Wettability of Nickel Alloys by Boron-Containing Brazes

Wetting characteristics are correlated to changes in filler metal composition and process variables

BY W. F. GALE AND E. R. WALLACH

ABSTRACT. The origins of a nonmonotonic trend in wetting of Ni-Si-B filler metals with a composition of Ni-Cr substrates, as observed during sessile drop wetting tests, has been examined. It is suggested that this trend arises from interactions between isothermal solidification and reduction of the substrate oxide by filler metal constituents.

Introduction

The joining of nonweldable gamma-prime or oxide-dispersion-strengthened nickel alloys for elevated-temperature service may be achieved by the use of fluxless vacuum brazing. Nickel-based brazes containing boron as a melting-point depressant are particularly attractive as filler metals for this process since it is possible, given a suitable postbraze heat treatment, to disperse the highly mobile interstitial boron in the substrate. This can raise the possibility of maintaining base metal service-temperature mechanical properties. Difficulties can, however, be encountered in forming sound joints due to the poor wettability of these filler metals, especially since the degree of wetting is very dependent upon exact compositional and process conditions. The work described in this paper forms part of a project examining the influence of filler metal/base metal interactions on wettability for a range of nickel-based filler metals.

The paper examines the wetting of Ni-Si-B filler metals on a range of model nickel-chromium substrates, rather than on commercial alloys, in order to assess the influence of gradual changes in composition on wetting and its interrelationship with process variables. The majority of previous studies (Refs. 1–3) have focused on the influence on wettability and/or joint formation of individual mechanisms, such as vacuum deoxidation or isothermal solidification due to diffusion of filler metal constituents into the substrate. However, new evidence is presented in this paper that suggests that such studies need to be extended to cater for interactions between the different mechanisms.

The work described in this paper follows studies (Refs. 4, 5) on the wetting behavior of the BNi-3 filler metal (Ni-4.5%Si-3.2%B) on nickel and nickel-chromium substrates in the range 0 to 20% chromium. A marked variation in spreading was observed with substrate chromium content. Peaks in wetting were produced at 1065°C (1949°F) on 10% and 20% chromium substrates, although the peaks were not evident as the brazing temperature was increased to 1150°C (2102°F). These peaks in wetting were correlated with a comparatively low rate of isothermal solidification of the filler metal compared to the rates on other substrate compositions. However, a mechanism for the nonmonotonic variation in isothermal solidification behavior with substrate chromium content could not be established. In addition, evidence was presented on a chemical reaction between the substrate oxide around the periphery of filler metal droplets and boron emanating from the filler metal. It is proposed, in the present work, that an interaction between isothermal solidification and such chemical reactions can account for the trend in isothermal solidification behavior observed previously.

KEY WORDS

Brazing Filler Metal
Ni-Si-B Filler Metal
Nickel Alloys
Wettability
Vacuum Brazing
Isothermal Solidification
Wetting Tests
Reactive Elements
Oxide Reduction
Composition Changes

Experimental Techniques

Sessile drop wetting tests were conducted using 3-mm (0.12-in.) diameter punched disks of 51-μm-thick BNi-3 (Ni-4.5%Si-3.2%B), MBF 35 (Ni-2.17% B-7.31%Si) and MBF 1005 (Ni-46.7%Pd-6.1%Si) rapidly solidified brazing foils. Nickel and nickel-5, -10, -15 and -20% chromium substrates were employed. Wetting tests were conducted in a 7×10^{-5} mbar vacuum using a 20-min hold at 1065°C for BNi-3 and MBF 35 or at 1110°C (2030°F) for MBF 1005. Wetting of the three filler metals was compared on substrates in the as-ground condition (600-grit silicon carbide paper finish). Also, sessile drop tests were conducted with BNi-3 on ground substrates that were preoxidized in air for 2 h at 900°C (1652°F). Details of the sessile drop technique may be found elsewhere (Ref. 4).

Results and Discussion

Isothermal Solidification

Isothermal solidification occurs during holding at a temperature in excess of the initial liquidus temperature of the filler metal as a result of compositional changes in the filler metal, which cause an increase in the liquidus temperature of the filler metal (Refs. 3, 6). In the case of Ni-Si-B filler metals, it has been found in earlier parts of the present investigation (as outlined in the introduction of this paper) that low wetting was correlated with a rapid onset of isothermal solidification and high wetting with a relatively low rate of isothermal solidification.

Compositional changes in the filler metal leading to isothermal solidification can result from diffusion of chromium from the substrate into the filler metal and/or diffusion of boron and silicon out of the filler metal into the substrate. The chromium content of the substrate could influence

W. F. GALE and E. R. WALLACH are with the Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, England.

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any of these interdiffusion processes; either directly (in the case of chromium diffusion) or indirectly (for boron or silicon). However, the extent of any interdiffusion and its effect on the liquidus temperature of the braze will be dependent upon the initial relative chemical potentials of the diffusing species. Thus, it would be expected that filler metals of widely differing initial compositions would show differing trends in isothermal solidification behavior, and hence wetting, with varying substrate chromium content.

In a comparison of the extent of wetting as a function of substrate chromium content (Fig. 1), all three filler metals produced peaks in wetting on 10% and 20% chromium substrates. A peak wetting for MBF 1005 was also observed on nickel substrates. In searching for a common compositional factor to explain the peaks in wetting on the 10% and 20% chromium substrates, it is noted that all of the filler metals examined contained silicon. However, comparison of the results for the high-boron, low-silicon BNi-3 filler metal with the high-silicon, low-boron MBF 35 filler metal suggests that the silicon content of the filler metal is not the predominant factor. This is concluded because the MBF 35 shows a consistently lower extent of wetting than BNi-3 throughout the range of substrate chromium contents studied. In addition, comparison of BNi-3 and MBF 35 shows that the extent of wetting is not a simple function of initial liquidus temperature because the liquidus temperature of MBF 35 (1035°C/1895°F) is 19°C (32°F) lower than the liquidus temperature of BNi-3.

Thus, in summary, the similarity of the wetting behavior of the three filler metals would tend to suggest that the presence of peaks in wetting on 10% and 20% chromium substrates is not directly attributable to modification of the filler metal liquidus temerature by interdiffusion between the filler metal and the substrate.

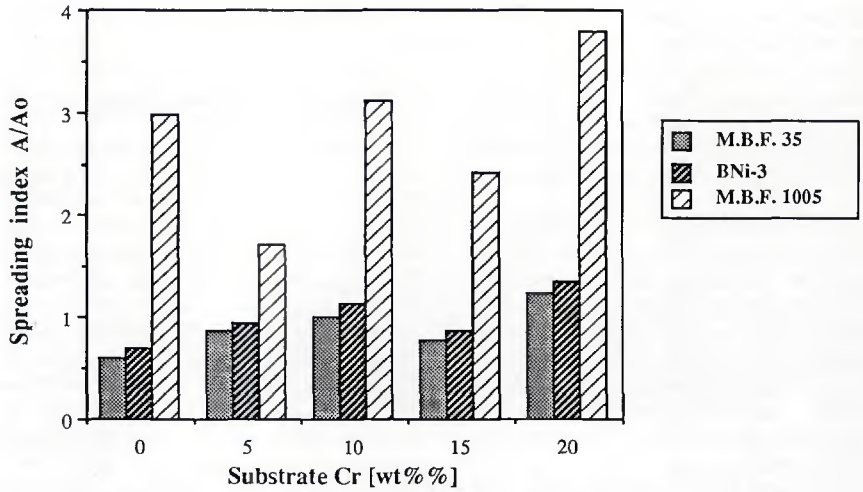

Fig. 1 — Wetting behavior on nonpreoxidized substrates.

Reactive Element Effects

An alternative explanation for the observed peaks in wetting on 10% and 20% chromium substrates might be associated with the presence of reactive elements (boron and/or silicon) in all of the filler metals. These reactive elements are capable of reducing nickel and chromium oxides under the prevailing experimental conditions, and reduction of the oxide layers on the substrates by boron and/or silicon originally emanating from the braze metal might occur. In fact, this has been observed experimentally (Refs. 4, 5).

In a system in which the extent of wetting is controlled by isothermal solidification, the occurrence of a chemical reaction may also be of importance because the reaction can deplete the liquid filler metal of the reacting species. If the reacting species is also a significant melting-point depressant in the filler metal, as is the case with boron and silicon, then its depletion will hasten the onset of isothermal solidification.

At first sight, it might seem unlikely that the reduction of an oxide layer of the order of tens of nanometers in thickness could significantly influence the overall composition of a braze droplet of the order of tens of micrometers in thickness. However, it has been observed experimentally (Ref. 5) that isothermal solidification needs to occur only at the edge of a droplet where the droplet is relatively thin (and not over the whole of the droplet surface) for wetting to be greatly impeded. Thus, the effect of the change in the composition of the filler metal will be dependent largely on the volume of the liquid in the vicinity of the droplet edge rather than on that of the entire droplet. Isothermal solidification of the edge of the drop may be delayed to some extent by homogenization of the droplet due to diffusion of the melting-point depressants in the liquid. However, as wetting takes place, an increase in the diffusion distance from the center of the droplet is produced. In addition, wetting reduces the liquid-solid contact angle and this results in a decrease in the volume of liquid at the edge of the droplet. Thus, any homogenization would be expected to decrease with increased wetting, although this requires further investigation.

The hypothesis that the termination of wetting is controlled by the volume of liquid at the droplet edge, rather than that of the bulk droplet, also serves to explain an apparent discrepancy between the wetting experiments described here and data on transient liquid-phase (TLP) bonding (Ref. 3), for which the rate of isothermal solidification was correlated directly with the extent of boron diffusion into the substrate. In the case of wetting, the onset of isothermal solidification in a small volume of material at the droplet edge is important. In contrast, in the TLP studies, it is the onset and completion of isothermal solidification throughout the width of a relatively thick braze joint that matters. Thus, for a given extent of reaction, the influence on the composition of the TLP bond would be less significant than for the edge of a braze droplet.

Influence of Oxide Reduction on Isothermal Solidification

Assuming that there is an interaction between the depletion of alloying elements in the filler metal due to reduction and isothermal solidification, its influence on the observed trend in wetting with substrate chromium content needs to be examined. The chromium content of the substrate determines the thickness and composition of the substrate oxide and hence the amount of the reducing species that will be required for the reaction. Thus, it is necessary to consider the variation in oxide thickness and composition with substrate chromium content.

The relative trend in parabolic oxidation rate constant (PORC) with substrate chromium content is shown in Fig. 2 for oxidation in air. The peak value of the PORC occurs in the region of 5% chromium and corresponds to the composition at which chromium ceases to dope NiO and the formation of $NiCr_2O_4$ and/or Cr_2O_3 commences. As the chromium content of the substrate is increased, further precipitation of Cr_2O_3 occurs and the PORC decreases (Refs. 7, 8). The relative trend in oxidation with substrate chromium content is a function of cation diffusion through the oxide layer (Ref. 9). Thus, it would be expected that only the absolute rates of oxidation, and not the relative trend with substrate chromium content, would be influenced by changes in oxy-

gen pressure, providing the oxide layer on the substrate remains stable. Thus, the trend in oxidation with substrate chromium content pertaining to air should also be relevant to a vacuum atmosphere. This is supported by the experimental observation, using hot-stage light microscopy under similar conditions to those employed in the brazing trials, that the 5% chromium substrate oxidized at a greater rate than the other substrate compositions studied. Additional support is provided by XRD studies of the oxide layer present on the substrates. It was observed that the largest NiO peaks were produced on 5% chromium substrates, which is consistent with the trend in oxidation described above.

In light of the above, the possible effect of oxide composition and thickness on the reduction reactions can be considered. However, a knowledge of the reactions that take place is necessary. The XRD studies conducted previously indicated that the boron oxides B_2O_3 and B_6O were formed as a result of reaction between boron and the substrate oxide layers (Ref. 5). Experimental evidence for the nature of the reaction products in silicon fluxing reactions has not been obtained, and it is therefore assumed that the oxide product of the reaction will be the stoichiometric oxide SiO_2.

Thus, the following reactions need to be considered:

$$NiO + \frac{2}{3}B = Ni + \frac{1}{3}B_2O_3$$
$$Cr_2O_3 + 2B = 2Cr + B_2O_3$$

$$NiO + 6B = Ni + B_6O$$
$$Cr_2O_3 + 18B = 2Cr + 3B_6O$$

$$NiO + \frac{1}{2}Si = Ni + \frac{1}{2}SiO_2$$
$$Cr_2O_3 + \frac{3}{2}Si = 2Cr + \frac{3}{2}SiO_2$$

It can be seen in all cases that, for any of the reducing species, the number of moles of the reducing species required to reduce a given quantity of oxide exists in a 3:1 ratio comparing Cr_2O_3 to NiO. Thus, under the experimental conditions used in the present investigation, for which it is thermodynamically possible to reduce both Cr_2O_3 and NiO, the amount of melting-point depressant that is depleted from the filler metal will increase as the substrate oxide changes from NiO to Cr_2O_3 associated with chromium additions to the substrate. Similar arguments apply to the reduction of the spinel phase $NiCr_2O_4$. However, simultaneously with this increased tendency to form chromium-containing oxides, a decrease in the thickness of the oxide layer occurs. Thus, the number of moles of the reducing agent required to deoxidize a unit area of the substrate will depend both on the number of moles of each substrate oxide phase present, which is a function of oxide thickness, as well as the number of moles of the reducing agent required to reduce one mole of the various oxide phases as discussed above. Therefore, minima in the extent of melting-point depressant depletion would be expected on substrates that have either easy-to-reduce oxides (Ni), very thin oxides (Ni-20%Cr) or a compromise between ease-of-reduction and thickness (possibly Ni-10%Cr). These minima would in turn be expected to correspond to delayed isothermal solidification, and hence enhanced wetting.

In order to verify that the trend in wetting observed experimentally could be attributed to the nature of the substrate oxide, an attempt was made to exaggerate the influence of the oxide by preoxidation, and hence reduce the influence of other variables. In this study (Fig. 3), peaks in wetting on 10% and 20% chromium were observed on preoxidized substrates. Since this trend correlates with that produced under vacuum brazing conditions, the experiment supports the hypothesis that the peaks in wetting are associated with the nature of the substrate oxide. However, a peak in wetting was also produced on the preoxidized nickel substrate, which was absent on the standard nonpreoxidized nickel substrate, and therefore further investigation of this is required.

A further area of anomalous behavior is the effect of vacuum quality on the wetting of MBF 1005 when compared to that of BNi-3. In the case of BNi-3, improvements in vacuum quality merely serve to reduce the influence of the oxide layer and produce a general enhancement of wetting (Ref. 5). For MBF 1005, however, as vacuum quality is enhanced a complete change in mechanism occurs to a process apparently dominated by tunneling under the substrate oxide (Ref. 10). The divergence between the behavior of boron-containing and nonboron-containing filler metals would seem to emphasize the importance of boron in the isothermal solidification processes as was discussed earlier.

The practical implications of the phenomenon described in this paper are as follows. In vacuum brazing practice, the occurrence of reactions between the filler metal and the substrate is usually considered to be advantageous. Moreover, comparison of the current investigation with studies using less mobile and/or less reactive filler metals, such as those containing phosphorus, suggests that extensive reactions with the substrate oxide are not always necessary in vacuum brazing. Therefore, in cases where the fluxing agent is both an important melting-point depressant and mobile, as is the case with boron, such reactions may be undesirable since they result in marked sensitivity of wetting to the nature of the oxide on the substrate as determined by vacuum quality, etc.

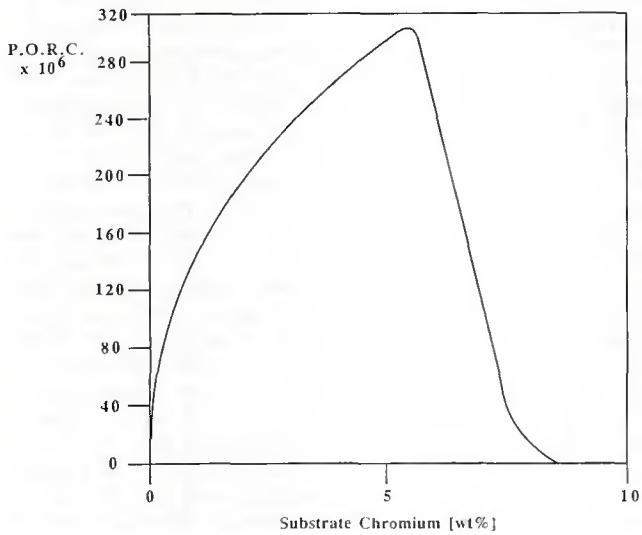

Fig. 2 — Parabolic oxidation rate constant in air (Ref. 8).

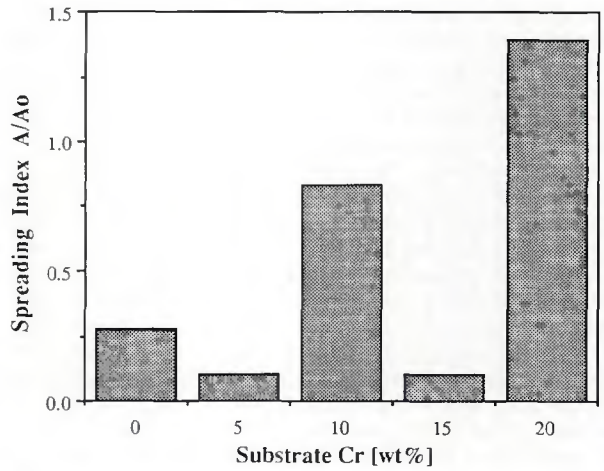

Fig. 3 — Wetting of BNi-3 on preoxidized substrates.

Conclusions

A study has been made of the causes of the variation in isothermal solidification with substrate chromium content during sessile drop wetting tests. In this study, the following conclusions were drawn:

1) The trend in wetting with substrate chromium content was not directly attributable to the nature of the alloying reactions between the filler metal and the substrate.

2) Reaction with the oxide layer on the substrate by filler metal constituents can deplete the filler metal of elements, such as boron and silicon, that also serve as melting-point depressants.

3) Depletion of the melting-point depressants from the braze joint by reactions with the substrate surface oxides hastens isothermal solidification.

4) The extent of wetting was correlated with the rate of isothermal solidification, which was in turn influenced by ease of reduction of the substrate oxide.

5) The occurrence of extensive reaction between the filler metal and the substrate oxide may not be desirable in vacuum brazing practice if the reacting agent is also an important melting-point depressant.

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