BY DAN KAY

Q: Our brazing shop has been doing nickel brazing in our vacuum furnaces for a number of years. I heard recently that I can use isothermal solidification in some high-temperature brazing processes in order to significantly raise the remelt temperature of a nickel brazement in subsequent service. How is this accomplished?

A: Yes, isothermal solidification can be a very useful brazing process for some brazing filler metals (BFMs), and can result in a significant increase in the re-melt temperature of the BFM in that brazed joint.

To better understand the process, first examine the component parts of the term "isothermal solidification." The prefix "iso" means "equal, or the same," and "thermal," of course, refers to temperature. So, we're looking at a BFM solidification process in which solidification takes place while the furnace is being held at the same, steady temperature. Although that may sound strange, there's some real logic to it. Isothermal solidification depends a lot on the diffusion capabilities of various components of the BFM while that BFM is being held at the brazing temperature.

You mentioned nickel (Ni) brazing in your question above, and it is an excellent example of how this process can be very useful for brazed components subjected to high temperatures in end-use service. AWS A5.8, Class BNi-2, also known in the industry as AMS 4777, is an example of a nickel-based BFM whose remelt temperature can be significantly increased by isothermal solidification. This BFM has almost 3.5% of boron (B) added to its chemistry as a temperature depressant, i.e., an element added to the BFM to significantly lower its initial melting temperature during brazing. Boron does this by forming low-melting eutectic compositions with the nickel into which it is alloyed. Boron is a very small atom compared to the much larger atoms of nickel, chromium, iron, and silicon that make up the rest of the BNi-2 chemistry. Thus, the boron atom does not fit as a so-called substitutional atom in the matrix of the BNi-2 alloy, but is, instead, known as an interstitial atom, i.e., one that fits into the small spaces between the much larger atoms, as shown in Fig. 1.

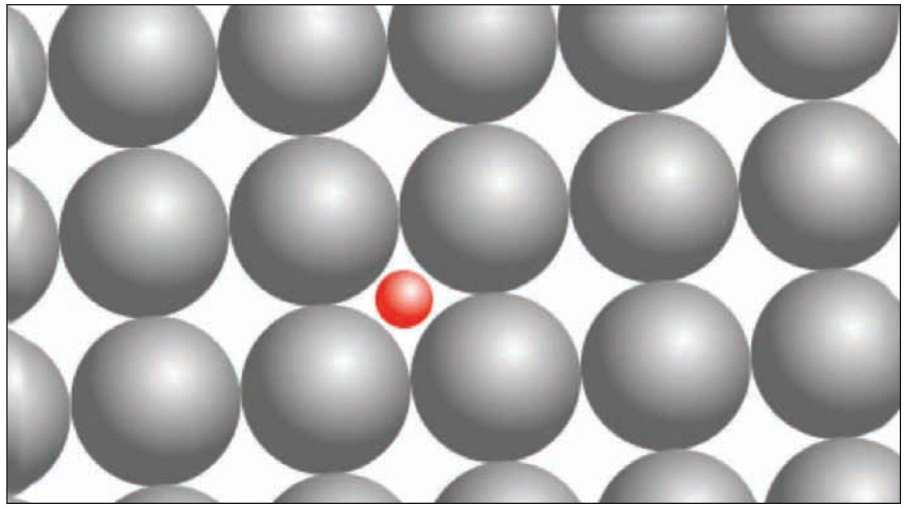

Fig. 1 — Note that small, interstitial atoms cannot substitute for the larger atoms in the matrix of atoms shown above, but must fit into the small interstices (spaces) between those larger atoms, as shown in this idealized conceptual diagram of atoms lining up with each other.

Interstitial atoms are not as strongly bonded into the matrix of atoms as substitutional atoms, which means that "interstitials" can enter or leave the matrix of atoms much more easily than substitutional atoms can. As you know, as a metal gets hotter and hotter, it will expand. It does this because atoms vibrate in place more and more when heated, occupying more and more space to do so. Thus, the overall dimensions of the metal get larger and larger as the metal gets hotter and hotter, since the spacing between each of the atoms in the alloy is increasing.

Here's where the tiny size of the boron atom comes into play. Because it is so small, and only weakly "bonded" into the BFM alloy structure (because it is an interstitial atom), the boron atom is able to escape, i.e., diffuse away, from the BFM when the brazing temperature has increased to the point where the spacing between the larger substitutional atoms is great enough for the small boron atoms to get through.

Remember, the boron was added into the BFM to lower its melting point. Therefore, does it not seem logical that when the boron leaves, i.e., diffuses away from the BFM, the melting point of the BFM should go back up? In fact, that does actually happen.

To understand this a little better, let's get into some of the metallurgy of brazed joints. Let's look briefly at a so-called phase diagram of the nickel-boron alloy system as shown in Fig. 2.

The varying amount of boron in the alloy is shown along the bottom of the graph, and temperature is shown on the vertical axis. It can be seen that as the amount of boron that is added to the alloy increases from zero up to 3.5%, the curved line labeled "liquidus" drops significantly, from about 2650°F (1455°C) down to only 2000°F (1093°C), whereas the line labeled "solidus" remains pretty steady from left to right at 2000°F. Let's now look at the same diagram in Fig. 3, with the vertical lines A (2% boron), and B (3.5% boron) added to it, as well as a horizontal line representing a theoretical brazing temperature.

At 2% boron content, you can see that as you increase the temperature of that specific alloy composition from room temperature up to 2000°F, you cross the solidus-temperature line. The solidus temperature is the temperature below which the alloy remains completely solid (hence the word "solid"-us). Thus, as soon as you cross the solidus temperature line during heating, the BFM will start to melt. It will continue to melt further and further until you reach the curved line labeled "liquidus," which, as you may have guessed, is the line representing the temperature above which that alloy chemistry is supposed to be fully liquid (hence the word "liquid"-us). Notice I said, "supposed to be." Please see my article about liquation published in the September 2010 *Welding Journal* for a lengthy discussion about this. Technically speaking, the liquidus temperatures are usually determined by cooling a liquid BFM and determining the temperature at which a particular composition begins to solidify.

Now, back to my discussion of isothermal solidification. Notice the difference between vertical lines A and B in Fig. 3. On vertical line B, the liquidus and solidus temperatures are the same. Such a junction is called a "eutectic point." This represents the lowest melting point for a given BFM alloy system, i.e., it is the composition at which the lowest melting temperature BFM-liquid can exist.

Notice now the horizontal line in Fig. 3 that is labeled "Brazing Temp." The brazing temperature used in any brazing operation should be at least 100°F (or 50°C) higher than the "melting point" (liquidus temperatures) of the BFM being used. We'll assume that's how you're brazing in your shop.

Now, remember that at brazing temperature, the boron begins to diffuse away from the joint into the base metals of the part being brazed (as the boron atoms move, i.e., diffuse away, to achieve an equilibrium balance of boron throughout the entire structure). As you can see, the liquidus line of the BFM in Fig. 3 begins to rise as you begin to move left from 3.5% boron in the joint down to 2% boron or less, i.e., as the boron continues to diffuse away from the braze-joint area. The boron concentration in the brazed joint won't go to zero, since the boron atoms are merely trying to achieve an equilibrium balance throughout the structure.

Notice in Fig. 3 that the brazing temperature crosses the liquidus line at about 2.5% boron (vertical line C). When the brazing cycle is held at brazing temp long enough until the boron in the BNi-2 BFM has diffused away to below 2.5%, there is then not enough boron left in the joint to keep the BFM liquid at that specific brazing temperature. Notice that when the boron is less than 2.5% the brazing-temp line is no longer in the "liquid" section of the chart, but is now situated in the "slush" zone between the liquidus and solidus lines. When this happens, the BFM will begin to solidify, even though the brazing temperature is being held constant. Isothermal solidification has begun.

Please note that isothermal solidification will not occur by merely holding the BFM at brazing temperature for a few minutes. Instead, it requires much longer times at temperature, typically 30 min minimum, and sometimes as long as an hour or two (depending on the load size in the furnace, it might require an even longer hold time). Experience will indicate the time required, depending on the mass of the parts, how much BFM is present, and thus, what clearance is being used in the joint.

Note: Wide joint clearances are not effective for trying to implement isothermal solidification. For good isothermal solidification results, the joint clearances should be tight at brazing temperature, typically 0.000–0.003 in. (0.000–0.075 mm), and the quantity of BFM applied should be just enough to fill the volume between the faying surfaces of the joint. Not only can thick braze joints be a deterrent to effective isothermal solidification, but excessively large amounts of applied BFM can result in large, heavy braze fillets that can behave in a manner identical to joint clearances that are too large.

In summary, if the joint clearances are large, or if too much BFM is applied, there will typically be too much BFM present in the joint area to be able to effectively diffuse away enough of the boron temperature depressant, and isothermal solidification will not occur, even for lengthy holds at brazing temperature.

Note, too, that because of the much larger size of silicon and phosphorus atoms used as the temperature depressant in many other nickel-based BFMs, isothermal solidification will be very difficult, if not impossible, with those BFMs using silicon or phosphorus as the temperature-depressant additives instead of boron.♦

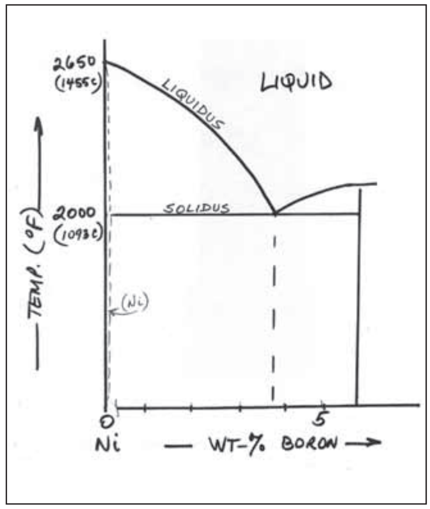

Fig. 2 — Simplified metallurgical phase diagram of the nickel-boron system.

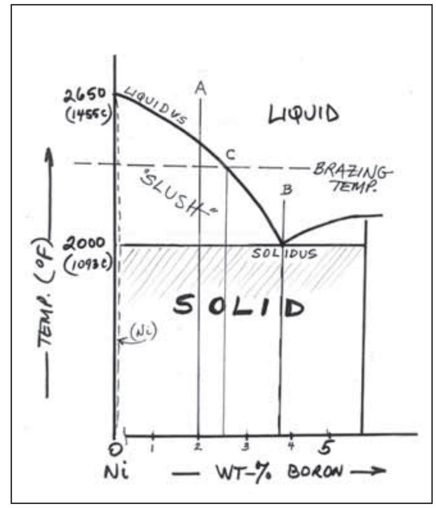

Fig. 3 — Ni-B phase diagram with a hypothetical brazing temperature shown.

This column is written sequentially by TIM P. HIRTHE, ALEXANDER E. SHAPIRO, and DAN KAY. Hirthe and Shapiro are members of and Kay is an advisor to the C3 Committee on Brazing and Soldering. All three have contributed to the 5th edition of AWS Brazing Handbook*.*

Hirthe (timhirthe@aol.com) *currently serves as a BSMC vice chair and owns his own consulting business.*

Shapiro (ashapiro@titanium-brazing.com) *is brazing products manager at Titanium Brazing, Inc., Columbus, Ohio.*

Kay (Dan@kaybrazing.com), *with 40 years of experience in the industry, operates his own brazing training and consulting business.*

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