BY ALEXANDER E. SHAPIRO

Q: We brazed titanium Grade 5 tubing to a flange of the same alloy. The brazing filler metal was AWS BAlSi-4, and we also used the flux RL3 A16. Both braze foil and flux were placed inside the joint, and the parts to be brazed were heated with a propane torch as uniformly as possible. When setting up the process, we added a ring of aluminum filler made from 1/16-in. wire on top of the joint, because the filler inside the joint was apparently insufficient. Now the joint has a sound quality; however, a "halo" or nonuniform spreading of the braze alloy appeared around the joint area with a pattern that cannot be removed by polishing with sandpaper. The pattern looks like two concentric circles differently colored. The outline is almost black and has the irregular shape, while the inner circle has a typical "aluminum cast" color. Since we cannot remove the halo, we want to know: What is the nature of these two colored patterns?; and does this affect the strength of the titanium flange?

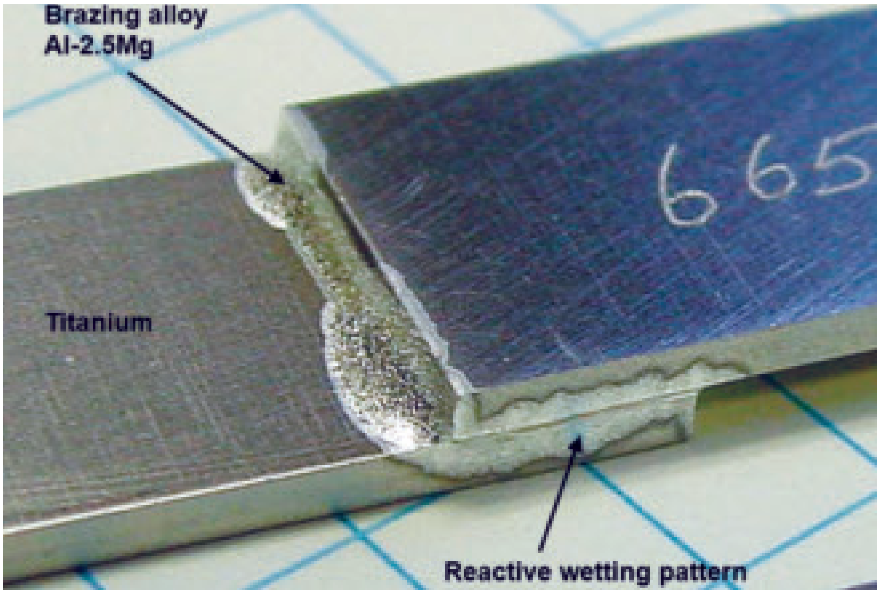

Fig. 1 — Reactive wetting pattern on titanium Grade 2 brazed in vacuum with filler metal TiBrazeAl-665 (Al-2.5Mg-0.3Cr).

A: The spreading pattern you describe has appeared due to the effect called "reactive wetting." It can be observed sometimes during brazing or soldering using such combinations of base and filler metals as nickel-plated copper printed circuit board (PCB) and tin-silver-copper solder, a superalloy and a braze of nickel-phosphorus, or nickel-chromium-phosphorus system, bronze and silver filler metals, titanium- and aluminum-based brazing filler metals, and others — Fig. 1. In other words, if liquid filler metal or solder reacts with base metal with formation of reaction products (especially, intermetallic compounds), this "halo" pattern may appear. And it is understandable why you cannot remove it by polishing. Some reaction products (in your case, likely $TiAl_3$ and TiAlSi intermetallic compounds) were formed at the interface between braze and base metal, and in order to remove them from the titanium surface, you have to remove the surface layer of titanium containing these intermetallics (supposedly, a layer several microns thick). Usually, manufacturers do not remove this layer because machining or abrasive treatment of brazed parts can damage the joint, and besides, the shape of parts is often not suitable for machining — for example, the PCBs mentioned previously.

Reactive wetting is a fairly sophisticated process that is accompanied by formation of different reaction products, mostly intermetallics, which have different reflective indexes (hence, different colors). These reaction products are formed during spreading of liquid braze or solder; therefore, we observe them as a number of concentric circles of a "halo" pattern of different colors — Fig. 1. A cross section of solidified braze filler or solder after reactive wetting is shown schematically in Fig. 2, where reactive product layers 2 and 3 are shaded in. Removal of peripheral circles would help only partially, because the same multilayer structure is formed at the interface, under the joint metal and fillet. If reactive wetting results in the formation of the halo pattern shown in Figs. 1 and 2, there is usually no reason to worry about the strength of the base metal. No evidence of decreasing the strength of the base metal have been found in practice. Moreover, I would consider the presence of such patterns after soldering as an indication of good wetting and the formation of quality joints, because wetting without the reaction of solder and substrate may led to voids and other defects.

However, sometimes reactive wetting may accompany erosion of the base metal as shown in Fig. 3. This can happen when the substrate is overheated during brazing or soldering; and holding time is too long and the reaction of the solder with the base continues, resulting in local dissolution of the base metal.

At this stage of the process, motion of the spreading liquid is controlled by the solute concentration gradient of base metal in the liquid. In order to avoid erosion, one can cut the brazing/soldering time, but the best solution is to substitute the combination of base metal and solder for a low-reactive pair of materials. Application of "stop-off agents" is also used in the industry. Sprays of yttrium oxide or boron nitride fine powders are very effective as stop-off materials. These compounds are deposited, before brazing, on the surface around the joint and limit spreading of filler metal or solder.

Reactive wetting has been studied fairly well, especially during the last decade (Refs. 1–3). According to the model called "Reaction Product Control" (Ref. 2), both final contact angle and spreading kinetics are governed by interfacial reaction. Here, we can only abstract this sophisticated model, which is supported today by many experiments and discussed in detail. Solder (or braze) spreading time in reactive systems is quite slow ($10–10^4$ s) vs. nonreactive wetting times (less than 10^{-1} s), which means that spreading in reactive systems can be observed visually. As a consequence, slow spreading rate in reactive systems is not limited by viscous dissipation, but the rate of interfacial reaction at the front of spreading liquid metal. This rate is controlled by the slower of three successive phenomena participating in reactive wetting: a) diffusive transport, if reacting elements approach or recede from the spreading front; b) local reaction kinetics; and c) local dissolution of base metal in the liquid.

Generally, overall spreading kinetics involved with reactive wetting can be described as follows (Ref. 3): Global mass

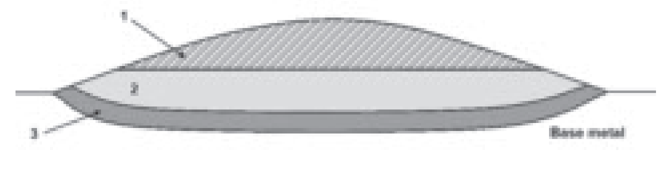

Fig. 2 — Cross section (model) of solidified braze or solder droplet after reactive wetting and spreading on the base metal surface. 1 = brazing alloy or solder; 2 and 3 are reaction product layers.

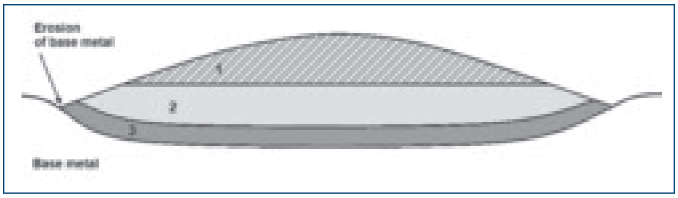

Fig. 3 — Cross section (model) of solidified braze or solder droplet after reactive wetting, spreading accompnied with local dissolution of base metal. 1 = brazing alloy or solder; 2 and 3 are reaction product layers.

transport in liquid braze metal or solder is controlled by convective transport and the formation of intermetallics dominated at early and intermediate times. This results in the formation of horizontal layers along the solid-liquid interface. And diffusive mass transport dominates at the late stages of reactive spreading.

In your case of the Al-12Si and Ti reactive system, I can suggest the following kinetics of the process: When aluminum and silicon contents exceed the reactivity limit, thin continuous layers of $TiAl_3$, TiSi, or TiAlSi compounds are formed along the entire interface, enhancing the spreading of liquid brazing filler metal Al-12Si. The reaction changes the composition of the liquid filler metal as a function of spreading. When the aluminum and silicon contents in the liquid alloy become insufficient for formation of the previously mentioned intermetallics, no new $TiAl_3$, TiSi, or TiAlSi compounds are formed at the liquid/solid interface, and spreading stops.♦

References

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Erratum

In the Oct. 2010 Brazing Q&A column, page 20, the volume ratio of oxide film to metal reads 1:214. It should read “1.214”.

This column is written alternately by TIM P. HIRTHE and ALEXANDER E. SHAPIRO. Both are members of the C3 Committee on Brazing and Soldering and several of its subcommittees, A5H Sub-committee on Filler Metals and Fluxes for Brazing, and the Brazing and Soldering Manufacturers Committee (BSMC). They are coauthors of the 5th edition of AWS Brazing Handbook*.*

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Readers are requested to post their questions for use in this column on the Brazing Forum section of the BSMC Web site www.brazingandsoldering.com.