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HI TEMP BRAZING ALLOYS

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Surface Preparation for High Vacuum Brazing

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The quality and strength of a brazed joint is determined by many factors including fit-up (joint clearance), brazing temperature and furnace atmosphere [1].

However the surface conditions of the base metal parts, which are often ignored, can also have a decisive influence on the success of the brazing process and joint properties.

Surface Cleanliness

Base metal surface condition is a key factor in producing a sound brazed joint. Good surface cleanliness is a pre-requisite for good wettability and helps ensure the molten brazing filler metal (BFM) flows freely over the substrate materials during the brazing process. Successful high temperature vacuum brazing requires clean and oxide free surfaces if optimum joint strengths are to be achieved.

It is very common for metallic sheets and preforms to contain organic contaminants such as lubricating oil or grease. Other surface impurities that can also inhibit capillary flow include dirt and oxide residues. A number of surface cleaning methods are available and their effectiveness depends on a number of factors such as the nature of the contamination, base material type and configuration. Chemical and/or mechanical techniques are used to both clean and condition the surface of the materials to be brazed.

Chemical Cleaning

Oil and grease are usually removed by dipping the part in a suitable degreasing solvent, or by vapor degreasing, alkaline (KOH, NaOH, phosphates) or aqueous cleaning. Residues which remain will form a barrier between the base metal surfaces and the brazing materials. An oily base metal, for example, will repel the flux, leaving bare spots that can oxidize when heated, resulting in voids as the BFM is not able to wet the surface in those areas. Oil and grease will also carbonize when heated, forming a film over which the filler metal will not flow [2].

However, if the surface is oxidized, the oxide layers cannot be easily removed by the majority of chemical processes. In these instances, a mechanical or chemical cleaning process such as acid pickling may be desirable. Pickling results in the removal of a thin layer from the substrate surface which may contain oxidized material.

Common industrial pickling methods include immersion, spray, or circulation pickling. The types of chemicals used for the pickling process are strongly dependant on the base material. Stainless steels, for example, are often treated using an acid mixture containing Nitric acid (HNO3) and Hydrofluoric acid (HF), whereas chloride containing acids such as Hydrochloric (HCl) should be avoided due to the risk of pitting corrosion.

Mechanical Cleaning

All surfaces should be chemically cleaned prior to a secondary mechanical process. Mechanical methods such as grinding, machining, filing, wire brushing, tumbling, vibratory polishing and blasting are all used. These methods can also remove oxide layers which may be present on the base metal surface. If coolants are used during any of these cleaning processes, they must be free from contaminants such as silicone residues and corrosion inhibitors.

Research has shown that grit blasting with non-metallic materials such as aluminium oxide and silicon carbide should be avoided as surface remnants of these materials can inhibit flow and wetting capabilities [3] by providing an oxide or physical barrier. The brazing of nickel-based substrates such as IN 718 can be improved by blasting with NicroBlast® grit nickel-based powder, prior to vacuum brazing. Chilled cast iron and hardened or stainless steel grits or powders, are recommended for carbon steels and stainless steels, respectively.

Mechanical cleaning processes produce surface compressive stress and a roughened surface. It is well established that wetting on a rough surface occurs much more readily than on a smooth surface of the same geometry. For most materials, the optimum surface roughness is 0.75 to 3.75 microns.

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Surface Conditioning

Although chemical and/or mechanical cleaning is extremely effective, some substrate materials and components require additional conditioning in order to provide a braze-friendly surface. Chemical composition and thermal history of the base metals can have an influence on the surface characteristics. For example, base materials which contain quantities of aluminium and titanium do not allow good flow of the BFM. This is due to the fact that these elements form very stable oxides within the surface region which prevent satisfactory wetting by the BFM.

The following surface conditioning techniques are well-known and are commonly used in the industry: [4]

Vacuum Cleaning – is a satisfactory method for removing oxides from stainless steel and some nickel-based alloys.

The main theory behind the use of a vacuum furnace in the brazing process is that a hard vacuum aids the removal of surface oxides. This effect is most commonly observed during the vacuum brazing of austenitic stainless steel as the dissociation of chromium oxide from the surface allows good flow of the BFM to be achieved.

While the oxides of Iron, Nickel and Chromium are readily dissociated under vacuum conditions at higher brazing temperatures, the oxides of aluminium and titanium do not dissociate easily. The surface oxides present cause interference with the flow of the BFM and often prevent brazing of the assembly.

The stability and the ease of dissociation of surface oxides is described by the "Ellingham diagram", Figure 1.

As shown in Figure 1, some of the most stable, and therefore, hard to remove surface oxides are the oxides of titanium and aluminium. Nickel-based alloys containing titanium and aluminium form complex spinel type oxides at the free surface which, if there in sufficient quantity, can inhibit wetting and subsequent brazing of these complex alloys.

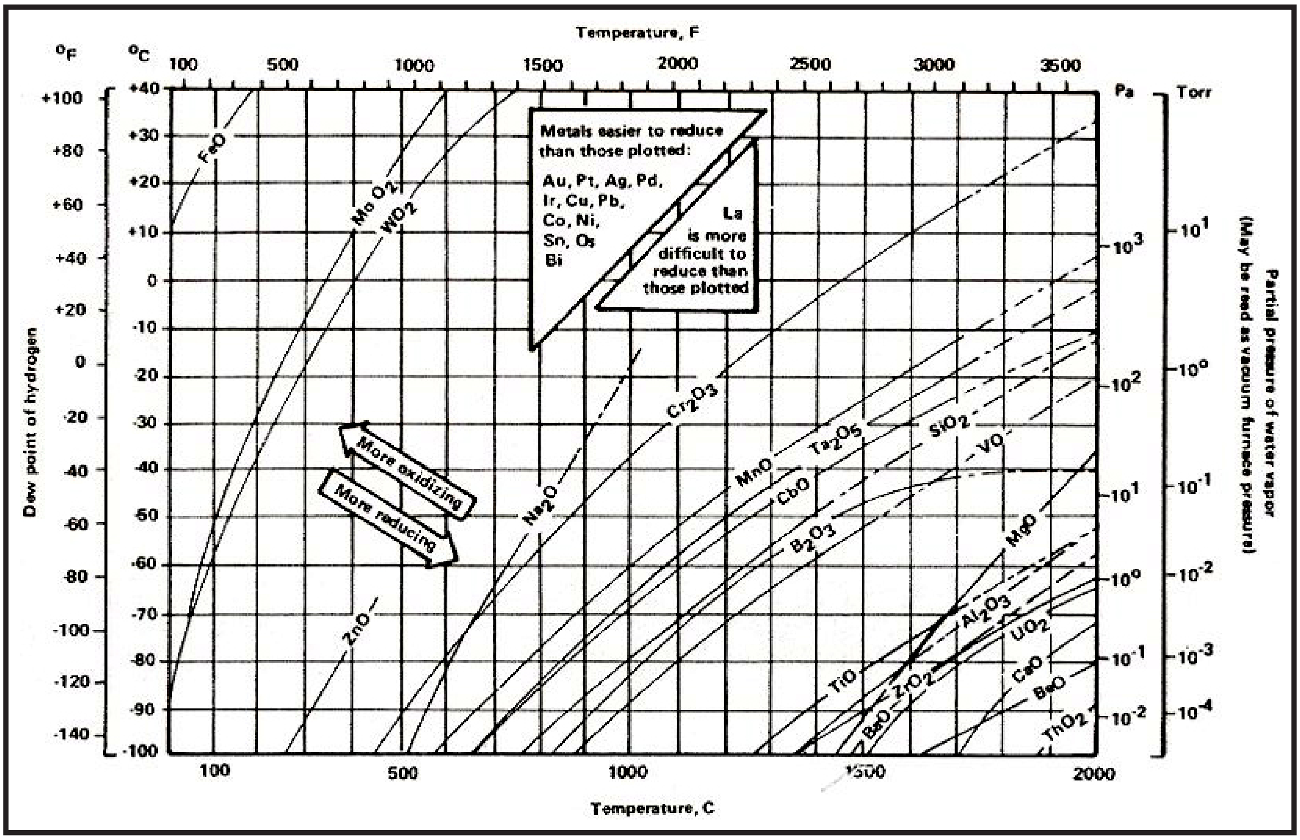

Figure 1: The "Ellingham diagram" which shows which surface oxides are relatively easy (to the left) and difficult (to the right) to remove during vacuum brazing.

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Therefore alloys containing significant amounts of Ti and Al (≥1% combined total) should be subjected to a regime of cleaning to produce a surface layer of between 20-50µm depth which is nominally depleted of Ti and Al oxides.

The Ellingham diagram reveals, with the exception of copper and nickel, that in order to achieve a decomposition of thermodynamically stable metal-oxides, oxygen partial pressures and temperatures are necessary which cannot be realized in vacuum brazing. Removal of the oxide layers in the vacuum yield can occur through other mechanisms affected by [5]:

- The mismatch of the thermal expansion between base metal and oxide layer and its brittle mechanical properties leads to the micro-cracking within the oxide layer. Molten braze filler metal can then infiltrate through micro-cracks in the oxide layer causing it to lift and detach.

- Dissolution of the thin oxide layers in the base material by diffusional processes under vacuum conditions.

- Reduction of the metal oxide by additions of elements with high oxygen affinity and high vapor pressure such as lithium, magnesium and calcium. They are introduced into the chamber as vapor or are alloyed with the filler metal and act as getter-metals, simultaneously reducing the oxygen and moisture content of the residual gas (this method is used as an example for the brazing of aluminium without flux)

Hydrogen Partial Pressure Cleaning (HPPC) – is a satisfactory method for removing oxides from stainless steels, cobalt based super alloys and some nickel-based alloys. Hydrogen provides the active ingredient to clean and also braze components, and can eliminate the need to use a flux.

The capability of pure hydrogen to reduce oxides on the surfaces of metals and alloys depends on three main factors: 1) temperature, 2) purity of the hydrogen (measured as dew point) and 3) pressure of the gas. In the case of any given metal-metal oxide, existing in equilibrium (Fig 1), at a given purity level and pressure of hydrogen, the breakdown of the oxide is favored by higher temperatures and is also time dependent [6]. Special caution needs to be exercised with metals which have a high affinity for hydrogen e.g. titanium as their properties may be significantly affected.

Fluoride Ion Cleaning (FIC) – is the only method capable of removing titanium and aluminium oxides from gamma prime precipitation hardened nickel-based super alloys (e.g. Inconel, Rene, Nimonic type alloys). This common surface cleaning method for Ti and Al rich alloys is seen as an extremely effective process and utilizes HF gas to offer a simpler, more precise and consistent alternative to other more complex techniques [7]. The chemical reactions are illustrated by the following:

1. $6HF + Al_2O_3 = 2AlF_3 + 3H_2O$
2. $4HF + TiO_2 = TiF_4 + 2H_2O$
3. $6HF + Cr_2O_3 = 2CrF_2 + F_2 + 3H_2O$

In addition to removal of the oxides present on the surface and within cracks, surface depletion of elements such as titanium and aluminium also occurs which enhances braze-ability by removing oxide reformers. These reactions are illustrated by the following:

1. $6HF + 2Al = 2AlF_3 + 3H_2$
2. $8HF + Ti = 2TiF_4 + 4H_2$

The depletion reaction is a function of the reaction temperature and time, the concentration of HF and alloy composition.

Nickel Plating – can be used in lieu of FIC. It covers, and thus prevents oxidation of base metals containing high volume of aluminium and titanium elements. Nickel plating may also be desirable for high nitrogen containing stainless steels. Nickel plating also improves surface wettability.

Plating can be carried out by either electrolytic or electroless (chemical) methods. In nickel brazing electrolytic Ni plating is often favored due to the presence of phosphorus commonly associated with the electroless process.

Electroless nickel plating phosphorus, present in the layer, acts as a melting point depressant causing the plated layer to become molten around 870°C (1600˚F). Once molten, the layer ceases to provide a stable barrier between the brazing filler metal and substrate material, leading to issues with the brazed joint.

Recommended Thickness of Electrolytic Nickel Plating

If the base metal is hot rolled and pickled with a matte finish, then it is likely that the surface has been completely depleted of Al, Ti and Cr and as such should braze without Ni plating. When the same base metal is machined or cold finished, oxides will be present and the typical colors of Al and Ti may be visible. In general, if the Al+Ti content of the material is <4%, 0.0025 - 0.015 mm (0.0001 – 0.0006 in.) of nickel plating will be satisfactory for vacuum processing. However, in pure dry hydrogen, 0.01 - 0.015 mm, (0.0004 – 0.0006 in.) thickness is recommended. In base metals with a Al+Ti >4% 0.008 - 0.015 mm, (0.0003 – 0.0006 in.) is required, while in dry hydrogen, 0.02 - 0.025 mm, (0.0008 – 0.001 in.) plating thickness is recommended. As a matter of fact some processors even use a Ni flash on 347 and 304 stainless steels, to improve brazing quality [8].

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About Wall Colmonoy and Brazing

Wall Colmonoy joins parts for high-temperature and corrosion applications using Nicrobraz®, Niferobraz®, and CuBraz™ brazing filler metals and brazing aids.

The pioneer of high-temperature brazing, Wall Colmonoy's expert brazing engineer, Bob Peaslee, invented a new brazing technology involving nickel-based filler metals and hydrogen atmosphere furnaces in 1950. As a result, the new filler metal - Nicrobraz® was created.

Today, Nicrobraz®, Niferobraz®, and CuBraz™ brazing filler metals are used in a variety of industries including aerospace, oil & gas, steel, energy, food, automotive, rail and defense meeting AWS, AMS, G.E., Honeywell, Pratt & Whitney and Rolls-Royce specifications. Nicrobraz products are available as powder, rod, paste, transfer tape and sheets in a full range of sizes and specifications. Wall Colmonoy also custom formulates brazing filler metals to meet customer requirements.

Aerobraze Engineered Technologies, a division of Wall Colmonoy, manufactures engineered components and provides technological solutions for the aerospace, energy, defense and transportation industries. This division meets aerospace quality standards in applications using the process of brazing, surfacing, welding, thermal processing, fabricating, machining and overhauling. Aerobraze Engineered Technologies has the engineering expertise to take concepts from design to prototype to production.

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