The Effect of Trace Elements on the Formation of Slag Spots During Gas Tungsten Arc Welding of 316 L Stainless Steel Tube Systems

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Introduction

Gas Tungsten Arc Welding (GTAW) is used in the manufacturing of longitudinally welded tubes and as a standard for the installation of tube systems in the semiconductor and pharmaceutical industries. During visual and/or boroscopic inspection of welds small grey spots might be conspicuous, especially in the downslope area of orbital welds. These slag spots are also referred to as *oxide islands*.

Apart from arc instability, an irregular weld bead and reduced penetration [1] slag spots are often considered as potential initiation sites for pitting corrosion and potential sources of particulate contamination into a flowing medium.

1 Slag spots — formation and chemical properties

1.1 Chemical composition of slag spots

Slags on welds of 304 and 316 stainless steels are generally composed of high melting point oxides of aluminium, calcium, magnesium, titanium, zirconium, cerium, silicon, chromium, manganese and iron [1]. In the majority of investigations carried out by the author slags on welds of 316 L stainless steel revealed high concentrations of aluminium, calcium and silicon and only small amounts of other metals. Fig. 1 shows a SEM[1] image (magnification $\approx 100\times$) of a typical small slag spot in the downslope area of a weld sample $38.1 \times 1.65\ mm$ (electropolished seamless tube, 316 L / 1.4404, heat 446612). Fig 2 shows the corresponding EDX[2] spectrum. Evaluation of this spectrum led to the analysis as listed in table 1.

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[1] SEM = Scanning Electron Microscopy

[2] EDX = Energy Dispersive X-ray Analysis

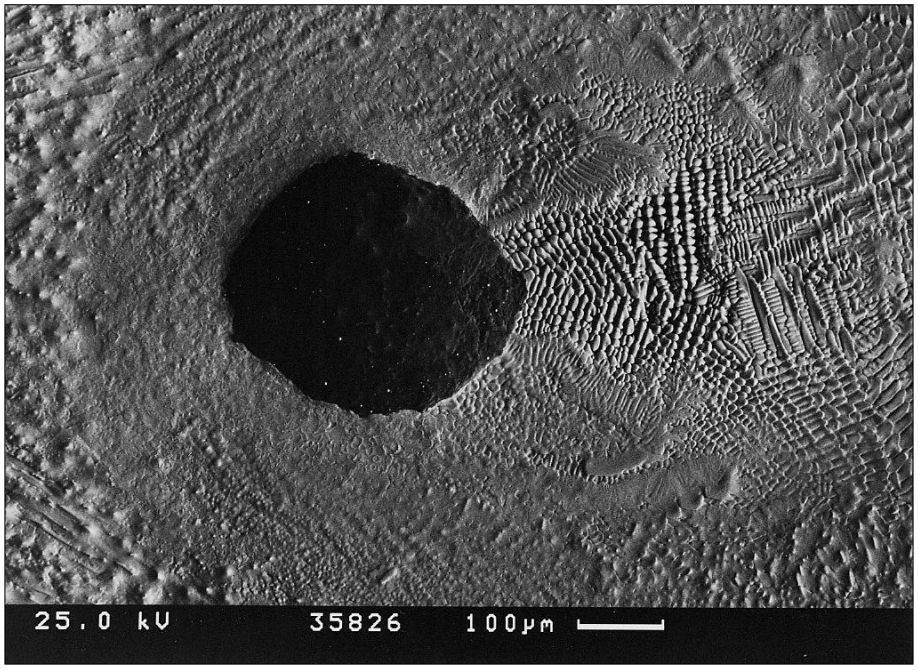

Figure 1: SEM image @ 100 × magn. (backscatter electron image) of slag spot at the downslope area of a weld sample 38.1 × 1.65 mm (seamless tube, 316 L / 1.4404, heat 446612)

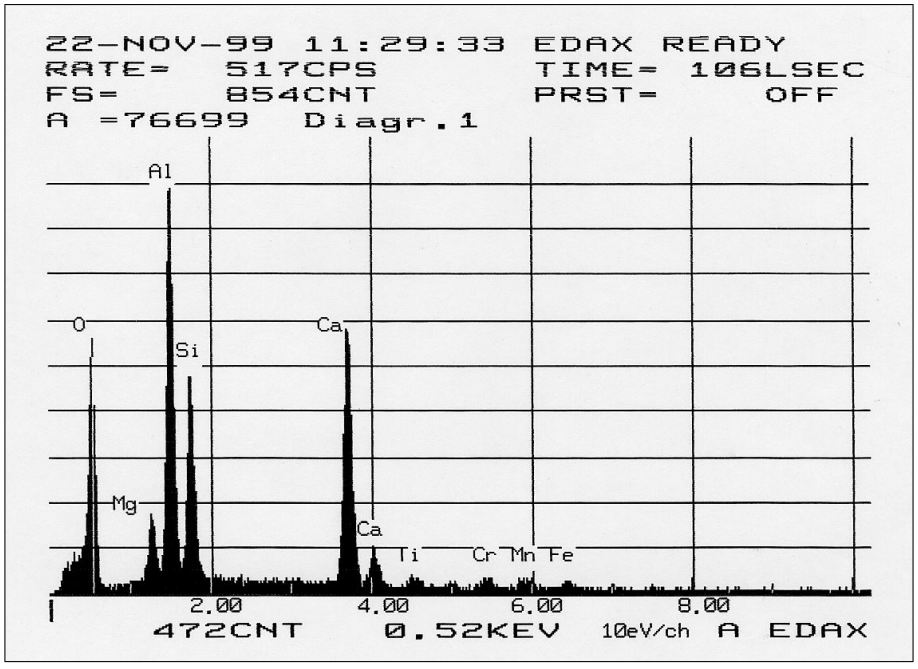

Figure 2: EDX spectrum of slag spot spot in the downslope area of a weld sample 38.1 × 1.65 mm (seamless tube, 316 L / 1.4404, heat 446612)

Table 1: Elemental composition of slag spot (fig. 1) determined by EDX spectroscopy (fig. 2)

Element	O	Mg	Al	Si	Ca	Ti	Cr	Mn	Fe
Weight %	54.87	3.69	16.82	8.28	13.94	0.84	0.86	0.45	0.25

The highest concentrations were measured for oxygen, aluminium, silicon and calcium. Furthermore small amounts of magnesium, titanium and manganese were detected. The high percentage of oxygen (> 50 weight %) shows that the elements found in the slag spot form binary (e.g. Al_2O_3) or complex oxides (e.g. calciumalumosilicates).

Corresponding results, i.e. high concentrations of Al, Ca and Si, were determined by several examinations of slag spots on welds of 316 L stainless steel. Furthermore it was found that small variations in the percentage of Al and Ca have a major influence on the slagging characteristics. An increase of the Ca content from an average value of 0.0006% up to 0.003% for instance led to severe slag spot formation on the OD of orbital welds of electropolished seamless tubes $\frac{1}{4}'' \times 0.035''$, $\frac{3}{8}'' \times 0.035''$ and $\frac{1}{2}'' \times 0.049''$. Therefore it can be concluded that especially Al and Ca should be strictly controlled to avoid formation of slag spots.

1.2 Origin of slag forming elements

Although most of the trace elements detected in slag spots are not specified by international standards their origin can be traced back to the steel melting and refining process.

Subsequent to the melting process in the steel mill the raw material is refined by *Argon Oxygen Decarburization* (AOD)[3]. To decrease the carbon content Ar and O_2 are blown through the molten steel. Carbon + oxygen form carbon oxide (CO). This exothermic reaction provides heat for further refining. In the next step reducing agents, e.g. aluminium or silicon, are added to reduce metal oxides back into the melt and aid deoxidization. These elements form the extremly stable oxides Al_2O_3 and SiO_2, respectively $(SiO_3)^{2-}$ or $(SiO_4)^{4-}$. The AOD process leads to steel with low sulfur content. Subsequently the percentage can be modified by addition of sulfur to increase the content or calcium oxide for further desulfurization. The resulting Al, Si and Ca compounds form together with contaminants the slag on the molten steel. After solidification of the melt a small amount of these elements remains in the steel as tiny inclusions. However, a certain amount of aluminium, silicon and calcium can be detected in all steels manufactured according to the standard process of AOD or VOD refinement.

It goes without saying that steel manufactured by a VIM/VAR[4] or VIM/E-BEAM[5] process [2] shows a higher degree of cleanliness with far lower concentrations of slag forming trace elements and therefore reveals a superior weldability with lower slag spot formation.

[3] alternatively *Vacuum Oxygen Decarburization* (VOD) is applied

[4] VIM = Vacuum Induction Melting; VAR = Vacuum Arc Remelting

[5] E-BEAM = Electron Beam Cold Hearth Refining

1.3 Mechanism of slag spot formation

If the steel is melted again, e.g. during welding, slag forming compounds can accumulate together and precipitate on the weld seam as visible spot. Number and appearance of slags do not only depend on the percentage of all elements but also on the ratio between them and on the solidification mode.

Pollard reported that slags can be classified into two types, i.e. patch-type and globular slags [1]. He found that large patch-type slags were formed when the ratio % silicon to % aluminium was less than 50 and less critical globular slags when it was greater than 50.

Furthermore Collins reported that the solidification mode has a major influence on slag spot formation [3]. Collins found that a 316 L composition that solidifies in the ferritic-austenitic mode will show a significantly decreased propensity for the formation of slags. These findings were explained by a higher solubility of slag forming elements, such as Al, Ca, Si, Zr, ot Ti, in a bcc[6] ferrite than in fcc[7] austenite.

2 Corrosion study

The effect of slags on the corrosion resistance was determined by electrochemical measurements on four samples of a welded, redrawn and solution annealed tube (316 L / 1.4435) which revealed major slag spots on the root of the longitudinal weld (tube i/d) [4]. These slag spots showed high concentrations of oxygen, aluminium, calcium, magnesium and small amounts of titanium as listed in table 2.

Table 2: Composition of slag spot on longitudinal weld determined by EDX spectroscopy

Weight %	> 10	1–10	< 1
Elements	Al, O	Ca, Mg	Ti

Plots of current density $[\mu A/cm^2]$ vs. potential $[mV/SCE]$ were recorded with 1 mV/s by utilizing an ec-pen[8]. 0.1 M Hydrochloric acid was chosen as electrolyte because halogenide induced pitting corrosion in acid environments was believed to be the most likely corrosion failure in the majority of applications.

The measurements were performed on the parent metal surface (**A**), on the root of the weld (**B**), in the center of the slag spot surface (**C**) and at the interface of slag and weld surface (**D**). In all experiments nearly the same plot was obtained and development of oxygen could be observed. Since these experiments did not result in any distinction between the different areas **A** to **D** the tests were repeated in 0.25 M hyrochloric acid. Since steel grade

[6] body centered cubic lattice type

[7] face centered cubic lattice type

[8] The ec-pen is a small electrochemical cell developed by the Swiss Society for Corrosion Protection (SGK). Stuctures in the range of a few millimeters can be resolve by this technique.

316 L / 1.4435 only shows a limited corrosion resistance against this medium the scatter of the obtained data was somewhat larger than in the previous tests. However, the results were generally the same, i.e. the areas **A** to **D** revealed the same resistance against corrosion.

The high level of corrosion resistance determined directly in the center of the slag could easily be explained by the thermo-dynamical stability of slag compounds. α-Al_2O_3 ($\Delta H_f = -1677\ kJ/mol$) for instance is one of the most stable compounds that are known and it can be assumed that it does not react with almost any kind of aqueous or non-aqueous media.

Somewhat surprising was the result that no significant drop in corrosion resistance could be detected at the interface of slag and weld surface (**D**). This area was assumed to show the lowest corrosion potential since the chromium enriched passive layer is definitely disturbed along this interface. Anyhow, in the reported experiments no detrimental effect on the corrosion resistance could be determined.

3 Embedding of slags into the weld metal

To determine the shape of a slag and its embedding into the weld metal a typical globular type slag was cross sectioned and prepared for optical microscopy [5]. The specimen was cut from an orbital weld of an electropolished seamless tube $38.10 \times 1.65\ mm$, 316 L / 1.4404, heat 446612.[9] The elemental composition determined by EDX spectroscopy is listed in table 3.

Table 3: Elemental composition of globular type slag spot determined by EDX spectroscopy

Element	O	Ca	Si	Al	Mn	Cr
Atom %	53.23	19.04	12.53	7.15	6.98	1.06
Weight %	32.77	29.37	13.54	7.43	14.77	2.12

The metallographic cross section at 500 × and 1000 × magnification is shown in figures 3 and 4. It reveals a lense-shape with a diameter of approx. 185 μm and a thickness of max. 26 μm. The specimen did not show any indication of cracks or crevices in the slag or between slag and weld metal. The slag appears embedded into the steel matrix and a separation of particulate matter from the slag which might contaminate a flowing medium seems to be very unlikely.

4 Conclusions

For the slag spots we investigated it can be concluded that a detrimental effect on the flowing medium inside the tube system seems very unlikely. Anyhow, for different slags on welds of a single tube manufacturing lot that were measured by means of EDX spectrocopy varying

[9] same production lot but different sample as described in section 1.1

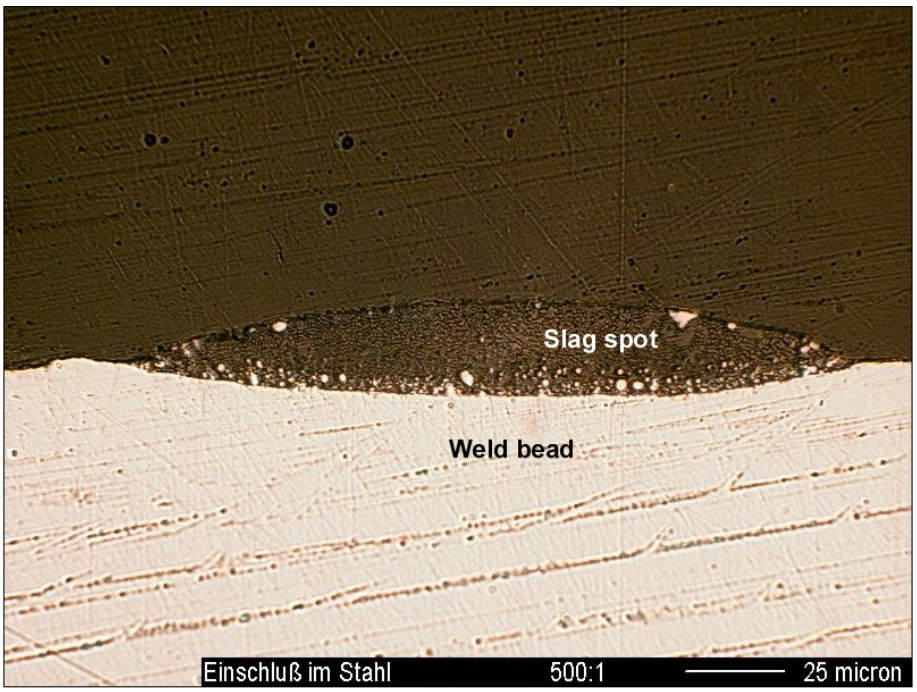

Figure 3: Metallographic cross section @ 500 × magn. through slag spot in the downslope area of an orbital weld 38.1 × 1.65 mm (seamless tube, 316 L / 1.4404, heat 446612)

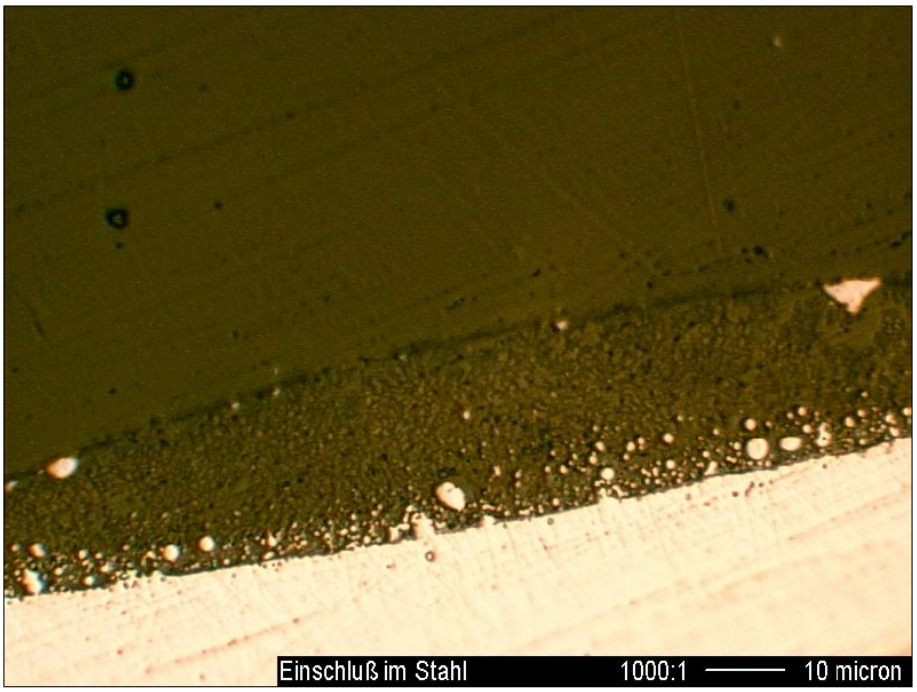

Figure 4: Metallographic cross section @ 1000 × magn. through slag spot in the downslope area of an orbital weld 38.1 × 1.65 mm (seamless tube, 316 L / 1.4404, heat 446612)

concentrations of slag forming elements were determined. Any of these slags might show a different behaviour in contact with bulk gases or process chemicals.

Furthermore it can't be excluded that more sophisticted electrochemical techniques may show a significant difference in the redox characteristics of slag and weld metal. Therefore the aim should be to minimize the formation of slags as far as possible although not all slags compromise the purity of the flowing medium.

The most promising approaches for minimization of slag spot formation are as follows:

1. Restriction of slag forming elements, e.g. aluminium and calcium. It was found that specification of Al max. 0.010 % and Ca max. 0.0010 % prevented heavy slagging. These levels can be maintained without extraordinary efforts (and costs) by standard AOD or VOD processing.

2. Adjustment of chromium and nickel equivalent as suggested by Collins [3]. Since a ferritic-austenitic solidification mode decreased the propensity for the formation of slags the chemical composition should be balanced accordingly. On the other hand δ-ferrite remaining in the weld should not exceed about 5 % to avoid a drop in corrosion resistance due to enhanced segregation of alloying elements. It was found that the *ideal* composition revealed approx. 3 % δ-ferrite after welding.

References

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[5] J. D. Schaefer, *Analysis of Inclusion in Welding Joint*, ATU GmbH — Analytics for Technology and Environment, Report no. 911066, 15 November 1999.