BY ALEXANDER E. SHAPIRO

Q: We need assistance to design and manufacture a structure for cryogenic work that will be immersed in liquid nitrogen with the upper tubing staying at ambient temperature. The application of low-weight metals is very desirable but the bottom plate or cup should be made from copper as the metal with the best thermal conductivity. The cylinder can be made of aluminum, titanium, or magnesium alloys. As any combination of these metals with copper is not weldable, we have to join the cylinder, the bottom, and tubing by brazing or soldering. But we cannot find any data about the mechanical behavior of brazed joints of dissimilar metals at cryogenic thermal cycling. How should we select a filler metal or solder for this job? What would be the best material combinations to provide reliable work for at least 2000 hours?

A: You are right, the properties of brazed joints subjected to low temperatures are not known for many base metal/filler metal combinations. Some data were published for brazed joints designed for use in nuclear industry applications, but the joining technique is definitely not suitable in your case. Therefore, I only can share with you some data obtained from my own experience (Ref. 1) — Figs. 1, 2.

As shown in Fig. 1, the first effect that you can face is shrinkage porosity in the brazed joints, especially at the interfaces between the base metal and the joint metal. The porosity results from thermal stresses appearing between two metals having slightly different coefficients of thermal expansion. The vacancies formed here during cycle-by-cycle of cryogenic treatment are accumulated to form tiny pores by coalescence. So, the first rule of designing joints projected for cryogenic thermal cycling is to use ductile metals that can release thermal stresses by their plasticity. The ductility of joint metal is more important here than shear or tensile strengths of the joints.

Secondly, we can expect that microstructures of both base metal and filler metal will be changed due to quenching by deep and fast cooling in liquid nitrogen. And this really happens — Fig. 2A, B. Microconstituents observed appear similar in these samples regardless of cryogenic cycle experienced, e.g., Fig. 2A reveals large needles, while in Fig. 2B small needle-like crystals appear. Consequently, the strength of brazed or soldered joints is changed, too. The needle-like microconstituent appears to be present in increased quantity in the sample that underwent one cycle of cryogenic cooling. Some improvement of joint strength can be expected resulting from the "hardening effect" of filler metal after cryogenic cooling. The tensile strength of soldered joints of aluminum cast Alloy A356 after cryogenic cooling reached 9.8 ksi (67.6 MPa), while joints "as soldered" failed practically immediately after loading, at <1 ksi (<6.9 MPa). The same effect significantly improves the strength of copper brazed joints made with standard silver filler metal BAg-24. Shear strength after brazing and one cycle of cryogenic cooling is 18.9 ksi (130.4 MPa), while after brazing only 14.1 ksi (97.3 MPa).

Not only microstructure and mechanical behavior of the joint metal can be changed by cryogenic cooling but also structure and properties of the base material. Cryogenic treatment is well known to improve hardness and wear resistance of alloy steels. Cryogenic cooling may result in complete martensitic transformation or precipitation hardening, which was not completed in the steel as delivered by the manufacturer.

The same effect causes an increase in the yield and/or tensile strength of aluminum or titanium alloys (Ref. 2). We found that ultimate tensile strength of aluminum cast Alloy A356 (Al-Si eutectic) grew, after cooling in liquid nitrogen, from 34 to 42–44 ksi (235 to 290–304 MPa), which is ~26% of improvement. The strength of cast magnesium Alloy AZ91C improved by ~9%: from 34 to 37.05 ksi (235 to 256 MPa). The strength of wrought titanium Grade 2 also went up after cryogenic treatment from 132.9 to 137.7 ksi (917 to 950 MPa). However, the increase of strength does not always occur.

If the base metal was heat treated properly, then cryogenic cycling may not improve its mechanical properties. For example, the strength of cold-rolled precipitation-hardened aluminum A7075 bars did not change during such processing. Cold-rolled copper bars also almost did not respond to cooling in liquid nitrogen (Refs. 1, 2).

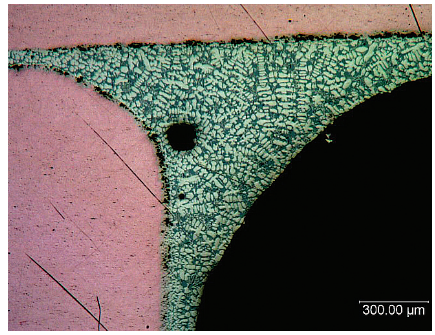

Fig. 1 — Shrinkage porosity at the interface of copper and P81 brazing filler metal after cycling in liquid nitrogen.

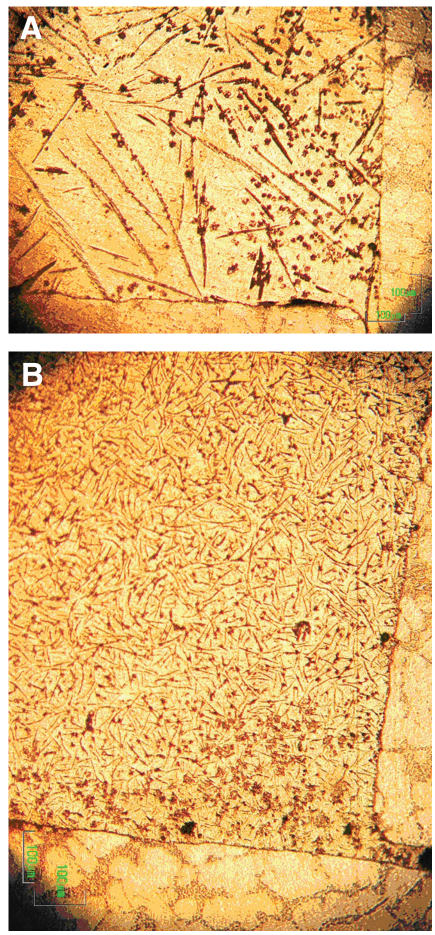

Fig. 2 — Fillet microstructure after soldering A356 aluminum cast alloy with Sn-20Zn solder. A — After soldering; B — after one cycle of cryogenic cooling.

The increased strength of the base

metal will definitely reflect strength of brazed or soldered joints. For example, brazed joints of titanium made with Al-5Mg-0.4Fe filler metal exhibited improved strength ~11.6 ksi (80 MPa) after brazing plus cryogenic cooling vs. 9.9 ksi (68 MPa) immediately after brazing.

Thirdly, very often, the brazing thermal cycle works as a tempering or even an annealing heat treatment of wrought base metals. For example, the brazing temperature of all aluminum alloys is in the range of 580°–610°C (1076°–1130°F); but most heat treatment operations are carried out below 450°C (840°F). Titanium alloys are mostly brazed above the $\alpha \rightarrow \beta$ transus temperature; or sometimes, alloy steels are brazed above or close to the temperature of martensitic transformation but they are cooled after brazing in a furnace or in air losing hardness and strength. Deep quenching in liquid nitrogen can be used for recovering mechanical properties of base materials after brazing and this point should be taken into consideration when one selects materials for brazed structures.

Summarizing the above factors, we can say that metallurgical compatibility of base and filler metals, as well as their possible structural transformations during deep cooling, are the most important points when designing brazed or soldered joints projected for operation in a cryogenic medium. Preliminary testing is necessary to find out the effect of cryogenic cycling on mechanical behavior and microstructure of base materials and brazed or soldered joints.

For your application, I would recommend a titanium cylinder with the thread connection to the copper cup that can be sealed by brazing either with a silver filler metal like BAg-24 or with aluminum filler metal BAlSi-4. An alternative solution is soldering of thread connection of aluminum cylinder with the copper cup using Sn-9Zn or Sn-20Zn solders.♦

References

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