Double Shroud Delivery of Silica Precursor for Reducing Hexavalent Chromium in Welding Fume

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The welding process yields a high concentration of nanoparticles loaded with hexavalent chromium (Cr^{6+}), a known human carcinogen. Previous studies have demonstrated that using tetramethylsilane (TMS) as a shielding gas additive can significantly reduce the Cr^{6+} concentration in welding fume particles. In this study, a novel insulated double shroud torch (IDST) was developed to further improve the reduction of airborne Cr^{6+} concentration by separating the flows of the primary shielding gas and the TMS carrier gas. Welding fumes were collected from a welding chamber in the laboratory and from a fixed location near the welding arc in a welding facility. The Cr^{6+} content was analyzed with ion chromatography and X-ray photoelectron spectroscopy (XPS). Results from the chamber sampling demonstrated that the addition of 3.2~5.1% of TMS carrier gas to the primary shielding gas resulted in more than a 90% reduction of airborne Cr^{6+} under all shielding gas flow rates. The XPS result confirmed complete elimination of Cr^{6+} inside the amorphous silica shell. Adding 100~1000 ppm of nitric oxide or carbon monoxide to the shielding gas could also reduce Cr^{6+} concentrations up to 57% and 35%, respectively; however, these reducing agents created potential hazards from the release of unreacted agents. Results of the field test showed that the addition of 1.6% of TMS carrier gas to the primary shielding gas reduced Cr^{6+} concentration to the limitation of detection (1.1 $\mu g/m^3$). In a worst-case scenario, if TMS vapor leaked into the environment without decomposition and ventilation, the estimated TMS concentration in the condition of field sampling would be a maximum 5.7 ppm, still well below its flammability limit (1%). Based on a previously developed cost model, the use of TMS increases the general cost by 3.8%. No visual deterioration of weld quality caused by TMS was found, although further mechanical testing is necessary.

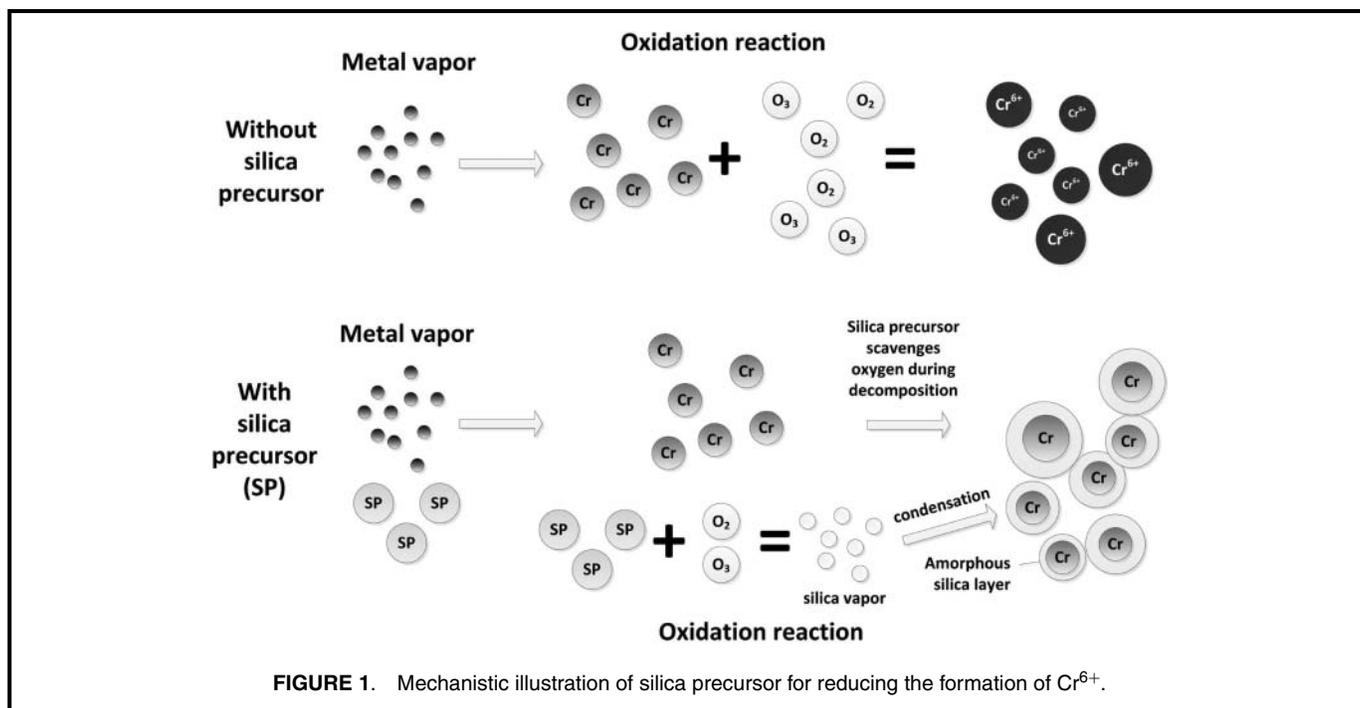**Keywords** hexavalent chromium, silica precursor, welding fume

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INTRODUCTION

S tainless steel welding, the joining of pieces of metal with stainless steel filler material, is a common industrial practice. The intense energy of the welding process yields fumes containing a high concentration of nanoparticles loaded with different metals.[1–5] The welding fumes pose potential adverse health risks to welders who may inhale toxic metals such as hexavalent chromium (Cr^{6+}), nickel (Ni), manganese (Mn), and other toxic components. The nanoparticles' small size allows the toxicants to travel deeply into the human respiratory tract where they can be easily absorbed and distributed.[6–8] Of all the metals present in welding fumes, hexavalent chromium (Cr^{6+}) draws the most concern due to its carcinogenic effect,[9] confirmed by extensive human and animal data.[10,11] By contrast, trivalent chromium (Cr^{3+}) is an essential nutrient for human metabolism activity.[12]

Chromium, because of its resistance to corrosion and discoloration,[13,14] is one of the major components of stainless steel. Cr^{6+} is formed as a result of Cr oxidation with reactive species such as oxygen and ozone in the welding arc zone.[15,16] Cr^{6+} exposure continues to be a troublesome issue in the industrial work environment.[17,18] The Occupational Safety and Health Administration (OSHA) lowered the 8-hr time-weighted average (8-hr TWA) permissible exposure limit (PEL) for Cr^{6+} from 52 $\mu g/m^3$ to 5 $\mu g/m^3$ in 2006.[19] The National Institute for Occupational Safety and Health (NIOSH) also proposed a 10-hr TWA recommended exposure limit (REL) of 1 $\mu g/m^3$.[20] Because of the residual risk of lung cancer even at REL,[21] NIOSH also recommended adoption of reasonable control technology to further reduce Cr^{6+}.

These tightened occupational standards pushed the development of Cr^{6+}-free welding technology to ensure welders' health and safety.[22] Metal inert gas (MIG) welding uses

FIGURE 1. Mechanistic illustration of silica precursor for reducing the formation of Cr^{6+}.

shielding gas to protect welds from surrounding atmospheric components such as nitrogen and water. The shielding gas also helps limit the oxidation of metals by preventing penetration of reactive oxygen species[16] and reducing fume generation rates.[23] However, there are numerous types of shielding gases,[24] and some combinations of these gases actually could increase ultraviolet (UV) intensity and ozone concentration.[16] Shielded metal arc welding (SMAW) uses vapor generated from flux coating to prevent oxidation and to ensure the purity of the weld.

Local exhaust ventilation (LEV) technology is commercially available to remove welding fumes from welders' breathing zones.[25,26] However, LEV is inconvenient in outdoor welding, where welders move frequently.[27,28] On-gun extraction was developed to collect welding fume near the welding arc, but the current type of extraction gun is bulky and heavy from an operational perspective and less effective in vertical and overhead welding.[28,29] There are also concerns that the suction force of LEV or on-gun extraction would disturb the flow of the shielding gas. The addition of reactive metals such as zinc (Zn) and aluminum (Al) to welding wires can reduce the formation of Cr^{6+}.[30] Reducing agents used as shielding gas additives, such as methane (C_2H_4) or nitrogen oxide (NO), can reduce ozone formation in the welding fumes and hence limit the formation of Cr^{6+}.

Dennis et al.[31] tested NO and C_2H_4 as shielding gas additives and found about 50~70% removal efficiencies. However, the flammability of methane and formation of toxic NO_2 are potential risks when using the two reducing agents. Carbon monoxide (CO) is also used in the metal industry as reducing gas,[32] yet is itself a hazardous air pollutant. Replacing the Cr content in the stainless steel wire with other materials with identical functions, such as ruthenium (Ru), can reduce the amount of Cr in welding fume,[33] but this option is limited by the lack of availability of these rare metals. In summary, there is currently no widely adopted technology conforming to the new standards to mitigate the formation of airborne Cr^{6+} emissions from welding.

Silica precursor technology is an effective measure for controlling metal nanoparticles emissions from pyroprocesses such as combustors and incinerators.[34–37] The use of shielding gas in the welding process provides a medium for the introduction of a vapor phase silica precursor. Silica precursor injected through the shielding gas decomposes in the high temperature of the welding arc zone and reacts with reactive oxygen species therefore providing a reducing environment (Figure 1). The in situ generated silica condenses on the metal particles and further insulates Cr from oxygen species by forming an amorphous silica layer. An *Escherichia coli* growth experiment demonstrated that in situ generated amorphous silica has much less biotoxicity than the particles of Cr and other metals.[38] The by-products from the decomposition of silica precursor are carbon dioxide and water.

Silica precursor technology applied to welding was described in previous studies.[39–41] A vapor phase silica precursor, tetramethylsilane (TMS), added to the shielding gas reduced Cr^{6+} concentration over 90% under the high primary shielding gas flow rate of 30 L/min. The inhibition of Cr oxidation was not considerable, however, under medium (25 L/min) and low (20 L/min) shielding gas flow rates. This ineffectiveness constrains the application to very specific operating conditions. High shielding gas flow can significantly increase welding operation costs, which would impede the use of silica precursor technology in industrial practice.

Medium and low shielding gas flows could not effectively disperse the heat generated from the welding process. TMS

premixed upstream with the shielding gas, being sensitive to high temperatures, decomposed before reaching the welding arc zone. Furthermore, a large quantity of silica powder was found deposited inside the welding gun under those conditions. A new welding gun design was needed to overcome these problems. Another question to be addressed was that the analytical method (NIOSH 7604)[42] used in the previous study could not verify the oxidation state of Cr sealed inside the amorphous silica shell formed during the process.

The objective of this study was to develop an alternative way to deliver silica precursor effectively into the welding arc zone. A prototype insulated double shroud torch (IDST) was designed to eliminate the premature heat transfer to the TMS. Laboratory experiments were conducted to assess its ability to reduce the Cr^{6+} concentration to below the limit of detection (LOD) in all shielding gas flow rates. A preliminary field test was carried out in an industrial site to evaluate the ease of implementing this technology. The hazard and cost associated with the technology were also assessed. Success of the reduction of Cr^{6+} generated by stainless steel welding would reduce the carcinogenic risk associated with this industrial process.

METHODS

Injection of Silica Precursor

To avoid the excess thermal energy transferred to the silica precursor, the silica precursor needs to flow separately from the primary shielding gas, which is a carrier of heat. Dennis et al.[31] first designed a double shroud torch using two nozzles to introduce the primary shielding gas and secondary shielding gas. However, their torch was designed only for conveniently mixing and switching different gas components. It did not address heat insulation and worked no differently from premixing the silica precursor.

A new double shroud torch was designed that incorporated a ceramic material to insulate against heat transfer between the primary and secondary shielding gases. Figure 2 shows the cross-sectional sketch of the new IDST. The IDST was hypoth-

esized to be able to minimize the premature decomposition of silica precursor by delivering the silica precursor directly to an effective position.

Traditional welding equipment was modified to introduce the silica precursor TMS into welding shielding gas (Figure 3a). TMS carrier gas argon (Ar) flowed through a Teflon impinger (T507G; Apex Instruments, Fuquay-Varina, NC) with TMS liquid covering the bottom. The impinger was immersed in an ice bath to lower the TMS vapor pressure, which prevented excess TMS vapor from getting in the system. The carrier gas became saturated with TMS vapor, which was delivered to the welding arc zone using the outer shroud of the IDST.

Welding Fume Sampling

Laboratory sampling of welding fumes was performed in an enclosed stainless steel welding chamber (Figure 3b). The design of the chamber followed the American Welding Society (AWS) F1.2:2006 design.[43] The conical chamber measured 36 inches in diameter at the bottom, 8 inches in diameter at the top, and 36 inches in height. A high-volume pump (GL-2000H; General Metal Works, Cleves, Ohio) with a sampling rate of 50 L/min was put on top of the chamber. Welding fume particles generated in the chamber mere collected on a 90-mm glass fiber filter (pore size 1 μm; Whatman, PLC, Maidstone, Kent, UK) mounted on the pump.

A welding machine (Power MIG 140C; Lincoln Electric, Cleveland, Ohio) was used in the laboratory study, with a constant voltage of 19.5 V and a wire speed of 100 inches/min was maintained throughout the study. The study used 0.035-inch-diameter 308L stainless steel wire, which has about 20% (wt) Cr. The IDST was kept in a fixed position by a metal stand, and the round shape mild steel base metal was positioned on a constantly rotating turntable (Aircrafter T-25; MK Products, Irvine, Calif.). The laboratory study simulated beading on the base metal at 1.5 min per sample.

The chamber study used 75% Ar/25% CO_2 as the primary shielding gas, following the welding machine's manufacturer
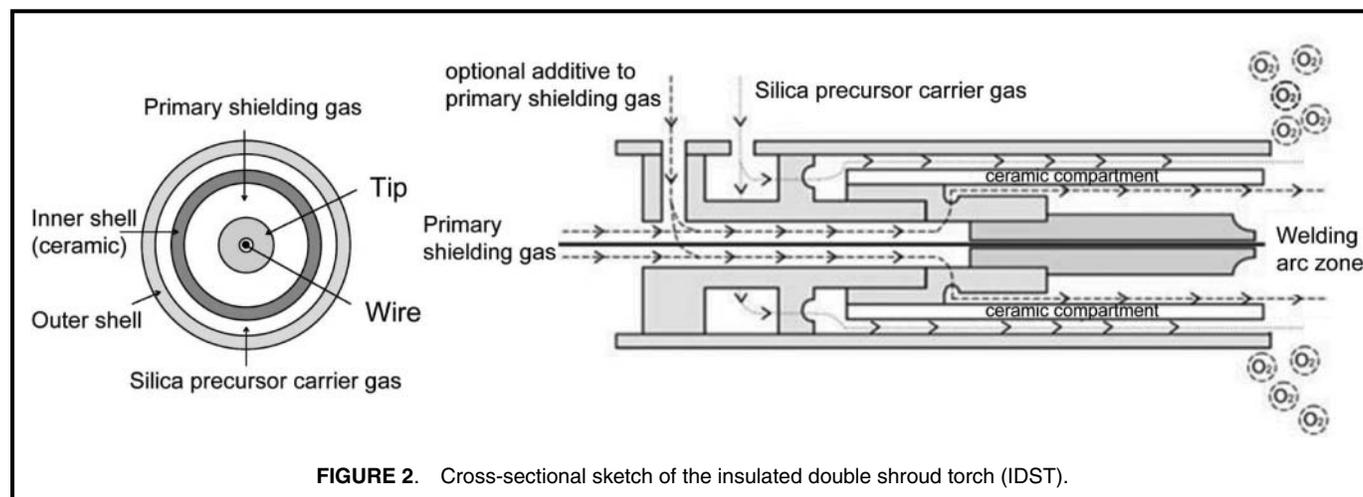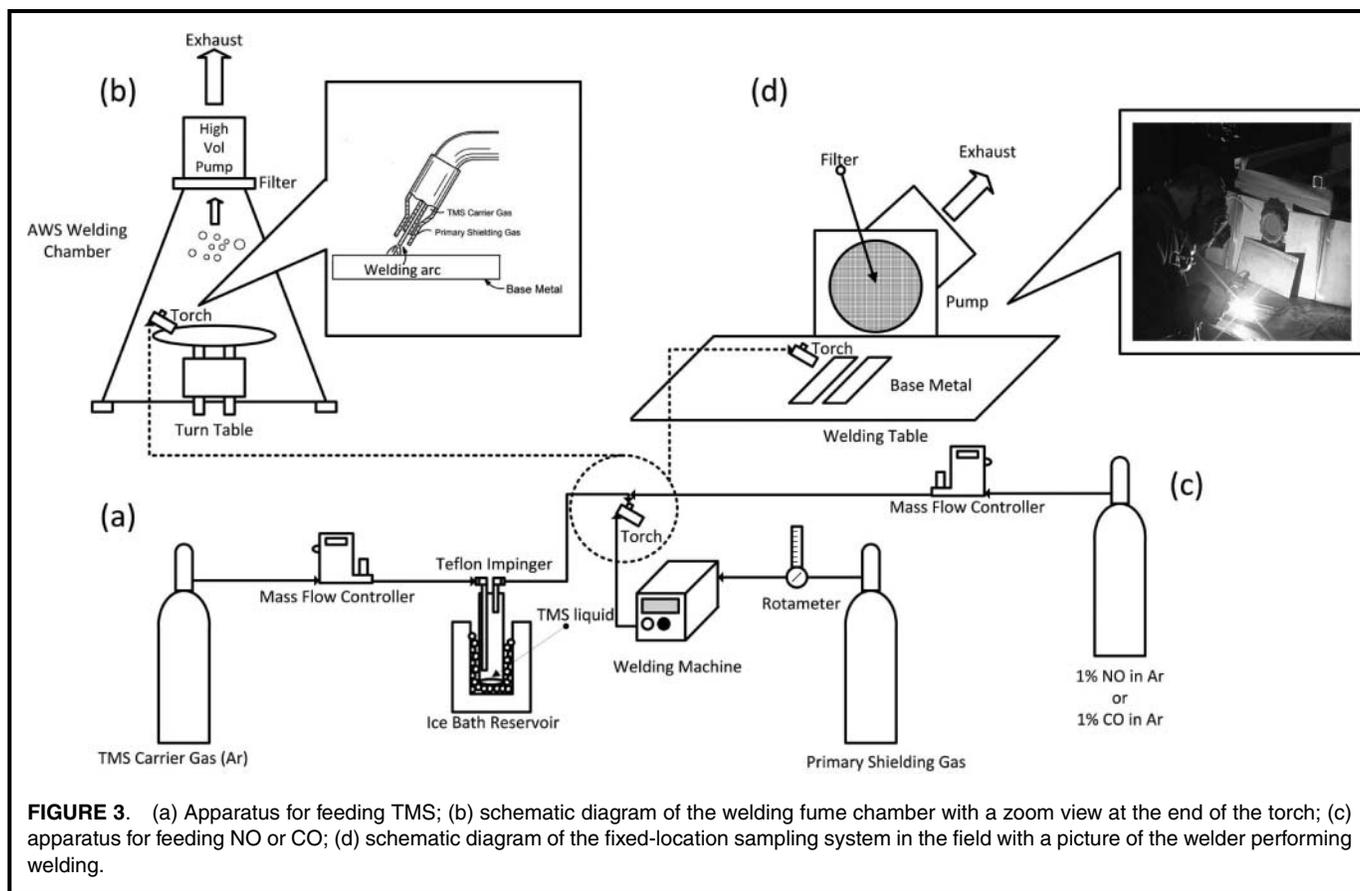
FIGURE 2. Cross-sectional sketch of the insulated double shroud torch (IDST).

FIGURE 3. (a) Apparatus for feeding TMS; (b) schematic diagram of the welding fume chamber with a zoom view at the end of the torch; (c) apparatus for feeding NO or CO; (d) schematic diagram of the fixed-location sampling system in the field with a picture of the welder performing welding.

suggestions. Three different flow rates of the primary shielding gas were selected based on previous studies to represent the low, medium, and high shielding gas flow conditions. Different injection rates of TMS carrier gas were tested; the testing conditions are listed in Table I. The injection rate of TMS carrier gas per each flow rate of the primary shielding gas started at 0.16 L/min and gradually increased to a percentage of the primary shielding gas that could eliminate the airborne

Cr^{6+} concentration to the LOD. The flow rates of the primary shielding gas and the TMS carrier gas were respectively controlled by a rotameter (HRF-1425-580; Radnor Welding Products, Radnor, Pa.) and a mass flow controller (FMA5500; Omega Engineering, Stamford, Conn.).

In addition to the silica precursor, nitric oxide (NO) and carbon monoxide (CO) were also tested during the study as alternative reducing reagents for comparison purposes. A

TABLE I. Testing Conditions of TMS and Shielding Gas Flows in the Chamber Sampling

Primary Shielding Gas Flow Rate (L/min)	TMS Carrier Gas Flow Rate (L/min)	Percentage of TMS Carrier Gas to Primary Shielding Gas Flow Rate (%)	Estimated TMS Concentration in the Shielding Gas (v/v)
20	0.16	0.8	2.8×10^{-3}
	0.32	1.6	5.6×10^{-3}
	0.64	3.2	1.1×10^{-2}
25	0.16	0.64	2.3×10^{-3}
	0.32	1.3	4.5×10^{-3}
	0.64	2.6	8.9×10^{-3}
	1.3	5.1	1.8×10^{-2}
30	0.16	0.53	1.9×10^{-3}
	0.32	1.1	3.8×10^{-3}
	0.64	2.1	7.4×10^{-3}
	1.3	4.3	1.5×10^{-2}

TABLE II. Testing Conditions of NO/Ar and CO/Ar in the Chamber Sampling

Primary Shielding Gas	Injection Rate (L/min)	Secondary Shielding Gas	Injection Rate (L/min)	Percentage of NO/Ar or CO/Ar
Ar	30	1% (v/v) NO in Ar	0.3	0.01
			0.9	0.03
			3	0.1
		1% (v/v) CO in Ar	0.3	0.01
			0.9	0.03
			3	0.1

commercially available NO/Ar shielding gas, MISON, consists of 300 ppm (0.03%) NO in argon. Theoretically, CO can absorb the ultraviolet (UV) light and react with oxygen species to provide a similar reduction. Different percentages of NO or CO in the final shielding gas (Ar) were tested. One percent (v/v) NO or 1% (v/v) CO in Ar were injected as the secondary shielding gas through the IDST (Figure 3c), while pure Ar was used as the primary shielding gas. The testing conditions are listed in Table II. A carbon monoxide monitor (Nighthawks KN-COPP-3; Kidde, Mebane, NC) was set near the chamber to determine the CO concentration in the air.

Field sampling was performed in an industrial facility that regularly conducts welding activities. A fixed-location area sampling setup was used in the field as shown in Figure 3d. A certified welder performed the welding task in front of the high-volume pump with glass fiber filter installed. The sampling period per each sample was extended to 5 min arc time to collect enough welding fume for analysis.

A welding machine (Invision 456MP; Miller Electric Mfg. Co., Appleton, Wis.) and a wire feeder (Miller 70 series 24 volt wire feeder) were employed in the field sampling. Voltage was controlled by a pulse program with an average of 26 volts; 310 stainless steel wire with a diameter of 0.045 inch and 310 stainless steel base metal with a thickness of 3/16 inch were used. The 310 stainless steel typically contains about 25% (wt) Cr. The wire speed was fixed at 192 inches/min. The primary shielding gas used was a mixture of 69% Ar, 31% He, and 1% CO_2. Flow rates of the primary shielding gas and the TMS carrier gas flow were kept constant at 15 L/min and 0.24 L/min, respectively.

Analysis of Cr^{6+}

An ion chromatography (IC) system (ICS-1500; Dionex, Sunnyvale, Calif.) was used to analyze Cr^{6+}. The IC was equipped with a cation analytical column (Dionex CS5A) for separating different ions, and a conductivity detector (Dionex DS6) to measure the Cr^{6+} concentration. Sample extraction followed NIOSH Method 7604.[42] Per manufacturer's specifications for the CS5A column, 5 mM sodium bicarbonate and 1 mM sodium carbonate were chosen as the eluent. The Cr^{6+}

content on the glass fiber filter was extracted using 20 mL eluent heated in a water bath to 100°C for 1 hr. The extracted solution was filtered to remove the solid residue to protect the ICS-1500 injection loop.

Standard solutions were prepared by diluting 1000 mg/L chromate solution (Acros Organics/Thermo Scientific, Fairlawn, NJ) with deionized (DI) water to a range of 1–60 mg/L of Cr^{6+}. The calibration plot was linear in the investigated concentration range with the correlation coefficient larger than 0.9999. The estimated Cr^{6+} concentration ($\mu g/m^3$) in the sampled air (C_{cr6+}) was calculated using the following equation:

$$C_{cr6+} = \frac{[Cr^{6+}] \times 20mL}{Q \times t} \qquad (1)$$

where $[Cr^{6+}]$ is the concentration ($\mu g/mL$) of Cr^{6+} in the 20-mL eluent measured by ICS-1500; Q is the flow rate of the sampling pump, 0.05 m^3/min; t is the sampling time, 1.5 min for the laboratory sampling, and 5 min for the field sampling. If $[Cr^{6+}]$ was less than the ICS-1500's LOD (about 10 ng/mL), the airborne Cr^{6+} concentration was conservatively assigned the corresponding values of the LOD (2.8 $\mu g/m^3$ in the lab, 1.1 $\mu g/m^3$ in the field).

In previous studies,[39–41] some fume particles were encapsulated in the amorphous silica layer generated by the condensation of silica vapor. However, the eluent used in the analytical protocol (5 mM $NaHCO_3$ and 1 mM Na_2CO_3) was not able to dissolve the amorphous silica shell. The use of a strong acid such as hydrofluoric acid (HF) could dissolve the silica shell; however, it could also change the valence state of the original Cr^{6+} as well as damage the instrument. In other words, ion chromatography cannot determine the Cr^{6+} encapsulated in the silica shell. X-ray photoelectron spectroscopy (XPS) is a non-destructive analytical process that could examine the valance state of Cr in the range of the penetration depth of an X-ray. A thin layer of fume particles was scratched down from the glass fiber filter to a silicon substrate. Only samples from one baseline and one optimal injection rate were analyzed. The XPS (5100; PerkinElmer, Waltham, Mass.) gives the intensity as an arbitrary unit (a.u.) for each peak; therefore, the relative ratio of Cr^{6+}/Cr^{3+} was calculated.

Chemical Reagents and Labware

All chemicals used were analytical grade or higher in purity. DI water used for dilution and cleaning was deionized and purified by a Nanopure system (Barnstead Nanopure/Thermo Scientific) to a conductivity of 18.2 mΩ-cm. All the shielding gases used were ultrahigh purity and certified by the manufacturers (Airgas, Praxair, and Air Liquide). All the glassware used in the study was cleaned in an ultrasonic cleaner (FS220) for 4 hr and dried in an oven (FS230G Isotemp/Thermo Scientific) in a laminar flow hood. The tubings in the sampling system were polytetrafluoroethylene (PTFE) or Tygon, and air leaking tests were performed regularly.

Hazard and Cost Estimation

Tetramethylsilane is a flammable and volatile liquid.[44] High concentrations of TMS vapor may cause flash fire or explosions in oxidizing environments. The toxicological properties of TMS to humans have not been fully investigated. However, high temperatures in the welding arc zone are expected to decompose the trace amount of TMS. In this study, the TMS concentration was estimated for a room based on test conditions in the field sampling and a worst-case scenario, i.e., all TMS vapor escaped without decomposition and ventilation.

The vapor pressure of TMS was calculated using the Antoine equation[44]:

$$\log_{10} Vp = A - \frac{B}{T + C} \tag{2}$$

where A, B, C are 3.97703, 1047.242, −36.057 (unitless), respectively, and T is the temperature of the ice bath (273 K). The ideal gas law was then used to calculate the concentration of TMS in the saturated carrier gas.

The increase in operating costs when using the silica precursor technology can be a major barrier for industrial implementation. A comprehensive cost assessment of the silica precursor was carried out using a model developed for estimating the welding cost.[45] Different scenarios of weld (pipe, butt, and fillet) production were utilized to compare the cost using the general welding technology and the silica precursor technology. The cost to acquire TMS is $65 per 100 mL, and its consumption rate is about 0.02 mL/min.

Statistics

All the samples were at least quadruplicate ($n \geq 4$) per each combination of the primary shielding gas flow rate and the TMS carrier gas flow rate in laboratory. The t-test was used to examine the mean concentration of Cr^{6+} under different circumstances. Statistical significance was evaluated using a significance level of $p = 0.05$. All statistical analyses were performed using SAS statistical software (version 9.3; SAS Institute, Cary, NC).

RESULTS AND DISCUSSIONS

Chamber Sampling Results

Figures 4a–c show the airborne Cr^{6+} concentrations under different combinations of the primary shielding gas and the TMS carrier gas flow rates. In addition to the current results from using the IDST and the LOD, the results from a previous study,[39] in which the TMS carrier gas and the primary shielding gas were premixed via a Y-fitting at the welding gun hose, are illustrated.

The Cr^{6+} concentrations in baseline samples were $25(\pm 5.2)$ $\mu g/m^3$, $35(\pm 4.1)$ $\mu g/m^3$, and $56 (\pm 8.9)$ $\mu g/m^3$ for the low, medium, and high primary shielding gas flow rates, respectively. The chamber sampling was a simulation of a continuous welding practice for 1.5 min, and it collected the full stream of welding fumes in an enclosed space. The concentrations measured in the chamber do not directly reflect breathing zone exposure concentrations and cannot be directly compared with the OSHA 8-hr PEL of 5 $\mu g/m^3$. The LOD of 2.8 $\mu g/m^3$ was used as lower reference for the Cr^{6+} reduction. The lower limit of the reduced airborne Cr^{6+} concentration was assumed to be equal to 2.8 $\mu g/m^3$, the previously cited LOD in the laboratory study.

Under the low shielding gas flow rate condition (Figure 4a), premixed TMS was unable to reduce the Cr^{6+} ($p > 0.1$) regardless of the increase of the percentage of TMS carrier gas to the primary shielding gas over the range studied (up to 6.3% v/v). In contrast, TMS injected by the IDST was able to reduce Cr^{6+} to below the LOD (2.8 $\mu g/m^3$) at 3.2% TMS gas/primary shielding gas. The percentage was also less than the needed percentage for the IDST to reduce Cr^{6+} below the LOD under the medium and high shielding gas flow rates. In the case of separate flowing of TMS carrier gas and the primary shielding gas, the low flow will create a relatively longer reaction time for the TMS in the welding arc zone, which reduces the ineffective reaction outside the microenvironment.

The medium and high shielding gas flow rates (Figures 4b and c) show similar reduction trends: as more TMS carrier gas was injected, the Cr^{6+} concentration gradually decreased to the LOD of 2.8 $\mu g/m^3$ ($p < 0.05$ for each conditions). The efficiency of the IDST was always higher than that of the premix mode at the same percentage of TMS carrier gas/primary shielding gas. This supports the hypothesis that the IDST could deliver more TMS without premature decomposition than the premix mode. Other benefits are that the costs associated with TMS consumption were also reduced and the nozzle showed less silica powder after the IDST experiment. This is direct evidence that the premature reaction of the TMS inside the nozzle that occurred in the premix mode was minimized with the IDST.

In sum, the chamber sampling results demonstrated that combining the IDST and the silica precursor technology could effectively reduce the airborne Cr^{6+} emission over 90%. The positive results prove that the IDST led to a greater Cr^{6+} reduction compared to the original premix mode. The lowest concentrations reported here all corresponded to the LOD (2.8 $\mu g/m^3$). Hence, the true reduction efficiency might be beyond this conservative estimate.

NO and CO Results

As previously mentioned, NO and CO were intentionally added to the shielding gas to test their reduction of the oxygen species, thus controlling the formation of Cr^{6+}. Figure 4d shows the results under different percentages of NO and CO in Ar. The mean Cr^{6+} concentration was 24 (± 5.8) $\mu g/m^3$ when NO was added to the Ar. Compared with the airborne Cr^{6+} concentration of 56 (± 8.9) $\mu g/m^3$ in the baseline, the difference indicated a mean reduction efficiency of 57%. The maximum reduction occurred at 0.1% of NO, which was much higher than that of the only commercially available NO/Ar shielding gas MISON (0.03% v/v or 300 ppm). A downside of NO is that excess NO may influence the welding arc and lead
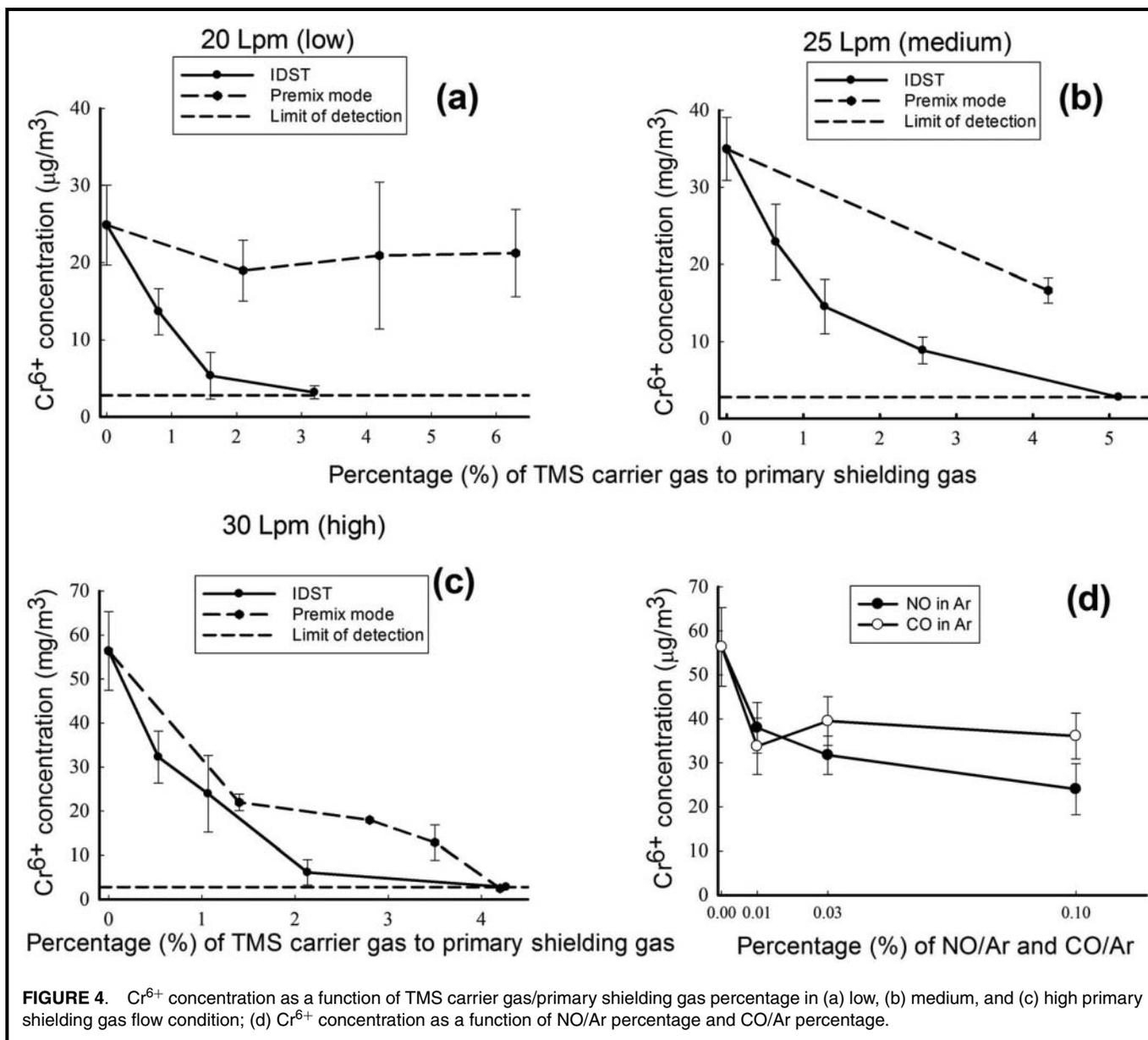
FIGURE 4. Cr^{6+} concentration as a function of TMS carrier gas/primary shielding gas percentage in (a) low, (b) medium, and (c) high primary shielding gas flow condition; (d) Cr^{6+} concentration as a function of NO/Ar percentage and CO/Ar percentage.

to mechanical failure of weld.[46] Furthermore, the control of NO has to be precise due to a NIOSH REL of 25 ppm for NO and OSHA PEL of 5 ppm for NO_2.[20]

There was no statistical difference among Cr^{6+} concentrations with different injection rates of CO ($p > 0.1$). The reduction of the UV intensity and the oxygen species due to CO could only lead to about 35% reduction of Cr^{6+}. The CO monitor also recorded a peak concentration of 100 ppm CO in the air while the percentage of CO in Ar was increased to over 0.1% (v/v), which could be hazardous with prolonged exposure.

Even without the injection of NO, nitrogen oxides (NO_x) can appear in the welding arc zone due to the reaction of ambient oxygen and nitrogen at high temperature. CO_2, the product of reaction between CO and oxygen, can also dissociate to CO at high temperature (>1000 K).[47] The thermodynamic

equilibrium here inhibited the reaction of NO and CO with the oxygen species. Another reason for the low reduction efficiencies of these gases was that these gases only protected the metal vapor from oxidation near the welding arc zone, while the amorphous silica layer formed on the metal particles by the silica precursor technology could insulate the metals from subsequent oxidation occurring outside the welding arc zone.

As seen in Figure 4d, the injection of NO or CO into the primary shielding gas as a reducing agent was much less effective at reducing the Cr^{6+} emission than the IDST silica precursor technology. In addition, the emission of unreacted NO or CO, as well as the generation of NO_2 potentially pose additional health hazards. Hence, the silica precursor technology is better suited for reducing Cr^{6+} in welding fumes.
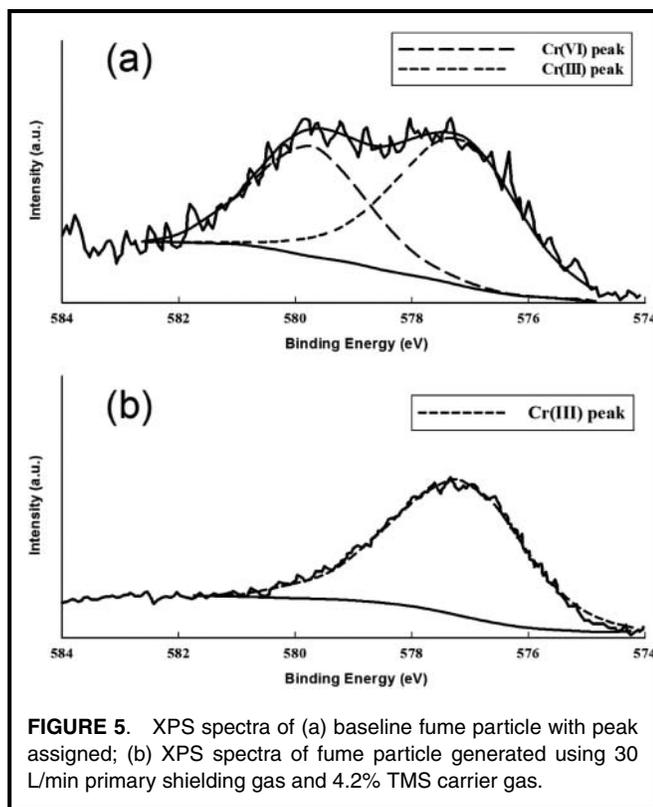
FIGURE 5. XPS spectra of (a) baseline fume particle with peak assigned; (b) XPS spectra of fume particle generated using 30 L/min primary shielding gas and 4.2% TMS carrier gas.

FIGURE 6. Photographs of weld surface from (a) baseline; (b) 30 L/min primary shielding gas and 4.2% TMS carrier gas.

XPS Results

Figure 5 shows the XPS spectra of selected samples. Significant bands were found at binding energies from 577.0–578.0 eV for Cr 2p3/2 and 587.0–588.0 eV for Cr 2p1/2. The Cr^{3+} peak was assigned by Cr^{3+} (577.2 eV) and Cr_2O_3 (576.3 eV), while the Cr^{6+} peak was assigned by CrO_3 (578.1 eV) and $Cr_2O_7^{2-}$ (579.2 eV). The ratio of the Cr^{6+} to Cr^{3+} was calculated by curve fitting. In this particular baseline sample (Figure 5a), the ratio of Cr^{6+} to Cr^{3+} was about 45:55. In the optimal TMS injected samples (Figure 5b), Cr^{6+} was absent. The XPS result provides semiquantitative evidence of the absence of Cr^{6+} inside the silica shell. This supports the hypothesis that elimination of the Cr^{6+} occurred before the formation of the amorphous silica layer.

Field Sampling Results

Due to limited study resources, the only comparison made was between the airborne Cr^{6+} concentrations using no TMS gas vs. using 1.6% TMS carrier gas/primary shielding gas. The Cr^{6+} concentration without using TMS was 9.8 (±3.4) $\mu g/m^3$, whereas the Cr^{6+} concentration was less than the LOD (1.1 $\mu g/m^3$) with 1.6% TMS carrier gas/primary shielding gas. The baseline airborne Cr^{6+} emission of 9.8 $\mu g/m^3$ was less than the baseline Cr^{6+} concentrations in the chamber samples (range: 25–56 $\mu g/m^3$) due to the greater dilution ventilation in the field setting.

The percentage of TMS carrier gas/primary shielding gas needed to achieve maximum reduction in the field (1.6%) was also lower than the laboratory (3.2%). The possible reason was
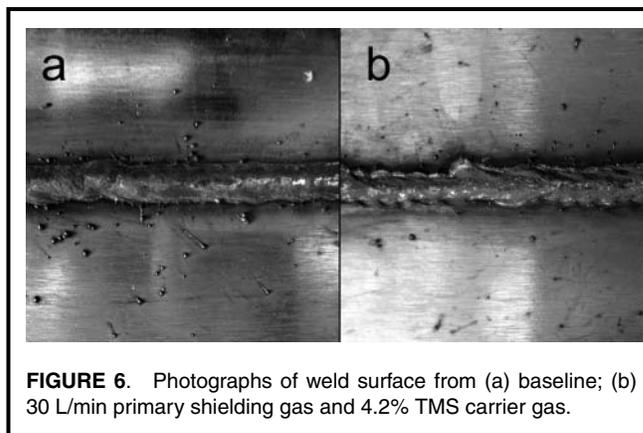
that the pulse welding process employed in the field sampling could decrease the heat input and increase the efficiency. This also indicates different welding machines and processes might have different optimal injection rates for silica precursor.

Effects on Weld Quality

Figure 6 shows photographs of two welds made using baseline (no TMS gas) and 4.2% TMS carrier gas added to 30 L/min primary shielding gas (75% Ar $+$ 25% CO_2), respectively. The welds were examined by a certified welder who reported no visual difference on buildup of the weld. The reaction between the TMS and oxygen species introduced extra heat input to the weld, which led to a longer cooling time for the weld puddle. This is similar to the role of CO_2 in the shielding gas. CO_2 is commonly added to the shielding gas to help weld penetration in cases where the welding machine does not have sufficient capacity. If extra heat is not desired, one can always use other components of the shielding gas to compensate for the heat, such as increasing the Ar content or increasing the primary shielding gas flow rate. The TMS vapor also increased the globular size in the globular transfer mode. The globular tended to bounce at the edge of the weld and create more spots. This problem did not occur in the short-circuit and the spray modes.

Apart from these two effects, there was no other evidence that TMS altered the welding process, and no mechanical structure change was expected. However, further in-depth mechanical test such as transverse tensile and bend tests should be performed to confirm the effects of introducing TMS on the generated weld.

Hazard and Cost Estimation

Equation 3 was used to calculate the worst-case volume concentration of unreacted TMS vapor in the air in a 5 m $\times$ 5 m $\times$ 3 m room with a 5-min duration of welding, which represents the conditions of the field sampling. This equation is based on dilution of the saturated carrier gas (TMS vapor in Ar) entering the TMS-free room air without ventilation. An assumption was made that the saturated carrier gas was at atmospheric pressure (760 mmHg). The saturation vapor pressure of TMS is 271 mmHg at 0°C (ice bath). The corresponding maximum

concentration was calculated to be 5.7 ppm when injecting 2.4×10^{-4} m³/min TMS carrier gas that was the flow rate (0.24 L/min) used in the field sampling. This maximum concentration was three orders of magnitude below the TMS' lower flammable limit/lower explosion limit (LFL/LEL) of 1%. This result indicates the use of TMS will not cause explosion risks for welding in a typically sized room, even without removal by ventilation.

$$C_{TMS} = \frac{271\,mmHg \times Qt}{760\,mmHg \times V} \times 10^6 \qquad \textbf{(3)}$$

where C_{TMS} is the concentration of TMS (vppm), Q is the flow rate of TMS carrier gas (2.4×10^{-4} m³/min), t is the duration of welding (5 min), and V is the space of the room (75 m³).

Using the model from SERDP PP-1415[45] to assess the additional costs of the TMS in various welding processes, the general material cost was calculated to increase by 3.8%. The cost of the shielding gas containing TMS was $0.6 per ft of weld. This cost does not include the initial capital cost of the IDST, which might vary significantly from laboratory phase to industrial bulk production. The details of these calculations are available in another report.[48] The costs of implementing the silica precursor technology are comparable to those of other control technologies such as LEV and on-gun extraction.[49,50]

CONCLUSION

Overall, the use of the IDST with the silica precursor technology was shown to reduce the airborne Cr^{6+} concentration to below the LOD (2.8 μg/m³) in the laboratory, under all primary shielding gas flow rates. The premature decomposition of silica precursor that occurred in the premix mode was minimized by injecting the primary shielding gas and TMS carrier gas separately. TMS was shown to be more effective and less hazardous than NO and CO as a reducing reagent in welding applications, with an acceptable cost. As observed in the previous studies, the in situ generated silica condenses on the fume particles that can insulate the metals from the analytical eluent of IC. XPS result confirms that at the optimal ratio, TMS prevented the formation of all the Cr^{6+} compounds.

In addition to the laboratory chamber sampling, a fixed location area sampling study was carried out in an industrial welding facility to examine the practicality of this technology. By adding 1.6% TMS carrier gas to the primary shielding gas, the Cr^{6+} concentration was reduced to below the LOD of 1.1 μg/m³. Furthermore, visual inspection of welds generated using the silica precursor technology showed no surface deterioration in weld quality. Nevertheless, a mechanical structure test will be helpful in determining if extra heat and increased globular size introduced by the TMS have any effects.

Besides reducing the Cr^{6+} concentration in welding fumes, the silica precursor technology also encapsulates other toxic metals such as nickel and manganese. The investigation of the impact of welding fumes on biotoxicity (e.g., bioaccessibility, cytotoxicity, and deposition pattern) will be essential before the application of the silica precursor technology in welding can be widely adopted.

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