Making Corrosion-Resistant Brazed Joints in Stainless Steel

ADVANTAGES OF PALLADIUM-BEARING BRAZING ALLOYS

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Stainless steel parts brazed with standard low-melting brazing alloys are susceptible to a specific kind of corrosion by water or humid atmosphere, generally known as interface or crevice corrosion. One of the advantages of brazing alloys of the silver-copper-palladium type is that they will produce joints in stainless steel resistant to this form of failure.

Joints made in stainless steel with certain low-melting brazing alloys (of the silver-copper-zinc-cadmium type) and exposed to the action of water or humid atmosphere are susceptible to corrosion of a rather unusual kind.

The attack in this case consists in the dissolution of a very thin steel layer along the joint interface, as a result of which the bond between the steel and the brazing alloy is completely destroyed. A failure of this kind is illustrated in Fig. 1, showing a laboratory stainless steel joint specimen in an advanced stage of corrosion.

Since the quantity of metal that has to be dissolved to produce this effect is extremely small, the rate of bond destruction is very fast. Cases are known of stainless steel parts brazed with unsuitable materials falling apart after a week's exposure to the action of ordinary tap water.

Another distinguishing feature of the corrosive attack of this kind, which is usually referred to as interface or crevice corrosion, is that neither the brazing alloy nor the stainless steel show any obvious symptoms of corrosion damage. Although iron dissolved at the joint interface is precipitated as a loose red rust deposit outside the joint area, once this corrosion product has been removed (by design or by accident), there is nothing to indicate that the separation of the brazing alloy from the steel was caused by corrosion. In fact, the usual reaction of an observer

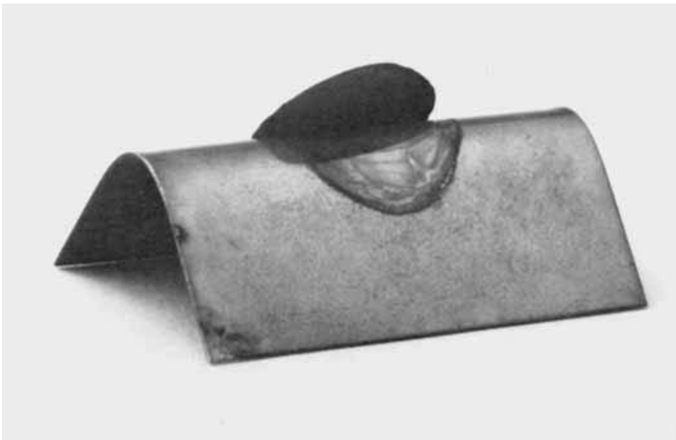

Fig. 1 A ferritic stainless steel (EN 60) specimen brazed with a 50Ag-15Cu-16Zn-19Cd alloy and held for eight days in running tap water. The specimen was bent to reveal the extent of interface corrosion resulting in the destruction of the bond between the brazing alloy and the steel

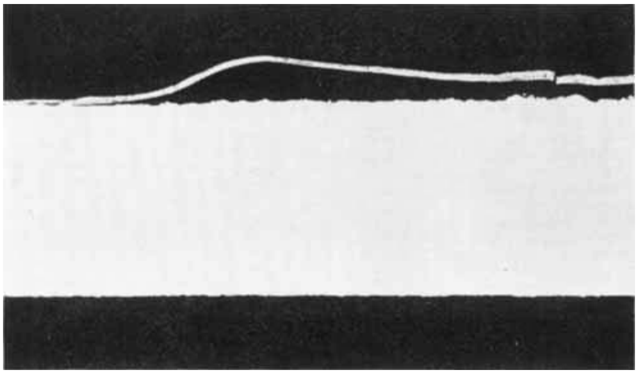

Fig. 2 Showing a blister formed in an austenitic steel (EN 58e) specimen brazed with a 54Ag-25Pd-21Cu alloy in dissociated ammonia under a flux cover and held for 106 days in running tap water. (×50)

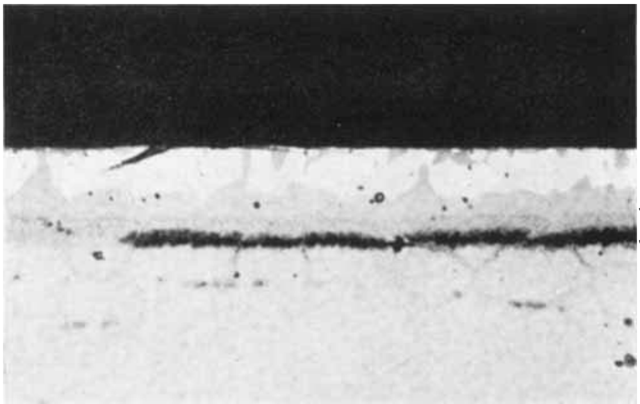

Fig. 3 A magnified view of a region of the specimen of Fig. 2 showing the presence of a partially oxidised steel layer at a certain distance from the joint interface along a plane coinciding with the path of the crack whose formation led to blistering. (×550)

faced with a failure of this kind is to conclude that the joint fell apart because no bond formation had actually taken place.

The mechanism of interface corrosion, which now appears to be a much more complex phenomenon than first thought, has not yet been elucidated. However, extensive researches in this field have made it possible to classify various standard and specially developed brazing alloys in the order of their usefulness for joining stainless steel when corrosion resistance of the joints produced is an important consideration.

It has been established for instance that, although there are several low-melting silver brazing alloys with which joints resistant to interface corrosion can be made, each of these materials has certain limitations. And so, most alloys that are convenient to use from the purely brazing point of view will produce corrosion-resistant joints but only when used on stainless steel of the nickel-bearing austenitic type. On the other hand, low temperature brazing alloys that are suitable (from the standpoint of interface corrosion resistance) for joining both austenitic and ferritic stainless steels are often distinguished by somewhat inferior flow characteristics. Finally, the corrosion resistance of stainless steel parts brazed with low-melting alloys of this kind may often be substantially affected by certain changes in the composition of fluxes used during brazing.

The only known materials that combine the freedom from the above limitations with many of the desirable properties of various silver solders are certain gold-base and palladium-bearing alloys. The latter are exemplified by the 54Ag-25Pd-21Cu composition which is one of the Johnson Matthey noble metal brazing alloys known as Pallabraze 950; its special advantages as a filler material for joining stainless steel can be summarised as follows:

(i) Pallabraze 950 will produce interface-corrosion resistant joints in both ferritic and austenitic stainless steels.

(ii) The corrosion resistance of joints made with this alloy is not affected by changes in the composition of the brazing flux, especially by the presence of free boron which is sometimes added to brazing fluxes to improve their flow-promoting properties and stability at elevated temperatures.

(iii) Joints made with Pallabraze 950 combine the resistance to interface corrosion with a relatively high strength at temperatures of up to 400°C.

(iv) Stainless steel parts brazed with this alloy are not damaged by erosion due to excessive interalloying during brazing.

(v) Due to its palladium content, Pallabraze 950 may be safely used when intergranular penetration of steel by a molten brazing alloy might otherwise lead to brazing failures.

(vi) Pallabraze 950 has excellent wetting and free-flowing characteristics and can be used both for brazing in air under a flux cover and for fluxless brazing in a reducing atmosphere.

In this last connection a rather unusual effect is worth reporting.

It is sometimes found in industrial practice that the oxide-reducing potential of a brazing furnace atmosphere which is sufficiently pure (dry) to preserve the initial bright finish of stainless steel parts is too low to make the steel surface wettable by the brazing alloy.

The usual remedy in such cases is to use both a reducing atmosphere and a small quantity of a suitable brazing flux. However, it has been recently found that this practice may have unexpected and rather puzzling consequences.

If an alloy is intrinsically capable of producing corrosion-resistant joints, it makes no difference whether the brazing is done in a reducing atmosphere or under a flux cover. When, however, both a reducing atmosphere and a flux are used in brazing with such an alloy (e.g. Pallabraze 950), the resultant joints —while resistant to interface corrosion—may be subject to failure of a different kind.

When observed under laboratory conditions on specimens tested in running tap water, the failure consisted in the formation of

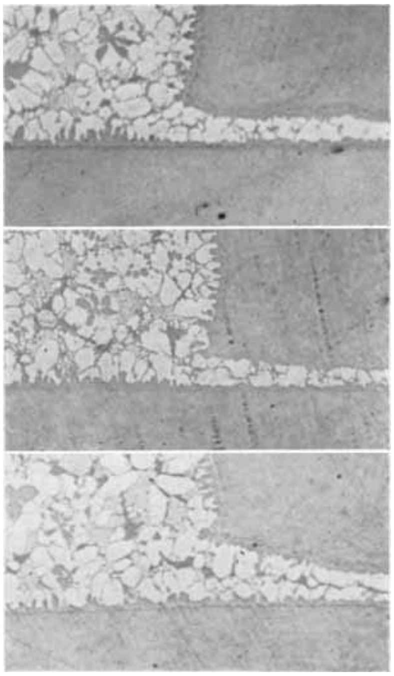

Fig. 4 Showing the absence of any obvious differences in the structure of joints brazed in an austenitic stainless steel (EN 58e) with a 54Ag-25Pd-21Cu alloy: (top) in dissociated ammonia; (middle) under a flux cover in air, and (bottom) in the presence of both a reducing atmosphere and a brazing flux. (×200)

a crack inside the joint. The crack was propagated in the steel itself along a plane parallel to, and at a distance of several microns from, the joint interface; it was often associated with the presence of a partially oxidised steel layer. The crack plane approximately marked the boundary of the zone into which palladium and copper had diffused into the steel during brazing. The only external evidence of the development of this failure was the formation of blisters in regions where the brazing alloy coating was sufficiently thin. Photomicrographs of a specimen that had failed in this way are reproduced in Figs. 2 and 3.

It should be added in conclusion that metallographic examination of specimens in the as-brazed condition revealed no differences between joints made with the same alloy under a flux cover, in a reducing atmosphere, and in the presence of both these fluxing media (Fig. 4).

Further studies will be necessary to establish the precise conditions leading to joint failure of the kind described above and to ascertain that the effects observed were not due to some extraneous, as yet unidentified factors. Nevertheless, the evidence available so far is sufficient to advise against using a brazing flux in combination with a reducing atmosphere in the joining of stainless steel parts that may be exposed to the influence of water or humid atmosphere in service.

Thermocouples Under Neutron Bombardment

CHANGES IN VOLUME AND COMPOSITION

Under severe neutron radiation thermocouples are known to be unstable although little data on the changes in composition which occur has hitherto been published. A recent report by C. B. T. Braunton, D. N. Hall and C. M. Ryall, of the Atomic Energy Research Establishment, Harwell, (U.K.A.E.A., A.E.R.E. – R5837, 1968), now provides information which will greatly simplify the selection of thermocouple materials for experiments carried out under radiation at high temperatures. Under such conditions lattice damage anneals out and changes of thermoelectric behaviour can be predicted from the compositional changes. These have been computed from differential equations which were developed to describe the exponential transmutation of isotopes, and curves defining the composition of the various alloys at successive stages of time and radiation are provided in this report.

Pure platinum when irradiated produces only gold and mercury, each reaching a maximum concentration of rather less than 1 per cent after a year's exposure to a flux of 10^{15}n/cm^2/sec. Under similar conditions, however, the rhodium content of rhodium-platinum alloys is almost completely consumed, to form palladium, mercury, gold and iridium.

Ruthenium alloys are far more stable. The ruthenium remains unchanged, all transmutation effects being confined to the platinum. The palladium content of palladium-platinum alloys is not greatly affected although small quantities of mercury, gold, cadmium, silver, iridium and rhodium are formed by transmutation. Molybdenum-platinum alloys are considerably more stable than rhodium-platinum alloys when irradiated being comparable to ruthenium-platinum alloys in this respect.

Tungsten, rhenium and tantalum all suffer severely in a neutron flux. Some 40 per cent of the rhenium is lost after one year at a flux of 2×10^{14}n/cm^2/sec; tungsten is rapidly replaced by rhenium, rhenium by osmium, and tantalum by tungsten. The compositional changes in molybdenum are small.

Platinum alloys increase in volume under neutron irradiation by amounts ranging up to 2 per cent after one year at 10^{15}n/cm^2/sec. Tungsten, tantalum and rhenium decrease in volume to a considerably greater extent.

A significant conclusion of this report is that tungsten-rhenium thermocouples will suffer more damage, and are likely to be less stable than platinum-based thermocouples under similar conditions of neutron bombardment. It will be interesting to see whether the results of the experimental programme now being carried out in mixed thermal and fast neutron fluxes, referred to in this report, confirm this prediction.

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