Chemical elements diffusion in the stainless steel components brazed with Cu-Ag alloy

I Voiculescu 1, V Geanta 1, I M Vasile 1, E F Binchiciu 2 and R Winestoock 3

1 University Politehnica of Bucharest, Romania 313, Splaiul Independentei, sector 6, 060042, Bucharest, Romania
2 S.C. Sudotim As SRL, 30, Bv. Mihai Viteazu, Timisoara, Romania
3 Ben Gurion University of the Negev, Beer-Sheva, Israel

E-mail: ioneliav@yahoo.co.uk

Abstract. The paper presents the study of diffusion of chemical elements through a brazing joint, between two thin components (0.5mm) made of stainless steel 304. An experimental brazing filler material has been used for brazing stainless steel component and then the diffusion phenomenon has been studied, in terms of chemical element displacement from the brazed separation interface. The filler material is in the form of a metal rod coated with ceramic slurry mixture of minerals, containing precursors and metallic powders, which can contribute to the formation of deposit brazed. In determining the distance of diffusion of chemical elements, on both sides of the fusion line, were performed measurements of the chemical composition using electron microscopy SEM and EDX spectrometry. Metallographic analysis of cross sections was performed with the aim of highlight the microstructural characteristics of brazed joints, for estimate the wetting capacity, adherence of filler metal and highlight any imperfections. Analyzes performed showed the penetration of alloying elements from the solder (Ag, Cu, Zn and Sn) towards the base material (stainless steel), over distances up to 60 microns.

1. Introduction

Nowadays, stainless steels like 304 and 316 are used extensively for steam pipes and exhaust systems, due their resistance to elevated temperature, oxidation, and corrosion, being the choice for food preparation equipment, including steam-heated boilers and storage tanks. The addition of chromium and nickel to the iron matrix creates a significant percentage of chromium and nickel atoms at the surface [1].

The corrosion resistance of stainless steel depends on the chromium content. Long maintenance at higher temperatures, in the range of 425-870 °C, causes the atoms diffusion and changes the metal's properties. Such high temperatures allow the chromium to diffuse away from the grain boundaries to form chromium carbides, its preferred crystalline structure at this temperature range [2]. During brazing, the assembly is heated from room temperature to the filler material melting temperature, and significant diffusion phenomena of chemical elements occur between the parent material and the filler metal. This process is particularly important when the filler metal layer is very thin [3].

To whom any correspondence should be addressed.
By dissolution of the base material into the molten filler, occurs the increase of width of the liquid zone. At the same time, the temperature increases from the melting point to the joining temperature. By lowering the temperature, isothermal solidification occurs, as a result of diffusion of one or more constituents of the filler into the base metal (and vice versa).

The minimum suitable temperature for a diffusion brazing of the stainless steels is not simply determined by the melting point of the filler material or that of the alloys generated by reaction. If it is desired that the end product of reaction is a solid solution across the joint and that there are no residual interfacial inter-metallic phases present, then the solubility limit of the minor constituents in the primary metal phase is also crucially important [4].

The brazed joints made in stainless steel can be frequently exposed to water or vapour during service. This specific medium can promote interfacial corrosion of failure of the joints. The special silver-copper brazing filler metal allows to avoiding the problems of interfacial corrosion and improves the strength of the joint. Most stainless steel types, with the exception of titanium or niobium stabilized grades, can be brazed. For brazing stainless steels in air, low-temperature silver brazing alloys are generally used [5].

One of the basic conditions to achieve a quality joint is to ensure proper wetting of the brazed surfaces. The stainless steel surface is difficult wetted by brazing alloys, due to the surface oxide that protect it from corrosion. The chemical composition of flows used for brazing must ensure rapid dissolution of oxide surfaces and to ease wetting by molten filler material [6]. Brazing alloy must be sufficiently fluid, in order to penetrate into gaps between components on large distances to ensure a good resistance of the joint. Melting temperature of brazing alloy that contains silver and copper must be well correlated with the type of base material. In the case of austenitic stainless steels, the effective maintenance in the 600-800°C temperature range is critical to avoid the inter-crystalline corrosion. In the case of very thin components, the effects of high temperatures are more critical [6].

The aim of the research paper was to establish the brazing behaviour of an experimental brazing filler material, named VIAg25SnSiPR. The filler materials used in the experimental study were produced through environmentally friendly technologies, without the use of highly toxic materials (cadmium free) and based on an optimized technology, with differences between the melting temperature up to 50°C, between metal rod and coating layer [7, 8, 9]. The increasing of tin content can improve the wettability and mechanical properties of the joints. However, when the tin content exceeds 5%, the shear strength of the joints decreases [5]. Following this observation, in the experimental filler material the tin content was kept lower than 2%Sn [10].

2. Experimental details

To be able to enter in the gap of the brazed joint, the brazing filler material contains a special covering that allows obtaining a difference between the melting temperature of coating and of the metallic rod. The filler material is in the form of a metal rod coated with ceramic slurry mixture of minerals, containing precursors and metallic powders, which can contribute to the formation of deposit brazed (Figure 1).

Figure 1. The production line of coated rods and the filler materials used in the experimental program.
At the low temperature (650-700°C) first ceramic mixture melting occurs, for the base material surface deoxidation. At higher temperatures, between 700-800°C, the second ceramic mixture and silver particles melting occur, completing the final chemical composition of filler material. In this way, the filler metal can spread rapidly and fill completely the gap. This alternance in melting that appears at filler material coating was evidenced by differential thermal analysis performed with the device Netzsch STA 449 F3, in Ben-Gurion University of Negev, Israel. Composite coatings contain 60 to 65% deoxidation flows, in accordance with EN 14045: 1999, 15 to 20% plasticizers and 10 to 15% binder. They also contain nano-powders with suitable properties, such as wetting and deoxidation agents, to improve the diffusion and to increase the strength tear.

In order to study the distance of filler material penetration, two type of samples were joined (figure 2), using flame brazing process. The average value of the gap between the 2 components was established in the range of 0.1 - 0.4 mm. Before brazing, the edges of the samples were mechanical cutted, and the surfaces was cleaned with propane, for eliminate all the contaminants (scale, oil/grease) and then were dried with hot air, for eliminate moisture.

An oxidizing flame type for brazing was chosen, for avoiding the evaporation effect of the chemical elements of the filler material. The total duration of the process was of 30 seconds, including heating the components and brazing period. This short heating period ensures a low deformation effects, considering the low thickness of the samples (0.5mm).

After the cooling period, the brazing zones were washed in hot water and were dried with hot air. The representative area from each brazed sample was removing using precision cutting machine with cooling agent, to avoid the alteration of the microstructure. To ensure the correct edge of samples during the polishing, those were embedded by compression in molten phenolic resin, at 175 °C, then it was applied the metallographic rough polishing procedure [1] using abrasive grit paper (400, 600, 800, 1000, 1500 grit) followed by final polishing using alumina alpha powder (Topol1, Topol, Topol 2 and 3, the grain size of 3 to 0.1 μm).

Metallographic analysis was performed with the aim of highlight the microstructural characteristics of brazed joints, for measuring the geometrical characteristics and to highlight any imperfections. The analysis was conducted using scanning electron microscope FEI QUANTA INSPECT F provided with the electron gun with field emission - EGF with a resolution of 1.2 nm and X-ray spectrometer energy dispersive (EDS) with resolution of 133 eV at MnK. Measuring conditions was: temperature + 24°C (reference temperature + 23 ± 5 °C); Humidity 50%.

3. Microstructural analysis
Metallographic analysis of brazed samples has targeted viewing of the distribution of the molten alloy in the joint gap, the correct sliding of the molten filler material and the absence of imperfections. For this purpose, some geometric measurements of joining areas have been done (joint width and stretching distance of molten metal). For "L" joint (Figure 3, 4 and 5) geometrical dimensions were:
penetration aperture of 42μm in the root and maximum width of 3.14mm, without misalignment of components, corresponding to the quality conditions imposed on this type of joint.

At higher magnifications (1000 x, Figure 4) it can see the correct geometry of the root and the absence of secondary fragile phases. Some pores are small (diameter of 1-2μm) with random spreading that do not endanger the bond strength (0.5mm diameter are admitted for imperfections according to EN 12799-2002). Also it can observe a good adhesion of molten material from the surface of the stainless steel component (Figure 5).

For the "O" joint (Figure 6) the average size of the gap was 412μm (Figure 6), with a continuous spreading distance of 4mm (Figure 7), without excess of molten material and correct shape of concavity, what meet the conditions imposed for this type of joint. The quality condition for required
maximum length of penetration is $5s$, where $s$ is the thickness of components. In this case, the effective length of penetration was $4\text{mm}$, which is higher than the required minimum value of $2.5\text{mm}$.

On examination with higher magnifications it can observe a good adhesion of brazing filler metal to components of stainless steel. The constituents that are present in molten metal have fine shape needle-like appearance of (Figure 8). Expanding heat affected zone (HAZ) is quite restricted ($270$-$315\mu\text{m}$) given the very small component thickness ($0.5\text{mm}$) (Figure 9).

3.1. **EDAX analysis on the cross section of "L" joint**

To evaluate the effects of diffusion, some analysis of chemical composition was made, performed using scanning electron microscope. The analyze was carried out in $105$ different points, located the area of the root and the seam, following a line that crossing successively the base material, the interface and filler material, then again in the base material (Figure 10).
Figure 10. Evolution of the chemical composition in 105 different points, on the line that cross by the joint between stainless steel components and filler material.

The measurements were carried out on the straight line, from left to right, between points 1 and 105, over a distance of 10 microns. The extension in the base material was of maximum 240 microns on both sides of the line of fusion (Figure 11).

Figure 11. Overall distribution of elements in the root zone of brazing joint, evidenced by EDAX analysis.

3.2. EDAX analysis on the cross section of "O" joint

Measurements of the chemical composition have been done in order to determine the distance of diffusion of chemical elements in "O" joint. The chemical composition values for each point are presented in table 1.

The measurements were performed in the base material and HAZ, in 5 points located at different distances from the brazing surface (Figure 12a). As results from the chemical composition values in table 1, diffusion effects are detected only at very small distances from the molten metal surface, at approximately 20μm length. It can be observed the diffusion of chromium, iron and nickel from the base metal towards the molten material, and diffusion of silver, zinc and copper from the filler metal towards the base material.

To estimate the effects of diffusion in the bulk of molten filler material the chemical composition was analyzed in other 5 points of the cross section of joining "O" (Figure 12b). Points "f" and "d" are placed outside of the diffusion zones, while "a" and "b" points are located in the transition zone, between base materials (overheated) and melted deposit (filler material).
Only at very small distances from the molten metal surface (points a and b), at approximately 20μm length, some diffusion effects of elements like chromium, iron, manganese and nickel can be observed, in direction towards filler material. In opposite direction, elements like silver, copper, zinc and tin diffuses from filler metal towards base material, the biggest diffusion effect being for copper (25%).

![Figure 12. The points location for determination of the chemical composition in “O” joint (400x).](image)

**Table 1.** Chemical composition measured in 5 points in cross section of base material.

| Measurement zone | Chemical composition, %wt |
|------------------|---------------------------|
|                  | Si | Cr | Mn | Fe | Ni | Al | Ag | Zn | Sn | Cu |
| 1- base metal    | 0.23 | 18.82 | 2.5 | 70.94 | 7.5 | - | - | - | - | - |
| 2 - HAZ          | 0.2 | 18.08 | 2.27 | 69.34 | 6.92 | 3.18 | - | - | - | - |
| 3 - HAZ          | 0.19 | 18.16 | 2.46 | 69.53 | 7.59 | 2.06 | - | - | - | - |
| 4 - HAZ          | 0.23 | 18.48 | 2.49 | 69.83 | 7.14 | 1.83 | - | - | - | - |
| 5 - near fusion line (20 μm) | 0.3 | 13.45 | 1.56 | 49.43 | 4.63 | - | 3.95 | 10.97 | 0.43 | 15.28 |

The chemical composition values for each point located in filler material zone are presented in table 2. As results from table 2 values, diffusion effects are not detected in the center of filler material.

**Table 2.** Chemical composition measured in 5 points through filler material and HAZ.

| Measurement zone | Chemical composition, %wt |
|------------------|---------------------------|
|                  | Si | Cr | Mn | Fe | Ni | Ag | Zn | Sn | Cu |
| a- base metal    | 0.28 | 15.12 | 1.58 | 56.99 | 4.92 | 3.19 | 6.99 | 0.21 | 10.7 |
| b- base metal    | 0.09 | 14.11 | 1.54 | 56.75 | 5.71 | 1.96 | 7.57 | 0.13 | 12.15 |
| c – center zone of filler metal | - | - | - | - | - | 21.36 | 34.5 | 1.16 | 42.98 |
| d- HAZ (164μm)   | 0.23 | 18.43 | 2.74 | 70.33 | 8.1 | - | - | - | - |
| f - HAZ (60 μm)  | 0.22 | 18.45 | 2.33 | 69.24 | 7.28 | - | - | - | - |
4. Conclusion
The experimental alloy used in the study has a good spreading behaviour and do not produce any cracking tendency. The only types of imperfections observed in the brazed area were: un-melted flux inclusions and pores (gas) resulted from the coating of the filler material.

In the brazed joints made by stainless steel components, at the interface between the base material and melted filler material, diffusion phenomenon can occurs, by migration of some chemical elements through the interface, even the time of maintain at high temperatures is short (30 minutes).

At approximately 20μm length from melting line, some diffusion effects of elements like chromium, iron, manganese and nickel can be observed, in direction towards filler material.

The elements with greater participation in the filler material (copper, zinc and silver) migrate by diffusion towards the base material, the biggest rate of diffusion being for copper (25%). These exchanges are extending only in a small area, of 20 to 60 microns form de interface, and do not affect the mechanical resistance or corrosion resistance of the base material.

The analyzes performed to determine the diffusion effects in the case of two types of brazed joints showed the penetration of alloying elements from the solder (Ag, Cu, Zn and Sn) towards the base material (stainless steel), over distances up to 20 microns. Concentration of alloying elements in base material was 3% Ag, 10% Cu and 7% Zn at 10 microns distance from the interface, and 2% Ag, 12% Cu and 7.5% Zn at 20 microns from the interface.

Acknowledgements
The research work was financially supported by the Romanian National Program for Research in the framework of the Project – PCCA 188/2012 ,,Materials and performant technologies designed to realize knives for milling the asphalt – MATFREZ.

References
[1] Millspaw M 1994 The Care and Feeding of Stainless Steel Brewing Techniques 2(4) pp 44-47
[2] Diffusion Brazing, Principle of Brazing ASM International 2005 pp 207-216
[3] An Introduction to Brazing 2014 Oerlikon Metco 4 pp 6 – 10
[4] Jhonson M Metal joining, Silver Brazing Alloys and Fluxes, pp 4 - 39 http://www.jm-metaljoining.com
[5] Xing F, Qiu X M, Li Y D 2015 Effects of Sn element on microstructure and properties of Zn–Cu–Bi–Sn high-temperature solder Trans. Nonferrous Met. Soc. China 25 pp 879 – 884
[6] Stainless Steel Cladding and Weld Overlays, ASM Speciality Handbook: Stainless steels, ASM International 1994 pp 109-110
[7] Voiculescu I, Geantă V, Binchiciu H, Binchiciu E et. all, Research Project – PCCA 188/2012 - Materials and performant technologies designed to realize knives for milling the asphalt – MATFREZ
[8] Binchiciu A, Voiculescu I, Geantă V, Binchiciu H, Ştefănoiu R and Binchiciu E 2010 Coated silver alloy rods of reduced hygroscopicity for brazing, comprises silver and tin deposited by extrusion deoxidizing flux made of synthetic vitreous precursors and metal powder additions (Patent Number: RO125836)
[9] Binchiciu A, Voiculescu I, Geantă V, Binchiciu H, Ştefănoiu R, Negriu R M and Binchiciu E 2012 Ecological coated core wires of silver alloys for brazing, made by extrusion coating with deoxidizing flux with metal powder addition (Patent Number RO125835)
[10] Voiculescu I, Geanta V, Binchiciu E, Moisa S, Vasile I M and Trusca R 2016 Study of Dilution Effects in the Joint Brazed with Cu-Ag Alloy for Stainless Steel Components, IMEC 17 The 17th Israel Materials Engineering Conference