1 INTRODUCTION

Generally the established thermal spray technologies like flame or arc spraying can be used for the defined deposition of solder/braze filler metal layers. But for those processes used under atmospheric conditions the achieved quality of the solder/braze joints is low. A high density of defects like inclusions or oxides, pores and contaminations are not avoidable. The novel technique of the cold gas spraying (CGS) works with very low process temperatures. Therefore the heating of spray particles is reduced to a minimum. The produced coatings are free of oxides and show very low porosity. So investigations concerning the potential of CGS for the application of solder/braze filler metals are self-evident.

In this work, substrates of different aluminium alloys (AA1050, AA3005, AA5754 and AA7022) are chosen. Depending on their particular solidification temperature, the used solder/braze filler materials are Al-, Zn- and Sn-based alloys.

2 SOLDERING / BRAZING

Soldering and brazing are thermal joining techniques. They are characterised by the process temperature $T_L$, which has to be lower than the solidification temperatures $T_{S1}$ and $T_{S2}$ of the partners to be joined, but depending on the material combination close to, equal to or higher than the melting temperature of the solder/braze filler alloy. As the filler is partly or totally molten, interactions (diffusion processes that result in alloying) between the partners to be joined and the filler material can occur. One major advantage in comparison to (conventional) welding processes is the possibility to join materials with very different chemical compositions (like steel with copper) and, by using active brazing filler alloys, different bond types (like steel with ceramics) [1]. Depending on the applied process temperature, soldering ($< 450 \, ^\circ\text{C}$), brazing ($450 - 900 \, ^\circ\text{C}$) and high temperature brazing ($> 900 \, ^\circ\text{C}$) processes are distinguished by standard [2].

Brazing of aluminium alloys

The manufacturing of aluminium heat exchangers is the most common industrial CAB (Controlled Atmosphere Brazing) process. Usually CAB processes are flux aided furnace brazing processes under an inert shielding gas (mostly nitrogen). For the joining of Al-based materials often AlSi alloys with melting temperatures between 595 and 610 °C are used as braze fillers. More expensive AlSiGe alloys (Ge for lowering the melting temperature) are used in vacuum brazing processes. Due to economical aspects their application is limited to small volume production only [3].
Aluminium CAB processes need fluxes. Fluxes have to cleanse the surfaces of the partners to be joined and to destroy the natural alumina film (Al$_2$O$_3$) on top of them. The alumina prevents the wetting by the braze filler material. So the flux agent additionally has to delay the reformation of the alumina skin for at least the brazing time. Carrying out the brazing process in an inert shielding gas atmosphere does not prevent the re-oxidation, because conventional technical inert gas atmosphere contains up to 3 % oxygen. In the past chloridic and/or fluoridic fluxes have mostly been in use, though their disadvantages are strong hygroscopic nature and corrosive attack on the aluminium. The brazed assemblies had to be cleansed, etched and passivated afterwards. Because of the additional costs and the ecologic risk in using aggressive cleaning agents, chloridic and pure fluoridic fluxes are not often used in industrial applications any more.

Flux-free brazing processes (in vacuum or ultrasonically assisted) require high quality surfaces and cannot be applied to all geometries and dimensions. Therefore their application area is limited to small series productions or special applications. For Al materials the industrially most frequently applied CAB process is the NOCOLOK® Flux CAB. It shows the advantages of an easily controllable flux aided brazing process without the need of a post-treatment by cleaning agents. The so called NOCOLOK® Flux agent mainly contains potassium-fluorine-aluminate, which forms non-hygroscopic reaction products that cannot be dissolved in water and do not cause corrosive attack on aluminium. In most cases (decorative effect not important) a cleansing process after brazing is not necessary [4].

3 COLD GAS SPRAYING

Cold gas spraying (CGS) is part of the group of thermal spray (TS) processes. TS is capable of coating defined surface areas of components with functional coatings (concerning corrosion, wear, thermal and electrical behaviour, etc.) or of repairing worn out areas. Generally all conventional TS processes are characterised by an energy source that melts or warms up a feedstock material and accelerates the spray particles onto a substrates surface, on which the coating forms. The substrate is not molten during the deposition process. Conventional energy sources of TS processes are flames, electrical arcs and plasmas. Depending on specific process characteristics the feedstock can be in wire, rod or powder shape.

During the time of interaction between particles and gas flow thermal and kinetic energy is transferred to the particles. Particle temperature and velocity at impact on the substrate determine the particles deposition characteristics and thereby coating properties like homogeneity, density, porosity, bond strength, etc. In high velocity (HV) spray processes more kinetic and less thermal energy is transferred to the spray particles. As a consequence of the particles high kinetic energy also warm solid particles can take part in the coating formation process and low porosity is achievable. The thermal load of the spray particles decreases, which results in less reactions with the spraying atmosphere.

CGS is a border case of thermal spraying and a consequent development of HV TS processes. The spray particles temperature is far below the solidification temperature and their velocity can (presently) amount to 1,200 m/s. CGS works by expansion of a process at high pressure through a convergent/divergent nozzle with spray particle injection in front of the smallest cross section. Heating of the process gas (T < 800 °C) results in increased particle velocities. Though the physical effects of the deposition process are not fully understood by now, it is known that the particles need to impinge on the substrate with a velocity exceeding a material
specific velocity to achieve a turn from abrasive effect to sticking [5,6]. However, GGS can only be applied successfully for coating materials with high ductility. Especially pure ceramic coatings cannot be produced.

In comparison to most other TS processes at atmosphere CGS permits manufacturing of coatings with very low porosity and oxide content. Especially substrate near coating areas are highly mechanically solidified. For coating materials with low thermal conductivity the bond strength can be increased due to small areas of metallurgical interactions (at particle/substrate as well as at particle/particle interfaces) due to local melting. Coatings with properties comparable to bulk material can be produced with high reproducibility [7,8].

4 MATERIALS

The aluminium alloys used in this work are listed along with their melting temperatures in table 1. Also the filler materials assigned to the specific substrates and their working temperatures are given.

*Tab. 1 Used aluminium substrates and solder/braze filler*

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Melting temperature ($T_s$)</th>
<th>Filler material</th>
<th>Working temperature ($T_w$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA 1050</td>
<td>646 °C</td>
<td>SnAg4Cu0.5</td>
<td>226 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn</td>
<td>420 °C</td>
</tr>
<tr>
<td>AA 3005</td>
<td>630 °C</td>
<td>AlSi12</td>
<td>578 °C</td>
</tr>
<tr>
<td>AA 5754</td>
<td>610 °C</td>
<td>Zn</td>
<td>420 °C</td>
</tr>
<tr>
<td>AA 7022</td>
<td>545 °C</td>
<td>ZnAl5</td>
<td>380 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ZnAl15</td>
<td>440 °C</td>
</tr>
</tbody>
</table>

The powder feedstock used for CGS are analysed concerning their morphology (by SEM) and chemical composition (by EDXS). The AlSi12 powder particles show homogeneous distribution of aluminium and silicon phases, spherical shape and size between 1 and 35 µm. EDXS analyses confirm the chemical composition of 12 wt.-% silicon in aluminium. The zinc based powders are blends of pure zinc and pure aluminium powder (EDXS results: 100 wt.-% zinc; 100 wt.-% aluminium). Both show non-spherical particle shape. The particle size fractions are 10 µm < d < 60 µm (zinc) and 5 µm < d < 20 µm (aluminium powder). Beside pure zinc powder, two composite powders are mechanically mixed: ZnAl5 (zinc, 5 wt.-% aluminium) and ZnAl15 (zinc, 15 wt.-% aluminium). According to the manufacturer the Sn95.5Ag4.0Cu0.5 powder shows spherical shape and a size fraction of 5 µm < d < 25 µm.
5 EXPERIMENTAL

Coatings are produced using the CGS system Kinetic 3000 (CGT Cold Gas Technology GmbH, Ampfing). The spraying process parameters gas pressure $p$, gas temperature $T$, spray distance $a$ and powder feed rate $m'$ are optimized by design of experiments applying $2^4$ experiments for each powder. Each coating is built up to a thickness of approximately 100 µm by moving the spray gun in meanders with 1 mm distance and spraying gun traverse velocity 0.35 m/s. For the CGS coating process using AlSi12 powder, also the influence of the spraying gun traverse velocity is investigated. In table 2 the powder specific values of the spraying parameters are given.

Tab. 2 Applied spraying parameters

<table>
<thead>
<tr>
<th>filler metal alloy</th>
<th>process gas pressure [bar]</th>
<th>process gas temperature [°C]</th>
<th>spray distance [mm]</th>
<th>powder feed rate [g/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td>Max</td>
<td>min</td>
<td>max</td>
</tr>
<tr>
<td>AlSi12</td>
<td>25</td>
<td>30</td>
<td>350</td>
<td>400</td>
</tr>
<tr>
<td>SnAg4Cu0.5</td>
<td>15</td>
<td>30</td>
<td>100</td>
<td>250</td>
</tr>
<tr>
<td>Zn</td>
<td>10</td>
<td>30</td>
<td>100</td>
<td>250</td>
</tr>
<tr>
<td>ZnAl5</td>
<td>10</td>
<td>30</td>
<td>100</td>
<td>250</td>
</tr>
<tr>
<td>ZnAl15</td>
<td>10</td>
<td>30</td>
<td>100</td>
<td>250</td>
</tr>
</tbody>
</table>

The soldering/brazing investigations concentrate on furnace processing with nitrogen atmosphere using industrially applied flux agents. The process is optimized concerning temperature-time function. For comparison samples with conventionally added filler materials (roll plated or as wire) are also joined.

Both CGS coatings and solder/braze joints are characterized by means of optical microscopy, SEM and EDXS analyses.

6 RESULTS

Production of CGS coatings

Depending on powder type and process parameters a different number of passes is necessary to reach the desired coating thickness of 100 µm. For each powder there is a transition from blasting to coating deposition depending on the process parameters. All coatings deposited by the same powder show comparable surface roughness and low porosity. Figures 1 to 3 show examples of the different coating types. The SEM investigations confirm very good bonding between coatings and substrates, partially with deep penetration of spray particles into the base material, especially in the case of the Sn based powder. Particularly the surfaces of AlSi12 coatings are very rough, while the Zn and Sn based coatings are rather smooth. EDXS analyses of both feedstock and coatings prove that no additional phases are formed and the
chemical composition remains constant. Only Zn-Al coatings show a difference in the composition of zinc and aluminium. The aluminium content is nearly doubled in comparison to the feedstock composition, which points at a significantly higher deposition efficiency of aluminium.

Assuming a constant coating density a factor $K$, which is proportional to the deposition efficiency, can be defined as:

$$K = \frac{d}{(N \cdot m')} \quad (1).$$

$d$: coating thickness [µm]

$N$: number of passes

$m'$: powder feed rate [g/min]

For constant powder feed rate $K_F$ already permits optimization of processing concerning deposition efficiency:

$$K_F = \frac{d}{N} \quad (2).$$
For including the gun traverse velocity \( v \) at constant powder feed rate into optimization considerations it has to be imparted in the characteristic parameter \( K_{Fv} \) due to its influence on the spraying time:

\[
K_{Fv} = v \cdot K_F
\]  

(3).

Generally CGS spraying with both high process gas temperature and pressure results in highest K-factors. Particularly AlSi12 coatings are only deposited, if high gas temperatures are applied. In Figure 4 a comparison of the K-factors depending on processing conditions for production of CGS AlSi12 coatings with process gas temperature of 400 °C is given. Apparently low powder feed rates result in increased deposition efficiency. The highest deposition efficiency is achieved for low levels of gas pressure, spray distance and powder feed rate.

The experiments concerning the influence of the gun traverse velocity show only small differences in morphology of the CGS AlSi12 coatings (velocities between 0.21 and 0.7 m/s). Therefore optimization is done according to pure economical considerations. Figure 5 comprises the \( K_{Fv} \)-factors depending on the gun traverse velocity. A maximum value is found for a velocity of 0.53 m/s. For further investigations the velocity yielding the highest K-factors is used exclusively.

In contrast to AlSi12 Zn-based coatings are also formed using low process gas temperatures (down to 100 °C). The maximum applied temperature in this case is 250 °C. The deposition efficiency increases with rising gas temperature. Also high process gas pressure and low powder feed rate contribute to increasing deposition efficiency.

Figure 6 comprises \( K_F \)-factors for CGS coatings produced using Zn, ZnAl5 and ZnAl15 powders and both high process gas temperatures and high powder feed rate. The different powder types do not show significantly different dependencies of deposition efficiency. Generally high process gas pressure results in high \( K_F \)-factors. In particular ZnAl15 are only formed, if high gas pressure conditions are applied. Also for ZnAl15 highest deposition efficiency is achieved for use of high process gas pressure. No difference depending on the spraying distance of 20 mm and 40 mm is observed for this powder type.
Also SnAg4Cu0.5 coatings can be produced using low process gas temperatures. However, like in the case of Zn-based coatings, in case of low process gas temperature high process gas pressure is necessary. For small spraying distances high deposition efficiency is achieved. Due to small quantity of available powder only very low powder feed rate is used. The $K_F$-factors of successfully deposited SnAg4Cu0.5 CGS coatings are given in figure 7.
Production of solder/braze joints

The applicability of the produced CGS coatings for soldering/brazing processes is investigated by CAB and atmospheric processes using heating plate or propane flame. With respect to the desired application field of heat exchangers the specimens are joint with angle-on-coupon geometry [9,10] (figure 8(a)), whereby CGS coated substrates are used as coupons. The angles are realized by 1 mm thick AA1050 strips.

Applying CAB in nitrogen atmosphere with NOCOLOK® flux perfect joints are produced with CGS AlSi12 coatings. The results are comparable to conventional methods of filler material addition like wires or roll plated coatings. In figure 8(b) an optical micrograph of a brazing seam for application of optimized temperature-time function (10 min at 610 °C) is given. In the braze joint only a negligible amount of defects like pores, inclusions or oxides can be detected. By SEM analysis a perfect metallurgical bonding between filler and base material is shown. EDXS analyses prove diffusion of silicon into the angle material. In the braze seam the silicon content amounts to 6 wt.-%. The precipitates located at grain boundaries are equal to those already in AA1050 substrates. The brazing seam microstructure compares to that of cast material.

Fig. 8 Angle-on-coupon sample (a) and optical micrograph of the braze seam (b) of an aluminium brazing joint using CGS AlSi12 coating filler.

Fig. 9 SEM image of a pure Zn CGS coated AA7022 sample after heat treatment according to a furnace soldering process (solder temperature 450 °C).

Fig. 10 Optical micrograph of a solder joint of AA1050-SiC(p) composite and AA5754 produced by ultrasonically assisted soldering using pure Zn CGS coating filler.
Zn-based CGS coatings do not permit production of high quality joints by CAB in nitrogen atmosphere and addition of different fluoridic Cs-based fluxes. Also tests performed under atmospheric conditions do not yield successful bonding. Always the wetting of the uncoated aluminium angle failed. Figure 9 shows a SEM micrograph of an AA 7022 sample coated with pure zinc after a heat treatment identical to the soldering process. Differences in comparison to ZnAl5 and ZnAl15 CGS coatings are not observed. Flux-free ultrasonically assisted soldering, however, produces perfect joints. An optical micrograph of a joint between AA1050 and AA5754-SiC(p) is given in figure 10.

All experiments on the solderability of specimens coated with CGS Sn-based filler coatings failed. Due to dewetting no bonding could be achieved [11].

7 SUMMARY AND DISCUSSION

AlSi12 Zn-Al and SnAg4Cu0.5 CGS coatings are successfully deposited on different aluminium alloy substrates. The coatings show identical chemical composition to the applied powder feedstock. For production of AlSi12 coatings comparatively high process gas temperature and pressure need to be used due to its low ductility. Low powder feed rate is beneficial to achieve maximum deposition efficiency. The investigations on the influence of the spraying gun traverse velocity on AlSi12 coating properties yield no differences. However, deposition rate and efficiency are strongly affected.

Zn-based feedstock (pure zinc, ZnAl5 and ZnAl15 blends) permits CGS coating production even at low process gas temperature or pressure. Just as for AlSi12 also for processing of Zn-based powders increased deposition efficiency is observed for low powder feed rate. EDXS-analyses prove a strong increase of aluminium content in comparison to the used ZnAl5 and ZnAl15 feedstock, which may not only be attributed to the different stress-strain behaviour and density but also to powder properties like particle size. In the case of the applied powder blend the zinc particles have three times larger diameter, i.e. roughly ten times larger volume and three times higher density compared to the aluminium particles, i.e. all in all 30 times higher mass of zinc particles. Therefore acceleration of aluminium particles occurs more effectively, which may result in a larger amount of particles reaching over-critical velocity. The applied SnAg4Cu0.5 feedstock permits production of dense CGS coatings both by low or high process gas temperatures and pressures due to tin’s high ductility and low melting temperature range.

For AlSi12 and Zn-based filler metal coatings a metallurgical reaction between the aluminium substrates and the coatings occurs during the soldering/brazing processes. As the flux agents do not approach the interface between coatings and substrate the natural oxide layer on top of the aluminium substrates must have been destroyed permitting its wetting by the filler melt. Despite deep penetration of particles during coating formation dewetting of the aluminium substrates is observed in the case of SnAg4Cu0.5 filler coatings.

CGS AlSi12 and Zn-based filler metal coatings permit production of perfect solder/braze joints by using a flux aided CAB process in nitrogen atmosphere or flux-free ultrasonically assisted soldering under atmospheric conditions.
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REFERENCES


