Welding fumes from stainless steel gas metal arc processes contain multiple manganese chemical species

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Received 2nd November 2009, Accepted 22nd January 2010
First published as an Advance Article on the web 23rd February 2010
DOI: 10.1039/b922840c

Fumes from a group of gas metal arc welding (GMAW) processes used on stainless steel were generated using three different metal transfer modes and four different shield gases. The objective was to identify and measure manganese (Mn) species in the fumes, and identify processes that are minimal generators of Mn species. The robotic welding system was operated in short-circuit (SC) mode (Ar/CO_2 and He/Ar), axial spray (AXS) mode (Ar/O_2 and Ar/CO_2), and pulsed axial-spray (PAXS) mode (Ar/O_2). The fumes were analyzed for Mn by a sequential extraction process followed by inductively coupled plasma–atomic emission spectroscopy (ICP-AES) analysis, and by X-ray diffraction (XRD). Total elemental Mn, iron (Fe), chromium (Cr) and nickel (Ni) were separately measured after *aqua regia* digestion and ICP-AES analysis. Soluble Mn^{2+}, Fe^{2+}, Fe^{3+}, and Ni^{2+} in a simple biological buffer (phosphate-buffered saline) were determined at pH 7.2 and 5.0 after 2 h incubation at 37 °C by ion chromatography. Results indicate that Mn was present in soluble form, acid-soluble form, and acid-soluble form after reduction by hydroxylamine, which represents soluble Mn^0 and Mn^{2+} compounds, other Mn^{2+} compounds, and (Mn^{3+} and Mn^{4+}) compounds, respectively. The dominant fraction was the acid-soluble Mn^{2+} fraction, but results varied with the process and shield gas. Soluble Mn mass percent in the fume ranged from 0.2 to 0.9%, acid-soluble Mn^{2+} compounds ranged from 2.6 to 9.3%, and acid plus reducing agent-soluble (Mn^{3+} and Mn^{4+}) compounds ranged from 0.6 to 5.1%. Total Mn composition ranged from 7 to 15%. XRD results showed fumes had a crystalline content of 90–99% Fe_3O_4, and showed evidence of multiple Mn oxides, but overlaps and weak signals limited identification. Small amounts of the Mn^{2+} in the fume (<0.01 to ~1% or <0.1 to ~10 $\mu g\ ml^{-1}$) and Ni^{2+} (<0.01 to ~0.2% or <0.1 to ~2 $\mu g\ ml^{-1}$) ions were found in biological buffer media, but amounts were highly dependent on pH and the welding process. Mn generation rates for the fractions were tabulated, and the influence of ozone is discussed. The conclusions are that exposures to welding fumes include multiple Mn species, both soluble and insoluble, and that exposures to Mn species vary with specific processes and shield gases.

Introduction

Welding is a major occupational activity in the US and worldwide, and includes workers in a number of industrial sectors, including manufacturing and construction. In excess of 462 000 workers do some welding as part of their duties in the US, about two-thirds in manufacturing industries.[1] Welding produces a significant number of hazards during operation, including fumes, gases, and physical agents such as heat and ultraviolet and infrared radiation.[2] Fumes contain a large number of metal compounds: for gas-shielded arc welding of stainless steel, this is mostly oxides of iron (Fe), manganese (Mn), nickel (Ni), and chromium (Cr); flux-containing processes may have fluoride compounds,[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.

Welding wire and the resultant fume may contain many metals, but most ferrous metal welding wire contains Mn as well as Fe; Mn improves hardness and other metallurgical properties of the weld. While Mn is an essential nutrient and is present in many important enzymes, it has been found that workers in some manganese industries, such as mining, ferroalloy smelting, and battery manufacturing have experienced neurotoxicity.[6] Prolonged exposure to Mn species in these industries may result in a disease, manganism, whose symptoms are similar to Parkinson's disease (PD), but may include additional neurological and behavioral symptoms.[7] The exact Mn chemical species, the exposures sufficient to cause manganism and the mechanism of disease induction are all not well understood.[8] Mn has total of 11 possible oxidation states[9] and forms many oxides, including MnO, Mn_2O_3, Mn_3O_4, Mn_5O_8, MnO_2 and several others of even higher Mn oxidation states. Studies that have attempted to

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develop animal models for manganism have used a number of different Mn compounds, such as $MnCl_2$[10] and $MnSO_4$[11] (both soluble), mixed Mn oxides,[12] and MnO_2[13] (all insoluble). Exposure routes have included inhalation, subcutaneous,[13] intravenous injection,[14] tracheal and nasal instillation[12] and oral gavage.[15] Mechanistic studies have shown that both soluble[10,16] and insoluble[12] Mn compounds can be transported to the brain.

Manganese has been identified and measured in welding fumes from ferrous metals, but a potential role of welding fume in manganism or other PD-like symptoms is even less clear than in the manganese mining and processing industries. Several recent papers have reviewed the scientific literature on this issue;[17,18] both these reviews concluded that there is no unequivocal link between welding fume inhalation and manganism or PD-like symptoms, with the exception of a few notable case studies.

It is clear that occupational exposure to excess levels of Mn is associated with adverse health effects, including manganism. The exact dose–response relationship and mechanism of action remain unclear, and the implications for workers routinely exposed to Mn fumes have not been established through toxicological studies of animals[19] or through additional scientific studies or meta-analyses. Research to resolve the exact role of Mn in the etiology of disease states is critical and ongoing. Parallel research paths have emerged to address unresolved issues in the etiology of manganism and manganese-related disease: (a) identification of the neurotoxic pathways, and (b) speciation of the exposures. The purpose of the current research is in support of the latter, and to identify welding processes that generate minimal rates of Mn species.

Speciation addresses the role of specific chemical forms (such as valence state) and chemical compounds in toxicity. While speciation is not crucial for all chemical agents, it is widely accepted that speciation can pinpoint the toxicological pathways of specific disease-causing chemicals. Further information on the role and importance of speciation in neurotoxicity can be found in a recent 'spotlight' article[20] and several critical reviews by Michalke *et al.*[21,22] Speciation for Mn and Ni has recently been critically evaluated at a welding plant for welders using several processes.[23] The current study will attempt to identify the chemical forms of Mn that are present in stainless steel welding fumes from 5 different process/shield gas combinations. Knowledge of the types and levels of Mn species can allow more focused toxicological studies of welding fumes and similar materials.

Common welding configurations

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 processes on stainless steel. There are in excess of 80 different welding processes, but most welding is done with electrical arc welding processes. The processes most used, based on consumable materials usage, are shielded metal arc (SMAW or stick welding) ~45%; gas metal arc (GMAW), ~34%, and flux-cored arc welding (FCAW) ~17%.[24]

SMAW requires the use of welding rods that have a filler metal rod coated with a flux mixture that provides a shielding environment to minimize degradation of the weld by atmospheric oxygen or nitrogen. GMAW uses a gas-shielded torch or gun, and the electrode is a consumable wire of the desired filler metal fed by a motorized feeder; shield gas is supplied from cylinders. The processes may use shield gases ranging from the completely inert (argon (Ar), helium (He) and their mixtures) to so-called active gases, which include carbon dioxide (CO_2), Ar mixtures with CO_2 or oxygen (O_2), and other gas mixtures; these gases may have chemical interactions with the weld or fume. FCAW is 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 only on GMAW.

Metal transfer modes in GMAW

More than one mode of metal transfer from the electrode into the weld pool is possible with GMAW, in contrast to other arc welding processes. When using relatively low applied voltages, the process is called short-circuit (SC) GMAW. The electrode wire is in direct contact with the weld pool, and a portion melts and is transferred into the weld pool. If the shield gas contains a high percentage of Ar, when the applied voltage is raised further, there is a transition to axial spray (AXS) transfer mode. Molten metal leaves the electrode wire tip and is transferred as a very fine spray into the weld pool. The technique is used primarily in flat or horizontal applications; overhead or vertical use may result in drip problems. There is a variation of spray transfer known as pulsed axial spray (PAXS) 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. Pulsed spray welds are generally high quality welds in any position with lower heat input, and have a low fume generation rate.

Specific aims

The specific aims of this study were to:

(1) Catalog and measure amounts of Mn species in fumes after serial extractions into fractions that contain Mn species of a single or a small group of Mn valence states.

(2) Analyze the fumes by X-ray diffraction (XRD) for Mn compounds and other crystalline compounds, and evaluate XRD as a study tool for welding fumes.

(3) Analyze fumes for the soluble metal ions Mn^{2+}, Ni^{2+}, Fe^{2+} and Fe^{3+} in a simple biological buffer that simulates typical cellular pH and phosphate levels.

(4) Identify process/gas combinations that are minimal generators of Mn species.

Materials and methods

Generation of GMAW fumes

The basic welding system used a six-axis robotic arm (Model 100 iB, Lincoln Electric, Cleveland, OH), a power supply (Power Wave 455, Lincoln Electric), 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 (see Table 1). A more detailed system specification is included in the reference by Antonini *et al.*[25]

Table 1 Welding operational conditions

Weld mode	Shield gas (%)	Gas flow/l min^{-1}	Wire feed rate/cm min^{-1}	Voltage/V	Current/A
Short circuit	He/Ar 75/25	35	445	22	130
Axial spray	Ar/CO_2 95/5	19	760	25	200
Short circuit	Ar/CO_2 95/5	19	320	17–18	120
Axial spray	Ar/O_2 95/5	19	760	23	200
Pulsed axial spray	Ar/O_2 98/2	19	760	(Variable)	(Pulsed)

Sampling strategies

Fumes from the weld area were drawn through ports around the torch circumference and passed through a peristaltic pump and entered the upper part of the exposure chamber (designed for animal inhalation exposures). Dilution air metered by a mass flow controller was mixed with the sampled fume stream in the upper part of the chamber. The concentration in the chamber was determined by two separate 1.0 l min^{-1} samples collected on 37 mm filters every 30 min; for a 3 h run this totaled 12 samples. The diluted fume aerosol exited through the bottom of the chamber, passed through a 254 × 305 mm filter, and through an exhaust fan operating under computer control that kept chamber pressure slightly positive at all times. The electrostatic filter material was Hollingsworth and Vose (East Walpole, MA) medium (PE 13060NA), cut to fit the filter housing. When sampling times were completed, filters were removed from the housing, folded inward, and put in sealed polyethylene bags. Samples were collected from 3-hour runs.

Sample recovery and processing

Filters from the chamber outlet filter housing were taken to the analytical laboratory within 5 min of the sampling completion time; the bags contained room air at room temperature. The welding fume was recovered from the filters by gentle suction and re-deposited onto a 47 mm, 0.8 μm polycarbonate filter. The 47 mm filter housing had a short piece of 6 mm i.d. silicone tubing, cut at 45° on the inlet end, and house vacuum was connected to the outlet end. A gentle blotting action was used across the filter area, and most of the particulate fume was removed from the filter. A sufficient quantity of fume was collected for multiple metals analyses; recovery exceeded 90% of collected mass. The fume concentrations were determined by the 12 gravimetric samples taken during the run, and the total flow was continuously monitored. After completion of the fume recovery, 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 recovered fume was treated with an antistatic device (Zerostat, Fisher Scientific, Pittsburgh, PA) immediately to prevent losses from electrostatic deposit to other surfaces. The fume was then ground in a metal-free apparatus to homogenize the sample for replicate analyses. The step of grinding is essential because results without grinding indicated large differences (with coefficients of variation typically >20%) between replicate samples weighed from material recovered from filters, while the grinding process resulted in much better precision for replicate samples, with coefficients of variation of typically 5–10%. The process 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. The material was antistatically treated again after grinding, and weighed into 20 ml scintillation vials with PTFE-lined caps; recovery was >95%. The vials were kept at 22 °C and remained sealed until samples were ready for analysis.

Metals analysis

For speciation of Mn compounds, 5 mg samples were weighed and transferred into the filter cups of 50 ml filter centrifuge tubes (MaxiSpin, Alltech, Deerfield, IL), as per the procedure of Thomassen *et al.*[26] The filter seals were supplemented with 2-PTFE O-rings above the filter disk and individually leak tested before use. Ten millilitres of 0.01 M ammonium acetate were added to the filter cup and the tubes were allowed to stand for 90 min at 22 °C. The tubes were then centrifuged for 10 min at 2500 × *g*. The recovered filtered liquid represents highly soluble Mn, and was saved for later analysis. The second extraction was prepared by adding 10 ml of 25% glacial acetic acid (Sigma, St. Louis, MO) in purified H_2O (18.2 MΩ cm) and agitating for 90 min at 75 °C in a shaking water bath. Samples were centrifuged as earlier and the liquid fraction, which contains acid-soluble Mn^0 and Mn^{2+} compounds, was saved for later analysis. The final extraction used 25% acetic acid supplemented with 0.5% hydroxylamine (Sigma) for 90 min in the 75 °C shaking water bath with subsequent centrifugation. Insoluble Mn subsequent to *aqua regia* digestion was not done due to the hazards of shipping the extracts for analysis; rather, total metals were determined separately, directly from separate 5 mg fume samples digested with *aqua regia* using NIOSH Physical and Chemical Analysis Method 7303 at Bureau Veritas, Inc. (Novi, MI).[27] The 5 mg samples were heated on a hot plate for 1 h at 95 C with 6 ml of *aqua regia*, an additional 4 ml of *aqua regia* was added, and heated for another 30 min at 95 C, before dilution with H_2O and ICP-AES analysis.

Fume generation rates, Mn generation rates, and normalized generation rates can be computed from the run variables; the rates need to be normalized since the wire feed rates to obtain optimal welds varied for some process/shield gas combinations. The fume generation rate is the product of the mass concentration and the total outlet flow. The concentration in the chamber is measured gravimetrically with 2 filter samples every 30 min, and the means of all flow and concentration measurements were used for subsequent calculations. The Mn generation rate is the product of the fume generation rate and the percentage of total Mn in the fume. The normalized Mn generation rate is the product of the Mn generation rate and the reciprocal of the wire feed rate in metres per minute.

Two preliminary assumptions were made concerning soluble metal ions in biological media: (1) they needed to be promptly analyzed so as to minimize valence state changes, and (2) since solubility products of transition metal phosphates are typically $<10^{-17}$, it would be surprising to find even micromolar concentrations present in PBS at neutral pH.

Therefore samples were analyzed in the laboratory by ion chromatography rather than ICP-AES analysis at a contractor laboratory. Soluble metals in biological buffers were determined by adding 5 mg of fume to 5 ml of prepared phosphate-buffered saline (PBS, Gibco, Grand Island, NY) at a pH of 7.2, or by adding concentrated HCl to PBS to lower the pH to 5.0. The samples were kept at 37 °C for 2 h in a rotary drum incubator, and centrifuged for 10 min at 2500 × *g*. Soluble Fe^{2+}, Fe^{3+}, Ni^{2+} and Mn^{2+} were measured by ion chromatography using a Dionex ICS 2500 (Sunnyvale, CA), with separation using a METPAK 5A column. An isocratic mobile phase of 7 mM pyridine-2,6-dicarboxylic acid; 66 mM KOH; 5.6 mM K_2SO_4; 74 mM acetic acid, at a pH of 4.2 ± 0.2 was used, and detection was made using absorbance at 530 nm after mixing with a post-column reagent containing 1 mM 2-dimethylaminoethanol, 0.5 M NH_4OH, and 0.3 M Na_2CO_3, at a pH of 10.4 ± 0.2. Analytical standards for each metal ion were made separately, in 0.85% NaCl, to avoid possible oxidation or reduction of ionic species; this has approximately the same ionic strength as PBS but has no phosphates that might precipitate metal ions.

X-Ray diffraction analysis

Ground 10 mg fume samples were examined using XRD at the West Virginia University Physics Department. A Rigaku (The Woodlands, TX) Model D/Max-B, using a Cu-Kα source with $\lambda = 0.154185$ nm was used, and diffraction peaks were identified with Jade 7 software and the International Center for Diffraction Data library.

Ozone sampling and analysis

Air samples were drawn from the exposure chamber into an Advanced Pollution Instrumentation Model 450 ozone analyzer (Teledyne, San Diego, CA). Ozone readings were acquired every 30 s and the values averaged over the entire run duration. The instrument was calibrated annually by the manufacturer.

Results

Total metals in the fumes for the 5 welding processes are shown in Table 2, expressed as a weight percentage of the fume. Amounts were calculated from the inductively coupled plasma–atomic emission spectroscopy (ICP-AES) concentrations, in mg ml^{-1}, multiplied by the volume of the sample solution, divided by the initial fume weight of 5 mg. Fig. 1 shows the Mn present in each of the extraction fractions, as well as total Mn after *aqua regia* digestion, for each of the 5 welding process/shield gas combinations (results are shown in Table 3). Calculations were done in the same way as the total metals determinations. Results are from triplicate samples from each of 2 different experiments; results are expressed as means ± standard errors of the mean.

Table 2 Fume metal elements content (elemental totals) in weight percent

Process/gas	Cr (%)	Cu (%)	Fe (%)	Mn (%)	Ni (%)
GMAW-SC 75% He/25% Ar	11 ± 5	0.13 ± 0.0	26 ± 0.5	11 ± 0.1	3.4 ± 0.5
GMAW-AXS 95% Ar/5% CO_2	7.8 ± 4	0.10 ± .03	24 ± 0.0	7.1 ± 0.0	3.4 ± 0.5
GMAW-SC 95% Ar/5% CO_2	6.0 ± 5	0.11 ± .03	20 ± 0.1	12 ± 0.5	2.7 ± 0.3
GMAW-AXS 95% Ar/5% O_2	8.1 ± 6	0.09 ± .06	24 ± 0.1	8.0 ± 0.5	3.6 ± 0.4
GMAW-PAXS 98% Ar/2% O_2	6.7 ± 8	0.12 ± 0.1	17 ± 0.3	15 ± 0.5	2.4 ± 0.4

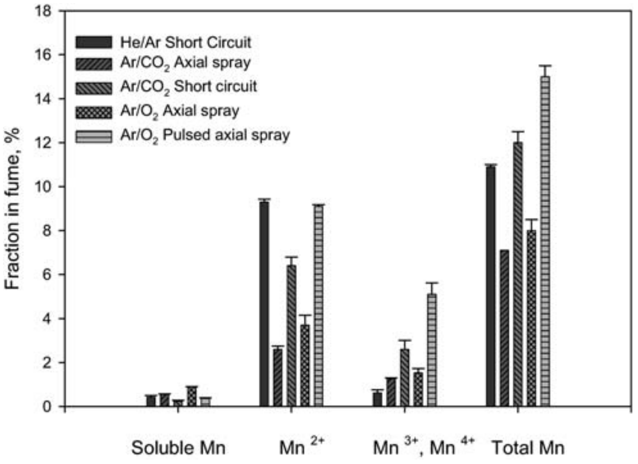

Fig. 1 Manganese content in 3 extraction fractions and total manganese for 5 processes.

Table 3 Total manganese % in fume, fume generation rates, Mn generation rates, and Mn generation rates/meter of welding wire

Process/gas	Fume gen. rate (mg/min)	Total Mn content (%)	Mn gen. rate (μg/min)	Wire feed rate (m/min)	μg Mn/m wire
SC He/Ar	1.4 ± 1.3	11 ± 0.1	150	4.5	33
AXS Ar/CO_2	1.7 ± 0.08	7.1 ± 0	120	7.6	16
SC Ar/CO_2	0.95 ± 0.13	12 ± 0.5	110	3.2	34
AXS Ar/O_2	1.2 ± 0.04	8.0 ± 0.5	96	7.6	13
PAXS Ar/O_2	0.50 ± 0.051	15 ± 0.5	73	7.6	10

Fig. 2 (A) through (D) show the concentrations of the soluble ions Mn^{2+} and Ni^{2+} in biological buffers at pH 7.2 and 5.0, simulating the pH and phosphate levels typical of cytosolic or lysosomal fluids in cells. Non-visible bars indicate the ion concentration was below the quantitation limit, but Mn^{2+} was detected in all of the samples. No Fe^{2+} or Fe^{3+} ions were observed in any of the samples under the experimental conditions. The detection limits for Fe^{2+} and Fe^{3+} are approximately 0.1 μg ml^{-1} in the assay used. Detection limits for Mn were approximately 0.3 μg ml^{-1}, and approximately 1 μg ml^{-1} for Ni.

The association of observed ozone concentration and manganese in the Mn^{2+} fraction, the Mn^{3+} plus Mn^{4+} fraction and total Mn are shown in Fig. 3. Results are shown in order of increasing O_3 concentration. Each column file of O_3 measurements has typically >150 observations.

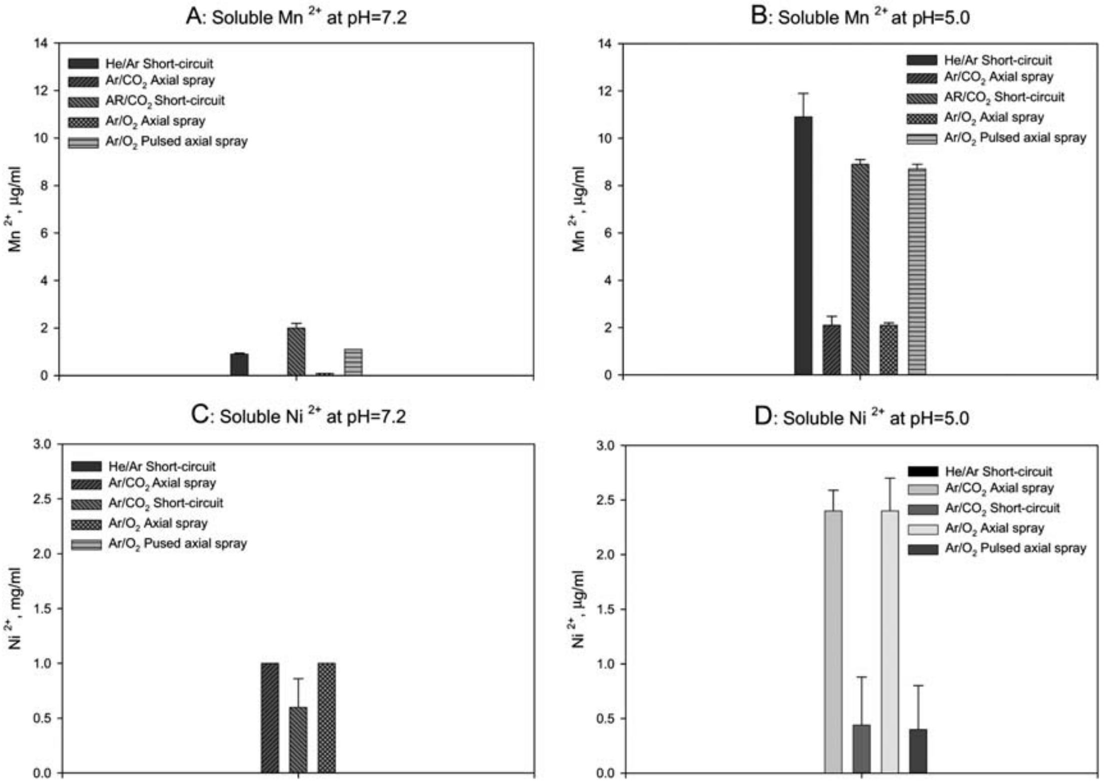

Fig. 2 (A–D) Soluble ions in biological buffers at pH 5.0 and 7.2.

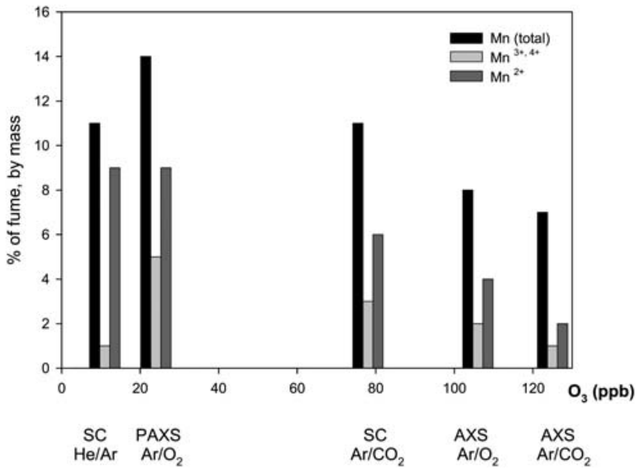

Fig. 3 Mass percent of total Mn and Mn in 2 extraction fractions and observed ozone concentration for 5 welding processes.

Table 4 Crystalline phases detected in welding fumes and semi-quantitative results for weight percent composition

Process/gas	Fe_3O_4	Fe	Mn oxides
SC He/Ar	90–95%	~5%	~2%
AXS Ar/CO_2	~98%	Not detected	~2%
SC Ar/CO_2	90–95%	~5%	~2%
AXS Ar/O_2	~99%	Not detected	~1%
PAXS Ar/O_2	~96%	~4%	Not detected

XRD results are shown in Table 4 and a representative spectrum is shown in Fig. 4. The diffraction spectrum shown in Fig. 4 was typical of all the fumes, with the exception that Fe peaks were also present for 3 of the fumes, as per Table 3. Reference diffraction spectra for the common oxides of Mn are shown below the XRD spectrum in Fig. 4.

Discussion

The results in Fig. 1 show that Mn found in welding fumes is present in multiple oxidation states, and amounts vary considerably with the process/shield gas combinations. While the acid-soluble Mn^{2+} fraction was the largest portion of all the fumes, there was a greater than 2 : 1 range for the different processes; for the Mn^{3+} and Mn^{4+} fractions, the range was greater than 4 : 1.

The three Mn extraction fraction amounts accounted for almost all of the Mn when compared to the results for total Mn for the SC He/Ar, the SC Ar/CO_2, and the PAXS Ar/O_2 modes (95, 80, and 100% respectively). The difference between the sum of the fractions and the total Mn amounts represents an "insoluble" Mn fraction in the procedure by Thomassen *et al.*[26] that is soluble only after very rigorous digestion with *aqua regia*, hydrofluoric acid and pressurized microwave heating; this fraction is not considered bioaccessible.[26] The sum of the 3 fractions was much less than the total Mn found for the AXS Ar/CO_2 and AXS Ar/O_2 modes (55 and 67%). A recent study of welding fume Mn speciation showed similar results for a GMAW process used on stainless steel (46% insoluble Mn),[23] although the metal transfer mode was not mentioned. There is no obvious single explanation for the large insoluble fraction for these two fumes,

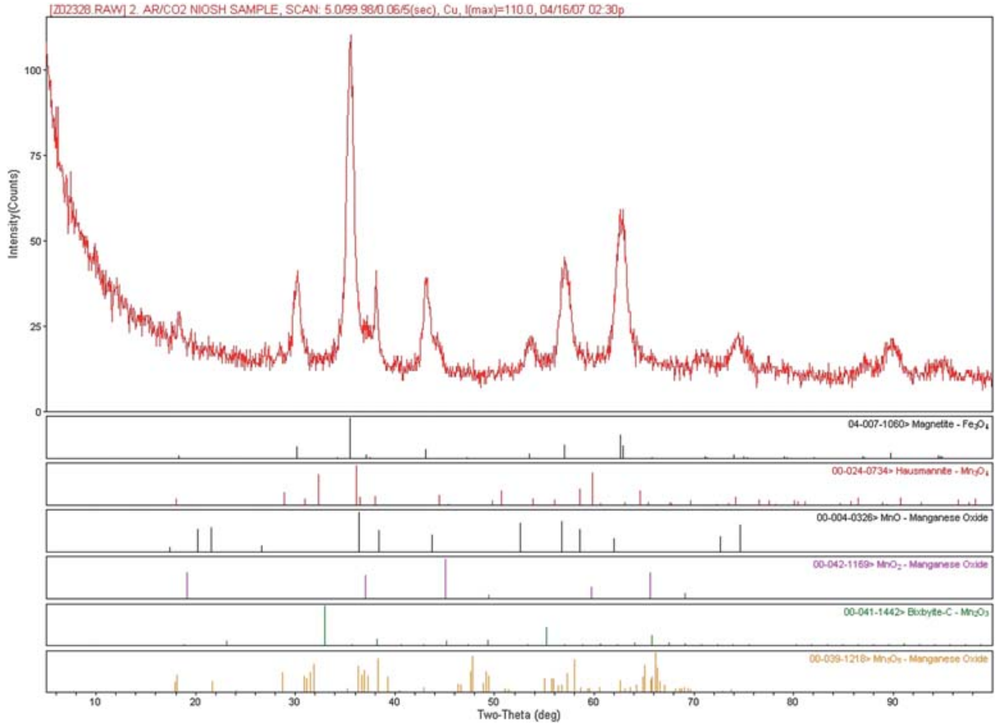

Fig. 4 X-Ray diffraction spectrum of 95% Ar/5% CO_2, axial spray welding fume.

but there were some notable differences in the AXS fumes relative to the others. It was evident that these two AXS fumes were more highly oxidized than the other fumes, since (1) XRD results (Table 4) showed no detectable quantity of unoxidized Fe in the AXS fumes, (2) their Cr^{6+} generation rate in a previous study[28] was higher than in the SC and PAXS fumes, and (3) the Fe_3O_4 content was higher in the XRD results (Table 4). Studies have shown that welding fume is highly heterogeneous, and has a core–shell structure that has been demonstrated by both X-ray photoelectron spectroscopy[3] and secondary-ion mass spectroscopy.[29] It is likely that there are more solution-resistant components on the outer shells of the fume particles that would occlude the more soluble interior Mn and other components. Chromium-containing welding fumes such as the stainless steel fumes of this study may incorporate chromium spinel compounds that are highly resistant to solubilization.[30] Incomplete recovery of welding fume constituents using *aqua regia* digestion and ICP-AES analysis has been noted in both a proficiency study involving welding fume[31] and a critical evaluation of sequential leaching procedures for welding fumes.[23] The possible occlusion of Mn species would also be consistent with the findings of lower total Mn for these 2 fumes, as shown in Fig. 1.

The sequential leaching scheme of Thomassen *et al.*[26] has been validated for many Mn oxides and mixtures of Mn oxides,[23,26] but has not specifically been validated for welding fumes of precisely known composition. The critical evaluation of that speciation method applied to welding fumes by Beringer *et al.*[23] concluded that although there are limitations of the method when applied to welding fume, it is nonetheless useful for identifying Mn and Ni species and for comparing fumes from different processes and materials. Manganese in all three fractions was identified and measured in all of the 5 processes examined, and the pulsed axial spray method was a minimal generator of Mn species, and the analytical recovery was very good in that case. The processes with the worst manganese material balance were the highly oxidized axial spray fumes; this problem will require improvements in sample digestion in future studies.

XRD results clearly showed that Fe_3O_4 was the dominant crystalline material present, and the remaining peaks in the diffraction spectra matched well with MnO, MnO_2 and Mn_3O_4 reference spectra. The spectra were weak and noisy, but this was not unexpected, noting the small size of the primary chain aggregates in the welding fume. Overall, both X-ray diffraction and the sequential leaching methods were limited in their ability to speciate the Mn in the fumes, but were still useful tools. The leaching method cannot differentiate Mn^{3+} from Mn^{4+} species, and XRD is inherently limited by the size of the crystalline domains in welding fume. X-Ray photoelectron spectroscopy with ion bombardment, X-ray absorption near-edge spectroscopy, selected-area electron diffraction and electron energy-loss spectroscopy may be able to shed additional light on valence states on Mn present in fumes, but were not available for this study. Due to the presence of large amounts of ferromagnetic material in the sample fumes, neither electron spin resonance nor magnetometry could be used to identify Mn species.

Soluble ion measurements in biological buffers at pH 7.2 and 5.0 indicate that Mn^{2+} ions were present from fumes from all 5 of the processes, and levels were generally higher at low pH than neutral pH. Nickel ions were present from some of the fumes, but at lower levels than Mn ions. A recent study[32] has shown "bioaccessible" Mn and other metal ions in simulated biological fluids, such as Gamble's solution and Hatch's solution, which were more complex than the phosphate-buffered saline used in

Table 5 Qualitative associations of metal species generation rates with observed O_3

Process/gas	O_3 (ppb)	Cr^{6+}/m^a	Mn total/m^a	Mn^{2+}/m^a	$Mn^{3+\text{ and }4+}/m^a$
SC He/Ar	Low	Low	High	High	Low
AXS Ar/CO_2	High	High	Med	Low	Med
SC Ar/CO_2	Med	High	High	High	High
AXS Ar/O_2	High	High	Low	Low	Low
PAXS Ar/O_2	Low	Low	Low	Low	Med

^{a} mg per meter of welding wire.

this study. It was significant that there were definite measurable Mn and Ni ions present, since most transition metal phosphates have very small solubility products, and there are millimolar concentrations of monobasic and dibasic phosphates present in PBS.

Ozone is regularly monitored in the chamber where fumes are collected, and a previous study in this laboratory showed a strong positive association of O_3 with hexavalent chromium generation rate.[28] Since this study used 5 different process/gas combinations, and there were so many variations in operating variables, a controlled study of ozone effects on metal generation rates was not possible. Nevertheless, it did appear that some associations were present. There was a general negative association of total Mn, the Mn^{2+} fraction, and the (Mn^{3+} and Mn^{4+}) fraction with ozone, shown in Fig. 3.

The leftmost observations in Fig. 3 seemed to differ from the prevailing trend of decreasing Mn in all 3 categories with increasing O_3; these were the He/Ar SC fumes. There were several aspects of this process that may account for the difference. The shield gas was totally inert, unlike the other processes, and had no oxygen content. The shield gas was also present at a significantly higher volumetric flow rate, which would have decreased oxygen diffusion into the area from the atmosphere. Additionally, the He/Ar shield gas had different thermal conductivity; this resulted in a much higher weld temperature, which facilitated the decomposition of O_3.

The previous study in this laboratory linked the He/Ar SC process and the Ar/O_2 pulsed-spray processes with minimal Cr^{6+} generation rates.[28] The results of this study showed high relative Mn^{2+} and total Mn associated with the He/Ar SC process, along with a high relative $Mn^{3+}$and Mn^{4+} generation rate. In contrast, the PAXS process had relatively reduced total Mn and Mn^{2+}, with its Mn^{3+}plus Mn^{4+}generation rate in the middle of the group. Qualitative associations of metal fraction generation rates and observed O_3 levels are shown in Table 5.

In conclusion, it is evident that multiple Mn forms are present in welding fumes, and the proportions of those forms vary with the process. None of the common oxides of Mn could be excluded from consideration as being present in the welding fumes studied, and there was some bioaccessible Mn^{2+} present in all of the fumes examined in this study at typical biological pH values. Once the crucial question of what Mn forms are causative for manganism can be established through further toxicologic studies, improved strategies for Mn-exposure control and reduction can be devised. This study was able to rank five GMAW processes for generation rates of total Mn, Mn^{2+} forms, and $Mn^{3+\text{ and }4+}$ fractions, which may allow selection of welding processes that will minimize or eliminate Mn species that pose the highest risks to welders. The pulsed axial spray method studied had the favorable characteristics of low generation rates of fume, all Mn species, and hexavalent chromium.

Disclaimer

The findings and conclusions in this paper are those of the author and do not necessarily represent the views of the National Institute for Occupational Safety and Health. The mention of any company names or products does not imply an endorsement by NIOSH or the Centers for Disease Control and Prevention, nor does it imply that alternative products are unavailable, or unable to be substituted after appropriate evaluation.

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