

Brazing Filler Metals Based on Reacting Ni-Cr-B-Si Alloys

Specific compositions determine the reaction whereby a low melting component with suppressed hard phases can solidify to form a higher melting braze metal

BY O. KNOTEK AND E. LUGSCHEIDER

The use of Ni-Cr-B-Si alloys for surfacing against wear is increasing. Various applications are found in industry, especially in glass, ceramic, cement, plastics and steel production (Ref. 1).

In Europe more than a half of the atomized Ni-Cr-B-Si metal powders — about 500 t/year in total — are used in the glass industry for surfacing various tools in the production of bottles and other glass parts (Ref. 2).

As a result of research work we have done on these alloys, we think they are suitable for brazing in production and repair work far more than they are used for this now (Ref. 3). But further research on melting and wetting properties is needed in connection with the structure of the quaternary system Ni-Cr-B-Si.

Structure of Ni-Cr-B-(Si) Alloys

A wide range of applications is suggested by the melting properties of these alloys, the most important of which is the lowering of the melting point by addition of boron to nickel. This effect can be seen in Fig. 1, a comparison of our results to those of

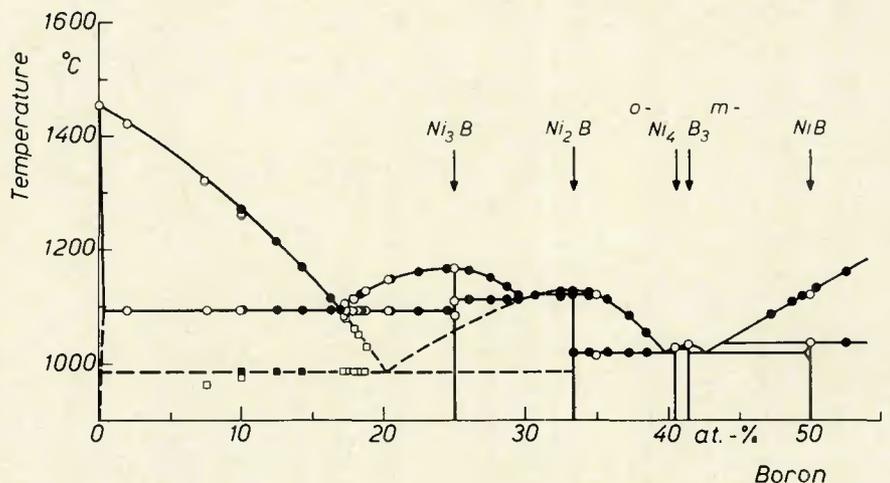


Fig. 1—Ni-B system. Circular points denote heating; squares, cooling. Solid black, after Schobel and Stadelmaier (Ref. 4); open points, present paper

Schobel and Stadelmaier (Ref. 4). The melting point of a nickel boron alloy decreases to 1092 C with increasing boron content; this is the eutectic temperature of the Ni-Ni₃B eutectic (17 at.% B). It should be noted that the crystallization of the phase Ni₃B can be suppressed in nickel-rich alloys. In this case a metastable eutectic Ni-Ni₂B is formed at 20.5 at.% boron and 986 C. The metastable Ni₂B is transformed into the stable boride Ni₃B at about 900 C. Therefore the alloys melt according to the stable Ni-Ni₃B system. The metastable crystallization of binary nickel-boron alloys can be observed up to 19 at.% boron.

We also found this metastable crystallization in nickel-rich Ni-Cr-B-(Si) alloys. The cooling rate and the over-heating of the molten alloy seem to have an important influence on the metastable crystallization of the Ni-Ni₂B system. The 100 C lower melting of the metastable eutectic is of interest from a brazing standpoint (Ref. 5). Thus boron is the main alloying element to change melting properties. Alloying these Ni-(Cr-)B alloys with silicon results in an additional reduction of the melting point. However, the plasticity of the alloys is also reduced by the addition of boron and/or silicon. Therefore the addition of these alloying elements is limited to

O. KNOTEK is Dr. Professor and E. LUGSCHEIDER is Dr. Ing., Lehrstuhl B and Institut für Werkstoffkunde, Aachen, West Germany.

Paper was presented at the 5th AWS International Conference held during the 55th AWS Annual Meeting at Houston, Texas, May 6-10, 1974.

some appropriate percent.

Technically used alloys consist of a relatively plastic nickel-chromium matrix with varying volumes of hard particles (borides) resulting in various properties. Two of the four ternary systems, the basis of the quaternary Ni-Cr-B-Si alloys, have been known for several years. These are the Ni-Cr-Si (Refs. 6, 7, 8) and the Cr-B-Si (Ref. 9) systems. The nickel-chromium-boron-system, the most important for technical alloys, was established at 1000 C by the authors (Ref. 10).

The importance is based on the fact that nickel can dissolve a large quantity of silicon, as substitution mixed crystals, but very little boron. In the binary system Ni-Si the solubility of silicon in nickel is 7.5 wt.% (14.6 at.%) at 1000 C; in the Ni-B system the solubility of boron is only 0.1 wt.% (0.2 at.%). Therefore just borides can be considered in technically used Ni-Cr-B(Si) alloys and knowledge of the Ni-Cr-B system is necessary. Figure 2 shows the phases of the Ni-Cr-B system we have found at 1000 C.

In ternary alloys there are the known nickel borides Ni_3B , Ni_2B , $o-Ni_4B_3$ and NiB . The binary $m-Ni_4B_3$ cannot be stabilized in ternary alloys. There are also the binary chromium borides CrB_2 , CrB_4 , CrB , Cr_5B_3 and Cr_2B and at high boron contents the ternary borides $Cr_2Ni_3B_6$ and Cr_3NiB_6 , observed by Kuz'ma (Ref. 11) first. These phases have the V_5B_6 and V_2B_3 structure. Contrary to former reports on Ni-Cr-B alloys, Cr_2B is the boride with the highest chromium content. Cr_4B could not be observed. The solubility of boron in nickel is not increased by the addition of chromium as expected.

In the nickel-boron-silicon system our investigations show a decreasing solubility of Si in Ni at increasing boron content. At 850 C the limit of the formation of the silicide Ni_3Si decreases linearly from 12.5 wt.% silicon at 0% boron to 0% silicon at 5.8 wt.% boron.

For instance, technically used alloys (10 at.%, 2 wt.% B) contain the silicide Ni_3Si at silicon concentrations higher than 5 wt.% Si. The formation of silicides will not be changed by addition of chromium in principle. This was found by x-ray diffraction and metallographic investigations with samples of Ni-Cr-B-Si alloys containing 10 at.% B.

Most of the Ni-Cr-B-Si alloys used for surfacing and brazing contain the nickel boride Ni_3B and the chromium borides CrB , Cr_5B_3 and Cr_2B as hard phases.

During our research on the Ni-Cr-B-Si alloys we determined the melting points of a series of ternary Ni-Cr-B alloys. The determination was made

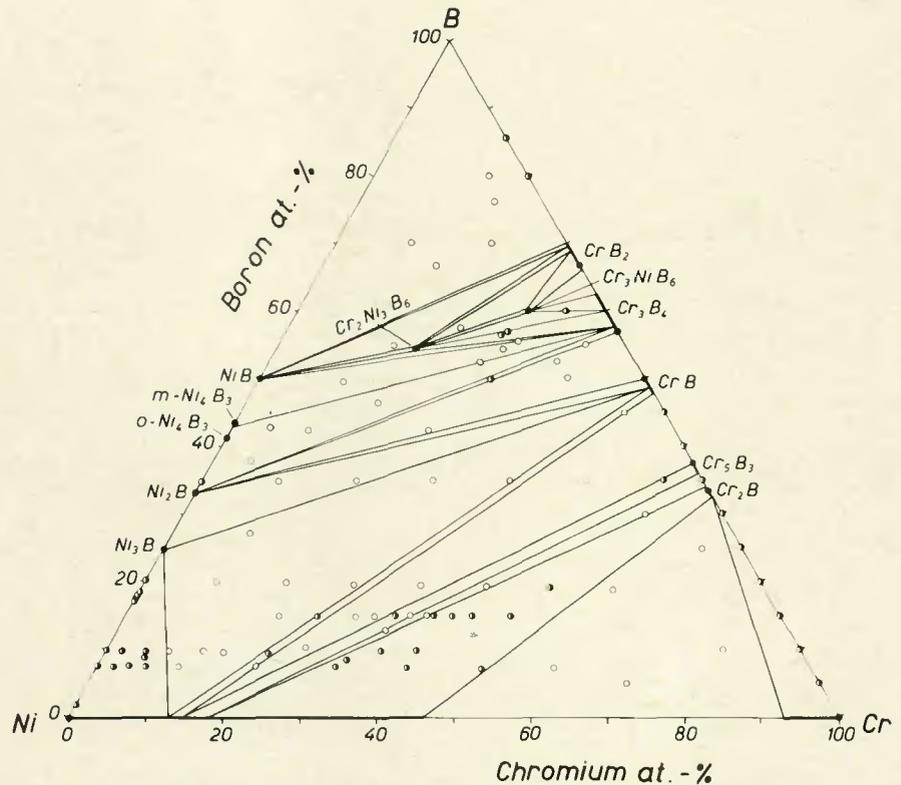


Fig. 2—Ni-Cr-B system at 1000 C. Solid black points, one phase; half black, two phases; open points, three phases

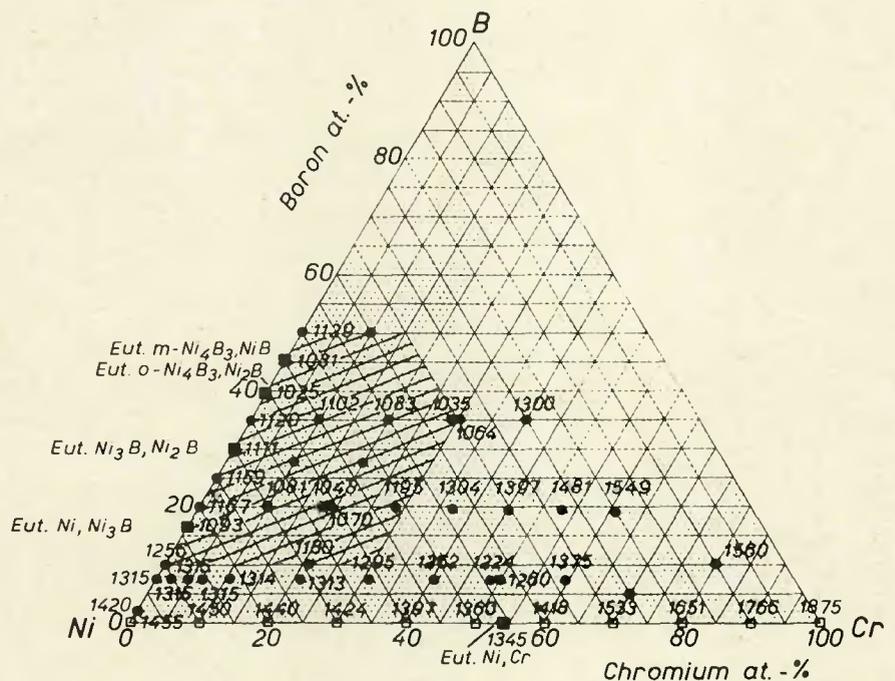


Fig. 3—Melting temperatures of Ni-Cr-B alloys; hatched lines indicate area suitable for brazing filler metals

by DTA in argon atmosphere. The weight of the samples was 5 g. The heating and cooling rate was 5 C/min, and 1600 C was the maximum temperature achieved. Figure 3 shows the results. The lower melting temper-

atures, which are advantageous for brazing, can be found in the nickel-rich area. This is the area of many hard surfacing alloys also.

Most of the hard surfacing alloys consist of three phases: nickel mixed

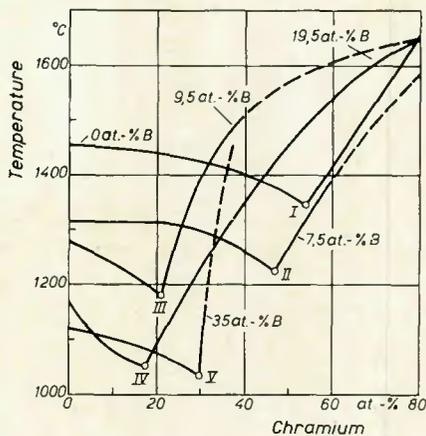


Fig. 4—Melting temperatures of Ni-Cr-B alloys (B constant) vs. chromium content

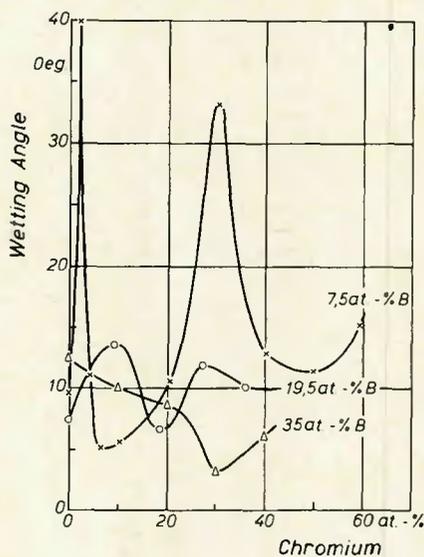


Fig. 5—Wetting angle of Ni-Cr-B alloys (B constant) vs. chromium content

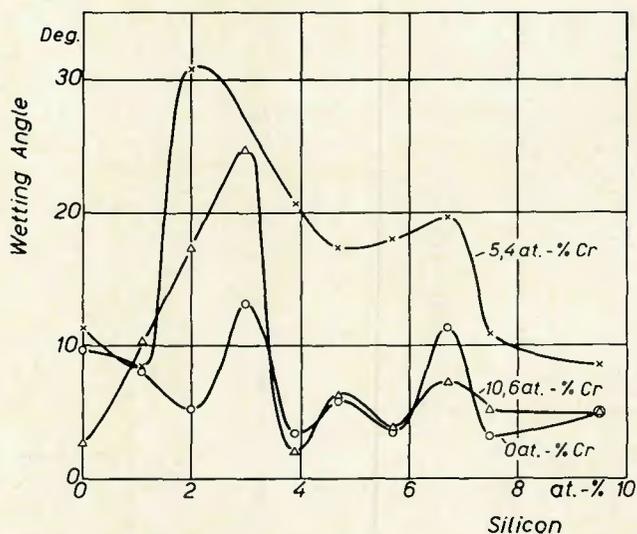


Fig. 6—Wetting angle of Ni-Cr-B-Si alloys (10 at. % B and zero, 5.4, and 10.6 at. % Cr) vs. silicon content

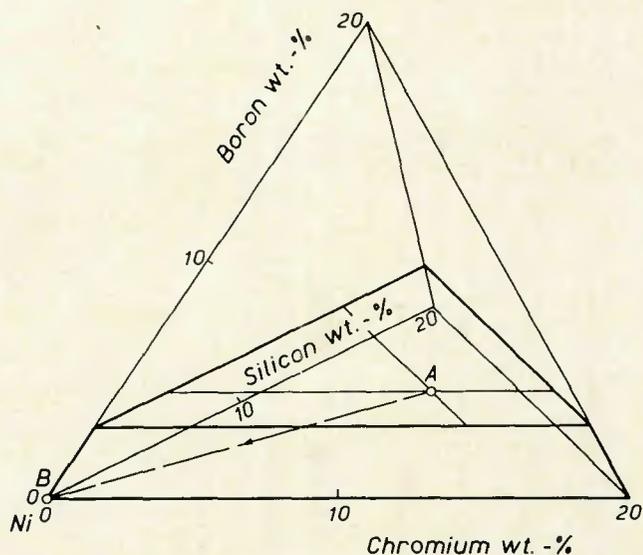


Fig. 7—Change of composition of a Ni-Cr-B-Si reacting alloy along the line A-B

crystal, Ni_3B and CrB , which can be seen by comparison of Figs. 2 and 3. Therefore the high wear resistance of these alloys is based on the monoboride CrB contrary to former assumptions which were based on the Cr_2B .

Other areas with low melting temperatures are in the range of high boron contents. These alloys are brittle and have no plastic properties. The melting points of ternary Ni-Cr-B alloys influenced by the boron content are shown in Fig. 4. The melting temperature is plotted against the chromium content at different but constant boron contents. The minimums of melting temperature, in form of binary eutectic points, decrease from 1340 C to 1020 C according to increasing boron content.

To achieve useful brazing temperatures silicon-free alloys should contain 10 to 20 at. % boron and 10 to 20 at. % chromium. In respect of plasticity these alloys can be improved by reducing the boron content and adding 2 to 6 at. % silicon. Then the melting temperature decreases 50 to 100 C.

Wetting Properties of Ni-Cr-B-(Si) Alloys

The wetting angle was determined to characterize the flowing and wetting properties of the Ni-Cr-B-(Si) alloys. The base metal was 316 stainless steel. In a microscope the angle was measured between the base metal and a tangent on the molten alloy. The testing samples were produced by melting the alloys on a 316 stainless steel sheet in an electric furnace with Ar atmosphere.

The results are plotted in Figs. 5 and 6. The minimum of the small and

useful wetting angle is shown in relation to increasing boron content and higher chromium contents (Fig. 5). Silicon-free alloys (10 to 20 at. % B, 10 to 20 at. % Cr, bal. Ni), which could be used for brazing according to their melting properties, have good wetting properties on 316 stainless steel. The wetting angle is less than 10 degrees.

Figure 6 shows the influence of silicon on the wetting angle of Ni-Cr-B-Si alloys. The angle of different alloys (10 at. % B; zero, 5.4 and 10.6 at. % Cr) is plotted against the silicon content. The alloying with small quantities of silicon improves the wetting properties of these alloys.

Alloys with low chromium content (5.4 at. %) have the poorest wetting properties. One can see (Fig. 6) the same dependence at the wetting angle on the silicon content in alloys with more than 3.5 at. % Si, and with 10.6 at. % and zero chromium contents, respectively. All alloys with 1 at. % Si have the same wetting angle independent on the chromium content.

Ni-Cr-B-Si Reacting Brazing Filler Metals

It is necessary to achieve useful working temperatures of Ni-Cr-B and Ni-Cr-B-Si alloys in order to have a wide field of applications in brazing and hard surfacing. In both types of application a low melting temperature is preferred. Because of the plasticity of the alloys the content of boron or/and silicon cannot be raised over a certain amount. This critical amount is different for surfacing and brazing filler metals. The ratio of hard phases/matrix should be high in wear

Table 1 — Tensile Strength of Usual Cast Ni Base Alloys

Composition, wt.% (bal. Ni)			Tens. strength,	
Si	B	Fe	MPa	ksi
1.7	1.2	0.5	255	37
2.4	1.5	0.3	335	49
2.5	1.5	0-1.5	343	50
3.3	2.5	0.4	417	60

resistant alloys. As mentioned earlier, the hard phases will be CrB, Cr₅B₃, Cr₂B and eventually Ni₃Si. To form these phases the content of boron and/or silicon will be reasonably high.

For brazing filler metals the ratio of hard phases/matrix should be small. Boron and/or silicon have to be added to achieve a useful working temperature only. Brazing filler metals do not have to be molten completely. A certain portion of a molten phase is necessary to assure the proper viscosity and related properties.

Based on this we developed brazing filler metals consisting of two components which react during the working time. The component A is liquid during the reaction; component B is solid. Component A has a high content of boron and/or silicon to achieve a very low melting temperature. Component A can be brittle at room temperature. Component B should have a high melting point. The boron and/or silicon content should be very low. The use of pure nickel or a nickel-chromium alloy is preferred. The powdered components should be mixed well before brazing and must react at the working temperature to form a new alloy.

Figure 7 shows an example of the change of the composition along the line AB. The example demonstrates the reaction of an alloy (72.5 wt. % Ni, 6.3 Fe, 10.0 Cr, 4.2 Si, 3.0 B) as component A and nickel as component B. The composition of the reacted alloy depends on the ratio A to B. This ratio depends on the portion of the molten phase and the melting point of component A which is connected with the overheating of the molten alloy during the reaction. Along the line AB the increasing content of component B raises the melting temperature of the reacting alloy. So brazed parts can be used at higher temperatures than the working temperature during brazing.

In Fig. 8 the solidus temperature after reaction is plotted against the A/B ratio. Starting with 970 C (first point above component A) the increase is very little up to 40 % of component B, but at ratio 1 it is 1430 C. The joints can be exposed for higher temperatures than the solidus temperature of

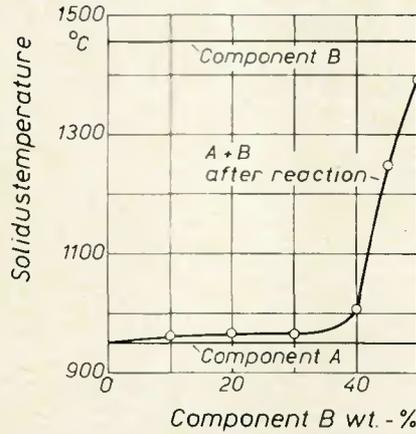


Fig. 8—Solidus temperature of a reacting brazing filler metal vs. component B content

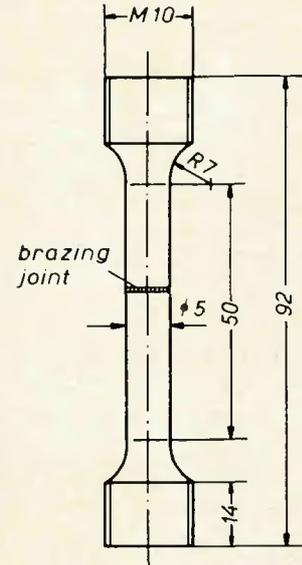


Fig. 9—Test specimen for tensile strength

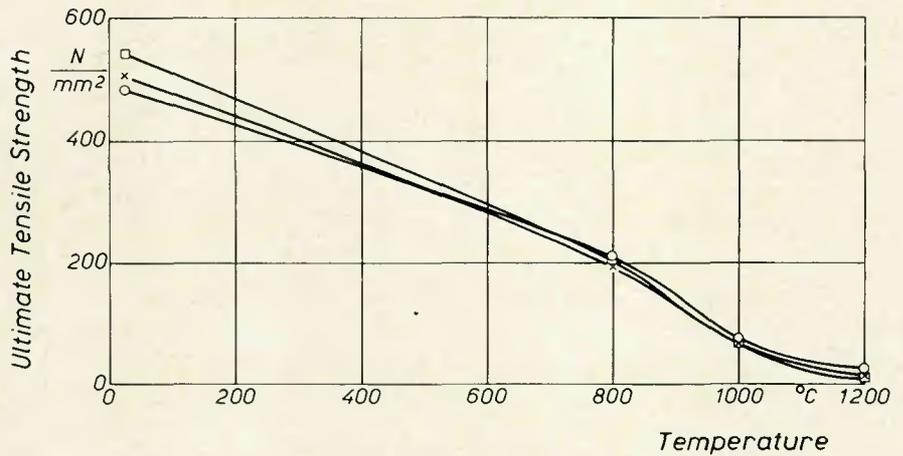


Fig. 10—Tensile strength of reacting brazing filler metals at elevated temperatures

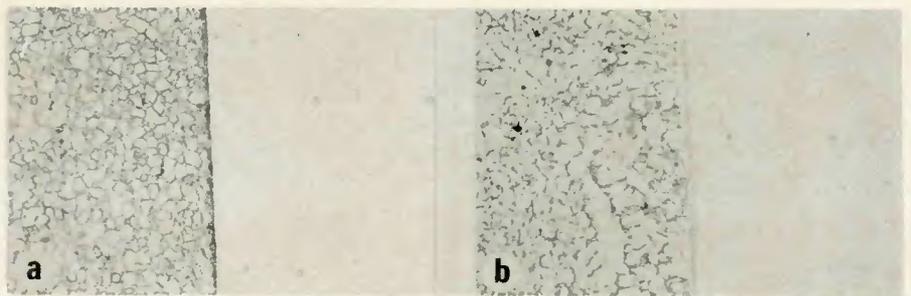


Fig. 11—Boron diffusion test of the brazing filler metal composition (wt. %: 2B, 5.3Cr, 2.6Si, 2.9Fe, Bal. Ni) at the joint interface with stainless steel 316. (a) sample as brazed, (b) brazed and heat treated (2 h, 1000 C)

the low melting component A which gives the working temperature during brazing.

The content of hard phases decreases during the reaction. Therefore the plastic and elastic properties of the reacted alloys increases by the additions of nickel (component B).

Figure 9 shows the specimen used

for the tensile strength test. The base material was 316 stainless steel. The reacting brazing filler metals were mixtures of 45, 50 and 55 % component B, balance component A. For brazing induction heating was used at approx. 1000 C. The joint clearance was 100 μm. The working time was 30 to 60 s.

Table 2 — Influence of Heat Treatment on the Tensile Strength (1000 C) of Reacting Brazed Joints

Component (wt. %)			Composition after reaction (wt. %, bal. Ni)				Tensile strength at 1000 C			
A	B	Cr	B	Si	Fe	as-brazed, MPa	ksi	brazed + 1 h at 800 C MPa	ksi	
55	45	8.25	1.65	2.3	2	74.6	10.8	66.7	9.7	
50	50	7.5	1.5	2.1	1.85	68.7	10.0	68.6	10.0	
45	55	6.75	1.35	1.9	1.7	64.8	9.4	67.6	9.8	

The results of the tensile test are shown in Fig. 10. The testing temperatures were 20, 800, 1000 and 1200 C. The last two were higher than the solidus temperature of component A. All three alloys have a similar tensile strength at elevated temperatures. At room temperature the tensile strength is 480 to 540 MPa (69.6 to 78.3 ksi) and at 1000 C is still 70 MPa (10.2 ksi). Since the fractures were always within the brazing alloy, the tests measured the tensile strength of the alloy. These tensile strengths are higher than those of the usual Ni-Cr-B-Si alloys listed in Table 1. No change of the 1000 C tensile strength could be observed after a 1 h heat treatment of the specimens for diffusion. Therefore the reaction is finished during the brazing operation (Table 2).

For high temperature application of reacting brazed parts the diffusion of boron into the base metal is very important. In steels we found that boron diffusion is of a volume diffusion type. Boron did not diffuse along the grain boundaries as supposed some years ago. In 316 stainless steel samples we could observe a narrow zone of

borides parallel to the brazing interface. The distance to the interface depends on the heat treatment and the composition of the brazing filler metal. This boride zone acts as a blocking layer (Fig. 11). The hardness is constant across the braze metal, drops clearly in the diffusion zone of the steel and has its maximum in the boride layer. Behind this blocking zone there is no influence on the hardness of the stainless steel.

In a parallel case, Bell (Ref. 3) reports on boron diffusion of Ni-Cr-B-Si alloy into stainless 45 and N-Xtra. When steel is boronized for increasing wear resistance, similar layers of Fe₂B and FeB are also found (Refs. 12, 13). Therefore the mechanical properties are less influenced by boron diffusion into steel than had been supposed before.

In our opinion carbon diminishes the diffusion activity of boron. There is a gradient of activity from the interface into the base metal. The boron diffusion starts with high diffusion rates which decrease very quickly and stop in an activation valley. The deactivation is also influenced by the other alloying elements of the steel.

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Correction

In the paper, "Techniques and Standards for Measuring Ferrite in Austenitic Stainless Steel Welds," appearing in the June 1976 issue, there is an error in labeling the axes of Fig. 8 shown on page 162-s. A corrected Fig. 8 is given herewith. The authors also state:

"We have changed the scale for the Ferrite Meter and also given the Magne Gage values as Ferrite Numbers (FN), as they should have been. In this form, the figure now serves as a

calibration for our particular instrument to FN, and an approximate calibration curve for other Ferrite Meters depending on the degree of reproducibility between instruments. It should be emphasized that this calibration applies only for ferritic stainless in austenite — not iron powder in austenite. Naturally a similar curve should be generated for each Ferrite Meter prior to using it to measure ferrite in austenitic welds. Also, the point of 6.1% was deleted since this was for Fe in austenitic 316 stainless steel, and not ferrite in austenite."

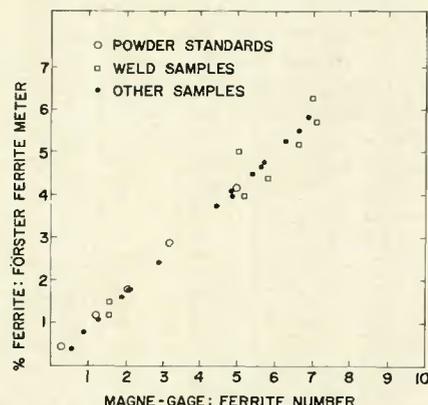


Fig. 8 — Ferrite Meter readings plotted versus those from the Magne Gage on a variety of samples. The data show that the Ferrite Meter measured regions of different ferrite content within the weld while the Magne Gage gave only a single average value