

Frequently asked questions #8

What is 'crevice corrosion'?

Particular care must be taken in the selection of filler materials for the **brazing of stainless steels** that **might** be exposed to **oxygenated moisture in service**. In such service conditions failure of the joint can result from a specific form of interfacial corrosion that occurs just a few microns into the steel **beneath** filler metal/ stainless steel interface. In the literature of brazing this form of failure is often referred to as '**crevice corrosion**', However, and to be strictly accurate, the phenomenon should be described as '**Interfacial corrosion**'!

Reference to '**Interfacial corrosion**' or sometimes **Crevice Corrosion** when '**Interfacial corrosion**' is really meant, is to be found in many Papers that are concerned with the brazing of stainless steels with low-temperature silver brazing filler materials. However, experience from industry clearly demonstrates that this form of corrosion is neither understood nor, in the main, even considered as a possible cause of joint failures that have occurred in brazed stainless steel assemblies. This may well be because detailed written information on the phenomenon is almost non-existent: this short Paper will attempt rectify this problem. What is abundantly clear is the fact that most people see 'corrosion' as a long-term thing, and so often discount the idea of its relevance to the service life of the assembly they are brazing. However, unless certain precautions are taken regarding the selection of the filler material and flux used to make the joints, it is a high probability that continuous exposure of brazed stainless steel parts to an aqueous environment will lead to failure of the brazed joint within **three months**, and that even in cases of intermittent exposure, failures can be expected within **six months**.

Interfacial Corrosion: Theory and practice

In the examination of joints that have failed by the mechanism of crevice corrosion it is usual to find that the mating surfaces of it appears bright and un-pitted, as though the joint had never been properly brazed. A further distinguishing characteristic feature of this mode of failure is the appearance of a thin 'deposition' of what appears to be conventional 'rust' along portions of the periphery of the filler metal fillet on the joint. See **Figs 1(a) & 1(b)**

As mentioned earlier in this Paper, written details and pictures of the phenomenon are almost non-existent. Consequently, before writing this Paper it was felt desirable to rectify the problem of the lack of photographic evidence by arranging for a number of samples to be prepared by using three filler materials that are widely available, two of which, (Samples **A & B**), were known to produce joints on stainless steel that would be susceptible to failure by interfacial corrosion, and one, (Sample **C**), that was known to be immune to this type of failure, and then to photograph the results obtained.

The filler metals used in the tests were as follows:

A. Specification: EN1044: 1999 Type AG 301

Composition: 50% Silver: 15% Copper: 16%Zinc: 19%Cadmium

Melting Range: 620 - 630°C

B. Specification: EN1044: 1999 Type AG 351

Composition: 50% Silver: 15.5% Copper: 15.5% Zinc: 16% Cadmium: 3%Nickel

Melting Range: 634 - 656°C

C. Specification: A proprietary material that does not have an EN reference number

Composition: 64% Silver: 26% Copper: 2%Manganese: 2%Nickel: 6% Indium

Melting Range: 730- 780°C

The samples were prepared by melting each of the filler materials onto several individual backing sheets of a martensitic stainless steel measuring 25mm x 25mm x 2mm thick under a

cover of a flux conforming to EN1045 Type FH10. The flux residues were removed after melting the filler metal onto the steel, and the resultant products were placed in individual containers that after filling with water were left open to the air. The samples were left immersed for a few days, but in the intervening period the water that had evaporated from the containers was topped-up as and when required. The results obtained were in-line with expectation:

(a) Sample A before testing



(b) Sample A after testing



Fig 1(a): The thin line of a brown deposit at the edge of the brazing alloy that has formed in the **after** testing picture is a sure sign that the interface between the filler metal and the stainless steel is being attacked by 'interfacial corrosion'

(b) Sample B before testing



(b) Sample B after testing



Fig 1(b): Here again the **after** testing sample shows evidence of interfacial corrosion attack. However the level is much lower than that experienced by **Sample A**. This is due to the presence of Nickel in **Sample B**, but note that **attack has still occurred!**

Sample C before testing



Sample C after testing



Fig 1(c): There is no evidence of interfacial corrosion in the '**after testing**' condition of **Sample C**, the very thin streak brown at the base of the alloy 'pool' and on its surface is mainly due to presence of manganese in the filler material: this is also visible in the '**before testing**' picture!

It is known that failure due to interfacial corrosion is much more likely to occur in martensitic and ferritic stainless steels than it is in austenitic materials. However, it is very important to recognise that if stainless steel is to be joined by brazing a useful 'insurance policy' is **always** to assume that it *will* be exposed to service conditions that can lead to interfacial corrosion failure occurring, and proceed accordingly! Unfortunately, once corrosion has begun the condition is irreversible!

One of the most interesting features of **Figs 1(a) to (c)** is the fact that filler **Sample B**, the one that contains a small amount of nickel in addition to both cadmium and zinc, is slightly less prone to attack than the nickel-free **Sample A** material. This seems to point to the possibility that the presence of nickel in a filler material **retards** the on-set of interfacial corrosion. This *might* explain the passing references in texts, initially written in the 1960's, that such materials are acceptable for use where joints in austenitic stainless steels are to be brazed, and where the resultant joints will be exposed to conditions where interfacial corrosion will be a service hazard. Be that as it may, the author of this Paper would **not** be happy to have a brazed austenitic stainless steel plumbing system installed in his home if the chosen filler metal that was to be used for the installation was other than the **Sample C** material!!

Research carried out in the mid-1970's in both the United Kingdom and Germany showed that if joints had been made with a filler metal that contained either one or both of cadmium and zinc, (elements that are found as major constituents in the majority of low-temperature silver-bearing filler materials), base-metal rich phases were produced during brazing. Intermetallic diffusion processes result in the formation of these phases along the joint interface during the brazing process and, essentially, those found were copper-zinc-cadmium-iron, and copper-zinc-iron. It is clear that the iron content of these phases is coming from the stainless steel while the brazing filler material is providing the other base-metal components. The Research Programme established that diffusion of these phases into the stainless steel is limited to a depth of only a few microns. The corrosion-cell that is generated when this diffusion layer is exposed to oxygenated moisture results in the base-metal phases being preferentially dissolved, this invariably leading to relatively rapid failure of the joint. It has also been shown subsequently that if brazing is carried out with the alloys that are to be found in **Table 2** later in this Paper, joint failure by the mechanism of interfacial corrosion is avoided.

Fig 2(a) & (b) are representations of the mechanism of interfacial corrosion

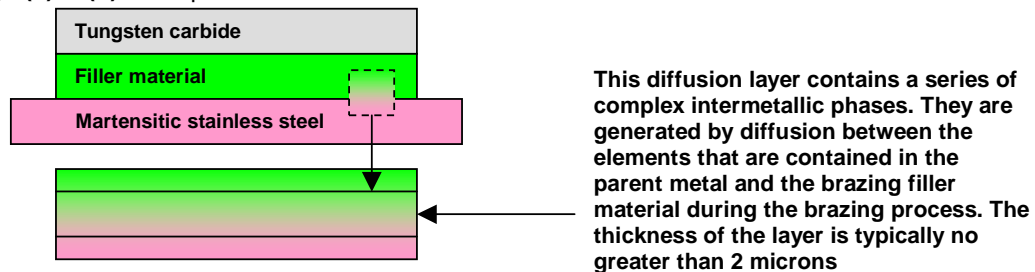


Fig 2(a): The diffusion layer that is generated during the brazing process

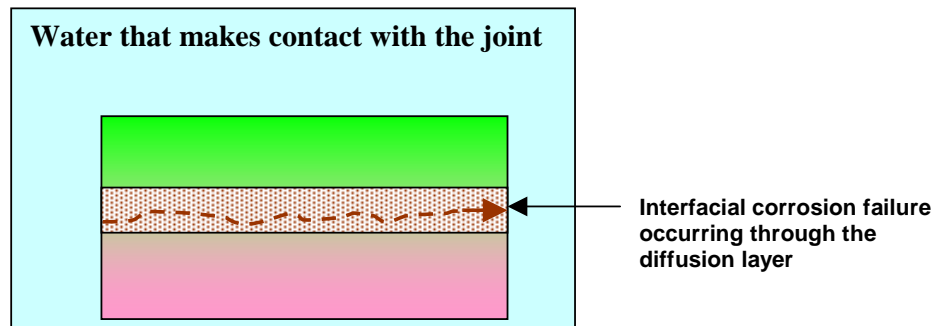


Fig 2(b): Interfacial corrosion failure through the layer of intermetallic compounds

What can be done to avoid this problem?

Brazing materials that can be used to avoid the problem of 'interfacial corrosion' are not 'thick on the ground', **and not all silver containing filler materials that are free from cadmium and zinc are immune to failure.** As a direct result of this situation the choice of technically suitable materials is **very limited**, and if economic viability is also taken into the equation the choice is restricted even further. Four potentially suitable, and cost-effective, silver-containing brazing filler materials are shown in **Table 2**.

Composition	Melting Range °C
56%Ag: 27%Cu: 14.5%In: 2.5%Ni	600 - 711
63%Ag: 28.5%Cu: 6%Sn: 2.5%Ni	690 - 800
60%Ag: 30%Cu: 10%Sn	600 - 730
64%Ag: 26%Cu: 6%In: 2%Mn: 2%Ni*	730 - 780

*Also available as a **tri-metal** foil

Table 2: Four filler materials that have been shown to be immune to failure by the mechanism of Interfacial Corrosion

While all the materials shown in **Table 2** can be described as low-temperature silver brazing filler materials, practical experience in the field points to the use of one or other of the Indium-bearing alloys as being the best choice. This is particularly true in situations where the material that is to be brazed to the stainless steel has a very low coefficient of linear thermal expansion, and where artificial thickening of the joint line will be necessary to overcome the potential distortion problems arising from the contraction stresses that will arise in the joint as it cools from brazing temperature. In this case a **tri-metal** foil will be required as the filler material, and as indicated in **Table 2**, only **one** of the suggested materials is available in that form.

Fluxing

Due to the presence of chromium in the material, the oxides that are developed on stainless steel when it is heated in air are very tenacious and quite difficult to remove. As a result due care has to be taken in respect of the selection of both the flux and the heating method that is to be employed.

The most appropriate flux for an 'in-air' brazing procedure in the majority of cases will be a conventional fluoride flux conforming to BS EN1045: 1999 Type FH10. However, when stainless steel is to be brazed a flux of the silico-fluoride type will give even better results, particularly if the heating cycle is longer than about a minute. The 'downside' of the use of this latter type of flux, however, is the fact that its residues are hard and virtually insoluble and have to be mechanically removed!

We have already commented that the surface oxides that are formed on the surface of stainless steels are tenacious. The need to deal with tenacious oxide layers when tungsten carbide is to be brazed led to the development of a variant of the 'standard' low-temperature brazing fluxes. These materials, which are formulated to include up to 1% of elemental boron, conform to BS EN1045 Type FH12. The presence of the elemental boron gives rise to their everyday name '**BROWN-**' or sometimes, '**BLACK- 'FLUX'**'

CAUTION: Where the joints brazed in stainless steels are to be exposed to moisture in service fluxes of this type **MUST BE AVOIDED!!**

This is because during the heating process the 'free' boron in the flux tends to diffuse into the surface of the stainless steel where it reacts with the chromium and nickel constituents of the stainless steel to produce both chromium- and nickel-boride. This action effectively 'locks up' these elements in the surface layer of the steel, and inevitably results in the properties of this layer being 'changed' so that, it becomes iron-rich, and so effectively 'non-stainless'. As a

result, if it is subsequently exposed to moisture, the surface layer simply rusts away as though it were an unalloyed steel, and premature joint failure is the inevitable result!

It is therefore of **fundamental importance** to ensure that **only** the '**white**' varieties of brazing fluxes are employed when stainless steel is to be brazed in air!

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