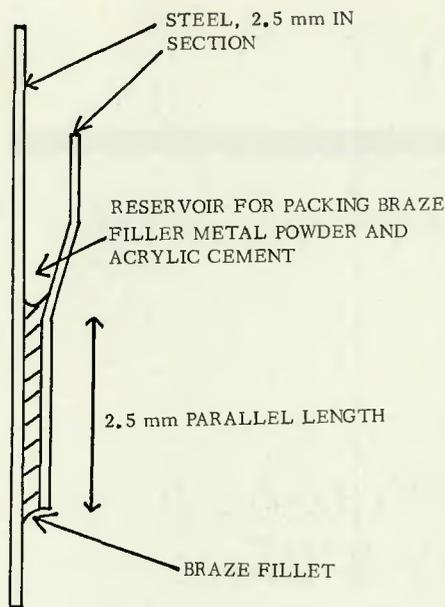


Fig. 1—Brazed joint assembly

with 2.5 mm (0.1 in.) thick blanks of steel and joint gaps between 25 and 100 μm as shown in Fig. 1. The braze filler metal powders were mixed with an acrylic cement binder, which should leave no residue after volatilization during the brazing cycle, and placed in the reservoir at the top of the specimens. The joints were brazed in a vertical position cold-walled vacuum furnace.

The standard brazing temperatures employed were 1150 C (2102 F) for BNi4 and 1100 C (2012 F) for BNi2, both being superheated about 100 C (180 F) above their liquidus temperatures.¹ The furnace was evacuated to 10^{-1} torr at room temperature and was then raised to 1000 C (1832 F) at a rate of 60 C (108 F) per minute, after which a 5 min hold at temperature was employed to permit the equalization to take place. The joints were then heated at the same rate to the selected brazing temperature and held at temperature for 2 min (standard heat treatment) or longer, after which the power to the furnace was cut. The furnace cooled to 800 C (1472 F) in about 8 min, whereat argon was flushed through to increase the rate of cooling so that 200 C (392 F) was reached within a further 15 min.

When tempering was required, it was performed in the same furnace for a standard time of 2 h at 750 C (1382 F). After heat treatment the specimens were spark machined into two along the vertical center line to show a transverse section of the joint. The pieces were then mounted in araldite and polished to a 1 μm diamond finish. The microstructures of the joints were revealed by chemical and electrochemical etching, using the solutions given in Table 2.

Table 2—Compositions of Chemical Etchants

Braze filler metals	2% conc. sulphuric acid 30% glycerol 68% water Etching potential 4.5 V
Steel	5 g ferric chloride 15 ml conc. hydrochloric acid 120 ml water

Microstructures of the Standard Specimens

The specimens were examined on both optical (Reichert) and electron microprobe (Camebax) microscopes in order to differentiate between and analyze the phases present. Optical pictures of the braze reservoirs are seen in Figs. 2 and 3. For the BNi4 reservoir in Fig. 2 there are three separate phases apparent, while in the BNi2 reservoir (Fig. 3) the same three phases can be seen together with a fourth.

A summary of the analyses of all phases is given in Tables 3 and 4 where it can be seen that the regions of similar appearance in the two braze reservoirs are indeed the same phases. The light phase adjacent to the steel is α -nickel, which contains silicon but no boron. The light grey phase that has a



Fig. 4—Braze reservoir of BNi4. $\times 800$ (reduced 40% on reproduction)

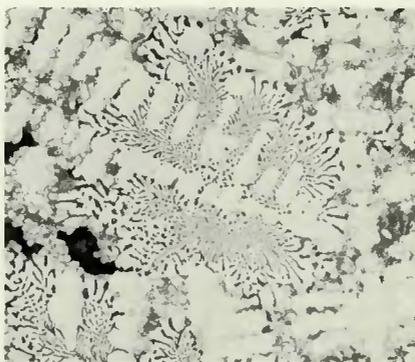


Fig. 5—Chromium carbide phase in BNi2. $\times 200$ (reduced 40% on reproduction)

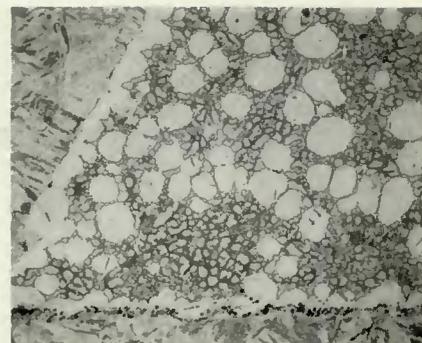


Fig. 2—Braze reservoir of BNi4. $\times 200$ (reduced 50% on reproduction)

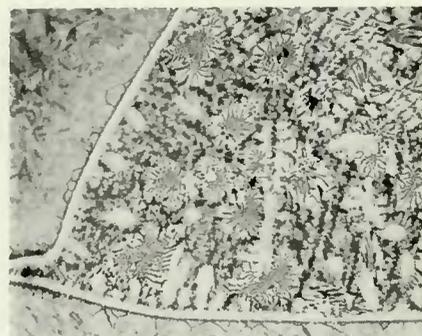


Fig. 3—Braze reservoir of BNi2. $\times 100$ (reduced 50% on reproduction)

rounded outline similar to the α -nickel is found to be a nickel boride that contains no silicon, while the mottled phase (which is seen in clear relief in the microprobe picture in Fig. 4) consists of the same nickel boride and a nickel silicide.

The fourth phase, seen only in BNi2, is a black and white lamellar or rod-like eutectic in the form of a rosette, the light phase being α -nickel and the black phase being essentially a chromium carbide. The eutectic is always formed adjacent to or around the arms of the initial α -nickel dendrites—Fig. 5. The analyses show that iron and chromium have entered from the steel, and not surprisingly are especially prevalent in the α -nickel adjacent to the steel. The new elements appear to segregate to the α -nickel phase within the bulk of the reservoir rather than into the boride or silicide.

Within the brazed joint, the phases present can number between four and one. The first phase to disappear is the final boride-silicide eutectic, and the next phase is the boride itself. Finally only the α -nickel remains in the joints, and it appears that the number of phases present decreases with the joint gap—Figs. 6 to 9. Within the brazed joints the ingress of steel elements is greater, as might be expected with the smaller diffusion distances involved.

While the braze filler metal is gaining in elements from the steel by erosion and diffusion, at the same time

Table 3—Microprobe Analysis of BNi4 Joint after Brazing, Wt-%^(a)

	Ni	Fe	Cr	Si	B	Other
<i>As-brazed</i>						
<i>Fillet:</i>						
Dendrite-at steel	69	23	2.6	3.5	0	—
-internal	71	22	2.3	4.7	—	—
Ni-B	75	15	2.3	0.2	1.7	—
Eutectic-average	74	11	1.8	8.3	0.7	—
-dark	73	14	2.6	2.5	—	—
-light	78	6.4	0.9	15	—	—
<i>Joint with eutectic:</i>						
Dendrite-at steel	74	19	3.0	3.4	0	—
Ni-B	80	11	2.0	0.2	2.0	—
Eutectic-dark	80	10	2.1	3.1	—	—
-light	79	4.5	0.8	15	—	—
Precipitate in steel	1.5	79	11	0.4	2.0	—
Steel	0	87	11	0.2	—	—
Black particles	14-45	31-38	3-5	1.7	0	+10% Ca + Al
<i>Joint with no eutectic:</i>						
Dendrite-at steel	43	43	5.8	1.6	—	—
-internal	64	25	4.0	3.1	0	—
Precipitate in steel	0-1	66-74	17-19	0.1-0.5	0-2.3	1.0-3.7%C + 1% Mo
Black particles-edge	13	18	2.3	23	—	—
-center	1.3	1.3	0.2	68	—	—
<i>Tempered</i>						
<i>Fillet:</i>						
Dendrite-at steel	2.0	64	10	0.2	—	—
-internal	71	22	2.6	3.3	0	—
Ni-B	75	15	1.9	0.6	1.2	—
Eutectic-average	74	15	1.0	6.8	0	—
Precipitate in steel	0-0.7	64-71	10-20	0.2-0.7	—	Some Mo
Precipitate in dendrite	72	17	1.8	6.2	0	Unresolvable.

^(a)All figures are corrected to two significant figures or one decimal place; estimated accuracy is about 67% ± 0.6%; 23% ± 0.3%; 3% ± 0.1%

Table 4—Microprobe Analysis of BNi2 Joint After Brazing, Wt-%^(a)

	Ni	Fe	Cr	Si	B	Other
<i>As-brazed</i>						
<i>Fillet:</i>						
Dendrite-at steel	69	19	6.3	3.8	—	—
-internal	74	16	4.5	4.8	—	—
Ni-B	78	11	2.9	0.1	1.6	—
Eutectic-dark	79	10	2.4	3.9	1.4	—
-light	78	5.2	1.0	12	0	—
Precipitate in steel	0.5-6	68	15-17	0.2	3.6	0-1.0%C
<i>Joint with eutectic:</i>						
Dendrite-at steel	70	18	5.0	4.6	—	—
Cr-C eutectic-light	70	19	5.9	4.0	0	0%C
-dark	5-26	6-17	19-55	0.1-0.5	0	3-21%C often holes
<i>Tempered</i>						
<i>Fillet:</i>						
Dendrite-at steel	64	22	7.1	3.6	0	—
-internal	74	15	7.5	4.1	—	—
Ni-B	81	8.6	3.1	0.2	1.2	—
Eutectic-average	81	8.1	2.1	9.1	—	—
Precipitate in steel	0.3	68	17	0.3	1.1-2	1.5%C
Precipitate in dendrite	78	13	3.5	5.7	0	Unresolvable
-dark	76	14	4.9	4.6	—	—
-light	76	13	3.4	5.7	—	—
Precipitate-free zone	80	12	3.6	3.9	—	—
Black particle	0.6	0.7	0.2	27	—	Oxygen = 100%
Cr-C eutectic-light	—	—	—	—	0	0%C
-dark	—	—	—	—	0.4-0.9	15-36%C

^(a)All figures are corrected to two significant figures or one decimal place; estimated accuracy is about 67% ± 0.6%; 23% ± 0.3%; 3% ± 0.1%

the braze filler metal elements are entering the steel. In BNi4 nickel and silicon enter by bulk diffusion to a distance of about 15 μm, but the boron which diffuses mainly along the austenite grain boundaries migrates to a

maximum distance of up to 140 μm. In BNi2 the respective values are 8 and 60 μm. It can be seen in Figs. 10 and 11 that the boron forms almost continuous stringers of iron boride along the boundaries. On the optical micro-

graph it can be seen that a dark-etching region surrounds the borides; this is not present after tempering. It was found by a process of autoradiography, a method that uses the bombardment of the specimen by

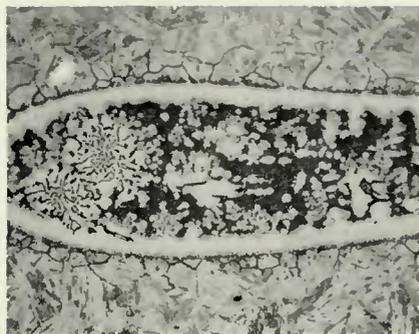


Fig. 6—Brazed joint of BNi2 with four phases present. $\times 200$ (reduced 50% on reproduction)

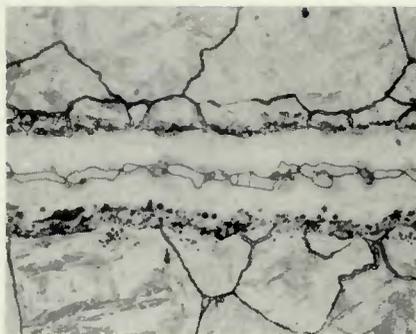


Fig. 10—Boride particles in the steel (BNi4). $\times 500$ (reduced 50% on reproduction)

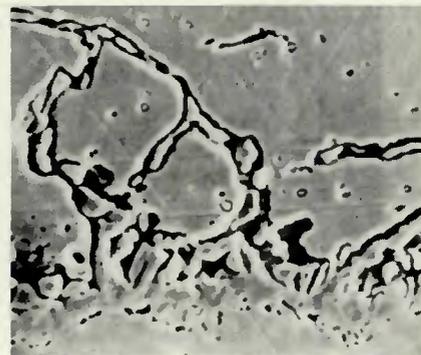


Fig. 11—Boride particles in the steel (BNi4). $\times 2000$ (reduced 50% on reproduction)

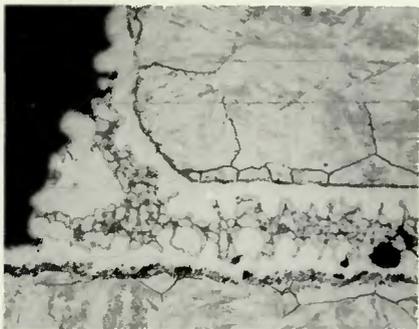


Fig. 7—Brazed joint of BNi4 with three phases present. $\times 200$ (reduced 50% on reproduction)

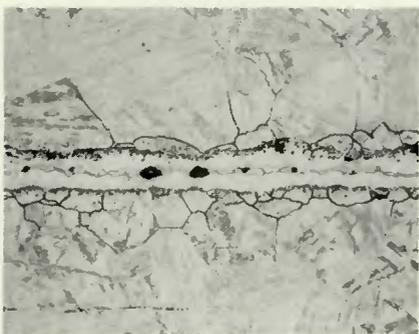


Fig. 8—Brazed joint of BNi4 with two phases present. $\times 200$ (reduced 50% on reproduction)



Fig. 9—Brazed joint of BNi4 with one phase present. $\times 200$ (reduced 50% on reproduction)

neutrons to cause the n, α reaction in which boron transmutes to lithium with the release of an α -particle, which is subsequently caught by the cellulose acetobutyrate film on top of the specimen. Autoradiography indicated that the boron had diffused to carbides either formed during the tempering operation or residual from the brazing cycle—Fig. 12. The intergranular iron borides were also seen to have spheroidized slightly during tempering.

It can be noted that there appears to be little effect of tempering on the morphology of the braze filler metal, except that a very fine silicon-rich precipitate could be seen in the α -nickel adjacent to the boride-silicide eutectic regions of the braze. There appeared to be little other change in microstructure, except that the nickel boride phase had spheroidized slightly after a temper of 240 h at 750 C (1382 F).

Microstructure of Non-Standard Specimens

Sometimes the brazing operation is not carried out in the optimized manner. Consequently, there can be excursions to longer times, perhaps when rebrazing, or to higher temperatures due to operator or machine malfunction. Accordingly, it was decided to incorporate variations in time and temperature into the program to see if any undesirable properties resulted from this. With this information it is possible to define the limits within which the brazing operation must be carried out in order to achieve the desired joint properties.

Some specimens were held at the brazing temperature for 10 and 50 min. It was seen that the main effect was on the extent of boron diffusion into the steel. In BNi4 this increased from the maximum of 140 μm at 2 min to about 155 μm after 10 min and to about 190 μm after 50 min—Figs. 13 and 14. For BNi2 the respective values were 60, 85

and 160 μm —Table 4. The only effect on the braze filler metal microstructure was that in BNi2 the morphology of the α -nickel and chromium carbide eutectic altered from a rosette form to a more parallel lamellar form—Figs. 15 and 16.

Other specimens were brazed with BNi4 at temperatures higher than 1150 C (2102 F), and it was macroscopically apparent that the aggression of the braze filler metal increased with temperature—Fig. 17. It was anticipated that the extent of boron diffusion would increase with temperature but a new reaction intervened at temperatures above 1180 C (2156 F). The angu-

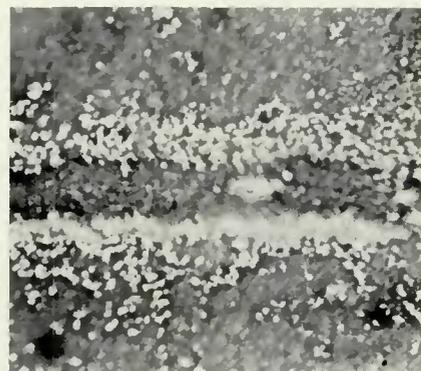


Fig. 12—Boron autoradiograph (top) and equivalent optical micrograph (bottom) of BNi4 brazed joint. $\times 500$ (reduced 50% on reproduction)

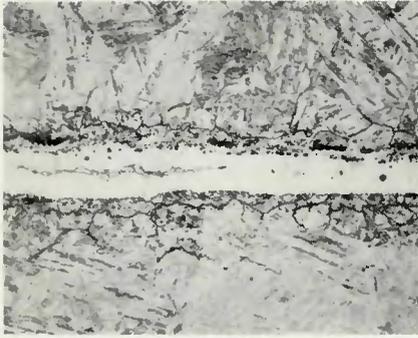


Fig. 13—Joint of BNi4 brazed for 10 minutes at 1150 C. $\times 200$ (reduced 50% on reproduction)

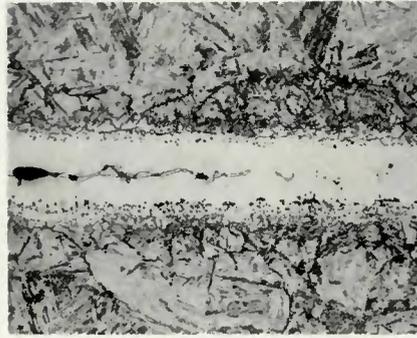


Fig. 14—Joint of BNi4 brazed for 50 minutes at 1150 C. $\times 200$ (reduced 50% on reproduction)

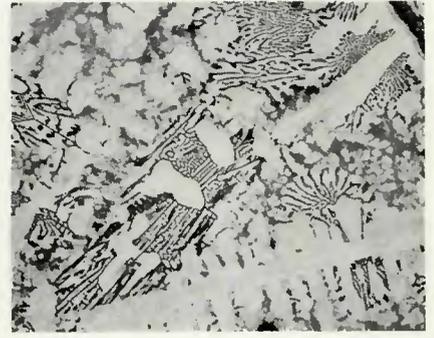


Fig. 15—Joint of BNi2 brazed for 10 minutes at 1100 C. $\times 200$ (reduced 50% on reproduction)

larity of the borides along the grain boundary was lost, and the grain boundary region contained a mottled phase. It was apparent that the grain boundaries had liquated during brazing and had solidified as an iron-iron boride eutectic.

The regions between the liquated boundaries were now seen not to etch up in the normal martensitic manner, but to remain unattacked—Fig. 18. It is interesting to note that, while the brazed joints liquate at the end away from the reservoir, at and near the reservoir there is no liquation even at 1225 C (2237 F)—Fig. 19. This was confirmed in tests placing some braze filler metal on top of a piece of steel and taking the specimen through a brazing cycle. With these specimens liquation was seen to start at about 1260 C (2300 F) for BNi4, but interestingly in the range 1175–1200 C (2147–2192 F) for BNi2.

As the temperature rises, the liquated grain boundaries become less apparent and the microstructure within the parallel joint and the braze reservoir changes—Figs. 20 and 21. The erosion within the braze filler metal reservoir and fillet increases with temperature as seen before, but within the joint the erosion is not as apparent. The white non-etching grains still delineate the extent of the diffusion of the braze filler metal, apart from

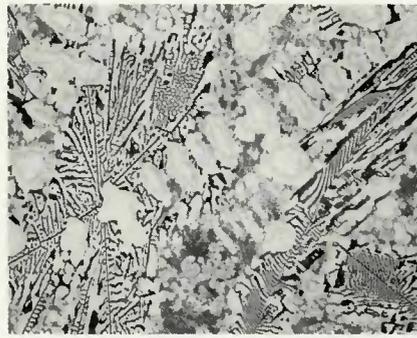


Fig. 16—Joint of BNi2 brazed for 50 minutes at 1100 C. $\times 200$ (reduced 50% on reproduction)

isolated grain boundaries that appear to be preferentially etched to some extent.

Discussion: Joints Brazed Under Standard Heat Treatment Conditions

Braze Filler Metal

There are few published phase diagrams for nickel-based braze filler metals, the work of Knotek and Lugscheider being a welcome exception.⁵ However, much information concerning the solidification processes within the braze filler metal can

be gleaned from the nickel-boron and nickel-silicon binary phase diagrams⁶ and the number and morphology of the phases seen within the braze reservoirs, fillets and joint gaps.

In the binary phase diagrams it can be seen that α -nickel can contain up to about 8 wt-% silicon but only about 0.2 wt-% boron. It is thus not surprising that in both braze filler metals the α -nickel contains about the average concentration of silicon in the melt, which is below 8 wt-%, but no boron. Where the dendrites in the reservoir are very close to the steel interface and there is substantial incorporation of iron and chromium into the phase, it appears the solid solubility of silicon within the α -nickel is somewhat reduced. At the steel interface the α -nickel phase extends some 15–30 μm uniformly into the reservoir, but further in there are signs of the classical dendrite morphology.

In the BNi2 braze filler metal alone the next phase to nucleate is the α -nickel and chromium carbide eutectic. It can be seen in Fig. 5 that this eutectic reaction is very closely associated with the primary α -nickel dendrites; filling the interstices between some dendrite arms and also at the ends of the dendrites. The morphology of the eutectic is similar to that of pearlite (albeit that the latter is a eutectoid reaction), except that there

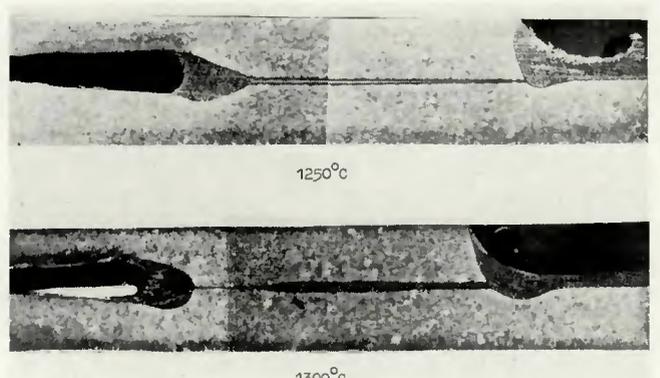
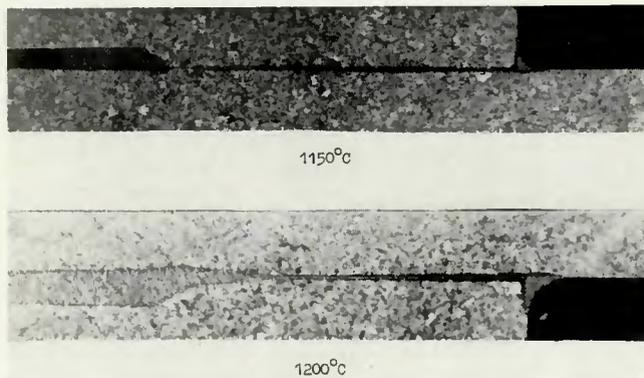


Fig. 17—Effect of increasing braze temperature on erosion of steel by BNi4. $\times 5$ (reduced 45% on reproduction)



Fig. 18—Joint adjacent to reservoir of BNi4 showing liquated microstructure. $\times 100$ (reduced 50% on reproduction)



Fig. 19—Joint adjacent to reservoir of BNi4 brazed at 1225 C. $\times 50$ (reduced 50% on reproduction)

are not lamellae but rather rods of carbide. The fact that it is not the dendrites that transform to this eutectic but the interstices, and also because α -nickel can contain no boron, means that the reaction in BNi2 is not of a eutectoid form.

Similar chromium carbide eutectics have been identified in several superalloys containing the two elements. It may be possible that the carbide phase contains some boron, even though the boron signal is low in most analyses, for it is known that substitution of boron for carbon is possible in an $M_{23}X_6$ lattice to form a mixed borocarbide.⁷ The carbide may not be of the $M_{23}X_6$ type but with the atomic radii and covalency of the two elements being so similar, some degree of substitution of one for another can presumably occur in other carbides and borides.

The next phase to be formed in both braze filler metals is the nickel boride. This may be formed with the α -nickel in a eutectic or peritectic reaction. In the plain binary nickel boron system the first eutectic at the nickel rich end is that between α -nickel and Ni_3B . However, later work by Knotek and Lugscheider on nickel-based braze filler metals has shown that the formation of Ni_3B can prove to be difficult and that the metastable eutectic between α -nickel and Ni_2B can form preferentially.⁵ So from the binary

phase diagram and the nickel-based alloy the existence of a eutectic is inferred.

There have been suggestions that the reaction may be a peritectic, and certainly in the braze reservoir of BNi4 the classical coating of the α -phase by the β -phase (nickel boride) seems to be prevalent around and between the arms of the dendrites. At the braze fillet (a term which is used here to define the region of braze filler metal at the opposite end of the joint from the reservoir) where a greater degree of alloying is present, the covering of α by β is not as apparent—Fig. 22. There is still coverage between the dendrite arms, but there are regions of α -nickel in the middle of the fillet (and reservoir) that have little or no nickel boride associated with them. If a peritectic reaction were occurring then the nucleation of α -nickel after the β -phase had begun to form would be impossible. So the presence of boride-free areas of α -nickel argues for the eutectic rather than the peritectic reaction.

The peritectic type of formation of nickel boride between the dendrite arms can also be explained by the eutectic reaction. As the boride grows, it rejects silicon into the last remaining liquid. Nickel can contain some 7-8 wt-% silicon at these temperatures. When there is little increase in iron and chromium contents that could reduce the solid solubility of other elements, the 3 wt-% of silicon in BNi4 would not saturate the α -nickel. The dendrites can thus continue to grow with the nickel boride; they can accommodate the excess silicon, and with the small amount of boride—and hence small amount of silicon rejection—this will continue until solidification is complete. With BNi2 the α -nickel and chromium carbide eutectic has filled many interstices between the dendrite arms, so the presence of borides there is not as frequently seen as in BNi4.

The eutectic between α -nickel and the boride does not have one of the typical morphologies associated with this reaction, the boride generally forming as a rounded phase. The reason for this could be partly the difficulty of nucleation of the phase and partly the high interfacial energy between that and the α -nickel, which is seen in the similar iron-iron boride eutectic reaction.⁸ The growth of large widely separated particles of boride would certainly not be hampered by the rate of boron diffusion: in steel at these temperatures it can diffuse about 10 μm in one second, so in the liquid braze filler metal the diffusion should be at least as rapid as that.

The question as to whether Ni_3B or Ni_2B is formed is unfortunately some-

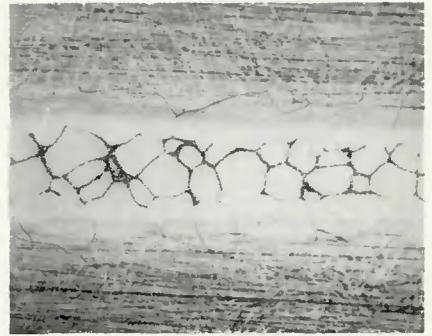


Fig. 20—Joint of BNi4 brazed at 1300 C. $\times 100$ (reduced 50% on reproduction)

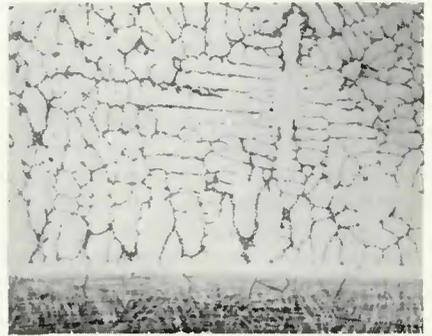


Fig. 21—Reservoir of BNi4 brazed at 1300 C. $\times 100$ (reduced 50% on reproduction)

what unresolved by the microprobe analyses. The direct boron estimation is somewhat low, due to absorption of the X-rays by other heavier elements; recommended procedure is to subtract the sum of the amounts of all other elements present from 100% for the boron content. In BNi4 and BNi2 this proves to be about 7-8 wt-% boron, which lies between the 5.5 wt-% required for Ni_3B and the 8.5 wt-% required for Ni_2B .

The content certainly lies nearer to Ni_2B , and BNi2 is similar to the braze filler metals used by Knotek and Lugscheider,⁵ in that it contains some chromium before there is any further enrichment by alloying with the steel; this would be further evidence to support the boride being Ni_2B . The levels of iron and/or chromium may, in fact, be important not only in determining which boride is nucleated, but also in making the separation of the boride a eutectic reaction with the α -nickel rather than a peritectic. However, without X-ray diffraction analysis, the confirmation of the boride as being Ni_2B cannot be made.

As the boride is forming, silicon is being rejected into the remaining liquid, because the boride contains no silicon. While the α -nickel can accommodate some increase in silicon content this is obviously limited and hence in the final eutectic a high silicon-nickel phase is formed. In fact, this eutectic does not appear to

contain any α -nickel at all. For this reason it should be termed pseudo-binary in nature rather than ternary.

The other phase in the final eutectic is the nickel boride. The morphology of the eutectic is as expected in eutectic reactions, with the two phases intimately mixed. Again, however, the nickel boride has a very rounded appearance again indicating a high interfacial energy.

The silicide that should be anticipated from the nickel-silicon binary phase diagram is the β -phase, containing some 13 wt-% silicon. From the silicon-rich end of the diagram this β -phase forms by a peritectic reaction between the γ -phase (containing 16 wt-% silicon) and the remaining liquid. Thus if there are any nucleation difficulties with the β -silicide, in a manner similar to the nickel boride, then the γ -phase may in fact develop from the eutectic reaction with α -nickel. It should be noted that this final eutectic is some 140 C (252 F) below that of the binary diagram, and this may aid the separation of the γ -phase rather than the β -phase. The microprobe analysis is again somewhat inconclusive in differentiating between the β and the γ , because the amounts of silicon measured vary between 12 and 16 wt-%. However, there may be evidence in the tempered specimens that the γ -silicide is formed, and this is discussed later.

It is interesting to note that in the fast freezing of the final eutectic that the nickel boride contains 3-4 wt-% silicon, with which it is normally incompatible. This again may have interesting consequences on the reactions that occur on tempering.

All of these phases are seen in the braze reservoirs and fillets. However, within the parallel joints themselves the number of phases present can be less. It appears that the number of phases is governed by the width of the joint gap—and the narrower the gap, then the smaller the number of phases. The reason for this is basically the loss of boron from the braze filler metal into the steel. With a large joint gap there is still a lot of boron left in the braze filler metal even after this loss, and all the phases are present. But as the joint gap width decreases, the amount of boron within the joint becomes critical. First, enough boron is lost to the steel to reduce the amount of nickel boride formed. This, in turn, means that the amount of silicon rejection is reduced until it is at a level that the α -nickel can contain the slight excess of silicon in the remaining liquid without recourse to the formation of the silicide. Thus no final eutectic is formed.

When the joint gap is so small that all the boron is lost to the steel, there is

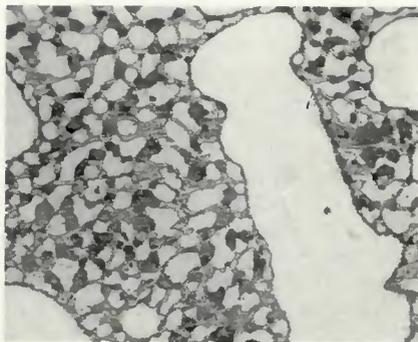


Fig. 22—Braze fillet of BNi4. $\times 500$ (reduced 50% on reproduction)

obviously no nickel boride formed, and in BNi4 only the α -nickel is seen within the joints. In BNi2 the formation of the α -nickel and chromium carbide eutectic is obviously dependent to some extent on the amount of carbon gained from the steel, as joints have been made in BNi2 with again only α -nickel present.

Tempering for 2 h at 750 C (1382 F) does not seem to have very much effect on the morphology and distribution of the phases. Indeed, there appears to be little or no decrease in the amount of nickel boride present to indicate that the boron was still being lost rapidly to the steel. One new phase was discerned, however, in the α -nickel regions adjacent to the final eutectic. The very fine particles (0.2-0.5 μm in diameter) precipitated in this region were too small to be resolved and individually analyzed on the microprobe. However, the general area showed an increase in silicon content, signifying that the particles were even richer in silicon.

The source of the silicon enrichment is not clear. Although the extremities of the dendrite regions will contain the maximum amount of silicon that is soluble at the solidification temperature (due to the rejection of silicon by the large nickel boride particles), this source would create these precipitate areas uniformly around the edges of the dendrites. The precipitates are, however, definitely localized around the regions of final eutectic, so presumably the source of the silicon is there. If γ -silicide were formed on solidification then this might degenerate to the β -form with the rejection of silicon during the tempering, and this silicon would then diffuse into the α -nickel to produce a silicon-rich precipitate.

The other source of silicon within the final eutectic is the nickel boride, which normally does not contain any silicon at all. It was found on analysis, however, that these regions of boride did contain 3-4 wt-% of silicon, due no doubt to the rapid solidification of the

last liquid braze filler metal. On tempering, this silicon that is effectively quenched *in situ* could be rejected into the α -nickel regions where it could combine with the free nickel to form a silicide. (The only way in which the excess silicon from the boride could be assimilated by the nickel silicide within the final eutectic is by forming a higher silicide, but this is not likely to be energetically favorable compared to formation of the lower silicide in the α -nickel.)

It is not possible to determine which of these two sources of silicon, or whether indeed both are operating to produce the excess silicon because the two phases were not individually analyzed in the tempered condition; the average analysis which was measured would see a drop in silicon content from either or both reactions occurring. The greater probability is that the nickel boride is rejecting the silicon contained therein. However, it is not clear whether or not there is any silicide degradation that may indicate the initial phase was γ -silicide.

Previous work on nickel-based braze filler metals has shown that temperatures around 900 C (1652 F) are necessary to cause the degeneration of the metastable Ni_2B to Ni_3B .⁵ Accordingly, the tempering treatment here of 2 h at 750 C (1382 F) is probably insufficient to begin this reaction. It is thus not surprising that no boron-rich particles are created within the α -nickel in the same manner as the silicon-rich precipitate, and the absence of these particles does not necessarily infer that the boride is not Ni_2B but Ni_3B .

The one specimen that was tempered for 240 h at 750 C (1382 F) showed very little difference in the morphology of the phases within the brazed joint, except that the nickel boride is slightly more spheroidized than it is after 2 h. This shows that the boron is still diffusing into the steel at these temperatures and that the boride is thus reducing its surface area of contact with the other phases.

Steel

Nickel and silicon diffuse into the steel through the grains, and their presence can be revealed by a dark-etching region adjacent to the α -nickel of the braze filler metal. In BNi4, which is brazed at 1150 C, (2102 F), the limit of this penetration is some 15 μm whereas in BNi2, which is brazed at only 1100 C (2012 F), penetration is some 8 μm . While the ingress of nickel and silicon have no effect other than slightly affecting the transformation and etching characteristics of the martensite, the ingress of boron into the steel has the more dramatic effect

of diffusing along the grain boundaries to form iron borides.

The iron borides can be seen as white particles in an almost unbroken line along the boundaries in optical micrographs of high magnification and the microprobe pictures; under the optical microscope they appear to have a dark-etching halo around them. Although this may be thought to be an enhanced etching effect due to the different chemical potentials of the particles and the steel, more likely it is an atmosphere of free boron around the particles as it diffuses along the boundaries. A reason for this interpretation is the fact that after tempering for 2 h at 750 C (1382 F) the atmosphere disappears; this obviously would not be likely to occur if it were merely an etching effect (the chemical etching potential of martensite and its associated strain energy is not greatly different from that of ferrite). This feature is discussed in more detail later.

The extent of the boron penetration is about 6-8 times that of the nickel and silicon. This is not altogether surprising when the sizes of the atoms and their diffusion coefficients in steel at the brazing temperature are considered. The particles are not just iron boride (Fe_2B) but contain the normal carbide-forming elements chromium and molybdenum, as well as an appreciable amount of carbon itself (especially when it is considered that the boron absorbs some of the carbon signal and so the true value of carbon concentration is underestimated).

There is little effect of the 2 h temper at 750 C (1382 F) on the bulk diffusing elements nickel and silicon. The iron borides do change somewhat, but not in the relative amounts of iron and chromium that might indicate that there is some change in crystallographic structure of the particles. Rather, there appears to be some replacement of the boron by the carbon that is rejected from the martensite on tempering. Additionally the free boron alongside the borides, that is thought to cause the dark etching characteristic in the as-brazed joints, disappears.

As the steel is tempered, the 0.1% carbon is largely rejected by the ferrite, and at 750 C (1382 F) the stable carbide formed is of the M_{23}C_6 type.⁹ This is also known to be able to accommodate boron substitutionally within the lattice in place of the carbon to form an $\text{M}_{23}(\text{C},\text{B})_6$ borocarbide.⁷

That the free boron at least has diffused to the newly-formed carbides in this manner would be impossible to verify by conventional optical microscopy, but it has been confirmed by a relatively new technique called autoradiography. As explained previously

the specimen is bombarded by neutrons and the positions of the boron atoms are revealed by the entrapment of the α -particles released by the degeneration of boron to lithium.¹⁰ This technique clearly shows that boron has diffused to the carbides in the grains and grain boundaries immediately adjacent to the iron borides.

The increase in boron penetration during tempering is very limited which is to be expected with a 400 C (752 F) temperature difference between the brazing temperature of BNi4 and 750 C (1382 F). Direct comparisons using standard diffusion equations are not permissible, because of the transformation from ferrite to austenite between the two temperatures. However, a rough guide to thermally activated processes is that often a reaction rate is approximately doubled by a rise in temperature of 10 C (18 F). Thus the diffusion rate at 1150 C (2102 F) would be approximately 2^{10} or 10^{12} times that at 750 C (1382 F) if there were no phase change. The increase in time from 2 to 120 min is clearly of little consequence when comparing the distance of penetration at 750 C (1382 F) to that at 1150 C (2102 F), for with those times the distances will be in the ratio 1:10⁹.

Variations in Microstructure

Variations with Brazing Time

The only effect of the extended times of 10 and 50 min at brazing temperature on the morphology of phases within the brazed joints was in the form of the α -nickel and chromium carbide eutectic in BNi2. Whereas with the 2 min brazing cycle the eutectic appeared to be a rosette or rod-like in form, after long holding times the appearance is much more lamellar and is quite similar to pearlitic morphologies seen in the eutectoid reaction in steels. The reason for this has not been confirmed by microprobe analysis, but it seems likely that the additional time at temperature allows for a greater ingress of iron and chromium from the steel into the braze filler metal.

BNi2 has been seen in this work to be more aggressive toward steel than BNi4, despite the higher brazing temperature used for the latter. The effect of this increased alloying content could be the reason why the morphology of the eutectic changes, since it is known that relatively minor differences in alloy composition can have marked effects on the solidification of an alloy. Indeed, this is a similar situation to the braze reservoir of BNi4 appearing to reveal a peritectic reaction by which the nickel boride separates, whereas the more highly alloyed braze fillet clearly exhibits a eutectic

reaction.

The effect of longer hold times at the brazing temperature is as expected qualitatively in that the penetration of both the intergranular boron and the bulk penetration of the silicon and nickel increased with time. The increase was not always what might have been expected quantitatively.

If a simple diffusion equation is assumed, where the distance diffused by the species entering the matrix, χ , is related to the diffusion coefficient for the temperature D_T and the time t :
$$\chi^2 = \text{constant} \cdot D_T \cdot t$$

We find $\chi_{t1}/\chi_{t2} = (t_1/t_2)^{1/2}$ as the constants cancel out. With time of 2, 10 and 50 min the expected ratio of penetrations should be 1:2.2:5. In Table 5 it can be seen that the bulk diffusion of both braze filler metal elements is in fair agreement with this ratio, but that the boron penetration is overestimated, especially for BNi4.

One complication with the boron is that it forms a compound with the matrix as it diffuses in. As a result, the diffusion profile is complex. Moreover, another effect could well be the exhaustion of the boron within the brazed joint. Since the BNi2 contains 50% more boron than the BNi4 and is being brazed at a temperature 50 C (90 F) below that of BNi4, it is not surprising that this exhaustion is reflected more in the penetration values of BNi4 than in those of BNi2. In the 2 min BNi4 specimen there was a little nickel boride formed along the center line of the joint, in the 10 min specimen only a trace and in the 50 min specimen none at all—this is with similar average joint gaps.

The greater amount of boron in BNi2 means that more boride is formed within the same joint gap so that depletion should not occur so readily. As a point in fact, however, the 10 min specimen (with a smaller joint gap) had only a little boride remaining and the 50 min specimen had only isolated traces left. With larger joint gaps the depletion of boron may not be so noticeable, and the increase in boron penetration would perhaps lie closer to that anticipated theoretically.

Variations with Brazing Temperature

A series of specimens were brazed at nominal temperatures of 1150, 1200, 1250 and 1300 C (2102, 2192, 2282 and 2372 F) in order to assess what detrimental effects could occur with a temperature overshoot during brazing. These tests showed the aggressive nature of the braze filler metal with respect to the steel, especially in the braze reservoir and fillet regions. That the joint region is not so greatly attacked is probably an indication that,

Table 5—Penetration into the Steel and the Joint Gaps of the Specimens Used, μm ^(a)

Time at temperature, minutes	Penetration into steel				Gap ^(c)	Eutectic ^{(c), (d)}	
	Pool ^(b)		Joint ^(b)				
	Boron	Bulk	Boron	Bulk			
<i>First Series</i>							
BNi4:							
2	105/95	12/10	150/100	15/10	25-50-70 70-30-20	0-20-55 40-(5)-0	
10	150/110	20/15	160/105	25/15	70-50-60 25-30-40	30-(10)-25 0-0-0	
50	190/140	25/20	185/120	35/25	40-50-60 50-40-35	0-0-0 0-0-0	
BNi2:							
2	60/45	8/5	65/40	10/8	60-50-60 45-35-20	20-20-25 (10)-(5)-0	
10	75/55	13/10	75/55	20/15	65-40-35 25-45-65	20-(5)-0 0-(5)-25	
50	160/120	35/25	150/105	45/30	50-45-60 60-75-80	0-0-0 0-0-(5)	
<i>Second Series</i>							
BNi4:							
2	135/90	10/8	140/95	10/7	50-45-65 110-85-60	15-(5)-20 70-40-20	
10	125/100	20/13	150/100	25/15	45-75-70 50-40-40	(10)-15-10 (10)-0-0	
50	175/115	30/25	175/115	35/25	25-45-50 85-55-40	0-0-0 0-0-0	
BNi2:							
2	85/65	13/10	70/55	15/10	20-15-10 40-50-25	0-X-X 20-15-(5)	No braze* < 5
10	115/80	25/15			10-10-5 25-10-10	0-X-X 0-X-X	< 3 < 15
50	175/140	45/35			35-10-25 40-15-10	0-X-X 0-X-X	< 10 < 5

^(a)All figures in μm are rounded to the nearest 5 except for those relating to the visible joint gap at which no braze flow occurred.*

^(b)Pool and joint penetration figures signify maximum/mean values.

^(c)Width of gap/eutectic measured at end-center-end of joint.

^(d)Brackets around figures indicate the center line eutectic is not continuous; X—signifies no braze filler metal present in the joint.

after the initial capillary flow of the braze filler metal through the joint, there is little interchange of elements along the length of the joint—also that the middle regions of the joint soon become saturated with the amount of steel elements they can contain and also lose boron and silicon to the steel, thus diminishing the aggressiveness of the braze filler metal to the steel.

It was anticipated that these tests would reveal the transformation of austenite to delta-ferrite, and indeed the ferrite can be seen to a limited extent in the two highest temperature brazed joints. The other anticipated feature was an increase in the extent of boron penetration with temperature; this was achieved in an interesting manner. In all brazed joint specimens, there was a white non-etching band in the steel along and parallel with the braze filler metal in the joints; and also the steel grain boundaries had liquated to form a mottled phase in these regions. Since no liquation had been seen before at 1150 C (2102 F) in BNi4 joints, the temperature control of the specimens was deduced to be poor and repeat specimens were required. A second series of specimens

were then brazed, at the temperatures 1130, 1180, 1200, 1225 and 1250 C (2066, 2156, 2192, 2237 and 2282 F) in order to define more closely the temperature at which the grain boundaries liquate. This series showed that there is no sign of liquation at 1180 C (2156 F) and below, but that it is present at 1200 C (2192 F) and above.

From the iron-boron binary diagram⁶ it can be seen that a eutectic between iron and iron boride, Fe₃B, exists at about 1175 C (2147 F) and at 3.5 wt-% boron. This means that below the liquation temperature the boron diffuses into the grain boundaries to form discrete particles of iron boride, but that above this temperature the presence of boron adjacent to the steel causes liquation to occur.

The width of the liquated zone will be about twice that of the discrete boride particles, and the presence of this liquation means that irrigation of the steel grains by nickel, silicon and even boron (as it is known that this element can diffuse transgranularly as well as intergranularly at high temperatures¹¹) can occur from all sides rather than from the line of the joint only. Since nickel and boron are austenite

stabilizers, the reason for the non-etching appearance in ferritic chloride of the steel adjacent to the braze filler metal could be the fact that austenite is retained during cooling.

Diffusion through liquid metals is very rapid. It appears that once the specimen has liquated at 1200 C (2192 F) there is no significant increase in boride penetration over another 100 C (180 F) rise in temperature. The limiting factor must be the amount of boron within the braze filler metal, and with BNi4 and these joint gaps the limit of penetration appears to be about 300 μm . As the steel is eroded, the iron and chromium can form similar eutectics within the braze filler metal and, as the temperature increases, the morphology of the filler metal changes. The nickel dendrites occupy a much greater volume in the reservoir and fillet as well as in the joint, and the boron forms a eutectic between the dendrite arms.

It is interesting to note that, in the 1200 and 1225 C (2192 and 2237 F) specimens, in the second series of specimens the liquation does not occur around the braze reservoir or the part of the joint immediately adjacent

to it. Previous discussion has mentioned the effect of alloying with the steel elements along the brazed joint; it appears that the liquation temperature with pure BNi4 can be somewhat lowered by this alloying.

Confirmation of this view has not been carried out by microprobe analysis but by the placing of pieces of BNi4 braze filler metal on top of specimens of the steel so that no capillary flow with the attendant alloying reactions occur. The first series of specimens went in 10 C (18 F) steps from 1160 up to 1260 C (2120 to 2300 F), and no liquation of the grain boundaries was discernible until the first signs were seen in the 1260 C (2300 F) specimen. If the interchange of braze filler metal and steel elements cause the decrease in liquation temperature, then the alloying effect is obviously time and temperature dependent; further tests must be performed before a complete understanding of this phenomenon is realized. In this context it is interesting to note that similar specimens using BNi2 braze filler metal reveal that liquation begins in the temperature range of 1175-1200 C (2147-2192 F), in agreement with the BNi4 brazed joints.

Implications

In order to make serviceable brazed joints, the braze filler metal should be ductile and contain no regions of weakness or brittleness. With these nickel-based filler metals this ideal is realized in narrow joints less than 40-50 μm , where only α -nickel is formed. Larger joint gaps allow the formation of borides and the boride-silicide eutectic along the center line of the joint. As these phases are known to have a high hardness (about 900 VPN) they obviously possess only very limited ductility and could crack if high tensile stresses are generated along or across the joint.

While a long hold time at brazing temperature increases the loss of boron to the steel to some extent, the normal method of eliminating the boron—using a very high temperature soak—is not a viable proposition if liquation of the grain boundaries within the steel is to be avoided. With regard to the corrosion properties of the braze filler metal within the joints the α -nickel will probably be almost as corrosion-resistant as pure nickel. When there are two or more phases present, there is the possibility of enhanced corrosion by galvanic coupling, although there are as yet no data to indicate that the resistance to corrosion of the boride and silicide is far lower than that of the α -nickel.

Within the steel the diffusion of nickel and silicon into the bulk grains

will probably not have a great effect on the mechanical or corrosion properties. On the other hand, the almost continuous array of boride particles along the prior austenite grain boundaries might be thought to be detrimental to the mechanical properties of the joints. Hard particles with limited ductility, similar to the nickel boride in the braze filler metal, might be capable of rupturing to form fatigue crack nuclei. However, it is known from work on grain boundary carbides that the matrix material must be plastically flowing, i.e. near its yield stress,¹² in order to generate fiber stresses on the particles that are high enough to cause rupture. It is not common practice to design brazed joints to accommodate plastic flow within the substrate. Although there is a potential source of crack nuclei within the grain boundary particles, in practice the necessary conditions for this cracking may not be attained.

Similar arguments can be used concerning the iron-iron boride eutectic present after liquation of the grain boundaries. This eutectic is known to be very brittle in high boron steels, but again high stresses are required and in many applications will not be attained. Whether or not the liquated joint is less tough than the normal non-liquated one has yet to be proved by mechanical testing.

The iron boride particles and the Fe_2B eutectic may adversely affect the corrosion resistance of the steel. Both can form a galvanic couple with the steel to promote corrosion, especially when it is remembered that this is a lean chromium steel and that the incorporation of chromium into the grain boundary phase will denude the adjacent regions of grains of that element.

A low resistance to corrosion may thus be endowed on these regions in the same way that the precipitation of carbides can cause weld decay in stainless-steels. However, there is one important feature of the brazed joint structure in this respect. It is that wherever this galvanic coupling and chromium denudation can occur, there will be an α -nickel barrier of some 15-25 μm thickness that the corroding medium must pass through before reaching the steel. Thus again, although a potential lowering of the corrosion resistance of the steel exists, in practice it is unlikely to be realized.

Conclusion

The solidification processes occurring in joints of a chromium steel brazed with BNi2 and BNi4 have been rationalized following the identification of the phases that can form therein. The number of phases seen in

the joint depends on the joint gap. The boron diffuses into the steel to form borides along the grain boundaries, and on tempering at 750 C (1382 F) further diffusion to form $\text{M}_{23}(\text{C},\text{B})_6$ boro-carbides occurs.

Prolonged hold times at the brazing temperature increase the amount of boron entering the steel, but increased brazing temperatures can cause liquation of the grain boundaries of the steel to occur. The possible effects of the different microstructures on the mechanical and corrosion properties of the joints have been discussed in the light of this work.

Acknowledgments

The author wishes to thank his colleagues—especially Mr. G. Brough, Mr. G. E. Sheward and Mr. A. F. Taylor—at SNL for their help in the preparation of specimens and discussions on the results obtained. The autoradiography and microprobe analysis were performed at Harwell by Mr. D. Mapper and Dr. H. E. Bishop respectively. The work was funded by NPC Risley and RNL Risley.

References

1. Peaslee, R. L., "Brazing Comes of Age," *Mechanical Engineering*, June 1962.
2. Sheward, G. E., and Bell, G. R., "Development and Evaluation of a Ni-Cr-P Brazing Filler Metal," *Welding Journal*, 55 (10), Oct. 1976, Research Suppl., pp. 285-s to 292-s.
3. Sheward, G. E., "Brazing Applied to the Development and Manufacture of Nuclear Fuel Elements," *Welding Journal*, 49 (7), July 1970, pp. 548 to 558.
4. Wall Colomoy Corporation, Nicobraz Data Sheets 2.1.3 and 2.1.17 Rev. B.
5. Knotek, O., and Lugscheider, E., "Brazing Filler Metals Based on Reacting Ni-Cr-B-Si Alloys," *Welding Journal*, 55 (10), Oct. 1976, Research Suppl., pp. 314-s to 318-s.
6. Smithells, C. J., *Metals Reference Book*, Butterworths, 1976.
7. Williams, T. M., and Talks, M. G., "Effect of Boron on the Precipitated Phases in Aged Type 316 Austenitic Stainless Steel," *J.I.S.I.*, Nov. 1972, p. 870.
8. Chadwick, G. A., *Metallography of Phase Transformations*, Butterworths, 1972.
9. Orr, J., "A Summary of the Properties of 9% Cr 1% Mo Steel," British Steel Corporation Report PROD/MEP/6600/-/72/D, 1972.
10. Hughes, J. D. H., and Rogers, G. T., "High-Resolution Autoradiography of Trace Boron in Metals and Solids," *J. Inst. Metals*, Vol. 95, 1967, p. 299.
11. Feduska, W., "The Nature of the Diffusion of Brazing Alloy Elements into Heat Resisting Alloys," *Welding Journal*, 40 (2), Feb. 1961, Research Suppl., pp. 81-s to 89-s.
12. Barnby, J. T., and Peace, F. M., "Influence of Carbides on the Low-Cycle Fatigue Strength of an Austenitic Steel," ISI Conference on the Effect of Second-Phase Particles on the Mechanical Properties of Steel, Scarborough, 1971.