

Control of Exposure to Hexavalent Chromium and Ozone in Gas Metal Arc Welding of Stainless Steels by Use of a Secondary Shield Gas

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Previous work has demonstrated that the shield gas composition in gas metal arc welding can have a considerable effect on hexavalent chromium [Cr(VI)] concentration in the fume and on ozone concentrations near the arc. Normally a single shield gas is used. This paper describes a double shroud torch that allows use of concentric shield gases of different compositions. A solid stainless steel wire was used for welding. The double shroud torch used secondary shield gases containing small amounts of the reducing agents NO and C₂H₄. The Cr(VI) concentration in the fume and ozone concentration at a fixed point relative to the arc were measured and compared with results when using a single shield gas. Use of the reducing agents in secondary shielding using the double shroud torch was found to offer advantages for ozone concentration reduction compared with use in a conventional torch, but this was not found to be an advantage for reducing Cr(VI) concentrations.

Keywords: chromium; control; ozone; weld fume

INTRODUCTION

Gas metal arc welding (GMAW) of stainless steel results in the production of a respirable fume containing chromium and nickel compounds including hexavalent chromium, Cr(VI), a suspected carcinogen. In addition, the toxic gas ozone is generated by the action of UV light from the arc on oxygen.

Concern regarding exposure to Cr(VI) has been expressed by the UK Health & Safety Commission, who specified a maximum exposure limit (MEL) (long-term limit) of 0.05 mg/m³. The occupational exposure standard (OES) (short-term limit) for ozone is 0.4 mg/m³ (equivalent to 0.2 p.p.m. on a volume basis). Ozone can cause severe irritation to the eyes and mucous membranes, and in severe cases pulmonary oedema. It is also known to exacerbate existing asthma. The OES for respirable fume is set at 5 mg/m³, at which level a fume containing >1% Cr(VI) would exceed the Cr(VI) MEL. This is

without considering the possible additive effect of nickel compounds, as some forms of nickel are also suspected carcinogens (Kazantzis, 1972).

Generally it is desirable to reduce exposure risk to both Cr(VI) and ozone. Ways to achieve this include local exhaust ventilation and various forms of process modification. In the case of manual metal arc welding, Kimura *et al.* (1979) described reduction of sodium and potassium in the covering and addition of lithium to replace them, resulting in substantial reductions in both fume formation rate and Cr(VI) in the fume. In the case of GMAW, surface cleaning of some stainless steel wires leads to slightly lower concentrations of Cr(VI) in the fume, probably due to the removal of traces of sodium and potassium compounds derived from wire-forming lubricants. Dennis *et al.* (1997) examined the effect of parameter changes in GMAW on UV light emissions, ozone and Cr(VI) formation. Ozone emission was much lower above 20 V compared with emissions between 15 and 20 V. Shield gas composition had a substantial effect on ozone and Cr(VI). Ozone emissions increased with shield gas flow rate for the shield gas studied. The formation of Cr(VI) in welding fume was linked

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to ozone generated by the arc. Madden (1987) exposed welding fume to concentrations of oxygen of up to 100% and to two different concentrations of ozone. None of the oxygen concentrations appeared to increase the Cr(VI)/total Cr ratio, but the ozone concentrations of 10 and 30 p.p.m. increased the ratio by 71 and 86%, respectively. Ozone is a strong oxidizing agent that can convert lower oxidation states of chromium to the Cr(VI) form. Measures to control ozone may also control Cr(VI).

The use of a second shield gas concentric with the first, in a modified 'double shroud' welding torch, in an attempt to control ozone and Cr(VI) is described in this paper. The description of the double shroud system and the results of its use with gas mixtures originally formed part of a paper by Mortazavi (1997).

The use of two concentric gas shields is not new. Glowicki and Sönnichsen (1974) described a GMAW process using an inner inert gas shield and an outer carbon dioxide shield in order to control spatter and improve the weld. Norrish (1992) described the 'dual shielding' gas tungsten arc welding technique (reported by Schultz, 1980) in which the inner shield is used to control arc characteristics and the outer shield to protect the weld pool. Whilst not being a concentric gas shield device, AGA AB Innovation of Sweden have produced a welding torch (described by Smårs, 1980) in which nozzles located some distance from the arc release MISON gas. MISON is an AGA product containing argon with 0.03% nitric oxide (NO). The idea is for the NO to react with ozone produced some distance from the arc and neutralize it before it can enter the welder's breathing zone. The welding arc produces strong UV radiation. The spectral distribution and intensity depends on the welding electrode composition, welding conditions, such as voltage and current, and shield gas. UV light of wavelength <240 nm can, theoretically, produce ozone from oxygen. For UV wavelengths <175 nm, most of the energy will be absorbed within a few millimetres due to strong absorption by oxygen between 125 and 175 nm, and strong absorption by argon (assuming argon based shield gas) below ~80 nm. Ozone formed close to the arc will be destroyed in part by thermal decomposition, in part by catalytic decomposition due to fume components and in part by reaction with NO, which is also formed in the arc. Wavelengths between 175 and 240 nm can travel further before being absorbed and so can create ozone some distance from the arc, where it is subject to greatly reduced decomposition by thermal or catalytic mechanisms. MISON was used as one of the secondary shield gases in the experiments reported in this paper. Ozone concentration at a fixed position relative to the arc and Cr(VI) mass% in the fume were measured.

Table 1. Bostrand 309L wire composition (mass%) and welding conditions

Wire composition	Fe (64 max)	Cr (23–25)	Ni (12–14)	Mn (1.0–2.5)
Wire size	1.2 mm			
Polarity	DC positive electrode			
Voltage	19.0 V			
Current	125–135 A			
Wire feed rate	2.016 kg/h			
Stand-off	20 mm			
Shield gases	See Tables 2–4			

MATERIALS AND METHODS

Welding system and wire

Welding took place on a variable speed rotating workpiece, above which a welding torch (BOC MG5/MXA503) was fixed so that a uniform weld could be achieved. The workpiece composition was mild steel. The height of the torch above the workpiece could be adjusted using a rotating ball screw, on a threaded shaft, to which the torch holder was attached. The welding set was a constant voltage direct current power source (BOC SMR500) with wire feed unit (BOC TF2.0S). Wire feed rate was evaluated by collecting and weighing the wire fed in a set time. The welding torch and workpiece were covered by a large conical fume box of similar construction to that recommended by the American Welding Society (AWS, 1979). For fume analysis, an extraction fan drew fumes to the top of the chamber, where they were collected on Whatman GF/A glass fibre filters. Fume was collected for analysis by carefully scraping it off the filter into a glass vial. For ozone determination the filter was removed and an electrostatic precipitator placed between the welding chamber and the extraction fan. This allowed a constant flow rate to be established in the chamber. A solid stainless steel wire (Bostrand 309L; Murex, Waltham Cross, UK) was used for welding, and its composition along with the welding conditions are given in Table 1.

Double shroud welding torch

A conventional welding torch consists of a central tube, through which the welding wire is fed surrounded by a nozzle that supplies a stream of shield gas concentric with the arc. A second nozzle, or 'shroud', was constructed consisting of an outer cylindrical sleeve (diameter 48 mm, length 75 mm) with one end closed apart from a 24 mm diameter central hole through which the torch head slotted and two 4 mm diameter holes into which the secondary gas inlet tubes screwed. Two concentric cylinders formed an annular gas flow chamber, which was

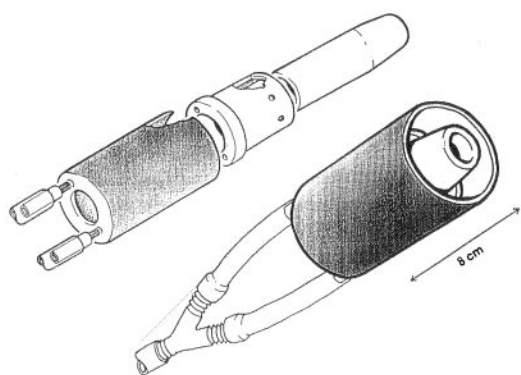


Fig. 1. Double shroud torch.

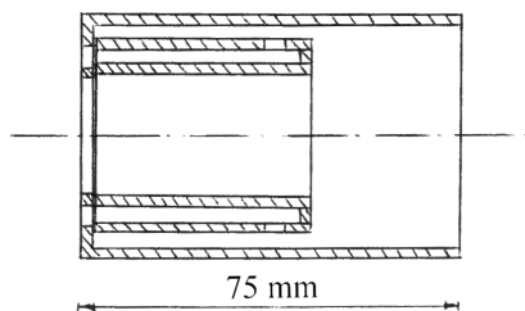


Fig. 2. Cross-section sketch of second shroud.

inserted inside the second nozzle. The chamber had two gas inlet holes corresponding to the 4 mm holes in the second nozzle. Gas flowed out of the chamber through six equally spaced holes on the outer surface. The original torch nozzle was inserted down the centre of the chamber and screwed onto the torch head, thus holding the two nozzles together. Figure 1 shows a picture of the double shroud torch and Fig. 2 shows a cross-sectional sketch through the second nozzle and gas flow chamber. The effective flow areas for the two shrouds, estimated gas flow rates and resulting gas velocities are given in Table 2.

Shield gases

The primary shield gas was Argoshield 5 (BOC Gases, UK) and the secondary shield gas was argon, MISON or argon with 0.03% ethene (C_2H_4). Comparison was made when using these gases in a single shroud system and also results are given for two argon/helium mixtures (H101 and H1) when used with a single shroud. The gases recommended for welding solid stainless steel wires are either low in CO_2 (e.g. H101 and H1) or contain no CO_2 (e.g. Ar + 2% O_2). The NO in the MISON and the C_2H_4 are both reducing agents, and they were used to react with ozone near the arc. The method for analysing ozone described below uses a chemiluminescent analyser that utilizes the reaction between ozone and C_2H_4 . Table 3 gives the shield gas compositions. Gas flow rates were measured using a variable area glass flow tube and float (PLATON, UK), with corrections for differences in gas densities to give the same volumetric flow rate for each gas. It was originally assumed that the pressure in the flow tube was close to atmospheric. Later it was found that there was a large pressure drop across the system downstream of the flow tube. Pressures at the flow tube were measured to allow estimation of the volumetric flow rate at the welding torch. For the single shield gas experiments there were large differences in volumetric flow rate at the torch between the helium-containing shield gases and other gases. MISON and Ar + C_2H_4 were assumed to be the same as argon for the flow rate estimation.

Cr(VI) analysis

Cr(VI) analysis involved the preliminary step of extraction using 2% NaOH/3% Na_2CO_3 solution. Accurately weighed samples of ~25 mg were placed in 150 ml conical flasks to which 40 ml of 2% NaOH/3% Na_2CO_3 solution was added together with 10 ml of deionized water. The solution was simmered for 20 min in covered flasks. Filtration, cooling and making up to 50 or 100 ml in volumetric flasks followed, and the Cr(VI) was determined on an atomic absorption spectrometer (Perkin Elmer 1100).

Table 2. Double shroud flow areas, gas flow rates and gas velocities (the flow rate for MISON and Ar + C_2H_4 is taken to be same as for Ar)

	Flow area (m^2)	Flow rate (m^3/s)	Flow rate (LPM)	Velocity (m/s)
Inner (primary) shroud				
Argon	2.01×10^{-4}	7.67×10^{-4}	46	3.81
Argoshield 5	2.01×10^{-4}	7.83×10^{-4}	47	3.90
Argoshield 20	2.01×10^{-4}	8.00×10^{-4}	48	3.98
Helishield H1	2.01×10^{-4}	3.33×10^{-4}	20	1.66
Helishield H101	2.01×10^{-4}	5.50×10^{-4}	33	2.74
Outer (secondary) shroud				
Argon	1.35×10^{-3}	5.33×10^{-4}	32	0.395

Measurements of ozone concentrations

Ozone concentrations were measured at a fixed sampling position relative to the welding arc at an angle of 60° from the horizontal and at a horizontal distance from the weld pool of 75 mm. The sampling probe was attached to the welding gun and connected via a 2 m poly(tetrafluoroethane) (PTFE) tube to a pre-calibrated chemiluminescent ozone analyser (Analytical Instrument Development Inc. model 650). The analyser was capable of measuring ozone concentrations in the range 0.001–100 p.p.m. Two 37 mm diameter, 0.2 µm PTFE filters were inserted in the connecting tube to prevent welding fume from entering the analyser. The first filter (nearest the sampling tip) was renewed after every test and the second filter was renewed after nine tests. Before undertaking any measurements on welding emissions, the sampling probe, PTFE tubing and filters were conditioned to prevent subsequent adsorption of ozone. Conditioning was by passage of 10 p.p.m. ozone from a Penwalt ozone generator (Wallace and Tiernan) for 10 min. Ozone measurements were averaged over a 60 s period after first welding for 60 s to allow for establishment of the welding regime. All experiments were performed in triplicate.

RESULTS

The shield gas combinations and resulting ozone and Cr(VI) concentrations are given in Table 4.

Considering first the comparison using the single shroud with Argoshield 5 and the double shroud with only a primary shield of Argoshield 5, the results are similar both for ozone and Cr(VI), as expected. Using the single shroud with argon and the double shroud

with a secondary shield of argon resulted in slightly lower ozone and slightly higher Cr(VI) concentrations with the double shroud.

MISON gas in the single shroud resulted in a 60% reduction in ozone concentration compared with Argoshield 5 and ~30–40% reduction when compared with H1 and H101. MISON also resulted in nearly 70% reduction in Cr(VI) concentration compared with Argoshield 5 and ~60–65% reduction compared with the H1 and H101, again using the single shroud. Using MISON as a second shield in the double shroud resulted in reduction in ozone concentration compared with Argoshield 5 alone of >90%, but the Cr(VI) concentration reduction was only 40%.

Ar + C₂H₄ in the single shroud gave ~30% reduction in both ozone and Cr(VI) concentrations compared with Argoshield 5, but gave slightly higher ozone and slightly lower Cr(VI) concentrations when compared with the H1 and H101. For the double shroud there is an ozone concentration reduction of >85% relative to Argoshield 5 alone. The Cr(VI) concentration remains about the same for Ar + C₂H₄ when it is used in the single or double shroud system.

DISCUSSION

Overall, the results show that ozone concentration reduction using MISON is much more effective when used as a secondary shield in the double shroud torch than when used as the gas in a single shroud torch. The same applies to the use of the Ar + C₂H₄ gas, although when used in the single shroud it gives no advantage over using the conventional H1 or H101 shield gases.

MISON is more effective at reducing Cr(VI) concentration in fume compared with Ar + C₂H₄ when they are used in the single shroud torch, but both gases are very similar in effect when used as the secondary shield in the double shroud torch. The measure for Cr(VI) used is mass% in the fume. For comparing exposure risk, it is really necessary to evaluate the Cr(VI) formation rate (mass per unit time) or the Cr(VI) generation coefficient based on weld bead mass [mass Cr(VI) formed per unit mass weld bead laid down]. Further work is therefore

Table 3. Shield gases and compositions (vol.%)

Gas	Ar	O ₂	CO ₂	He	NO	C ₂ H ₂
Argon	100.00					
Argoshield 5	93.00	2.00	5.00			
MISON	99.97				0.03	
Ar + C ₂ H ₄	99.97					0.03
Helishield 1	13.50		1.50	85.00		
Helishield 101	60.00		2.00	38.00		

Table 4. Single and double shroud: ozone and Cr(VI) results

Conventional torch (single shroud)			Modified torch (double shroud)			
Shield gas	O ₃ (p.p.m.)	Cr(VI) (%)	Primary shield gas	Secondary shield gas	O ₃ (p.p.m.)	Cr(VI) (%)
Ar	1.32	0.61	Argoshield 5	Ar	1.10	0.64
Argoshield 5	0.95	0.57	Argoshield 5	None	0.83	0.58
MISON	0.39	0.18	Argoshield 5	MISON	0.05	0.35
Ar + C ₂ H ₄	0.69	0.38	Argoshield 5	Ar+C ₂ H ₄	0.11	0.37
H1	0.57	0.45				
H101	0.68	0.51				

necessary for valid comparison of Cr(VI) using the gases described. The results so far indicate that, for Cr(VI) reduction, addition of 0.03% NO or 0.03% C₂H₄ to existing shield gas mixtures and use in a single shroud would be advantageous.

Examining the results for ozone and Cr(VI) concentrations using the argon-containing gases and assuming a linear relationship between ozone and Cr(VI) concentrations gives values for the Pearson product moment correlation coefficient squared (r^2) of 0.902 for the single shroud data set and 0.998 for the double shroud data set. The values for r^2 indicate a link between ozone and Cr(VI) concentrations, but the much greater reduction in ozone concentration in the double shroud system using MISON or Ar + C₂H₄ gases is not reflected in lower Cr(VI) concentrations. It is not easy to draw conclusions about a link from these results. The region where Cr(VI) is formed is not necessarily the same as the region where ozone concentration is measured, and Cr(VI) concentration is not a measure of amount of Cr(VI) formed. Further work would be necessary to establish in what region Cr(VI) is formed and then to measure ozone concentrations in that region.

For ozone concentration reduction there is an obvious advantage in using a double shroud system with either MISON or the Ar + C₂H₄ mixture. There are, however, other considerations to take into account in assessing overall exposure risk when using either NO or C₂H₄ additions in single or double shroud systems. In the case of NO, it is a toxic gas, with an OES of 30 mg/m³, and the product of its reaction with ozone is NO₂, which has an OES of 5 mg/m³. It is important not to supply NO to the arc in excessive amounts. The reaction products of C₂H₄ oxidization are H₂O and CO₂, although there may be some CO formation. The use of gases with NO or C₂H₄ additions may change the concentrations of other components in the fume, such as nickel compounds. A complete analysis of fume produced with and without the use of the additions would allow better evaluation of exposure risk change as a result of using the additions. As well as considering exposure risks, it is also necessary to consider possible changes to weldability and weld quality, and also to consider the cost implications of using a double shroud system.

Although the experiments carried out here used GMAW with a stainless steel wire, ozone and Cr(VI) are not generally considered the main exposure risk in GMAW with solid stainless steel wires. Ozone is found to be a major exposure risk in aluminium welding using metal inert gas (MIG) and tungsten inert gas (TIG) processes. Ozone could also be a problem in TIG welding of other metals and also possibly in some MIG welding of mild steel. In the application of high-current MIG welding to thick plates, the Osaka Transformer Co.

Ltd, Japan, has used a double shroud system. Their objective was to weld aluminium very fast, using currents of up to 900 A on wires of up to 4.8 mm diameter. Normally, this would give rise to surface puckering of the weld as a result of oxidation from air drawn into the arc by convection. The double shroud produced a more stable gas shield and so gave a good weld finish, allowing joints up to 75 mm thick to be welded in two passes. This would seem an ideal application for an ozone-reducing gas.

In TIG welding the tungsten electrode can be deteriorated by the presence of oxygen in the shield gas, particularly at levels >0.05%. Argon or helium is generally used as the shield gas, and so the ozone must form outside the shield gas zone. Use of an ozone-reducing gas as the secondary shield in a double shroud system may be a way of effectively controlling ozone without the components of the secondary shield contaminating the electrode, altering the arc characteristics or adversely affecting the weld.

Development of a double shroud system would need to include refinement of the double shroud design to provide effective action whilst at the same time keeping the secondary shield gas flow rate low.

As was explained in Materials and methods, the estimated shield gas volumetric flow rates were not always constant between gases. For the single shield gas experiments there were large differences in volumetric flow rate at the torch between the helium-containing shield gases and other gases. This may have partially contributed to some of the observed differences in ozone and Cr(VI) concentrations between shield gases.

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