New hermetic sealing material for vacuum brazing of stainless steels

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Abstract. For vacuum brazing applications such as in vacuum interrupter industry Hermetic Sealing Materials (HSM) with low partial pressure are widely used. AgCu\textsubscript{28} dominates the hermetic sealing market, as it has a very good wetting behavior on copper and metallized ceramics. Within recent decades wetting on stainless steel has become more and more important. However, today the silver content of HSMs is more in focus than in the past decades, because it has the biggest impact on the material prices. Umicore Technical Materials has developed a new copper based HSM, CuAg\textsubscript{40}Ga\textsubscript{10}. The wettability on stainless steel is significantly improved compared to AgCu\textsubscript{28} and the total silver content is reduced by almost 44\%. In this article the physical properties of the alloy and its brazed joints will be presented compared to AgCu\textsubscript{28}.

1 State of the art

Brazing is a technology for joining, in general, two metal or metallized parts without introduction of major microstructural changes into the base materials. This is in contrast with technologies such as welding [1].

A prerequisite for brazing is the sufficient wetting of the brazing filler metal of both base materials as well as spreading on the parts subsequently. A characteristic for the wetting is the wetting angle \( \theta \). The wetting angle is influenced by the surface energies of the brazing filler metal and the base material as well as the brazing atmosphere.

[2]. Therefore, the absence of scale forming oxygen on the surface is required to allow a proper wetting process. Among others, this can be achieved by the application of reactive fluxes, brazing in a protective gas atmosphere, or in a vacuum [3]. The vacuum brazing process of metal parts results in high quality brazing joints with low porosity, because fluxes and other gas forming impurities that could lead to gas pores inside the brazing joints are avoided. In addition, vacuum brazing allows the sealing of high purity vacuum inside of e.g. vacuum interrupter tubes, if high purity and non-evaporating brazing filler metals are utilized [4].

The purity of the vacuum as well as the surface condition of the parts to be joined, can have a significant effect on the wetting and therefore joining behavior of the HSM [5]–
A prominent example of a typical HSM is the eutectic alloy AgCu28 [4]. AgCu28 features excellent wetting on copper base materials while the wetting on steels could be improved by additions such as Ge, Pd, Ni, and Co [4]. The aim of the present study is to investigate a new alloy CuAg40Ga10 that exhibits independently improved wetting behavior on stainless steels compared to AgCu28. The improved wetting behavior is an advantage since the chemical concentration and therefore the quality of the stainless steel parts can vary within the limits of the steel grade standard. Furthermore, significantly less silver is required while still maintaining a similar brazing temperature to AgCu28 [8]. In order to demonstrate the performance of the new HSM its characteristics and properties of its joints will be discussed.

2 Methods

2.1 Material’s selection

The HSM’s evaluated in this study were manufactured according to the tolerances for volatile elements and impurities of standard DIN EN ISO 17672 (special vacuum requests: class 1) and with the tolerances of the alloying components given by table 1.

| Alloy name     | guaranteed chemical concentration | identical to standardized alloy of DIN EN ISO 17672 |
|----------------|-----------------------------------|---------------------------------------------------|
| AgCu28         | 71-73 % 27-29 % -                 | Ag272                                             |
| CuAg40Ga10     | 39-41 % bal. 9,5-10,5 %           | not applicable                                    |

Hence wetting and brazing on copper and nickel is due to the high solubility of copper and nickel in Ag-Cu brazing alloys not challenging and the interactions of the brazing material and the substrate are well investigated[9, 10]. The present study focusses on application tests of the HSM’s on two typical stainless steel grades well-known in the vacuum industry: 1.4307 and 1.4404. These steel grades are specified according to DIN EN 10088-3 and also known under the following material names X2CrNi18-9 and X2CrNiMo17-12-2 respectively. In figure 1 ring-shaped preforms can be seen.
2.2 Melting range, density and coefficient of thermal expansion (CTE)

Essentially for the technical function of HSM’s is their brazing temperature influenced by their melting range. Therefore, liquidus and solidus temperatures were determined by thermal analysis using a TGA/DSC 1 machine from Mettler-Toledo. Samples of 150-200 mg weight were heated in aluminum oxide crucibles. The heating rate was set to 10 K/min and flowing argon atmosphere was used. Liquidus and solidus temperatures were derived from the measured data as described by Schnee et al. [11]. The density of the brazing alloys was evaluated with a hydrostatic balance according to the Archimedes principle [12].

The CTE was measured by dilatometry using a Netzsch 402S. Samples with a length of 30 mm of HSM were applied while the heating rate was constant at 2 K/min. An argon atmosphere was injected to avoid oxidation of test samples during measurement. The CTE was determined for the temperature range from room temperature up to 600 °C.

2.3 Wetting behavior and spreading factor

The formation of the brazing joint and therefore the later strength and vacuum tightness of the joint depends on the wetting and spreading of the HSM on the base materials. By in-situ measurement of the wetting angle between liquid HSM and base material the wetting process was quantified. For determining the wetting angle the sessile drop method was used [13]. The wetting behavior of AgCu28 and CuAg40Ga10 on two standardized stainless steels (1.4307 and 1.4404) was evaluated. The HSM was positioned on a horizontal sheet of stainless steel base material, 15 x 15 x 1 mm³ in size. The wetting tests were performed in a vacuum chamber with gas pressures below 5·10⁻⁵ mbar. A molybdenum wire spiral was used to heat the sample while the local temperature was measured with a thermocouple positioned in a distance of only 2 mm above the sample. The wetting angle measurement was conducted in a temperature-dependent mode by applying a constant heating rate of 5 K/min throughout the experiment. Left and right wetting angles of the HSM droplet on the base material were examined optically and averaged afterwards. The spreading factor S is a crucial property for the technical performance of the HSM combining wetting behavior and the kinetics of flowing of the liquid at a given temperature. It was determined, by measuring the wetted area $A_1$ of the HSM on base material after a temperature treatment of 820 °C for 5 min. $S$ is calculated with the equation 1, where $A_1$ and $A_0$ are the areas of the applied alloy before and after temperature treatment, figure 2.
For cleaning the stainless steel base materials, they were mechanical ground (No chemical cleaning or degreasing). Initial surface $A_0$ of the alloy discs is given by their diameter of 10 mm$^2$. The thicknesses of the discs were 0.15mm.

$$S = \frac{A_1}{A_0} \quad (1)$$

**Figure 2.** Determination of the spreading factor $S$ from brazed HSM discs

2.4 Micrographs and ultimate tensile strength of brazing joints

Typically for brazing joints there is a strong structure-property relationship between features in the microstructure and their mechanical behavior such as the responsiveness to tensile loads. Therefore, in this study micrographs were taken from brazed samples by mechanical metallographic preparation and optical microscopy. During optical microscopy, bright field imaging was applied to render the material contrasts.

The typical load case during the application of a vacuum interrupter during its lifetime is tensile load in the brazing joints. The ultimate tensile strength of the brazing joints can provide a quantitative degree for the maximum resistance of the brazing joint against tensile loads. The ultimate tensile strength was tested according to DIN EN12797:2000. The geometry of the tensile specimen is shown in figure 3.

**Figure 3.** Tensile strength specimen according to DIN EN 12797:2000

The two identical stainless steel cylindrical rods were brazed at 1·10-6 mbar with a temperature of 830 °C for 10 min. Before the tensile test was performed, the brazed rod was machined to comply with the geometry requirement of DIN EN12797:2000. Both stainless steel grades in this study (1.4307 and 1.4404) were mechanically evaluated by this method.

3 Results

3.1 Physical properties of HSM

The melting range of a HSM is one of the core properties of the material, because it is influencing other technological parameters of the material such as the brazing temperature. Compared to AgCu28, which is a eutectic alloy with a melting point at 779 °C, the CuAg40Ga10 has a melting range. The
melting range is about 100 K from 726 °C to 831 °C, table 2. In consequence liquid of CuAg40Ga10 is already available at lower temperatures than 779 °C ($T_S$ of AgCu28).

Table 2. Chemical concentration ranges of investigated HSM’s

| Material     | TSolidus [°C] | TLiquidus [°C] | Density [g/cm³] | CTE 0°C-600°C [10⁻⁶/K] |
|--------------|---------------|----------------|-----------------|------------------------|
| AgCu28       | 779           | 779            | 9.97            | 23.60                  |
| CuAg40Ga10   | 726           | 831            | 9.33            | 21.56                  |

From figure 4 it can be seen that the main melting event is at 756 °C. Under the assumption that latent heat consumed for melting at 780 °C (~70 % of total heat according to measurement) correlates with the molten volume fraction it can be concluded that the major volume fraction of the material is melted below 780 °C.

![Figure 4: Melting range of CuAg40Ga10](image)

The density of CuAg40Ga10 is slightly lower than that of AgCu28, which is beneficial hence the required volume and not the required weight for filling a brazing joint is constant, table 2. For CuAgGa10 less weight and therefore again less silver per brazing joint is required by the applicant. The thermal expansion coefficient of CuAg40Ga10 is very similar to AgCu28, table 2. Therefore, additional thermal residual stresses between the base materials caused by use of CuAg40Ga10 instead of AgCu28 are not expected if the base materials are not exchanged.

3.2 Brazing joint properties

3.2.1 Wetting and spreading behavior during brazing

In the literature, it is reasoned that partial wetting occurs for wetting angles $\theta < 90^\circ$ [14]. From an application perspective the working point of the HSM is achieved at the temperature when the wetting angle falls below 90°. Figure 4 and figure 5 show the measured development of the wetting angle over temperature. The critical temperatures for $\theta < 90^\circ$ are summarized in table 3.
Table 3: Temperature $T[\theta < 90^\circ]$ for which wetting is initiated

| T[\theta < 90^\circ] in °C | HSM |
|---------------------------|-----|
|                          | AgCu28 | CuAg40Ga10 |
| Steel Grades 1.4307      | 827    | 829        |
| Steel Grades 1.4404      | 861    | 821        |

The wetting angle measurements show that especially for the case of the 1.4404 stainless steel CuAg40Ga10 leads to significantly lower wetting angles than AgCu28. For 1.4307 the difference is smaller, but still measurable. In addition, for the wetting on 1.4404 steel the temperature for $\theta < 90^\circ$ is significantly lower than for AgCu28. Therefore, it can be concluded that the wetting behavior on the two tested steels grades is improved for CuAg40Ga10 compared to AgCu28.

Figure 5. Temperature-dependent wetting of AgCu28 and CuAg40Ga10 on 1.4307
**Figure 6.** Temperature-dependent wetting of AgCu28 and CuAg40Ga10 on 1.4307

**Figure 7.** Spreading factor $S$ of AgCu28 (black) and CuAg40Ga10 (grey) on 1.4307 and 1.4404 after a temperature treatment of 840 °C for 5 minutes
Next to the wetting, behavior the other important property is the tendency to spread on a base material. It describes the extent to which the HSM increases or decreases the contact area with the base material without external force.

For AgCu28 on plain stainless steel surfaces without any specialized surface treatment such as e.g. electro-polishing this test can be considered as an extreme test setup. So especially under these conditions for AgCu28 instead of spreading a reduction of the contact interface is observed. This can be seen in the following figure 6, figure 7 and figure 8. For CuAg40Ga10 it could be observed on both stainless steels, that the wetted area after spreading test is significant larger than for AgCu28.

### 3.2.2 Metallographic cross sections of brazing joints

The microstructure of CuAg40Ga10 is dominated by copper-rich primary crystals. At the interface of brazed steel parts a pronounced diffusion zone can be observed, figure9a and figure10a. In the cross sections shown in figure 9b and figure10b the eutectic microstructure of AgCu28 is visible. For AgCu28 there is almost no diffusion zone observable in the steel base material.
3.2.3 Mechanical strength of brazing joints

Tensile tests were conducted with brazed and non-brazed rods, heat-treated rods both according to the geometry requirement of DIN EN 12797:2000. The non-brazed solid steel rods were heat treated at 790 °C and 890 °C to simulate the microstructural changes and therefore changes in ultimate tensile strength of the base materials. This means that Rm values of the brazing joint (830 °C) can be at maximum as high as a value between these two values. The results are provided in table 4.

**Table. 4.** Ultimate tensile strength Rm in MPa.

|                          | stainless steel 1.4307 | stainless steel 1.4404 |
|--------------------------|------------------------|------------------------|
| after brazing with AgCu28 at 830 °C | 480                    | 468                    |
| after brazing with CuAg40Ga10 at 830 °C | 535                    | 519                    |
| 790 °C annealed steel     | 679                    | 625                    |
| 890 °C annealed steel     | 625                    | 583                    |
It is obvious that with CuAg40Ga10 the strength of the brazing joint can be increased on both stainless steels. Therefore, with the new HSM, joints can be produced that exhibit a higher tolerance against catastrophic failure of the brazed parts.

4 Conclusion

CuAg40Ga10 is a silver-reduced specialized vacuum grade brazing alloy developed to show an improved technical profile for applications involving the joining of stainless steels.

As shown with the technical characterization of CuAg40Ga10 the new HSM exhibits superior ultimate tensile strength and wettability on the tested steel grades compared to AgCu28. Explanations for the favorable characteristics of CuAg40Ga10 as the improved cohesion within the joint can be found in the abundance of a diffusion zone formed between the HSM and steel. Secondly, the effect of mixed crystal hardening of the third alloying component gallium in the CuAg40Ga10 alloy might have its contribution to the higher strength of its brazing joints.

Hence, the melting range of the CuAg40Ga10 is enclosing the melting point of AgCu28, users do not have to change the parameters of the brazing process in many applications. Future investigations will have to show if additional surface pre-treatment steps of stainless steel surfaces such as electro-polishing are still required when using the improved wetting potential of the new material.

In addition, the new alloy provides two ways to reduce the silver consumption for the vacuum brazing processes: The absolute silver content could be reduced by 32 wt-% and the density was reduced by 6.4 %: resulting in lower alloy mass per identical brazing preform consumed by the applicant.

Examples taken from published papers:

5 References

[1]  DIN ISO 857-2; Schweißen und verwandte Prozesse. DIN Deutsches Institut für Normung e.V., 2007.
[2]  Young, T.: An essay on the cohesion of fluids. In: M. D. For. Sec. R. S. (1804.)
[3]  Messler, R.W.: Joining of Advanced Materials. Butterworth-Heinemann, Stoneham, (1993), S. 303 et seq.
[4]  High Purity Vacuum Brazing Metals (http://technicalmaterials.unicore.com/CPM/en/Products/HermeticSealingMaterial/), Umicore AG & Co. KG : Datasheet, 2013.
[5]  McGurran, B.; Nicholas, M.G.: A Study of factors which affect wetting when brazing stainless steel to copper. In: Proceedings, BABS Autumn Conference (1984.)
[6]  Schwartz, M.: Brazing for the engineering technologist. Chapman and Hall, London, (1995), S. 12.
Asthana, R.; Kumar, A.; Dahotre, N.: Kapitel 2: Materials Science in Manufacturing. Elsevier, Burlington, 2006, S. 280–281.

[8] Technical Data Sheet AgCu28, Umicore AG & Co. KG, 2009.

[9] Nicholas, M.G.: Joining Processes. Kluwer Academic Publishers, Dordrecht, (1998), S. 57 et seq.

[10] Jacobson, D.M.; Humpston, G.: Principles of Brazing. ASM International, Ohio, (2005), S. 52.

[11] Schnee, D.; Wiehl, G.; Starck, S.: Development of Ag-Cu-Zn-Sn brazing filler metals with a 10 weight-% reduction of silver and same liquidus temperature. 2014 International conference on Brazing, Soldering and special Joining Technologies, Beijing, China, June 2014, pp. 53–58.

[12] N.N.; Seilnacht Verlag (http://www.seilnacht.com/versuche/dichteb.html), 2016.

[13] Eustathopoulos, N.; Sobczak, N.; Passerone, A.; Nogi, K.: Measurement of contact angle and work of adhesion at high temperature. In: J. Mater. Sci. 40 (2005), S. 2271–2280.

[14] Starov, V.M.; Velarde, M.G.; Radke, C.J.: surfactant science series. Bd. 138: Wetting and Spreading Dynamics. CRC Press, London, (2007), S. 2–3.