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Gaseous Shielding Gas Additives as Flux Substitute for TIG Arc Brazing

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Abstract: Brazing is one of the key technologies in the field of joining of metal components. To improve the wetting of brazing material and work-piece surface, it is often required to fall back on the use of flux. The application of these substances requires accuracy and is often connected with considerable expenditure and it is, just as the removal of flux residues, often an additional working step which has to be carried out manually. Within the framework of a DFG research project it has been investigated to which degree gaseous substances as addition to the shielding gas may replace conventional flux in TIG arc brazing. To this end, investigations have been carried out using different combinations of base and filler materials. Mainly monosilane as a gaseous flux substitute has been added in low concentrations to the shielding gas volume flow. The resulting brazed joints have been quantified with regard to their geometry, their fusion conditions and their chemical compositions. These qualities were then correlated and evaluated with the provided quantity of monosilane in order to identify dependencies.

Key-words: Flux; Silane; TIG; Arc brazing.

1. Introduction

The technology of brazing is increasingly gaining in importance in production technology. In light-weight construction and in the field of automotive engineering, brazing methods are often the only joining methods which are capable to join coated and temperature-sensitive materials economically while maintaining the required technological properties of the joining point.

Due to the heat input into the base material which is low in relation to fusion welding, the influence on the material properties of the base material is only minimal. Thermal changes in the base material can thus be avoided, compared with classic fusion welding methods. It is, moreover, possible to reduce distortion sustainably which allows to dispense with labour-intensive and expensive post-treatment, especially when coated sheets are welded. On galvanised steel sheets, the anti-corrosive zinc layer remains potentially intact in close proximity to the welding zone, whereas it is most definitely destroyed in welding processes due to the low evaporation temperature of zinc. For this reason, subsequent coating work will not be required and additional costs moght be avoided when brazing methods are applied.

Brazing, however, requires a more complex preliminary work. An important technological parameter for the evaluation of a brazed joint is the wetting behaviour of the brazing material on the base material. For the improvement of the wetting behaviour, often flux is used. The flux is applied in the form of paste on the base material, this is often done manually, and residuals are removed after the arc brazing process has been concluded. Due to these required preliminary and subsequent works, the application of the brazing technology in automated production is estimated to be time-consuming and planning-intensive. The drying time of the flux is, moreover, to be considered since it is an additional impediment to the integration of the brazing process into the production cycle.

Against this background, the demand for a brazing technology where the required working steps which are connected with flux application can be reduced and/or be dispensed with must be determined.

2. State of the Art

Depending on the working temperature of the brazing material which lies within the range of the melting point of the brazing material, it is systematically differentiated into soldering processes (T_{liq} < 450 °C), brazing processes (T_{liq} > 450 °C) and high-temperature

brazing processes (T_{liq} > 900 °C) [1]. The arc brazing processes which are, in this work, used for making the brazed joint are assigned to the field of brazing and or high-temperature brazing. The following expositions about the state-of-the art are therefore limited to these last-mentioned groups.

A pre-condition for the fusion between brazing material and base material during the brazing process are the occurring phase boundary reactions. The selection of an appropriate flux promotes these reactions by removing inhibiting thin oxide layers and by preventing their new formation during heating up to brazing temperature.

In accordance with DIN EN ISO 9453 a flux is a "[...] non-metallic matter which, when molten, supports wetting by removing existing oxides or detrimental coatings from the surfaces which are to be joined and by preventing their new formation during the joining process".

In brazing, a clean work piece surface is essential for a good fusion of the brazing material since proper phase boundary reactions occur only then. For this reason, the surface shall always be cleaned before brazing takes place in order to remove grease and other impurities from the surface. Fluxes are used in order to remove the wetting-inhibiting oxide layer from the base material and to prevent renewed oxidation during the brazing process. The oxide layer would otherwise cause lack-of-fusion defects since it impedes the phase boundary reactions, just as the impure surface of the base material would do. Moreover, the application of flux helps to avoid oxide inclusions in the brazed seam which would lead to embrittlement of the seam.

It is, under certain circumstances, possible to dispense with the application of flux [2], when

- brazing materials which are self-fluxing in air are used,
- brazing is carried out under shielding gas or vacuum using special brazing materials,
- the brazed surfaces are pre-treated immediately before joining and when high heating speed is achieved during brazing,
- measures for the destruction of the oxide layers are taken during the brazing process.

The main constituents of the fluxes are boron, phosphorus, silicon and halogen compounds. In most cases, different individual or multi-component compounds are used as flux. The fluxes which contain several components and have thus different functions are, at that, particularly effective. Depending on the type of oxide, the constituents are acting on the surface of the base material. For basic oxides, fluxes with acidic character and for acidic oxides fluxes with basic character are accordingly required.

So far, gaseous fluxes are mainly used for braze welding. At that, brazing methods such as, for example, the gas flux method are used. Normally, brazing materials which are melting at approximately 900°C are applied. These are, in most cases, brass brazing materials and alpaca brazing materials. Brazing with gaseous flux does not leave any residues and, in contrast with the use of solid fluxes, flux inclusions do not occur [3]. The application is as follows:

First, the flux which consists of alkali fluorides, alkali borates, boric acid ester and easily vapourable solvent as the carrier medium [4], is liquid (In [5] it consists of alcohol and boric anhydride, in [6] of tetrafluorethylmethylether "Boropur"). The flux turns into gas while it is flowing through the fuel gas in the carburettor. Subsequently, the mix reaches the brazing flame. During the burning inside the flame of a gas torch which is taking on a green colour, the flux is changed into different boron compounds [7] which are condensing on the heated work-piece [8]. As fuel gas, normally, an acetylene oxygen flame is used. The application of such a flame allows brazing of the materials bronze, brass and steels without needing addition of flux in the form of powders, pastes or coatings of brazing bars.

The application of aerosols as used in gas flux welding according to [4-8] is difficult in GMA brazing. According to Wilden and Müller [6], increased porosity occurs at flow rates above 1,4 l/min. The flux addition also exerts influence on the seam geometry. The fluxes Boropur and NocolokZnFlux have been used.

In furnace brazing, also gaseous agents such as monosilane (SiH4) [9-14] have of late been applied. These are easier to handle since they are dispensed directly into the furnace atmosphere. The balanced application of conventional fluxes is sometimes difficult, this problem is thus avoided. Here, the results gained by Bach et al. [9-12] are pointing to a high effectivity.

The components which are active in conventional solid fluxes can basically be developed from the gas phase by application of the required activation energy, i.e. their production takes place most beneficially in the

arc itself. As starting materials (educts), and thus as “gaseous fluxes”, here compounds such as monosilane (SiH4, gaseous) come into consideration which, on the one hand, form the arc plasma with argon and which, on the other hand, react with the existing oxygen from the air in situ towards the known effective components. Simple, thermo-dynamical considerations are instrumental for a prognosis. In the easiest case, the standard enthalpy of formation of the starting materials with those of the desired products are considered [15-18].

Monosilane is mainly used in the semi-conductor and solar cell industry. It is especially used for methods where silicon or silicon compounds shall be separated from the gas phase.

Normally, monosilane disintegrates during the pyrolysis in the plasma into hydrogen and silicon. Current research via mass spectrometry in plasmas establishes, however, the formation of various charged and uncharged radicals at the substrate surface which are highly reactive due to their unpaired electrons [19]. Depending on the type of plasma generation (radio frequencies, arc, laser, etc.) and the conditions in the closed system, different species and reactions are observed [20,21]. Various silyl radicals, radical cations and various hydrogen species and argon ions are specified which are, by recombination, capable to react with one another. The exact chemical reactions in the arc plasma are, however, not predictable. Processes in the plasma state are, normally, part of physical research and have, so far, been specified only for at least closed systems [22,23].

Another possible quality of the application of the gaseous components is the reaction with oxygen and hydrogen in the immediate environment of the arc. The reaction of monosilane towards silica and/or quartz is strived for. Through this chemical reaction the substance which is acting as flux is developed and the undesired oxygen is also kept away from the brazing point.

Basically, the highly reactive behaviour of silane is relevant as regards occupational health and safety. Silane is self-igniting as from a concentration of 1,4% in atmosphere which must be considered in technological application.

3. Objective, Research Hypothesis and Methodology

The scientific aim of the research work was to determine in how far monosilane as addition to the shielding gas can replace the application of fluxes in arc brazing. Moreover, the effective concentration of the additive was to be determined, the effects were to be investigated, quantified and documented.

Monosilane (SiH4) represents the initial member of the silanes. The striking reactive property of silane is the strong oxygen affinity. As additive gas in arc brazing, silane shall extend thus the property of the shielding gas with regard to the binding of free oxygen and also activate the joining partners’ surfaces. Through the reactions of the silane with the oxygen, oxygen partial pressures in the region of the shielding gas are developing which are very similar to those in vacuum brazing, Equation 1:

$$SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O \quad (1)$$

It is expected that the oxide layer on the base material is reduced by the products of the applied silane. Moreover, the low oxygen partial pressures shall prevent renewed oxidation of the less noble joining partner during the process [3].

Against this background, tests have been carried out where TIG surface brazing under variation of the process parameters, the base material and the shielding gas composition were produced. The resulting brazed joints have been quantified with regard to their geometry, their fusion conditions and their chemical compositions. These qualities have then been correlated and evaluated with the provided quantity of monosilane in order to identify dependencies.

4. Experiments and Results

In order to obtain a defined gas mixture, an argon-silane mixture has been prepared by means of two mass flow controllers. At that, a pure argon mass flow has been combined with a 99% argon / 1% silane mixture. First TIG tests without filler material served the purpose of identifying possible peculiarities in the arc process.

Regardless of the quantity of the added silane and the electrode polarity, changes of the electrode tip geometry could be observed, Figure 1. The undefined change of the electrode geometry resulted in the undefined burning of the arc.

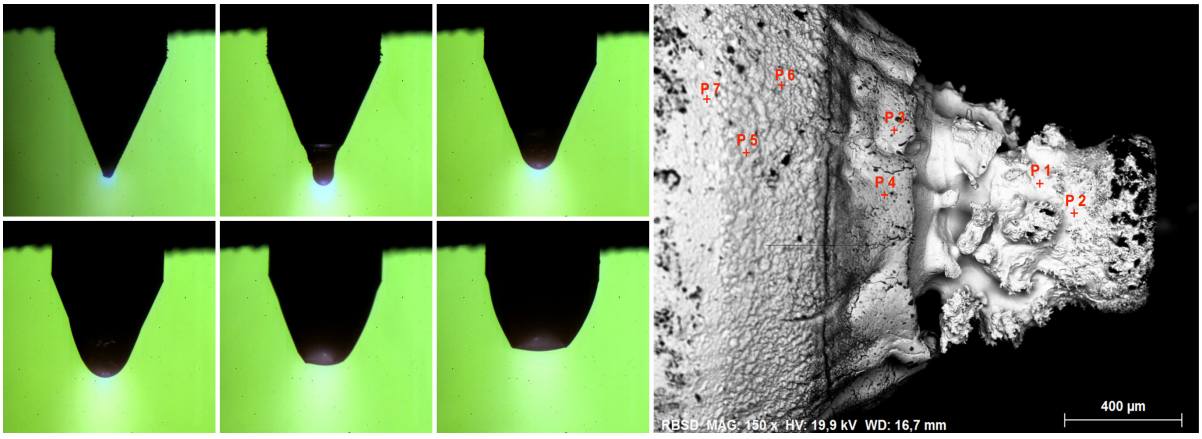

Figure 1. Integrity loss of the electrode geometry (left), electrode condition after silane influence (right).

In order to comprehend the deformation of the electrode, the identification and concentration of the elements at the electrode surface were decisive, and they were analysed via energy-dispersive X-ray analysis (EDX). The analysis showed that silicon enrichment close to the surface of up to 60 atom-% could be identified. This is caused by the formation of the low-melting W-Si phases so that successive enrichment of the tungsten with silicon and molten mass of the developing phases leads to the destruction of the electrode geometry. Apart from the loss of the geometrical integrity, this leads also to inhomogeneities in the charge carrier exchange with the free electrode surface and thus to irregularities in the arc behaviour.

The test set-up has been expanded by an additional nozzle which serves for the dedicated silane addition within distance from the electrode, Figure 2. It is decisive that the tip of the nozzle within the shielding gas shroud is positioned in the absolute vicinity of the arc so that the argon silane mixture is sucked into the arc through the gradient in the dynamic pressure component. By the silane input within distance from the electrode, the electrode geometry and thus the arc behaviour remained stable.

In order to determine possible energetic differences of the different gases and gas combinations, the processes which were setting with the tested gases, gas mixtures and gas combinations have been compared at constant current. Since in the TIG method the current is controlled as a process parameter, process voltage is setting as a system answer, depending on the given process boundary conditions. This way, the integrated electric behaviour of different gases and gas mixtures can be estimated via the measurement of the process voltage relative to one another.

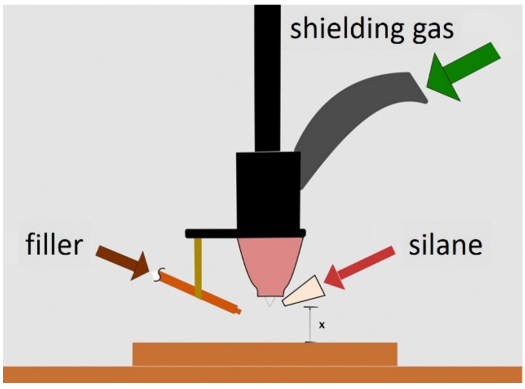

Figure 2. Principle of silane addition without direct electrode contact.

Argon has been used as the primary shielding gas. The tests were carried out once without injection of additional process gas and once with injected silane/argon mixture (0.5 l/min) and once with injected argon (0.5 l/min). The result of these measurements is depicted in Figure 3. The differences which have been determined with the different current intensities lie within the range of measuring accuracy and statistical process reproducibility. The arc system behaviour is, within the framework of statistical process behaviour, electrically invariant towards the input of secondary process gas in the specified quantity. In the tests which were carried out with silane addition, a constriction of the arc was observed, therefore silane might affect the energy density in the arc, despite the constant all-electric behaviour.

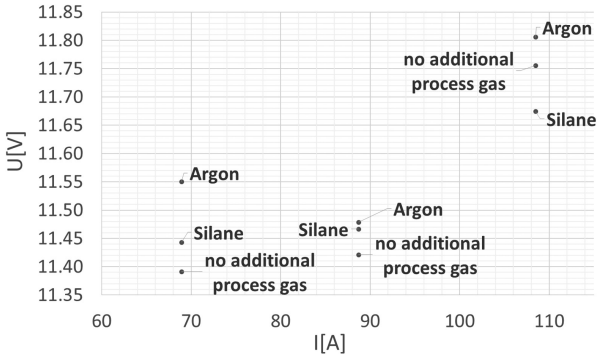

Figure 3. Energetic consideration of the TIG process with addition of silane without direct electrode contact.

The first tests which were carried out were surface brazings of AlCu7 on uncoated S235 with a thickness of 2 mm.

Representative for the tests which have been carried out, Figure 4 depicts a series of surface brazings of AlCu7 on structural steel S235JR with a thickness of 2 mm according to DIN 10025. The rolled surface of the steel was cleaned and the silane addition was, with equal process parameters, successively increased. Table 1 contains the relevant information with regard to the silane addition and resulting seam geometry. Here, the change of the seam geometry becomes clear. The wetting behaviour is specified by the dihedral angle (also called wetting angle). With increasing silane addition, the wetting angle is decreasing and the seam is widening. As from an addition of 0,6 l/min 1% of silane in 99% argon, the seam geometry is converging, a further increase does not bring about improvement of the wetting behaviour. It was, thus, possible to exert influence on the weld geometry which was reproducible and dependent on the silane addition.

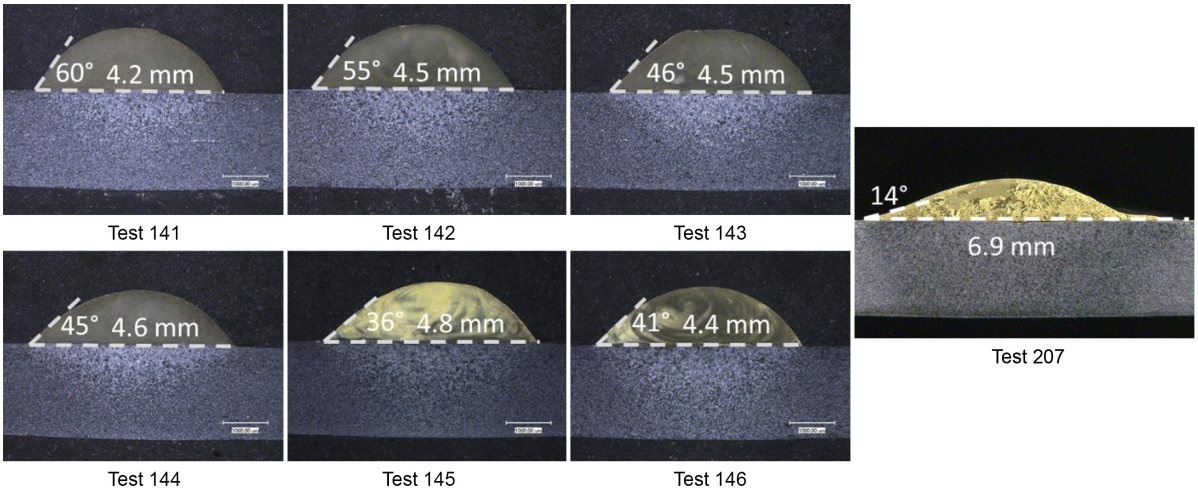

Figure 4. CuAl7 on S235JR, convergence of the geometry when silane addition is increased. Tests 141-146, wetting behaviour when conventional fluxes are used, Test 207a.

Table 1. Comparison of seam geometries with silane addition and conventional flux CUAl7 on S235JR.

sample	1% silane (l/min) / flux	wetting angle	weld width (mm)	current (A)	wire feed speed (m/min)	welding speed (m/min)
141	-	60°	4.2	70	1.5	0.3
142	0.3	55°	4.5	70	1.5	0.3
143	0.4	46°	4.5	70	1.5	0.3
144	0.5	45°	4.6	70	1.5	0.3
145	0.6	36°	4.8	70	1.5	0.3
146	0.7	41°	4.4	70	1.5	0.3
207a	Brazetec FH20s	11°	6.9	70	1.5	0.3

For a direct comparison, brazings with conventional fluxes and equal process parameters were also carried out. The influence of the flux is, here, much more obvious, Figure 4, Table 1.

If the silane addition is increased, a contraction of the arc system in the arc attachment is observed. The current working hypothesis is based on the assumption that the processes which are required for the activation of the work-piece surface promote the local charge carrier transport which is accompanied by a local increase of the energy density. The accumulation of embedding structures of iron in the brazing material in the centre of the cross-section of the seam which, this way, has not been observed in the reference brazings made without silane, Figure 5, points to this. The increase of the global energy level by increasing the process current results, in the case of silane addition, also in premature local melting of the base material.

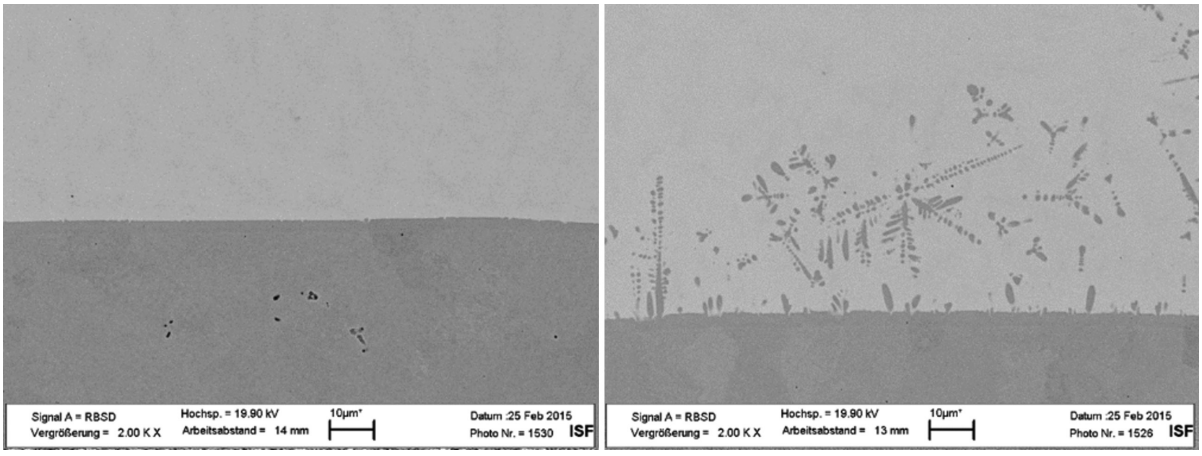

Figure 5. Comparison of embedding structures of iron in brazing material matrix. Right: brazing without silane addition, left: brazing with silane addition.

The addition of silane in surface brazings of CuAl7 on galvanised steel, here: DX51D+Z did, as expected, not bring about significant improvement of the wetting conditions. Minimum additions (0.2 l/min) of 1% silane reduced the dihedral angle and resulted in lesser widening of the seam, Figure 6, Table 2. The increase of silane addition did not bring about any further improvement.

In analogy to the tests made with unalloyed steel, test series using austenitic chromium nickel steel (1.4301 according to EN 10088-1) and CuAl7 as brazing material were carried out, Figure 7, Table 3. Here, similar effects were observed. The seam geometry is converging fast when the silane addition was increased, wetting angle and seam width were also increasing. Here, the increase of the melting of the base material with rising silane proportion must be pointed out. It can be assumed that the passivating chromium oxide layer is, as from a critical silane addition, locally more strongly interacting with the silane and that locally higher current densities are setting which are sufficient for obtaining the melting temperature of the base material.

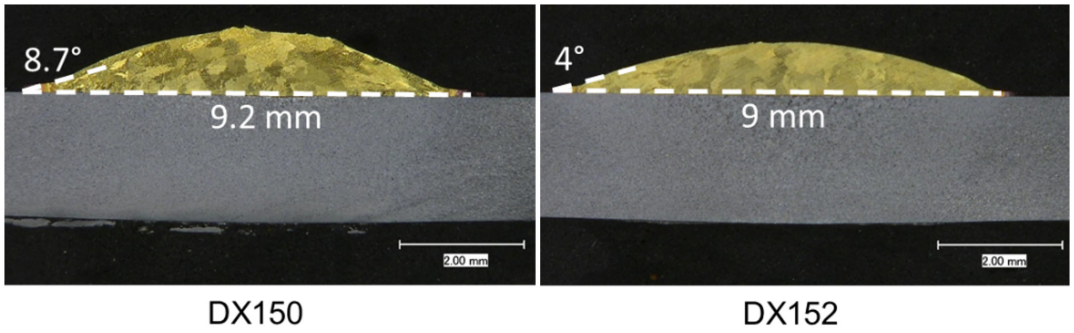

Figure 6. CuAl7 on DX51D+Z, comparison with and without silane addition.

Table 2. Comparison of seam geometry with silane addition, CuAl7 on DX51D+Z.

sample	1% silane (l/min)	wetting angle	weld width (mm)	current (A)	wire feed speed (m/min)	welding speed (m/min)
DX150	-	8.7°	8.9	90	1.5	0.25
DX152	0.2	4°	9.2	90	1.5	0.25

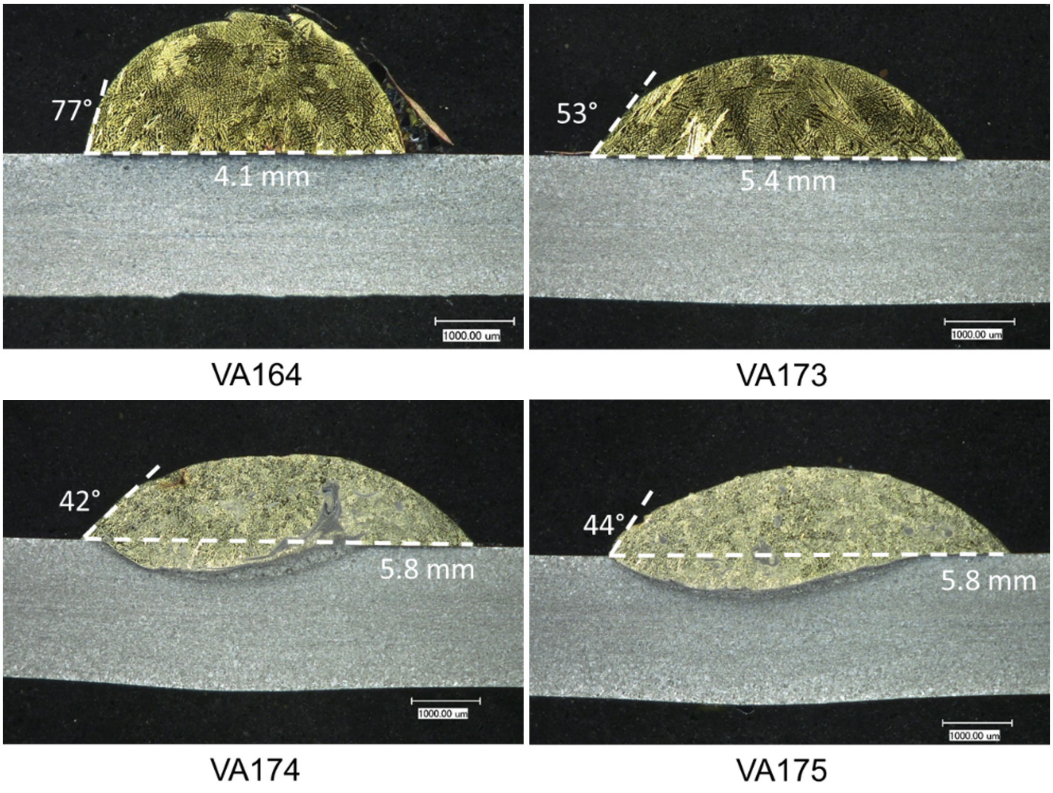

Figure 7. CuAl7 on 1.4301, comparison with and without silane addition.

Table 3. Comparison of seam geometries under silane addition, CuAl7 on DX51D+Z.

sample	1%silane (l/min)	wetting angle	weld width (mm)	current (A)	wire feed speed (m/min)	welding speed (m/min)
VA164	-	77°	4.1	90	2	0.5
VA173	0.2	53°	5.4	90	2	0.5
VA174	0.3	42°	5.8	90	2	0.5
VA175	0.4	44°	5.8	90	2	0.5

The reducing action of silane and its products becomes particularly clear by the suppression of tempering colours during the processing of high-alloy austenitic chromium nickel steels. Figure 8 depicts remelting tests made with and without silane addition. As from an addition of 0.3 l/min 1% silane, tempering colours on and besides the seam are suppressed reproducibly.

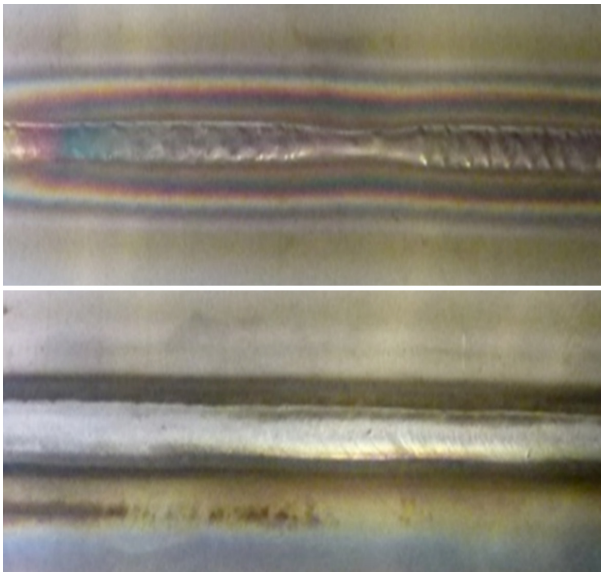

Figure 8. Remelting tests on 1.4301, comparison with and without silane addition.

5. Summary and Outlook

Within the framework of the research it has been investigated in how far silane has a flux effect on the brazed joint when added to the shielding gas volume flow in TIG brazing.

Basically, the application of silane as additive in the shielding gas can exert a positive influence on the fusion quality, i.e. wetting angle. The addition cannot be made in the actual shielding gas flow since a chemical reaction of the silane with the tungsten electrode occurs which leads to the destruction of the electrode integrity. It is, thus, not possible to add silane directly as additive to the shielding gas in the process. In order to maintain the electrode integrity, a test set-up has been developed which allows to add silane via an additional gas nozzle into the process area in such a way that the destruction of the electrode does not occur.

Within the framework of the quantification of the effects of the silane input during brazing, different combinations of filler and base materials were applied.

When galvanised sheets are applied, the addition of flux can normally be dispensed with. When additional flux is used, there is hardly a positive influence on the brazed seam geometry. There is also no significant difference with regard to the seam geometry between brazings made with and without silane. However, the dihedral contact angle under silane addition was easy to optimise where the optimisation was also reproducible. This effect is, however, so insignificant that the application of silane is not deemed necessary.

Brazing on uncoated steel shows different qualities. The untreated work-piece surfaces are clearly inhibiting the wetting of the brazing material. The addition of silane allowed to exert a reproducible, positive influence on the wetting behaviour. The dihedral contact angle is, under silane addition, clearly decreasing. This results, moreover, in a flatter and wider seam and thus in the increase of the structurally relevant wetting area. Moreover, an increase of the local energy density recognisable in the form of arc contraction at the arc attachment point and the increase of embedding structures of iron in the brazing material is possible. Within the framework of the tests it has been established that silane as additive in the shielding gas volume flow has similar, if not so pronounced, effects during brazing of steel as the use of conventional fluxes.

Future research will focus on the transfer of the achieved results from the TIG arc to GMA brazing. Since, here, the problem of the self-destroying electrode is not existing, the complex shielding gas addition can be dispensed with.

Acknowledgements

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