Control of Cr$^{6+}$ Emissions from Gas Metal Arc Welding Using a Silica Precursor as a Shielding Gas Additive

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Hexavalent chromium (Cr$^{6+}$) emitted from welding poses serious health risks to workers exposed to welding fumes. In this study, tetramethylsilane (TMS) was added to shielding gas to control hazardous air pollutants produced during stainless steel welding. The silica precursor acted as an oxidation inhibitor when it decomposed in the high-temperature welding arc, limiting Cr$^{6+}$ formation. Additionally, a film of amorphous SiO$_2$ was deposited on fume particles to insulate them from oxidation. Experiments were conducted following the American Welding Society (AWS) method for fume generation and sampling in an AWS fume hood. The results showed that total shielding gas flow rate impacted the effectiveness of the TMS process. Increasing shielding gas flow rate led to increased reductions in Cr$^{6+}$ concentration when TMS was used. When 4.2% of a 30-lpm shielding gas flow was used as TMS carrier gas, Cr$^{6+}$ concentration in gas metal arc welding (GMAW) fumes was reduced to below the 2006 Occupational Safety and Health Administration standard (5 µg m$^{-3}$) and the efficiency was $>90\%$. The process also increased fume particle size from a mode size of 20 nm under baseline conditions to 180–300 nm when TMS was added in all shielding gas flow rates tested. SiO$_2$ particles formed in the process scavenged nanosized fume particles through intercoagulation. Transmission electron microscopy imagery provided visual evidence of an amorphous film of SiO$_2$ on some fume particles along with the presence of amorphous SiO$_2$ agglomerates. These results demonstrate the ability of vapor phase silica precursors to increase welding fume particle size and minimize chromium oxidation, thereby preventing the formation of hexavalent chromium.

Keywords: aerosol size distribution; hexavalent chromium; shielding gas; vapor phase sorbent; welding fume

INTRODUCTION

Gas metal arc welding (GMAW) is a commonly used process that uses mild or stainless steel wire as filler material to join pieces of metal. Shielding gas is used to protect the superheated weld site from gaseous species that degrade the weld’s mechanical properties.
and destabilize the welding arc. The operator controls welding parameters such as voltage, shielding gas composition, shielding gas flow rate, and wire feed speed to obtain desired weld characteristics. The operating parameters impact fume formation as well as weld characteristics, the complexity of which creates a challenge for the industry to balance maximum product quality with minimum emissions.

The intense energy of the welding process results in the formation of fumes containing a high number concentration of particles containing toxic metals as well as gaseous species including ozone and nitrogen oxides (Hewett, 1995b; Jenkins et al., 2005; Liu et al., 2007). Fume aerosols generated during arc welding are typically <1 μm in diameter and the primary particles are often in the nanometer range (Zimmer et al., 2002; Biswas and Wu, 2005; Jenkins et al., 2005). The fume characteristics are influenced by a variety of parameters, including shielding gas composition, welding wire composition, voltage, and metal transfer mode (Zimmer et al., 2002; Hovde and Raynor, 2007).

Stainless steel welding fumes contain manganese and iron as well as chromium and nickel (Castner and Null, 1998; Heung et al., 2007). About 1–5% of the chromium found in GMAW fumes is in the hazardous hexavalent state (Heung et al., 2007; Serageldin and Reeves, 2009). These metals are layered in a core-shell structure that typically has a core made up primarily of iron with other metals making up the outer layers along with surface enrichment by lighter elements such as silicon, chlorine, and fluorine (Konarski et al., 2003; Maynard et al., 2004).

Welding uses a shielding gas to maintain arc stability, produce desirable weld penetration, and reduce fume formation rate (Dennis et al., 1997; Ebrahiminia et al., 2009). The shielding gas chosen has an impact on ultraviolet (UV) light, ozone generated, particle size distribution of aerosols, and the amount of Cr$^{6+}$ (Dennis et al., 1997; Zimmer et al., 2002). The use of shielding gas in GMAW decreases overall fume formation rate; however, the formation rates of UV light, ozone, and Cr$^{6+}$ all increased with shielding gas flow rate (Dennis et al., 1997). Hexavalent chromium and ozone in welding fumes lead to many adverse health effects following occupational exposure (Antonini, 2003; Lillienberg et al., 2008). Cr$^{6+}$ is a known human carcinogen, with extensive human and animal data available (IARC, 1990). Studies of welding emissions in California found that welding is the primary source of airborne Cr$^{6+}$ in the state (Chang et al., 2004). Nickel is also a known human carcinogen (IARC, 1990), while manganese exposure can cause a number of adverse neurological effects, including a Parkinson’s-like disorder known as manganese (Antonini et al., 2006; Bowler et al., 2006).

The aerodynamic diameter and shape of welding aerosols impact where welding fume particles deposit in the respiratory system and how rapidly the particles are cleared once deposited in the lungs. Few welding fume particles deposit in the upper respiratory system where clearance occurs rapidly. Welding fume particles deposit more readily in the lower regions of the respiratory system where clearance from the lungs is less effective (Hewett, 1995a; Yu et al., 2000; Kleinsteuuer et al., 2008). Toxicity of nanoparticles is unique because the solid particles can be translocated across pathways other than the respiratory system that are typically not considered for larger particles (Biswas and Wu, 2005). For example, manganese nanoparticles can be translocated through the olfactory nerve directly to the brain where manganese expresses neurotoxic effects (Elder et al., 2006). The soluble fraction of welding fumes is responsible for toxicity due to oxidative stress and free radical production (Taylor et al., 2003; McNeilly et al., 2004). Welding particles differ from other metal aerosols in that the insoluble and soluble fractions of the fumes are both significant contributors to toxicity (Antonini et al., 2004).

Occupational Safety and Health Administration (OSHA) recently lowered the permissible exposure limit for Cr$^{6+}$ in occupational air from 52 to 5 μg·m$^{-3}$ (OSHA, 2006). The 2006 regulation included a 4-year extension until May 2010 for industry to install engineering controls to reduce exposures. This change placed pressure on industry to develop new control technologies to limit emissions of Cr$^{6+}$ from arc welding. The simplest method of controlling welding fume exposure is removing the fumes from the breathing zone of the welder although preventing exposure to Cr$^{6+}$ is preferred to evacuating the fumes using exhaust ventilation. High-velocity/low-volume local exhaust systems can reduce exposure to metals in welding fumes by about half if the hose for the pump is placed 5.1–7.6 cm (2–3 inches) from the welding torch (Meeker et al., 2007). The use of reducing agents as shielding gas additives can reduce ozone formation in the welding fume (Dennis et al., 2002). Similarly, the addition of reactive metals, such as zinc and aluminum, to welding wires can reduce Cr$^{6+}$ formation (Dennis et al., 1996). However, these technologies have not controlled formation of Cr$^{6+}$ effectively enough to gain acceptance in industry. Hence, it is necessary to develop a control technology that will limit exposure to these pollutants while maintaining the integrity of the welded metal.
Sorbent injection into combustion systems has been examined as a means for removing trace metals. Sorbents are capable of scavenging a variety of metals in vapor phase in combustion systems to prevent nucleation of metallic aerosols (Biswa and Wu, 1998). Injection of bulk solid phase sorbents is not feasible for welding systems. Fortunately, vapor phase sorbent precursors have recently emerged as an alternative to solid phase materials. Previous research has shown that vapor phase silica precursor (e.g. tetraethylxosilane) is capable of lowering Cr\textsuperscript{6+} emissions from gas tungsten arc welding (Topham et al., 2010). Amorphous silica, formed from pyrolysis and subsequent oxidation of precursor chemicals, has been proven effective as a sorbent for lead produced during combustion. It is capable of forming an amorphous web that effectively captures ultrafine metal aerosols and increases their particle size (Owens and Biswas, 1996a,b; Biswas and Zacharias, 1997; Lee et al., 2005). Amorphous silica may cause respiratory inflammation, emphysema, and other respiratory problems. However, epidemiological evidence does not suggest that amorphous silica persists in the respiratory system and causes cancer and fibrosis in the way that crystalline silica does (Reuzel et al., 1991; Merget et al., 2002). In this study, tetramethlysilane (TMS) was used as a shielding gas additive during GMAW to prevent formation of Cr\textsuperscript{6+}. The total shielding gas flow rate and the flow rate of TMS carrier gas were varied to investigate their effects on the efficacy of Cr\textsuperscript{6+} control and to determine the optimal feed conditions. Aerosol size distribution was monitored to assess the impact of TMS additive on resultant particle size, which has implications for subsequent respiratory deposition.

**EXPERIMENTAL METHODS**

The welding fume generation and sampling system (Fig. 1) followed a modified American Welding Society fume hood design (AWS, 1999). A conical chamber 91.4 cm (36 inches) in diameter at the base, 20.3 cm (8 inches) in diameter at the pump, and 91.4 cm (36 inches) in height was constructed. A Lincoln Power Mig 140C welder was used for producing welding fumes using ER 308L (0.09 cm diameter, 18 g·min\textsuperscript{-1} wire feed rate) stainless steel welding wire, which has an average chromium content of 19.5–22.0%. This wire also contains 9.0–11.0% Ni, 1.0–2.5% Mn, and 0.35–0.65% Si, according to its material safety data sheet. The sampling time, pump flow rate, and welding wire feed rate were kept constant throughout the experiment. This allows for conversion of the results, presented in micrograms Cr\textsuperscript{6+} per cubic meter, to micrograms Cr\textsuperscript{6+} per mass of welding wire consumed by multiplying the values presented by 0.07 (this value is derived by dividing the pump flow rate by the welding wire feed rate). Mild steel base metal was used for sampling in order to avoid interference from chromium emitted by the base sheet metal. The welder was operated in short-circuit mode with a contact tube working distance of ~1.9 cm (0.75 inches). The welding torch was modified to allow injection of TMS (CAS # 75-76-3) by inserting a Y-fitting to connect the torch and the gas hose. The wire guide was lengthened to ensure it was long enough to reach the contact tip. The trigger was removed and the wires inside the trigger were extended outside the chamber to allow remote operation of the welding gun. The welding gun used was a Lincoln Magnum 100L and the gas nozzle had an inner diameter of 0.95 cm (3/8 inches). The hose from the shielding gas cylinder was connected to a T-fitting to allow the gas flow to be split into two parts. The main shielding gas flow was passed through the welder as in normal operation while the remainder of the gas was used as the TMS carrier gas.

The recommended minimum shielding gas flow rate designated for this model of welder is 15 lpm (liters per minute). An initial shielding gas flow rate of 20 lpm was chosen to produce quality welds after preliminary testing demonstrated that this flow rate produced welds with good bead appearance and free of porosity upon visual inspection. The silica precursor feed rate was controlled by varying the flow rate of carrier gas that was passed over the liquid TMS reservoir, maintained at 0°C, with a mass flow controller. The carrier gas saturated with TMS vapor was then rejoined to the main shielding gas flow prior to reaching the welding torch. The base metal was placed on a rotating turntable (MK Products Aircrafter T-25) placed in the hood to maintain a constant weld speed. A 90-mm-diameter glass fiber filter (Millipore APFA 090) was placed at the top of the hood and connected to a high-volume [Hi-Vol; 1.27 m\textsuperscript{3}·min\textsuperscript{-1} (45 ft\textsuperscript{3}·min\textsuperscript{-1})] pump for collecting the aerosols. The sampling time was 85 s throughout the experiments. A mixture of 75% Ar and 25% CO\textsubscript{2} was used as the shielding gas, which acted as the needed carrier gas for TMS without requiring a secondary carrier gas. TMS is highly volatile with a vapor pressure at room temperature of 598 mmHg (Aston et al., 1941). The TMS reservoir was placed in an ice bath to lower the vapor pressure (~270 mmHg at 0°C).
Baseline samples using 75% Ar and 25% CO₂ as a shielding gas (i.e. no flow going through the TMS reservoir) were run to determine emissions of Cr₆⁺ during normal welding operation using short-circuit metal transfer. This scenario represents the standard welding method currently used in industrial environments. Experimental set A was performed using three TMS carrier gas flow rates (2.1, 4.2, and 6.3% of total shielding gas flow rate) at 20 lpm of total shield gas flow rate to determine the effect of TMS carrier gas flow rate on Cr₆⁺ formation. In experimental set B, total shielding gas flow rate was increased to 25 lpm, and 5.0% of the shielding gas was used as TMS carrier gas. Experimental set C used a total shielding gas flow rate of 30 lpm and TMS carrier gas flow rates of 1.4, 2.8, 3.5, and 4.2%. Experimental sets B and C were performed to test the effect of shielding gas flow rate on the efficacy of this technology.

Ion chromatography (IC; Dionex ICS 1500, CS5A analytical column, DS6 conductivity detector) was used to measure the soluble hexavalent chromium species, chromate (CrO₄²⁻). Sample extraction for IC followed a modified National Institute for Occupational Safety and Health (NIOSH) Method 7604 (NIOSH, 1994). The analytical column differs from the anionic column recommended in the NIOSH method. The manufacturer of the ion chromatograph recommends the cationic CS5A analytical column that is also capable of separating certain anionic species, such as chromate. The eluent chosen for the current study was sodium bicarbonate (5 mM) and sodium carbonate (1 mM) rather than the sodium bicarbonate and sodium hydroxide eluent used in the NIOSH method, as per manufacturer’s specifications for the analytical column used in this study. Soluble Cr₆⁺ species were extracted using the eluent and heated in a water bath to 100°C for 1 h. Additionally, transmission electron microscopy (TEM; Model 2010F; JEOL) was used to observe SiO₂ coating formed on fume particles and particle morphology. Specialty grids designed for TEM (Pelco, Lacey Carbon Type-A, 300 mesh) were directly loaded with fume particles for imaging. A scanning mobility particle sizer (SMPS; TSI Model 3081 Long DMA) was used to obtain aerosol size distribution data. For aerosol size distribution measurement, welding was performed for 10 s and stopped at which point the SMPS pump was turned on. After the SMPS completed its 135-s sampling run, the Hi-Vol pump was turned on to clear the chamber of particles. One-way analysis of variance (ANOVA) was conducted to verify difference among groups.

**RESULTS AND DISCUSSION**

20 lpm shielding gas flow rate

The impact of TMS addition on Cr⁶⁺ generation during GMAW using a total shielding gas flow rate of 20 lpm is shown in Fig. 2a (filled circles indicate data points). There was no statistically significant difference between the amount of Cr⁶⁺ mass concentration in the fumes regardless of the amount of TMS added ($P = 0.229$, ANOVA single factor, $\alpha = 0.05$). A large amount of white powder was observed on the
head of the welding torch after sampling (Fig. 3). It likely resulted from premature thermal decomposition of TMS inside the head of the welding torch. When this happened, TMS did not function as an effective oxidation inhibitor or coat fume particles in a SiO₂ film because the TMS had already reacted before reaching the area where fume particle formation was occurring.

The addition of TMS led to an increase in fume particle size as shown in Fig. 4a. During baseline welding, a large number of particles with a mode size of ~18 nm were observed by SMPS measurements. As increasing amounts of TMS were added, this peak decreased and eventually vanished when 6.3% TMS was added. The particle size distribution shifted toward larger particles with the nanoparticles being replaced with particles >100 nm in diameter.

25 lpm shielding gas flow rate

There was an increase in baseline Cr⁶⁺ mass concentration when the shielding gas flow rate was increased from 20 to 25 lpm (Fig. 2b; filled squares indicate data points). When 5.0% of the shielding gas flow rate was used as TMS carrier gas, there was a significant decrease in Cr⁶⁺ concentration of ~40% with a P value far below 0.05 (Student’s T-test, two tails, unequal variance). The reduction in Cr⁶⁺ indicated that some of the TMS was surviving until reaching the area where reactive oxygen species were present. After sampling, there was still some white powder observed inside the head of the welding torch, although not as much as in the 20-lpm case.

The SMPS particle size data for 25 lpm shielding gas flow rate followed the same pattern as that for 20 lpm, as displayed in Fig. 4b. When welding without TMS, a large peak was seen at ~20 nm. As TMS feed rate was increased, the peak in the nanometer size range shrank relative to the peak >100 nm.

30 lpm shielding gas flow rate

The results indicate adding TMS to shielding gas of 30 lpm reduced formation of Cr⁶⁺, as seen in Fig. 2c (filled triangles indicate data points). When 4.2% of the shielding gas was used as TMS carrier gas, the Cr⁶⁺ concentration was successfully reduced to below the IC detection limit for all replicate samples. For display purpose, the concentration for all non-detectable samples was set equal to the detection limit. This was a reduction in Cr⁶⁺ concentration of at least 93% compared to baseline conditions. There was not as
much white powder inside the head of welding torch as observed in the 20-lpm case. The reduction in Cr6+ concentration achieved when using TMS as a shielding gas additive exceeded the results seen in previous studies that incorporated reducing agents into shielding gas or welding wire (Dennis et al., 1996, 2002; Topham et al., 2010). The differences in Cr6+ mass among TMS feed rates were statistically significant ($P = 6.8 \times 10^{-11}$, ANOVA single factor, $\alpha = 0.05$).

As increasing amounts of TMS were fed into the system, the metal nanoparticles were scavenged by SiO2 agglomerates and the particle size distribution shifted toward larger particle sizes (Fig. 4c). The count mode diameter increased from 18 nm in the nanometer

Fig. 4. GMAW fume particle size distributions at (a) 20, (b) 25, and (c) 30 lpm shielding gas flow rate. Note: total particle number concentration decreased as shielding gas flow rate increased.

Fig. 5. TEM images of welding fume particles collected at 4.2% of TMS carrier gas flow rate with 30 lpm of total shielding gas flow rate: (a) GMAW fume agglomerate without SiO2 coating (scale = 20 nm); (b) GMAW fume agglomerate with SiO2 coating indicated by arrows (scale = 20 nm); (c) amorphous SiO2 agglomerate (scale = 20 nm); (d) metal-SiO2 agglomerate formed by intercoagulation (scale = 50 nm).
range to 270 nm as TMS feed rate was increased to 4.2%. The increase in particle size observed when TMS was added agreed with previous studies that utilized silica precursors to control lead emissions from combustion systems. In those studies, adding silica precursors increased particle size out of the nanometer range (Owens and Biswas, 1996a,b).

TEM images were obtained to determine whether a SiO2 coating was present on fume particles when 4.2% TMS was used as an additive. For baseline samples without TMS feed (Fig. 5a), the images show metal nanoparticles without SiO2 coating. Careful examination of Fig. 5a reveals that some surface enrichment with lighter elements did occur, which mirrors results of previous studies of welding fume particle structure exhibiting surface enrichment with silicon, chlorine, and fluorine (Maynard et al., 2004). With TMS feed, Fig. 5b shows an agglomerate particle that had a coating of SiO2 encapsulating the entire agglomerate rather than surface enrichment of individual primary particles. The coating in Fig. 5b was more significant than the surface enrichment seen on individual primary particles under baseline conditions in previous research (Konarski et al., 2003; Maynard et al., 2004). Meanwhile, not all silica formed in the process ended up as the coating; Fig. 5c displays an agglomerate particle made up of amorphous SiO2. There are also agglomerates of metal fume particles with amorphous SiO2 particles, as shown in Fig. 5d. This result is consistent with previous research demonstrating that intercoagulation can scavenge nanoparticles (Lee and Wu, 2005). This is also echoed by the shift in mode size shown in Fig. 4. Twenty-nanometer particles have high deposition efficiency in the alveolar area (~50%), while 300-nm particles have the minimum deposition efficiency in the respiratory system (<15% for total deposition and <8% for alveolar deposition) (ICRP, 1994). Size increase out of the nanometer range to reduce respiration deposition, as shown, may be another potential benefit of the TMS process though full characterization of the impact of particle size shift on health effects is needed to validate the benefits.

The TEM images obtained show that coating by SiO2 was not uniform for all fume particles. Some particles were not coated, some agglomerate particles were covered in a thin layer of SiO2, and some separate amorphous agglomerates composed mostly of SiO2 were also present. Figure 5b indicates that silica precursor additives can possibly encapsulate all types of metals in welding fume particles through the formation of a SiO2 film on metal particles. This phenomenon is similar to that observed in previous research where metal nanoparticles formed in combustion systems can be trapped in a web of amorphous SiO2 (McMillin et al., 1996; Owens and Biswas, 1996a; Biswas et al., 1997). Metal nanoparticles that are coated in SiO2 may take longer to exhibit toxic effects because the SiO2 coating could take weeks to dissolve in the respiratory system (Roelofs and Vogelsberger, 2004). This would provide the respiratory system’s removal mechanisms more time to remove the particles before exposure to the toxic metals occurs. Indeed, Yu et al. (2010) showed significant reduction in biotoxicity of welding fume particles tested with Escherichia coli when TMS was added to the shielding gas, and amorphous silica produced in such a process was demonstrated to possess no biotoxicity to the bacteria. Meanwhile, the results also indicate that process optimization is needed to further lower the toxicity by more complete coverage, which will also lead to reduced consumption of TMS. Comparing the baseline results (i.e. no TMS) of all shielding gas flow rates, it can be seen that Cr6+ concentration increased as shielding gas flow rate increased, which is in agreement with prior studies (Dennis et al., 1997). By avoiding premature decomposition, high shielding gas flow rate yielded better Cr6+ reduction when TMS process was adopted. Hence, measures to ensure proper timing of TMS decomposition will allow more effective amorphous silica coverage with more efficient utilization of TMS.

The shield gas flow rates used in this study were within the normal range of operation for the welding machine used. However, an optimized delivery system is necessary to transition this technology use in industrial settings. The modifications required to the shield gas system and laboratory equipment used in this study may present operational or safety concerns in an industrial setting. Some of the process parameters, such as the use of carbon steel plate, the shield gas mixture chosen, and the working distance chosen, may have introduced some error into the data. For example, stainless steel sheet metal would contribute some Cr6+ to the welding fumes. The error introduced from these variables could be eliminated through process optimization; however, any error would be relatively consistent across the samples in this study.

CONCLUSIONS

Silica precursors led to reduction in Cr6+ in GMAW fumes of >90% when 4.2% of the shielding gas was used to carry TMS at 30 lpm total shielding gas flow rate. The use of TMS as a shielding gas
additive greatly brought Cr\textsuperscript{6+} concentration down from a level that exceeded the OSHA permissible exposure limit to within regulatory limits. This result may help industry keep pace with tightening occupational limits for this hazardous air pollutant. The increase in particle size observed when TMS was added may be another benefit for using these chemicals. Further research to evaluate whether the increase in particle size achieved using TMS could help personal protective equipment protect workers from welding fume particles by reducing penetration through filters is desired. New technologies to scavenge nanoparticles from effluent gas streams will be required as nanomaterial manufacturing spreads. Silica precursors may provide a tool for dealing with this challenging problem. TEM imagery demonstrated that some particles were coated in a film of amorphous SiO\textsubscript{2}. All of the metals contained in the particles that were coated in SiO\textsubscript{2} were insulated regardless of speciation.

More research is needed to determine whether this technology alters the toxic effects of welding fume particles containing nickel and manganese through encapsulation in amorphous silica. Further research is also necessary to verify that using silica precursors as shielding gas additives has no adverse effects on the mechanical properties of the materials being welded.

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