Development of Nickel-Chromium-Silicon Base Filler Metals

Alloying with small amounts of phosphorus decreases melting temperatures during development on low melting boron-free brazing filler metals for high temperature service

BY E. LUGSCHEIDER, O. KNOTEK AND K. KLOHN

Introduction

For some applications—mainly in the nuclear industries—boron-free nickel base filler metals are preferred. One of the important filler metals used in these fields in West Germany is the nickel-chromium-silicon filler metal BNI-5. This nickel base filler metal, containing 19 wt-% chromium and 10.2 wt-% silicon, has a considerably high liquidus temperature of about 1408 K or 1135 C (2075 F) in comparison to boron-containing filler metals such as BNI-2, BNI-3 or BNI-4.

Although the suggested brazing temperature of BNI-5 is high, this filler metal is used in non-nuclear industries because of the possibility to get very ductile joints using a heat treatment after brazing. The brittle silicide hard phases of the brazing gap can be eliminated during the diffusion heat treatment because of the high solid solubility of silicon in the base metal. This most important improvement of joint ductility for high strength components is very difficult in cases using boride-containing filler metals because of the very low solid solubility of boron in the base metal.

In developing boron-free low melting nickel base filler metals, the melting behavior of nickel-chromium-silicon alloys (depending on the chromium and silicon content) has been investigated systematically. Further, the influence of low content of phosphorus on the melting and flowing behavior has been examined.

Selected Ni-Cr-Si and Ni-Cr-Si-P alloys were used for brazing experiments. Their strength properties were tested using the AWS single-lap standard method. The ability of the investigated alloys for high temperature brazing filler metal is discussed.

Properties of Ni-Cr-Si and Ni-Cr-Si-P Alloys

Melting Behavior of Ni-Cr-Si Alloys

In the nickel-rich part of the Ni-Cr-Si system, the filler metal BNI-5 is the only alloy used in high temperature brazing. BNI-5 (19 wt-% Cr, 10.2 wt-% Si, bal. Ni) has a liquidus temperature of 1408 K or 1135 C (2075 F). Systematic investigations on the melting behavior of ternary alloys dependent on the chromium and silicon content should show if there are concentration areas of lower melting temperatures.

The element silicon is essentially responsible for reducing the melting point of Ni-Cr-Si alloys. On the other hand, silicon stabilizes brittle silicide hard phases distributed in the nickel solid solution. Therefore, a compromise has to be made between lowering the melting point and raising the volume of hard phases; this leads to an upper limit corresponding to a silicon content of about 10 to 15 wt-% in the filler metal. The decrease of the melting points of ternary Ni-Cr-Si alloys can only be given by nonvariant reactions influenced by eutectic reactions of the binary systems.

In the nickel-silicon binary system, one eutectic reaction exists at significant silicon concentrations. The eutectic is formed between nickel solid solution and the silicide Ni$_3$Si at 11.5 wt-% silicon and 1423 K or 1150 C (2102 F). Ni$_3$Si results by a peritectic reaction between the melt and the silicide Ni$_3$Si at a temperature of 1438 K or 1165 C (2129 F).

In the nickel-chromium binary system, only one eutectic reaction exists between the solutions of nickel and chromium at 49 wt-% chromium and at a temperature of about 1618 K or 1345 C (2993 F). Besides its importance for the melting characteristic of the alloy, silicon improves the flowing behavior and—similarly to the chromium—the corrosion and oxidation resistance.

The determination of the melting behavior of nickel-base alloys was done by differential thermal analysis. The test conditions were an argon atmosphere and heating and cooling rates of 5 K (i.e., 5 C or 9 F) per minute. The results are shown in Fig. 1, which indicates the relationship between the liquidus temperature and the concentration of the alloying elements in the nickel-rich part of the system nickel-chromium-silicon.

About 350 samples prepared by induction heat melting under argon inert gas atmosphere were investigated. Raw materials for the preparation of these alloys were nickel, chromium, nickel silicides and chrom-
Figure 1 shows that—in the investigated concentration range of 0-40 wt-% chromium, 0-14 wt-% silicon, and the balance nickel—a ternary eutectic exists at a temperature below 1350 K or 1077 °C (1971 °F). The ternary eutectic is given by the point of intersection between melting grooves (dark lines in Fig. 1) and was found at 20 at-% chromium and 21.3 at-% silicon; this corresponds to 20.5 wt-% chromium and 11.8 wt-% silicon.

The melting grooves are the lines of intersection of the melting planes (planes of primary crystallization). The plane of the primary crystallization of the nickel solid solution slopes steadily from the melting temperature of nickel to the temperature of the ternary eutectic for 376 K/C (676 °F). In other words, the temperature of the primary crystallization of the nickel solid solution decreases with increasing concentrations of silicon and chromium, but the influence of silicon is much more pronounced as shown by the isoliquidus curves drawn in steps of 50 K, i.e., 50 °C (90 °F).

The melting planes in concentration areas with silicon contents of more than about 11 wt-% show a slope similar to the part of the melting plane at high nickel concentration. Of great importance for developing Ni-Cr-Si filler metals is the strong influence of the composition on the liquidus temperature in concentration ranges near the ternary eutectic. This fact can be better demonstrated by concentration-temperature sections.

Figure 2 shows such sections at constant chromium content of 19 wt-% containing the filler metal concentration of BNi-5—and of 20 and 21 wt-% chromium. All sections are near the concentration of the ternary eutectic. The dependence of the liquidus temperature on the silicon content in Fig. 2 indicates that a small change of silicon silicides, all of at least 99.8% purity.

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the composition of filler metal BNi-5 leads to alloys with liquidus temperatures of about 56 K/C (104 F) below the liquidus temperature of BNi-5. For further investigations an alloy near the ternary eutectic with 21.5 wt-% chromium, 11.6 wt-% silicon and balance nickel was selected.

Melting Behavior of Ni-Cr-Si-P Alloys

Besides the elements silicon and boron, phosphorus is also an effective element to lower the melting temperature of nickel base alloys as it is known from the melting behavior of the filler metals BNi-6 and BNi-7. In Fig. 3 the influence of phosphorus on the liquidus temperature of the approximate ternary eutectic alloy with 20.4 wt-% chromium, 11.6 wt-% silicon and balance nickel is shown. The graph demonstrates that only small amounts of phosphorus of about 0.5 wt-% give an additional decrease of the melting point of alloys in concentration areas of the ternary eutectic.

The alloy with 20.3 wt-% chromium, 11.5 wt-% silicon, 0.5 wt-% phosphorus, and balance nickel has a liquidus temperature of 1333 K or 1060 C (1940 F). This means that this boron-free filler metal BNi 20.3Cr 11.5Si 0.5P which was selected for further investigations has a 75 C or 75 K (135 F) lower melting temperature than the filler metal BNi-5 and a similar melting behavior in comparison to used boron-containing filler metals.

Further investigations in alloying Ni-Cr-Si alloys with phosphorus show that a decrease of the silicon content in the alloy in respect to lowering the hard phases requires higher amounts of phosphorus of about 3 wt-% to give similar melting behavior to alloy BNi 20.3Cr 11.5Si 0.5P. For instance, an alloy with 14.8Cr 8Si 3Fe 3P balance nickel has a melting range of 1269 K or 996 C (1825 F) to 1336 K or 1063 C (1945 F).

Flow Behavior and Structure of BNi 21.5Cr 11.5Si and BNi 20.3Cr 11.5Si 0.5P

Besides melting characteristic, the flow behavior is a very important property for the manufacturing of high temperature filler metals. As a characteristic value for the wettability, the contact angle was measured between the liquid filler metal and a plain base metal surface at different temperatures. The investigations were made under vacuum (< 10^{-4} torr) in the temperature range of 1323 K or 1050 C (1922 F) to 1383 K or 1110 C (2030 F). The base metal was stainless steel (W. No. 1.4541, X 10 CrNiTi 18 9).

The filler metals BNi 21.5Cr 11.6Si and BNi 20.3Cr 11.5Si 0.5P with liquidus temperatures of 1350 K or 1085 C (1985 F) and 1333 K or 1060 C (1940 F) show good wettability even at temperatures below their liquidus temperature, whereby the phosphorus-containing alloy indicates a slightly better flow behavior. The wetting angles in the investigated temperature range for both alloys in any case were below 3 deg as seen in Fig. 4.

The structure of the alloy BNi 21.5Cr 11.6Si is the same as that of filler metal BNi-5. The main silicide Ni$_2$Si$_3$ is distributed in the nickel solid solution. Additionally, very small amounts of a ternary silicide Cr$_2$Ni$_5$Si$_3$ (n-phase) like in the case of Ni-5 were found.

The phosphorus-containing alloy BNi 20.3Cr 11.5Si 0.5P has a structure similar to that of Ni-5. Also, small amounts of the nickel phosphide Ni$_3$P are added because of the very little solid solubility of phosphorus in the nickel matrix.

Brazing Experiments

With selected filler metals BNi 21.5Cr 11.6Si and BNi 20.3Cr 11.5Si 0.5P, brazing experiments were made to get the optimum brazing temperature in regard to their diffusion behavior and joint strength.

The AWS single-lap standard method was used to determine strength properties. The ratios of overlap to thickness were 0.5 to 6. The clearance was 25 pm (0.001 in.). The brazing was done in an electric heated vacuum furnace at a vacuum better than 1.33 x 10^{-4} Pa (1.0 x 10^{-4} torr) according to the brazing cycle shown in Fig. 5. This brazing cycle with a brazing time of 10 min and a diffusion heat treatment at 1273 K or 1000 C (1832 F) for 60 min after brazing, is typical for processing the filler metal BNi-5 in nuclear industries to get ductile joints. The base metal used was stainless steel (W. No. 1.4541, X 10 CrNiTi 18 9) with a yield strength of 214 N/mm$^2$ (31 ksi) and an ultimate tensile strength of 575 N/mm$^2$ (83.4 ksi). Both values were determined after the base metal was heat treated in the same way as the brazed joints. The filler metals were used as powders and placed with cement.

The results of the strength tests of joints brazed with the filler metal BNi 21.5Cr 11.6Si at temperatures of 1363 K or 1090 C (1994 F) and 1368 K or 1095 C (2003 F) are shown in Fig. 6. It can be seen that, at both brazing temperatures, the tensile stress of the joints is slightly above the ultimate tensile strength of the base metal at ratios of overlap to thickness greater than about 1.5. At the brazing temperature of 1368 K or 1095 C (2003 F), the joints fail at any ratios in the base metal except the joints with ratios of 2 and 6 where we find brazing defects in the brazing gap. In any case, the tensile stress of the joints is above the yield strength of the base metal which indicates a good ductility of the brazing seam.

Joints brazed at a temperature of 1343 K or 1070 C (1958 F) have tensile stresses above the yield strength of the base metal. However, the values are in general lower. The reason can be that this brazing temperature in connection with the diffusion heat treatment is not sufficient to eliminate silicide
phases of the brazing gap by diffusion—Fig. 7. For the most part, joints brazed at a temperature of 1363 K, 1090 C (1994 F) or 1368 K, 1095 C (2003 F) according to the brazing cycle in Fig. 5 show no silicide phases in the brazing gap—Fig. 8. Therefore, for the filler metal BNi 21.5Cr 11.6Si a brazing temperature of 1368 K, 1095 C (2003 F) should be suggested if high joint strength has to be required.

The results of the strength tests of joints brazed with the phosphorus-containing filler metal BNi 20.3Cr 11.5Si 0.5P at 1363 K or 1090 C (1994 F) and 1368 K, 1095 C (2003 F) are shown in Fig. 9. It seems that the tensile stress of these joints also at a ratio of overlap to thickness of 1.5 is equal to the ultimate tensile strength of the base metal (compare to Fig. 6). Because of the fact that samples with ratios of 2, 4 and 6 failed in the filler metal, further tests should be made to confirm the dependence shown in Fig. 10. On the other hand, joints with overlap ratios below 1 show failure in the base metal. Although brazing tests at lower brazing temperatures—for instance, at 1343 K, 1070 C (1958 F)—demonstrated a good filling of joints at gaps of 25 µm (0.001 in.) (Fig. 10), the suggested brazing temperature for the filler metal BNi 20.3Cr 11.5Si 0.5P should be 1363 K or 1090 C (1994 F) to 1368 K or 1095 C (2003 F).

In any case, no optimization of the value of the clearance has been done.

Summary

In developing boron-free nickel-base low melting, high temperature
Table 1—Characterization of New Filler Metals in Comparison to BNi-5 and BNi-1

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<tr>
<td>BNi 21.5Cr 11.6Si</td>
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<td>Liquidus 1358 K</td>
<td>1343-1383 K</td>
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<tr>
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<td>1333 K</td>
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<td>14Cr, 38, 4.5Si 4.5Fe, 0.7C, bal. Ni</td>
<td>1250 K</td>
<td>1311 K</td>
<td>1338-1478 K</td>
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1. 273 K = 0 °C.

brazing filler metals for applications in nuclear industries, the melting behaviors of nickel-chromium-silicon alloys in the concentration range of 0-40 wt-% chromium, 0-14 wt-% silicon, and the balance nickel were investigated systematically.

The lowest liquidus temperature of 1350 K or 1077 C (1971 F) in this nickel-rich area was found at a ternary eutectic concentration of 20.5 wt-% chromium, 11.8 wt-% silicon, the balance nickel. This means that a small change of the concentration of filler metal BNi-5 [19 wt-% Cr, 10.2 wt-% Si, the balance Ni; T_L = 1408 K, 1135 C (2075 F) ] leads to a 58 K/C (104 F) lower melting filler metal. Alloying with small amounts of phosphorus indicates an additional decrease of the melting temperature to values of 1333 K or 1060 C (1940 F).

For testing the brazing behavior and the joint strength, two alloys—BNi 21.5 Cr 11.6Si and BNi 20.3Cr 11.5Si 0.5P—which are characterized in Table 1—were selected. Both alloys have a structure and diffusion behavior similar to that of BNi-5 and show good flowing behavior on stainless steel with wetting angles between 0-3 deg dependent on the temperature.

Strength tests using the AWS single lap standard method show that, at higher overlap ratios for joints of stainless steel brazed with both filler metals, tensile stresses equal the ultimate tensile strength of the base metal.

The suggested brazing temperature for the investigated filler metals is 1368 K or 1095 C (2003 F). This means that these boron-free filler metals give ductile high strength joints at a brazing temperature 95 K/C (171 F) and 80 K/C (144 F) below the brazing temperature normally used for processing the boron-free filler metal BNi-5 or the boron-containing filler metal BNi-1.

Compared to other well known boron-containing filler metals, the alloys BNi 21.5Cr 11.6Si and BNi 20.3Cr 11.5Si 0.5P should have higher oxidation and corrosion resistance because of the higher content of chromium and silicon.

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References


AWS Filler Metal Specifications

AWS A5.25-78, Specification for Consumables Used for Electroslag Welding of Carbon and High Strength Low Alloy Steels and AWS A5.26-78, Specification for Consumables Used for Electrogas Welding of Carbon and High Strength Low Alloy Steels are now available.

The classification system used in the specifications follows as closely as possible the standard pattern used in other AWS filler metal specifications. This allows the user to more readily select the proper filler materials. However, the inherent nature of electroslag and electrogas welding has necessitated specific changes to more ably classify the electrodes.

Each specification contains 24 pages and they are saddle-stitched, soft cover, 8½ x 11 in., three-hole punched, priced at $5.00 per copy. Discounts: 25% to A and B members; 20% to book stores, public libraries and schools; 15% to C and D members. Send your orders to the American Welding Society, 2501 N.W. 7th St., Miami, FL 33125. Florida residents add 4% sales tax.
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