Hexavalent chromium content in stainless steel welding fumes is dependent on the welding process and shield gas type†

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Occupational exposure to welding fumes is a known health hazard. To isolate elements in stainless steel welding fumes with high potential for adverse health outcomes, fumes were generated using a robotic gas metal arc system, using four shield gases of varying oxygen content. The objective was to measure Cr^{VI} concentrations in a broad spectrum of gas metal arc welding processes, and identify processes of exceptionally high or low Cr^{VI} content. The gases used were 95% Ar/5% O_2, 98% Ar/2% O_2, 95% Ar/5%CO_2, and 75% He/25% Ar. The welder was operated in axial spray mode (Ar/O_2, Ar/CO_2), short-circuit (SC) mode (Ar/CO_2 low voltage and He/Ar), and pulsed axial-spray mode (98% Ar/2% O_2). Results indicate large differences in Cr^{VI} in the fumes, with Ar/O_2 (Pulsed) > Ar/O_2 > Ar/CO_2 > Ar/CO_2 (SC) > He/Ar; values were 3000 ± 300, 2800 ± 85, 2600 ± 120, 1400 ± 190, and 320 ± 290 ppm respectively (means ± standard errors for 2 runs and 3 replicates per run). Respective rates of Cr^{VI} generation were 1.5, 3.2, 4.4, 1.3, and 0.46 µg/min; generation rates were also calculated in terms of µg Cr^{VI} per metre of wire used. The generation rates of Cr^{VI} increased with increasing O_3 concentrations. Particle size measurements indicated similar distributions, but somewhat higher >0.6 µm fractions for the short-circuit mode samples. Fumes were also sampled into 2 selected size ranges, a microspatter fraction (≥0.6 µm) and a fine (<0.6 µm) fraction; analysis indicated that Cr^{VI} is primarily associated with particles <0.6 µm. The conclusion of the study is that Cr^{VI} concentrations vary significantly with welding type and shield gas type, and this presents an opportunity to tailor welding practices to lessen Cr^{VI} exposures in workplaces by selecting low Cr^{VI}-generating processes. Short-circuit processes generated less Cr^{VI} than axial-spray methods, and inert gas shielding gave lower Cr^{VI} content than shielding with active gases. A short circuit He/Ar shielded process and a pulsed axial spray Ar/O_2 process were both identified as having substantially lower Cr^{VI} generation rates per unit of wire used relative to the other processes studied.

Introduction

Welding is a major occupational activity in the US and worldwide, and includes workers in manufacturing, construction and a number of other industrial sectors. In the US, in excess of 462 000 workers do some welding as part of their duties,[1] about two-thirds in manufacturing industries. Welding produces a significant number of hazards during operation, including fumes, gases, and physical agents such as heat and UV and IR radiation.[2] Fumes contain a large number of metal compounds; for gas-shielded arc welding of stainless steel, this is mostly oxides of Fe, Mn, Ni, and Cr; flux-containing processes additionally have fluoride compounds of K and Ca,[3] as well as other flux components, such as TiO_2 and SiO_2. Occupational health studies indicate a number of occupationally related adverse health effects, including bronchitis, decreases in pulmonary function, pneumoconioses, and lung cancers.[2] Mortality from pneumoconioses shows a proportionate mortality ratio (PMR) of 1.58, while lung cancer PMR is 1.21, as reported in the 2002 NIOSH Work-Related Lung Disease Surveillance Report.[4] The PMR figures are compiled for welding on all types of metals. Most welding operations are performed on low-alloy or high-carbon steels, but stainless steel may account for up to 5% of welding,[5] and is an important segment of some industries, such as shipbuilding.

However, welding on stainless steel presents a unique occupational-risk exposure: known carcinogens—hexavalent chromium and nickel—have been identified in stainless steel welding fumes.[6] This hazardous exposure is well recognized and critical enough to merit evaluation by the International Agency for Research on Cancer (IARC). Findings from that evaluation were presented in the IARC monograph: *On the Evaluation of Carcinogenic Risks to Humans, Volume 49: Chromium, Nickel, and Welding*.[5] That monograph reviewed a number of studies that measured hexavalent and total chromium exposures or generation rates. That review, along with an additional Environmental Protection Agency review,[7] found a very wide range of Cr^{VI} concentrations; this suggested that different welding processes and conditions could account for the 20:1 range of Cr^{VI}

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concentrations. The current study is predicated on these findings and suggestions for additional research. The general purpose of this study is to extend the initial IARC and EPA findings to determine the amount of Cr^{VI} generated from a range of common welding processes, and additionally seek to determine whether the amount of Cr^{VI} in welding fumes can be lowered by altering factors in the welding process.

Common welding configurations

Analysis of welding-based hazards is dependent on an understanding of the range of welding processes and conditions. While numerous combinations of processes and conditions are found in various industrial settings, the purpose of this study was to examine a defined group of welding-based aerosols with significant potential to induce morbidity. More than 80 different welding processes[8] are commonly found, but most welding is done with electrical arc welding processes. The most prevalently used variations, based on materials usage, are shielded metal arc (SMAW or stick welding or manual metal arc welding) ~ 45%; gas metal arc (GMAW) ~ 34%, and flux-cored arc welding (FCAW) ~ 17%.[7]

SMAW has the simplest equipment requirements: a power supply, an electrode holder, welding rods, and a ground clamp. The welding rods have a coating over the filler metal rod that provides a shielding environment to minimize degradation of the weld by atmospheric oxygen or nitrogen. GMAW uses more complex equipment; besides a power supply, it uses a gas-shielded torch or gun and the electrode is a consumable wire of the desired filler metal fed by a motorized feeder. The shield gas is supplied externally from cylinders. Shield gases range from the completely inert (Ar, He and their mixtures) to so-called active gases, which include CO_2, Ar mixtures with CO_2 or O_2, and other gas mixtures; these gases may have chemical interactions with the weld or fume. FCAW uses equipment similar to GMAW, but the wire electrode has an internal flux material for weld shielding; the process may be used with or without an external shield gas. In this study, the focus is on GMAW.

Metal transfer modes in GMAW

GMAW differs from other arc welding processes in that more than one mode of metal transfer from the electrode into the weld pool is possible. At relatively low applied voltage, the process is called short-circuit GMAW. The end of the electrode wire is in direct contact with the weld pool, and a portion melts and is transferred into the weld pool. The melting breaks the short circuit, and the arc forms. The arc is intermittent (up to 200 times per second), and not perfectly stable; this may generate spatter, where relatively large droplets may be released outside the weld bead.

When the voltage is increased above the short circuit range, another mode of operation known as globular transfer occurs. The wire end melts, forming large drops that typically are larger than the wire diameter. The droplets fall by gravity into the weld pool. This limits usage to flat or horizontal welding positions.

With shield gases containing high percentages of Ar, as the applied voltage is raised further, there is a transition to axial spray transfer mode. Metal leaves the electrode wire tip and is transferred as a very fine spray into the weld pool. This produces a high quality weld with lower spatter. The technique is used primarily in flat or horizontal applications; overhead or vertical use may have drip problems. A variation of spray transfer is pulsed spray transfer, where current pulses are added to a steady-state background current; this allows the total current to periodically exceed the required transition current and permit spray mode. This allows high quality welds in any position with lower heat input, and a low fume generation rate.

Objectives

Hexavalent chromium was determined in a spectrum of stainless steel welding fumes generated in this laboratory. The specific objectives of this study were to:

(1) Determine the Cr^{VI} content of stainless steel welding fumes from a range of GMAW processes, using shield gases spanning a wide range of oxygen contents, with the goal of identifying fumes of especially high or low Cr^{VI} content. Fumes will be generated according to welding equipment manufacturer's recommendations and the system will be optimized to assure high quality welds.

(2) Examine the coarse "microspatter" fraction of fumes and compare its Cr^{VI} content to the fine (<0.6 μm) fraction to determine whether the coarse fraction is a major contributor to overall Cr^{VI} content.

(3) Compare the fumes that were generated in this study for physical differences, including particle size distribution, morphology, and crystalline content.

Material and methods

The basic robotic welding system included a six-axis robotic arm (Lincoln Electric 100 iB), a power supply (Lincoln Power Wave 455), a water-cooled arc welding torch (Tregaskiss 450 Amp "Tough Gun", Lincoln Electric), and a wire feeder capable of rates to 300 inches (762 cm) per minute. A detailed system description is included in the reference by Antonini *et al.*[9]

Aerosols were drawn from the torch vicinity with a peristaltic pump at typical flow rates of 5–20 litres/min and diluted with metered filtered air. The approximate chamber aerosol concentration was monitored with a DataRam 4000 (Thermo Electron, Franklin, MA, USA) and the concentration was controlled to a relatively constant level by altering dilution air. Exact gravimetric chamber concentration in mg/m^3 was determined using periodic 30 min samples collected on 37 mm PTFE filters from near the center part of the chamber with 2 pumps operating at 1.0 litres/minute.

Stainless steel welding wire was Lincoln Electric E308 LSi, 0.045 in. (1.14 mm) diameter, fed from a 225 kg drum. The high-volume samples analyzed for Cr^{VI} in this study were sampled from a single lot of wire, Lot 308Y. The manufacturer's nominal composition of the wire is 2% Mn, 19–25% Cr, 10–13% Ni, and the remainder Fe.

Shield gas was taken from cylinders, pressure-regulated, and set to deliver 19 litres/min. (Ar/CO_2 and Ar/O_2 mixtures) or 35 litres/min. for He/Ar 75/25. The welding material in the base-plates was ¼ inch (6.35 mm) A-36 carbon steel. Operation with all shield gases and welding process types used similar conditions,

Table 1 Operating variables for generated welding fume samples

Shield gas	Gas flow	Weld mode	Wire feed	Voltage (V)	Current (A)
Ar/CO_2 95/5	19 l/min	Axial spray	760 cm/min	25	200
Ar/CO_2 95/5	19 l/min	Short circuit	320 cm/min	17–18	120
Ar/O_2 95/5	19 l/min	Axial spray	760 cm/min	23	200
He/Ar 75/25	35 l/min	Short circuit	445 cm/min	22	130
Ar/O_2 98/2	19 l/min	Pulsed Spray	760 cm/min	(variable)	(pulsed)

but was adapted to good welding practice, generally as recommended by welding supply manufacturers. All welding operations were adjusted for good bead appearance with good penetration of the baseplates. Operating variables are shown in Table 1 below.

Sampling strategies

Fumes from the weld area were sampled through ports around the torch circumference, which were combined and passed through 1 inch inside diameter electrically conducting tubing, through a peristaltic pump and passed into the upper part of the exposure chamber. The stream was mixed with dilution air, which was metered by a mass flow controller. The diluted fume aerosol was exhausted through the bottom of the chamber, passed through a 254 × 305 mm filter, and through an exhaust fan that was operated under computer control to keep chamber pressure slightly positive at all times. The filter material was Hollingsworth and Vose (East Walpole, MA, USA) electrostatic medium (PE 13060NA), cut to fit the filter housing. After sampling times were completed, filters were removed from the housing, folded inward, and put in sealed polyethylene bags. Two-fraction samples were obtained with a cyclone/filter system. The aerosol was taken from a probe in the upper central part of the chamber, entered a cyclone (InTox #4 cyclone, Moriarity, NM, USA), passed though a 4 inch (102 mm) electrostatic filter, and through a vacuum pump, whose discharge line was exhausted back into the uppermost part of chamber. The aerodynamic cutoff diameter of the cyclone operated at 30 litres/minute was approximately 0.6 μm.[10] The filter was monitored for pressure drop; if it exceeded 60 in. (152 cm) of H_2O, the pump was halted and the filter changed. The flow was measured at the sampling line inlet in the chamber with a mass flow meter (TSI, Inc.) before sampling began and after sampling was completed, and the mean value of the two values used for the flow. Flow was also monitored by an inline rotameter, and adjusted with an inline metering valve if necessary. No other samples were taken during the cyclone sampling period. Samples were also taken for particle size distribution of the welding fume aerosol at 30 litres/min from the same sampling line as the cyclone sampler at separate times, sampling for typically 20 min.

Samples were normally collected over 3 hour runs. There have been a number of problems associated with the sampling and subsequent analysis of welding fume for Cr^{VI}, primarily changes in the oxidation state of Cr, especially when sampling onto filters and storing for extended periods of time before analysis.[12] To address these issues, a 30 minute high volume sample was collected from the chamber bottom and rapidly recovered, processed, and analyzed for Cr^{VI}, in the same manner as the 3 h samples. Additionally, samples from the Ar/O_2 AXS mode was analyzed repeatedly at times ranging from 3 min to 3 months to check for storage effects on the fume Cr^{VI} content.

Sample recovery and processing

Filters from the high-volume filter housing were folded, bagged, and taken to the analytical laboratory within 5 minutes of the sampling completion time; the bags contained room air at room temperature. Welding fume particulate matter was recovered from the filters by gentle suction onto a 47 mm, 0.8 μm polycarbonate filter. The 47 mm stainless steel filter housing had a short piece of 6 mm ID silicone tubing, cut at 45° on the inlet end, and house vacuum was connected to the outlet end. Using a gentle blotting action, most of the particulate fume was removed from the filter. Sufficient quantity was collected for Cr^{VI} and other metals analysis, but quantitative recovery was not necessary, since fume concentrations were determined by the 12 separate gravimetric samples taken during the run, and the total flow was continuously monitored. After completion, the polycarbonate filter was removed from the housing over a tared 75 × 75 mm weighing boat, and material brushed from the filter and housing interior with a #3 artist's brush. The fume was treated with an anti-static device at this point to prevent losses. The dust was then ground in a metal-free apparatus to homogenize the sample for replicate analyses; preliminary results indicated large differences between replicate samples weighed from material recovered from filters and subsequently analyzed, with coefficients of variation typically >20% for replicate samples. The process below resulted in much better precision for replicate samples, with coefficients of variation of typically 5–10%. The system used was a disposable polyethylene vial with two 1/8 inch silicon nitride coated ceramic balls, shaken for 30 s in a Wig-L-Bug grinder. After grinding, the material was anti-static treated again, and weighed into 20 ml scintillation vials with PTFE-lined caps. Storage in the vials was at room temperature, in air, and vials remained sealed unless samples were removed for analysis. For Cr^{VI} analysis, 5 mg samples were weighed into 15 ml polypropylene centrifuge tubes. Cyclone samples were recovered by dissembling the cyclone, and brushing the material from the cup and cyclone interior into a tared weighing boat. The entire cyclone sample was analyzed, since masses were small, typically 5 mg or less. The filter downstream of the cyclone was treated as the high volume samples above.

Analysis for Cr^{VI}

Samples were treated and analyzed using NIOSH Physical and Chemical Analysis Method 7703, Hexavalent Chromium by Field-Portable Spectrophotometry.[12] The estimated limit of detection is 0.08 μg, and the method range is 1 to 400 μg of Cr^{VI}. Ten ml of extraction solution (0.05 M $(NH_4)_2SO_4$/0.05 M NH_4OH for soluble Cr^{VI}; 0.10 M Na_2CO_3/0.02 M $NaHCO_3$ for insoluble Cr^{VI}) were added to each 5 mg sample, and the tubes sonicated in a bath for 30 minutes. Samples were removed and centrifuged 10 minutes at 3000 × g. Solid-phase extraction began with activation of the 3 ml (1 g of sorbent) strong anion exchange columns (Supelco) with 1 ml of water, and adding 5 ml of the supernatant liquid of the centrifuged samples to the column. Columns were then rinsed with 1 ml of H_2O to remove any cations. Anionic Cr^{VI} was eluted from the columns with three 3 ml portions of 0.5 M $(NH_4)_2SO_4$/0.1 M NH_4OH. Samples were acidified with 100 μl of concentrated HCl, and 2 ml of 20 mM diphenylcarbazide in CH_3CN added. The color was allowed to develop for 5 minutes, and the absorbances at 540 nm were read, with the instrument blanked on a reagent blank. Standards were made from K_2CrO_4, 1 mg Cr^{VI}/ml in ammonium extraction buffer, diluted 1:10, and working standards made fresh for that day's analysis. Standards spanned the range of 0.1 to 1.0 mg/ml. Triplicate samples were analyzed for 30 minute and 3 hour fume samples, and 2 separate experiments were done. Cyclone and downstream filters were single samples.

Fume particle morphology

Aerosol particle samples were periodically collected at 1 l/min using the gravimetric sampling port onto 47-mm Nuclepore polycarbonate filters (Whatman, Clinton, PA) with Formvar®-coated grids on the filter to assess particle morphology. The particles on the grids were viewed using a JEOL 1220 transmission electron microscope (JEOL, Inc., Tokyo, Japan), operated at 80 kV, using magnifications of 25 000×.

X-Ray diffraction sampling and analysis

Fume samples from the 3 hour collected fume were ground as above, and 10 mg samples were examined using X-ray diffraction at the West Virginia University Physics Department. The Samples were analyzed with a Rigakyu Model D/Max-B (Rigaku, The Woodlands, TX, USA), using a Cu-Kα source with $\lambda = 0.154185$ nm, and diffraction peaks were identified with Jade7 software and the International Center for Diffraction Data library.

Ozone sampling and analysis

Ozone samples were drawn from the exposure chamber through a ¼ inch (6.35 mm) ID PTFE line to an Advanced Pollution Instrumentation Model 450 (Teledyne, San Diego, CA, USA) ozone analyzer. Ozone readings were taken every 30 s and the values averaged over the entire run duration. The instrument was calibrated annually at the manufacturer's facility.

Particle size distributions

Particle size distributions of different welding fumes were determined by using two Micro-Orifice Uniform Deposit Impactors (MOUDI and Nano-MOUDI, MSP model 110 and 115; MSP Corp., Shoreview, Minn.). By combining the two MOUDI impactors in series, the particles were size-classified and collected into 15 fractions ranging from over 18 μm down to 10 nm. Besides the special feature of being able to classify nano-size particles, the MOUDI consists of rotating stages to obtain a nearly uniform particle deposit on the collection substrates, which can reduce particle bounce and is useful for subsequent analysis. Although the total flow rate for the impactors is operated at 30 litres/min, only 5 litres/min samples were taken from the chamber upper central area to avoid any potential flow turbulence in the chamber as a result of drawing high air flow. Dilution air of 25 litres/min was added prior to the inlet of the impactors to fulfill the flow requirement. The impactors were typically operated for 20 minutes. A data inversion method was used to determine the MMAD and GSD that minimizes the differences between the measured mass fractions and those computed under the assumption the aerosol is perfectly unimodal and lognormally distributed. The detail of this method can be found in a paper by O'Shaughnessy and Raabe,[13] where the application of a spreadsheet to this method is described and made readily available.

Statistical approaches

Mixed models were used to analyze the data and test for differences between processes and times. Tukey's adjustment was used to correct for the possibility of inflated type I errors, due to multiple comparisons.

Results

The stability of recovered and ground fume samples over a 3 month period showed very little change in the Cr^{VI} content; Fig. 1 shows concentration as a function of time for a selected fume.

Hexavalent chromium results for all of the generated samples are shown in Table 2. All results were soluble Cr^{VI}; all analyses for insoluble Cr^{VI} were less than the limit of detection. The rapidly sampled, recovered and analyzed samples were not different from the 3 h samples at the $p = 0.05$ level for any of the samples. Since the fumes were not generated at precisely the same conditions, results were normalized with respect to their respective fume generation rate, yielding a generation rate of Cr^{VI} under the experimental conditions. Additionally, some of the differences in total fume generation rate and Cr^{VI} generation rates were

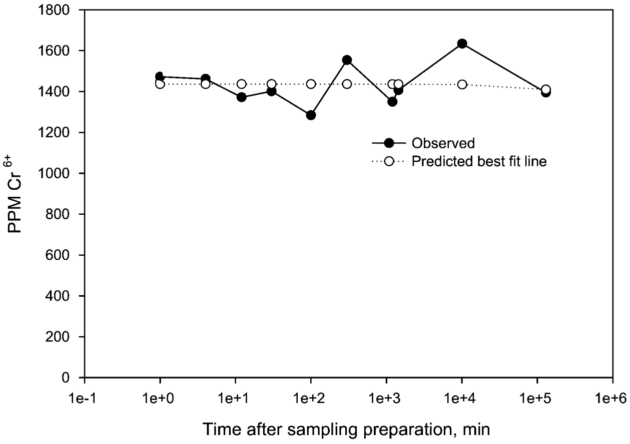

Fig. 1 Sample stability after capture and processing.

Table 2 Fume soluble Cr^{VI} content, fume and Cr^{VI} generation rates, and normalized generation rates for 5 processes (2 experiments, 3 replicates/experiment; $N = 2$)

Process	Cr^{VI} (μg/g) (±std error) (3 h sample)	Cr^{VI} (μg/g) (±std error) (30 m sample)	Fume gen. rate (mg/min)	Cr^{VI} gen. rate, (μg/min)	μg Cr^{VI}/m wire
Ar/CO_2 AXS	2600 ± 120	2600 ± 130	1.7 ± 0.08	4.4 ± 0.2	0.58 ± 0.03
Ar/CO_2 SC	1400 ± 190	1300 ± 101	0.95 ± 0.13	1.3 ± 0.18	0.41 ± 0.06
Ar/O_2 AXS	2800 ± 85	2900 ± 300	1.2 ± 0.04	3.2 ± 0.098	0.42 ± 0.01
He/Ar SC	320 ± 290	44 ± 38	1.4 ± 1.3	0.46 ± 0.42	0.10 ± 0.09
Ar/O_2 AXS-P	3000 ± 300	2900 ± 122	0.50 ± 0.05	1.5 ± 0.15	0.20 ± 0.02

influenced by the different wire feed rates necessary to maintain optimum welds. Therefore, generation rates were re-normalized with respect to wire feed rates, and also shown in Table 2. All of these normalized data were calculated from the 3 h samples. The fume generation rate was calculated from the product of the chamber concentration (a column average of all concentrations during the sampling period, 2 samples every 30 min) and the total outlet flow (again, a column average of all observed flows during the generation interval). The Cr^{VI} generation rate was calculated as the product of the observed Cr^{VI} fraction of the fume (ppm) and the fume generation rate (g/min). The results normalized for wire feed rates were calculated as the product of the Cr^{VI} generation rate (μg/min) and the reciprocal of the wire feed rate (m/min). To convert to mass units of wire per minute, the wire feed rate may be multiplied by the (measured) value of 7.9 g/metre for the lot of wire used.

Table 3 gives the results from the 2-fraction cyclone/filter sampler. The second column is the ratio of Cr^{VI} content (ppm) in the cyclone collected material to the Cr^{VI} content (ppm) in the fine fraction. The third column is the ratio of the cyclone-collected mass to the total mass collected.

Two MOUDI particle-size-distribution graphs are shown below in Fig. 2. This shows that the fractions exceeding ~0.6 μm are enhanced in the short-circuit mode relative to axial spray mode for Ar/CO_2 95/5 GMAW fumes. Particle size distributions were similar for those of a given process; short-circuit were similar, as were all axial spray processes. The summary data (means and geometric standard deviations) are shown in Table 4

The relation between Cr^{VI} generation rate and chamber ozone concentration are shown in Table 5. The Cr^{VI} generation rate correlated with the measured O_3, with a Pearson correlation coefficient of 0.8935, and with a p-value of 0.0411. The Cr^{VI} generation rate per metre of wire also correlated with the measured O_3, with a Pearson correlation coefficient of 0.9795, with a p-value of 0.0035.

Transmission electron microscopy showed that all of the fumes in this study contained both the very small chain-aggregates and the larger, spherical particles. Comparison of the two Ar/CO_2 fumes (axial spray and short circuit) indicated that the morphology is similar between the two processes, but the proportion of larger, spherical microparticles was increased in the short-circuit mode fumes, as shown in Fig. 3.

Table 3 Relative Cr^{VI} content in the coarse (>0.6μm) and fine (<0.6μm) fractions of welding fumes

Gas/process	Cr^{VI}_{Coarse} (ppm)/Cr^{VI}_{Fine} (ppm)	Mass % Coarse
Ar/CO_2 AXS	0.7	16
Ar/CO_2 SC	0.3	4
Ar/O_2 AXS	0.6	2
He/Ar SC	0.6	9
Ar/O_2 Pulsed-AXS	0.5	7

Table 4 Mass mean aerodynamic diameters (MMADs) and geometric standard deviations (GSDs) for different shield gases and welding processes, from MOUDI data

Sample: gas/process	MMAD (μm)	GSD
Ar/CO_2 AXS	0.26	1.4
Ar/CO_2 SC	0.33	1.5
Ar/O_2 AXS	0.32	1.5
He/Ar SC	0.41	1.4
Ar/CO_2 Pulse AXS	0.26	1.3

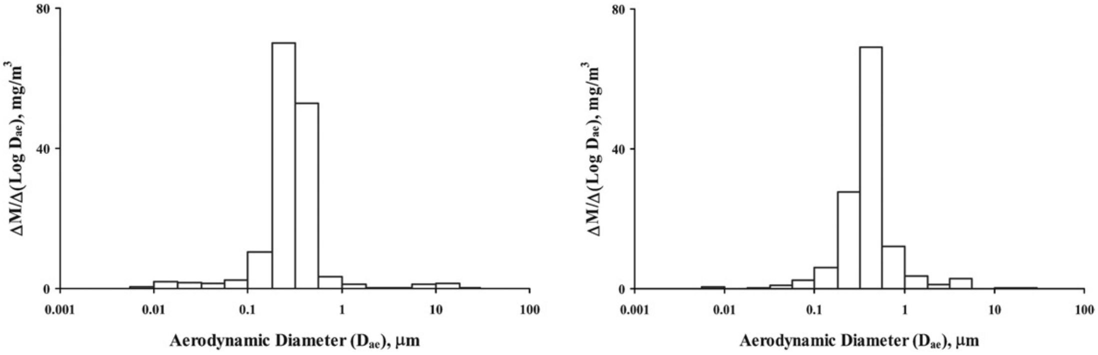

Fig. 2 MOUDI particle size distribution for Ar/CO_2 axial spray mode (L) and short-circuit mode (R) welding fumes.

Table 5 Ozone concentrations and Cr^{VI} generation rates for the generated welding fumes (sorted in order of the measured O_3)

Welding shield gas/ process type	Measured O_3, ppm	Cr^{VI} generation rate, mg/min	Cr^{VI} generation rate, mg/metre of wire
He/Ar short circuit	0.011	0.46	0.01
Ar/O_2 pulsed spray	0.024	1.5	0.02
Ar/CO_2 short circuit	0.078	1.3	0.41
Ar/O_2 axial spray	0.106	3.2	0.42
Ar/CO_2 axial spray	0.125	4.4	0.58

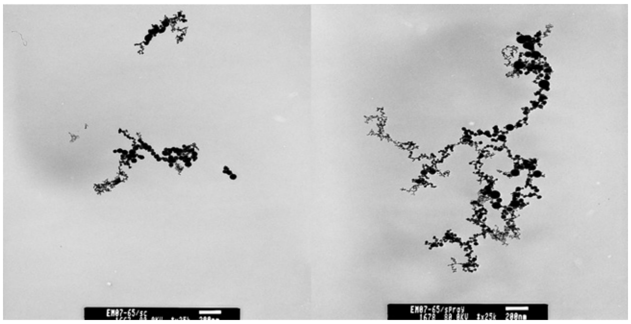

Fig. 3 Transmission electron photomicrographs of short-circuit (L) and axial spray (R) welding fumes. Scale bar is 200 nm.

X-Ray diffraction results were similar for all of the fumes, with a crystalline composition of 90–98% Fe_3O_4, 1–2% Mn_3O_4, and two of the SC fumes, the He/Ar and the Ar/CO_2, showing ~5% of metallic Fe. No chromium compounds were detected.

Discussion

The results indicate a wide range of hexavalent Cr, in terms of concentration in the fume, generation rate, and in generation rate per unit of welding wire. Fume concentrations ranged over an order of magnitude; Cr^{VI} generation rates varied 8:1, and generation rates per unit of wire ranged 6:1. All of these measures are important in exposure assessment and the design of engineering controls in the workplace. Although many studies have examined fume generation and Cr^{VI} for various processes, many of those studies do not report sufficient data for calculation of all these measures. Hexavalent chromium content in welding fumes has been reviewed by IARC[5] and the USEPA;[7] most studies include a fume concentration in mg/m^3 and a percentage of soluble, insoluble or total Cr^{VI} in the fume or as a fraction of total Cr. The study by Moreton *et al.*[14] cited in the EPA review includes sufficient data (for GMAW stainless steel) for conversion to generation rates of Cr^{VI} in μg/min and μg Cr^{VI} per metre of wire. Ranges from that study were 2000–4000 ppm Cr^{VI}; 9–22 μg/min generation rate, and 0.5–2.8 μg Cr^{VI}/m wire. The findings of this study are similar in general with those of that study; fumes ranged from ~300 to 3000 ppm, the generation rates were ~0.5–4.4 μg/min, and 0.1 to 0.6 μg Cr^{VI}/m wire. The fact that the samples of this study were generated by the highly stable and reproducible robotic system with very stable arc length, drag angle, and gas shielding is probably an important reason why the Cr^{VI} levels tended to be lower than results from the Moreton *et al.* study.

The finding that freshly generated and rapidly analyzed Cr^{VI} results were not significantly different from the 3 h samples suggests that significant oxidation or reduction are not important issues under the conditions of this study. The study of Pederson *et al.*[11] that found major problems in Cr^{VI} analysis in welding fumes used different sampling media, handling techniques, and analytical methods, some of which were shown to directly affect the results. There may be differences between the fresh and aged samples from the He/Ar shielded fumes, but the large variances in those samples may have obscured the differences; the Cr^{VI} levels were also small on those samples, which also added to the uncertainty in results. The sample stability study showed that samples changed only by negligible amounts after storage times out to 3 months time. Further research may more completely determine decay rates for welding fume samples, in the event that longitudinal sampling of health exposures was undertaken within specific industries, to determine whether there were long-term health outcomes from different welding processes. This might be of significance for innovative and automated welding processes performed on specialty materials that might be considered as having potential to introduce hazardous exposures. Given the increased innovation rate in material science, and the rapid introduction of new materials, the necessity of archiving samples of welding fume to determine health exposures may become of greater significance.

The results for the separately sampled and analyzed microspatter and fine fractions demonstrated that the microspatter fraction is consistently lower in Cr^{VI} content than the fine fraction, confirming that the enhanced spatter fractions in short-circuit welding processes examined in this study did not contribute much to the overall Cr^{VI} content or the total mass of the fume. This is in agreement with the findings of Jenkins[15] and Kura,[16] who found that total Cr increased with increasing particle size, but the Cr^{VI} content decreased.

The Table of Cr^{VI} generation rate and O_3 content in the chamber shows a strong association, even though the processes are very different. So many process variables differed between the 5 fumes studied that a systematic study of the dependence of Cr^{VI} generation rate on observed O_3 was not possible. The study by Dennis *et al.*[17] was able to study Cr^{VI} generation rate dependence on O_3 and other factors very systematically in a single GMAW process study, and found that increasing Cr^{VI} rate parallels increasing O_3 under much of the conditions studied. This study confirms that finding even across the 5 different processes of this study. Furthermore, this suggests that controlling O_3 generation may be a crucial factor in the control of hexavalent Cr.

Virtually all of the fume fractions were respirable, with >97% of the particles capable of penetrating into the deeper portions of the lung, with high probabilities of deposition, including the microspatter fractions. X-Ray diffraction results showed only a single Fe oxide and a single Mn oxide, along with metallic Fe for the SC processes, but X-ray diffraction only detects crystalline content; there may be other components that are amorphous or whose crystalline domain size is not large enough to be detected, or whose concentration is too small, so other chemical species cannot be ruled out at this point.

A number of studies have examined Cr^{VI} exposures from stainless steel welding, and some have explored methods for reducing Cr^{VI} content in the fumes. Studies by Kimura *et al.*[18] and Dennis *et al.*[19] successfully reduced Cr^{VI} content in the fume by using altered fluxes in FCAW. Studies by Dennis *et al.* examined the dependence of Cr^{VI} on UV radiation, O_3 and other factors[16] and also examined the use of secondary shield gases to reduce Cr^{VI} in the fumes.[20] Another study examined work process changes, welding process type and engineering controls to limit Cr^{VI} exposures in the workplace.[21] This study examined common, popular techniques with common shield gases, with the possible exception of the He/Ar SC process; while this is one of many recommended choices for stainless steel welding, it is relatively uncommon, primarily due to the increased gas costs of He/Ar relative to Ar mixtures with CO_2 or O_2, or 100% CO_2.

Conclusion

Findings from this research indicate that there is no single, representative stainless steel welding fume; the compositions and generation rates vary widely when using common welding processes and shield gases. Likewise, it is unlikely that there is a best, lowest-Cr^{VI}-producing welding process for all conditions. It is therefore unlikely that a single and straightforward set of recommendations can be established to minimize Cr^{VI} exposure across a variety of industrial settings, industries and processes, and the hierarchy of engineering controls should be utilized, whenever possible, as a primary means to reduce exposures. The technical requirements for welding are much too diverse and complex to devise a universal approach to minimizing hexavalent Cr generation. Nevertheless, there are some choices that may be made to minimize Cr^{VI} exposures, especially in situations in which there may be practical limitations on the use of substitution, ventilation or other engineering controls. Two welding processes—a He/Ar shielded short-circuit mode and an Ar/O_2 shielded pulsed axial-spray mode—were identified in this study, as generating much-reduced Cr^{VI} per unit length of welding wire. These processes should be considered for adoption under conditions involving the potential for pulmonary exposure. This study was not exhaustive in its analysis of welding processes, but sought to include a representative spectrum of common processes and shield gases; further research may identify additional processes with reduced Cr^{VI} exposure potential.

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