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Brazing Filler Metals of Limited-Noxiousness

Abstract: The recent results of technological process and composition-related research performed at Instytut Spawalnictwa in Gliwice and dedicated to brazing filler metals and fluxes of limited noxiousness. The brazing properties of newly-developed low-melting cadmium-free silver filler metals in the form of flux-coated rods and low-fluoride fluxes. The quality and mechanical properties of joints brazed using the newly developed filler metals.

Keywords: brazing, filler metals, fluxes, limited noxiousness

Introduction

The development of brazing is strictly connected with the development of brazing consumables, i.e. filler metals and brazing fluxes, having high brazing properties and complex chemical composition. Such materials, for ensuring the obtainment of required technological properties, often contain chemically active yet harmful substances posing hazard to humans and environment. The obligations of determining production and application-related safety regulations are contained in the Labour Code and related Regulations of the Council of Ministers, taking into consideration Poland's obligations in relation to the International Labour Organisation and the European Union (Regulations and Directives of the European Parliament).

As regards brazing metals, the year 2011 saw a change in the Regulation of the European Parliament and of the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) in relation to Appendix XVII concerned with cadmium [1]. Cadmium is rated as carcinogenic and toxic in the water environment. On 10.01.20012 EU countries practically banned the use of cadmium in brazing metals (maximum permissible content – 0.01% by weight). On an exceptional basis, brazing filler metals containing more cadmium can be used in the military and aviation industries as well as for national security-related purposes.

Presently, poorly brazeable materials are brazed using high-fluoride fluxes (containing approximately 50% by weight of toxic fluorides) characterised by significant toxicity, chemical noxiousness and high chemical activity. However, in recent years the EU, and thus Poland, has adopted Regulations of the European Parliament and of the Council [1, 2], whose primary assumption is controlling and reducing the use of toxic chemical compounds. The use of such compounds has been restricted by various requirements, e.g. a new more rigorous classification of chemical mixtures (including also brazing fluxes) and the registration of some particularly hazardous chemical compounds. This move has urged brazing flux manufacturers to develop the chemical compositions of fluxes characterised by limited noxiousness without compromising their high brazing properties. Such efforts were also undertaken at

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Instytut Spawalnictwa in Gliwice and focused on replacing potassium fluoride (contained in flux) with less toxic potassium fluoroborate (KBF4) as well as on eliminating boric acid and replacing it with more complex boron compounds, i.e. K2B4O7 or KB5O8. In this way the fluxes (containing little or no toxic fluorides) for brazing stainless steels and brasses have been developed [6 ÷ 8].

This study presents cadmium-free equivalents of low-melting silver filler metals and fluxes containing small amounts of noxious fluorides developed at Instytut Spawalnictwa in Gliwice.

Cadmium-free Low-melting Silver Filler Metals

The basic advantage of the Ag-Cu-Zn-Cd type filler metals containing noxious and carcinogenic cadmium (15÷25% by weight) is a relatively low melting point, lower than that of the Ag-Cu-Zn type filler metals (having a similar Ag content as Ag-Cu-Zn-Cd types) and good brazing properties [3]. For this reason, such filler metals have been used for brazing elements sensitive to overheating, in the production of metal accessories, model-making, production of tools with inserts of tool steels or inserts of diamond or ceramic element-reinforced sinters [9]. Among previously developed silver filler metals, the Ag-Cu-Zn-Sn type filler metals can be used as equivalents to cadmium-containing brazing metals. Although cadmium-free brazing metals do not have such a low melting point as cadmium-containing silver filler metals, yet their advantages, including relatively lower melting points than those of the Ag-Cu-Zn type silver filler metals (having a similar Ag content), advantageous brazing properties, relatively small solidification ranges, high corrosion resistance and good mechanical properties, increase their application areas [3,4]. Such filler metals containing 25÷56% Ag and having a full melting point (liquidus) of 655÷760°C are covered by the PN-EN ISO 17672:2010 standard. Their equivalents are also contained in AWS standard (USA) [3]. Among these filler metals, special attention should be paid to the Ag 145 (Ag45Cu27Zn25.5Sn2.5) filler metal (melting point range: 640÷680°C), universally applicable for brazing steels and non-ferrous metals and their alloys. The Ag 156 (Ag56Cu22Zn17Sn5) and Ag 155 (Ag55Cu21Zn22Sn2) filler metals have the lowest fusibility (liquidus temperatures 655°C and 660°C respectively). The filler metals mentioned above are characterised by very good wetting properties as well as by advantageous influence limiting stress corrosion-induced cracking in alloy steels and nickel alloys. Brazes made with these filler metals have a bright silver colour. Particularly recommendable applications of the aforesaid filler metals include brazing of food industry equipment, cutlery, jewellery and metal accessories. However, joints made with these filler metal wires are more sensitive to dynamic loads if compared with joints made using the Ag-Cu-Zn type silver brazing metals without tin additions [10].

The Ag-Cu-Zn-Sn type filler metals are usually produced and offered by manufacturers in the technically convenient form of flux-coated rods. Such a filler metal (PO-AG104 grade (Ag 145 according to PN-EN ISO 17672:2010)) has also been developed and manufactured in this form by Instytut Spawalnictwa in Gliwice on an individual order basis [5].

Fig. 1. Macrostructure of the joint made of the X2CrNi18 stainless steel, brazed with the Ag 145 grade coated silver filler metal, etchant: $FeCl_2$

The filler metal is characterised by good brazing properties and ensures the obtainment of high quality joints (Fig. 1). The mechanical properties are manifested by the shear strength amounting to 269 MPa and 166 MPa for the stainless steel and brass respectively.

Brazing Low-fluoride Fluxes

For many years Instytut Spawalnictwa has conducted research on specialist low-fluoride active fluxes for brazing of high-alloy steels and brasses using silver filler metals. In 1996 a Lutosil (commercial name) flux in the form of a technologically convenient paste was developed and implemented [6]. Although the flux does not contain alkali metal fluorides, it contains a significant amount (over 50%) of fluoroborates. In addition, the flux is characterised by relatively low chemical stability – a few months after manufacture it undergoes crystallisation and becomes problematic in applications. In 1999 another low-fluoride flux (commercially designation: F25), also for brazing high-alloy steels and brasses was developed [7]. However, due to the excessively complex chemical composition (as many as 9 components) the production of this flux is highly problematic (the content of fluorides in the flux composition amounts to 25% by weight, and that of fluoroborates - 15% by weight).

In 2007 an innovative flux, containing only 6% by weight of toxic fluorides, was developed [7]. The flux, containing also amorphous boron, was designated as F6B. The experience of previous investigation of fluxes for brazing of high-alloy steels directed matrix composition-related tests towards the mixtures of such compounds as tetraborate or potassium pentaborate. The matrix mentioned above is activated by the mixture of potassium fluoride and potassium tetrafluoborate. The flux is characterised by good brazing properties, particularly by the high Ag 245 (B-Ag45CuZn-665/745) filler metal spreadability on the X2CrNi18-9 grade stainless steel substrate (spreadability area of approximately 283 mm²). Figure 2 presents a test piece after the spreadability tests involving this flux. As can be seen, the flux leaves very little flux slag on the test piece.

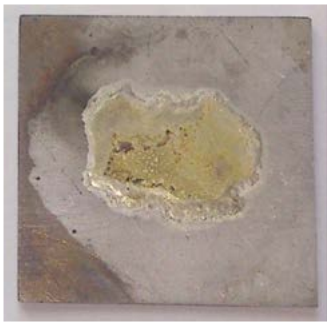

Fig. 2. Spreadability of the Ag 245 filler metal on the X2CrNi18-9 grade stainless steel using the F6B flux

In related metallographic and strength tests, the flame brazed overlap joints made of the X2CrNi18-9 steel using the Ag 245 filler metal and the F6B flux revealed good quality (Fig. 3) and a high shear strength of approximately 200 MPa.

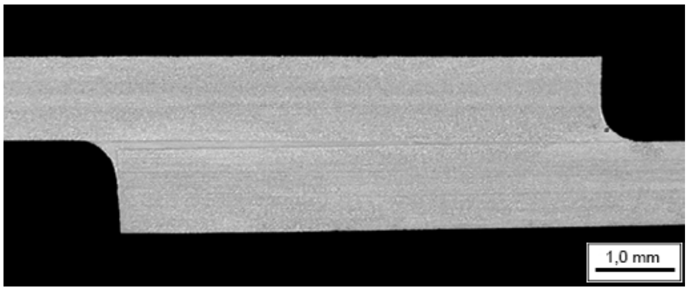

Fig. 3. Macrostructure of the joint made of the X2CrNi18-9 steel using the Ag 245 silver filler metal and the low-fluoride boron-containing F6B flux, Adler's etchant

A certain limitation to the F6B flux use is its relatively high price, 3 times higher than that of a typical high-fluoride flux. The high price of the F6B flux results from the presence of expensive amorphous boron in the flux composition. Due to the relatively high price of the F6B flux, in 2012 Instytut Spawalnictwa undertook technological and composition-related tests aimed to develop a low-fluoride flux characterised by good brazing properties, yet not containing amorphous boron. The matrix of the new flux included such compounds as tetraborate and potassium pentaborate. The analysis of reference publications as well as the overview of documented tests results related to the development of brazing fluxes had enabled the selection of potassium fluorides (KF, KHF_2) and potassium tetrafluoborate

(KBF4) as the activators of the matrix mentioned above. The flux developed was designated F10 and contains only a slight amount of toxic fluorides (10% by weight) in its composition [8]. The flux is characterised by good brazing properties – the Ag 245 filler metal spreadability area on the X2CrNi18-9 grade stainless steel substrate amounts to approximately 415 mm2. Figure 4 presents a test piece after spreadability tests. As can be seen, the F10 flux, similarly to F6B, leaves very little flux slag.

Fig. 4. Wettability of the Ag 245 filler metal on the X2CrNi18-9 grade stainless steel using the F10 flux

The F10 flux underwent more detailed examination of brazing properties including testing the penetrability into brazing capillary gaps as well as the quality and mechanical properties of flame brazed overlap joints. The base metal used in the tests was in the form of a sheet made of the X2CrNi18-9 grade stainless steel and the CW508L (CuZn37) grade brass, whereas the filler metal was the Ag 245 silver brazing metal. Figures 5÷6 present the cross-sectional macrostructures of the joints made. The width of a brazing gap amounted to 0.05 mm and 0.17 mm for brass and stainless steel respectively. The joints did not reveal any brazing imperfections such as gas cavities or flux residue. In addition, the use of the flux enabled the obtainment of a smooth braze face free from surface imperfections and of the properly shaped fillet flash at the brazing gap outlet.

The overlap joints of the X2CrNi18-9 steel made using the Ag 245 silver brazing metal under the F10 flux cover are characterised by a high shear strength of approximately 200 MPa.

Fig.5. Macrostructure of the overlap joint made of the CW508L brass using the Ag 245 silver filler metal and the F10 flux, etchant: $FeCl_3$

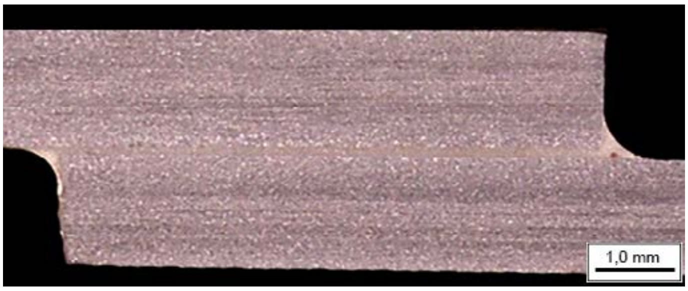

Fig.6. Macrostructure of the overlap joint made of the X2CrNi18-9 stainless steel using the Ag 245 silver filler metal and the F10 flux, etchant: $FeCl_3$

It should be emphasized that the brazing fluxes developed at Instytut Spawalnictwa are manufactured as waterborne pastes by wet milling in closed tumbling mills. Such a production method ensures advantageous Health and Safety conditions during manufacture as well as favours maintaining proper environmentally friendly conditions.

Concluding remarks

1. In the light of global requirements related to the detoxication of brazing processes, among brazing filler metals developed and manufactured at Instytut Spawalnictwa in Gliwice, special attention should be paid to the following:
   - Po-AG104 (Ag 145 according to PN-EN ISO 17672:2010) grade low-melting silver filler metal with a tin addition manufactured in the form of rods with a mechanically stable flux coating;
   - F6B low-fluoride flux (fluoride content approximately 6% by weight) with amorphous boron for brazing stainless steels and poorly brazeable copper alloys;

- F10 low-fluoride flux (fluoride content approximately 10% by weight) for similar applications as F6B.

2. The PO-AG104 low-melting cadmium-free silver filler metal with a tin addition in the form of a coated rod is characterised by good brazing properties (wettability, spreadability, penetration into capillary gaps) and ensures the obtainment of joints characterised by high quality and good mechanical properties (for stainless steel 269 MPa, for brass 166 MPa).
3. The F6B and F10 low-fluoride fluxes reveal required chemical activity and good brazing properties as regards brazing stainless steels and copper alloys. The fluxes ensure proper wetting of stainless steels and copper alloys with silver filler metals (e.g. Ag245 according to PN-EN ISO 17672:2010) as well as the good quality of brazed joints and their good mechanical strength.
4. Due to Health and Safety requirements and environmental protection, the fluxes developed are waterborne pastes produced by wet milling in closed tumbling mills.

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