Arc Welding Health Effects, Fume Formation Mechanisms, and Characterization Methods

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1. Introduction

Welding fume health effects, fume formation, and characterization are reviewed. The applicability of several collection and characterization methods is discussed. Detailed work on Flux-Cored Arc Welding (FCAW) consumables is presented along with current trends in welding fume particle characterization.

2. Health effects of welding fume exposure

Worker exposure to welding fume is most often associated with acute and chronic lung damage, but there are a number of other health concerns. While exposure to specific gases and metals are associated with certain disease outcomes (such as hexavalent chrome and lung cancer), health effects have also been well documented for total welding fume exposure.

2.1 Routes of exposure

Workers can be exposed by inhaling, ingesting, and coming into skin contact with the fume. All three can be important contributors to disease outcome. Inhalation is the primary, but not only, route of exposure. Welding worker exposures are usually measured in the breathing zone. To evaluate actual exposure, the filter or other sampling media should be placed under the welding helmet (sample adapters are available). As the worker lifts up and puts down the helmet, the device collects a more representative sample. Particle size affects respirability, but virtually all welding fume is in the respirable range. However, it's important to note that the mass collected in typical exposure measurements is not all metal fume. A study found that worker welding fume exposure was 25-55% of the mass collected was metal fume, with the balance of the metal mass collected was due grinding and spattering (Linden & Surakka, 2009).

Workers can also be exposed to welding-related metals through ingestion and skin contact. This needs to be taken into account when evaluating worker exposure as welders eating with dirty hands or eating or drinking contaminated food/liquids can ingest a significant dose. This route is important because lung cancer has been associated with human consumption of drinking water containing high levels of arsenic and chromium. Additionally, a number of metals (including beryllium, chromium and cobalt), can directly affect the skin (irritation and allergic impacts) or be absorbed through the skin and cause

lung damage and other health effects. Skin absorption is enhanced by small particle size and by cuts or other damage to the skin. Surface wipe sampling has been used to evaluate fume distribution in facilities (Nygren, 2006). Biomonitoring of blood and urine can be used to evaluate total exposures.

2.2 Acute health effects

Short term exposures to welding fumes can cause shortness of breath, irritation to eye, nose and throat, and other nonspecific effects such as headache and nausea. These effects are similar to those from exposures to just ozone and/or nitrogen dioxide, important components of welding fumes, but metal fume components also contribute to lung effects (Antonini et al, 2004).

Welding-related asthma, which has been related in the past to fluoride exposures, can also be seen in non-fluoride aluminum welding exposures (Vandenplas et al, 1998). Metal Fume Fever, defined in one study as "having at least two symptoms of fever, feelings of flu, general malaise, chills, dry cough, metallic taste, and shortness of breath, occurring at the beginning of the working week, 3-10 hours after exposure to welding fumes", may also be an indicator of welding-related asthma (El-Zein et al, 2003). In addition to fluoride and aluminum, it is thought that chromium, nickel and/or molybdenum are some welding fume components that may contribute to asthma (Hannu et al, 2007).

There is some suggestion that Manual Metal Arc welding may result in acute decreased lung function compared to other processes (Leonard et al, 2010). Generation of Reactive Oxygen Species (ROS) is theorized as one mechanism for welding fume acute adverse health effects, (Taylor et al, 2003) with stainless steels containing chrome and nickel producing more reactive oxygen species (ROS) than mild steel (Leonard et al, 2010).

2.3 Chronic health effects

Primary concerns with chronic exposures include chronic bronchitis (a component lf COPD), and lung cancer (discussed in more detail in chromium section) (Christensen et al, 2008). Welding fume exposures have also been associated with:

- Susceptibility to infections (Palmer et al, 2009).
- Decrease in semen quality and other adverse reproductive effects (welding-related heat and electromagnetic field exposures may also be contributors) (Meeker et al, 2008).
- Sino-nasal cancer (d'Errico et al, 2009).
- Sarcoid-like (immune response) lung disease (Kelleher et al, 2000).
- Peripheral Artery Disease, particularly cadmium (Navas-Acien, 2005).
- Cardiotoxicity (Fang et al, 2010)

A potential mechanism for cardiovascular disease, acute systemic inflammatory response, has been found in welding-exposed workers (Kim et al, 2005). Siderosis, once thought to be an iron fume related "benign pneumoconiosis" without health effects, has been associated with pulmonary fibrosis. (McCormick et al, 2008).

Inorganic dust pneumonias: the metal-related parenchymal disorders

Liberating coatings on surfaces being welded (such as the well-known risk of metal fume fever from zinc coating) is an important source of welder exposure. While not a metal exposure, heating polyurethane-containing coatings to as little as 150°C can release free isocyanates, potentially resulting in severe acute lung damage and debilitating respiratory sensitization. This can occur even without visible smoke generation, as even grinding and

power sanding to remove the coatings before welding can be sufficient to release isocyanates.

2.4 Health effects of elements

2.4.1 Manganese

Chronic manganese exposure has long been associated with central nervous system (CNS) effects which are similar in nature to Parkinsonism. There is considerable controversy to whether manganese exposure can cause Parkinsonism itself, or whether Manganism is a separate disease entity. Either way, manganese can cause a degeneration of CNS function that gets progressively worse after symptoms first appear. (American Conference of Governmental Industrial Hygienists, 2011b). Note that Vanadium exposure may also be related to Parkinsonism. (Afeseh Ngwa et al, 2009).

2.4.2 Beryllium

Beryllium is recognized as a known human lung carcinogen (U.S. Department of Health and Human Services, 2011). Workers can become sensitized to beryllium, exhibiting an asymptomatic immune response (Committee on Beryllium Alloy Exposures, 2007). Sensitization can lead to chronic beryllium disease, a granulomatous disease primarily affecting the lungs. Beryllium contact with skin may play a role in sensitization, so this should be considered in addition to fume levels when evaluating and controlling exposure. (Committee on Beryllium Alloy Exposures, 2007)

2.4.3 Cadmium

Cadmium is a known human lung carcinogen (U.S. Department of Health and Human Services, 2011). High short-term exposures can result in chemical pneumonitis (lung symptoms similar to pneumonia). Sometimes an acute overexposure to cadmium may cause death. Chronic exposure can cause kidney damage and osteoporosis. (Bernard, 2008) (Nawrot et al, 2010). Cadmium exposure may also increase the risk of prostate and bladder cancer. (Yi-Chun Chen, 2009) (Kellen et al, 2007)

2.4.4 Chromium

DNA damage in welders has been associated with hexavalent chromium exposure. (Sellappa et al, 2010). This is consistent with the classification of hexavalent chromium as a human lung carcinogen. (U.S. Department of Health and Human Services, 2011) This risk may be independent of smoking. (Halasova, 2005). The chromium valence state appears to be critical, and with water soluble compounds being more carcinogenic. Unfortunately, chromium welding exposures can be difficult to control. An exposure survey by National Institute for Occupational Safety and Health (NIOSH) found "Most operations judged to be moderately difficult to control...involve joining and cutting metals with relatively high chromium content." (Blade, 2007)

2.4.5 Nickel

There is considerable ongoing research on the effects on toxicity of nickel speciation, solubility and particle size. Ni (II), which is water soluble, is recognized by IARC as a "known" human carcinogen causing lung, nasal, and sinus cancers. (IARC, 2011). Nickel metal and other nickel alloy materials are classified as a "possible" human carcinogen by

IARC. However, The US Report on Carcinogens states that metallic Nickel is "reasonably anticipated to be a human carcinogen, and classifies Nickel compounds as known human carcinogens that can cause both lung and nasal cancer (Report on Carcinogens, 2011).

2.4.6 Aluminum

Chronic aluminum exposure is associated with Alzheimer's disease, although concerns have been raised about the strength of the epidemiology studies. (Ferriara, 2008). (Santibáñez, 2007). A recent review identified mechanisms of how aluminum may contribute to the formation of Amyloid proteins in the brain, a marker of Alzheimer's Disease. (Kawahara, 2011).

2.4.7 Other welding-related metal carcinogens

Both lead and lead compounds are also "reasonably anticipated to be human carcinogens" (12th Report on Carcinogens). Arsenic is a recognized human carcinogen, implicated in both lung and bladder cancer (IARC, 12th Report on Carcinogens, Marshall et al, 2007). Antimony is "possibly carcinogenic to humans", but the studies suggested that lung cancer may be associated with the arsenic co-exposures (McCallum, 2005).

2.5 Threshold limit values

The Threshold Limit Values (TLVs(r)), published by the American Conference of Governmental Industrial Hygienists (ACGIH), provide guidance for controlling exposures (Table 1). The TLV for each material has formal documentation that should be reviewed before using a TLV to understand the bases and limitations of the recommended control levels. (American Conference of Governmental Industrial Hygienists, 2011a) A common misunderstanding (perhaps because they are called "Thresholds") is that keeping worker exposures below TLV(r) concentrations will protect all workers against "all" health effects. TLV(s) are based on protecting against "known" health effects, and some workers exposed to sub-TLV(r) concentrations can still experience those known adverse effects (and other unknown effects). TLVs are periodically revised as new information emerges. Using the TLV(r) as a control value without these considerations can put workers at risk.

2.6 Welding fume

Toxic substances produced during welding include heavy metals, ozone, carbon monoxide, carbon dioxide, and nitrogen oxides. Ozone, or O_3, is a strong oxidant that generates reactive oxygen species in tissue, which can cause DNA damage. Ozone is produced within 30 seconds during welding, depending on the arc power. The highest O_3 levels, 195 parts per billion (ppb) occurred during the welding operation (Liu et al, 2007). Welding fume is generated primarily by fusion welding processes, such as arc welding and to a lesser extent laser beam welding. Fume formation as a result of other processes, such as friction welding, a solid state process, are generally very minimal. Welding fume is produced when the filler material or electrode is melted and vaporized in the presence of a high temperature heat source. The combination of the molten metal with the compounds in the flux or electrode coating can cause chemical reactions that can change the composition of the fume particles. Fume particle morphology and composition are therefore a product of the electrode composition and shielding atmosphere. The materials typically found in welding fume include aluminum, beryllium, cadmium oxides, chromium, copper, fluorides, iron oxide,

lead, manganese, molybdenum, nickel, vanadium, and zinc oxides. Welding also produces gases, which can contain carbon monoxide, fluorine, hydrogen fluoride, nitrogen oxide, and ozone. All welding processes produce fume, but most fumes are produced via arc welding process such as Shielded Metal Arc Welding (SMAW), Flux-Cored Arc Welding (FCAW), and Gas Metal Arc Welding (GMAW). High heat from an electric arc that is maintained between the electrode and workpiece is used to melt and fuse the metal at the joint. The heat from the arc vaporizes a portion of the electrode in the air, thereby creating a weld plume.

Substance	Threshold Limit Value-8 Hour Time Weighted Average
Aluminum metal and insoluble compounds	1 mg/m^3
Antimony and compounds, as Sb	0.5 mg/m^3
Arsenic and inorganic arsenic compounds, as As	0.01 mg/m^3 (A1)
Beryllium and compounds as Be	0.00005 mg/m^3 (A1)
Cadmium	0.01 mg/m^3 (A2)
compounds, as Cd	0.002 mg/m^3 (A2)
Chromium and inorganic compounds, as Cr	
Metal and Cr III compounds	0.5 mg/m^3 (A4)
Water-soluble Cr VI compounds	0.05 mg/m^3 (A1)
Insoluble Cr VI compounds	0.01 mg/m^3 (A1)
Cobalt and inorganic compounds, as Co	0.02 mg/m^3 (A3)
Iron Oxide	5 mg/m^3 (A4)
Lead and inorganic lead compounds, as Pb	0.05 mg/m^3 (A3)
Manganese and inorganic compounds, as Mn	0.2 mg/m^3 *
Nickel, as Ni	
Elemental	1.5 mg/m^3 (A5)
Soluble inorganic compounds	0.1 mg/m^3 (A4)
Insoluble inorganic compounds	0.2 mg/m^3 (A1)
Zinc oxide	2 mg/m^3

A1: Confirmed Human Carcinogen
A2: Suspected Human Carcinogen
A3: Confirmed Animal Carcinogen with Unknown Relevance to Humans
A4: Not Classifiable as a Human Carcinogen
A5: Not Suspected as a Human Carcinogen
* ACGIH issued a notice of intended change - TLV may be lowered

Table 1. 2011 Threshold limit values (TLV) for selected metals.

2.6.1 Fume formation mechanisms

There are several mechanisms by which welding fume can originate. More than 90% of the particulates in welding fume is formed by vaporization of the electrode filler metal in addition to the core and coatings (Brown, 1997). Particles form when the metal vapor condenses. About 1% of the electrode condenses into metal oxide nanoparticles which

aggregate together to form particle agglomerates (Haider, 1999). Welding fume can be present in different morphologies. Individual spherical particles less than 20 nm are formed by vapor condensation, while aggregates of 20 nm particles are formed by the collision of primary particles. Welding fume particle size can be divided into three groups: ultrafine ($0.01<d<0.1\mu m$), fine ($0.1<d<2.5\mu m$), and coarse ($d>2.5\mu m$) (Jenkins & Eager, 2003).

Inert atmospheres, such as those used in GTAW, facilitate fume formation through vaporization and condensation of elemental material with some light oxidation. Fume formed from FCAW and SMAW results from vaporization, condensation, and subsequent oxidation of elemental and lower oxide species, and the vaporization/condensation of oxide and fluoride flux species and compounds. The chemical composition of fume is, therefore, highly dependent on flux composition since a significant amount of low melting point components are contained within the flux and wind up in the fume particles themselves (Heille & Hill, 1975). Micro and nano-particles of fume are comprised of metal oxides and unoxidized metals and compounds, such as fluorides and chlorides (Konarski et al, 2003). There are five main forms that the metal from the electrode can assume. These include metal droplet, metal vapor, primary metal oxides, volatile element vapor, and volatile metal oxides.

Figure 1 shows the various methods of fume formation. Metal alloy droplet expulsion occurs when heating of the liquid metal occurs rapidly. What results is small droplets being forced off of the parent metal droplet. When this metal droplet cools and solidifies outside the presence of oxygen, as in an inert argon or helium atmosphere, mostly metallic particles with a slight oxide layer will occur. In cases where inert gas shielding is not used, such as with SMAW or self-shielded FCAW, the liquid droplet is in direct contact with oxygen and will readily oxidize. That the welding process require flux or an electrode coating is not a prerequisite for oxidation. For inert processes, such as GMAW or GTAW, oxygen may be incorporated from the surrounding atmosphere or may be an inherent component in the gas mixture, as in Ar-O_2 mixtures or even Ar-CO_2 mixtures. If heating of the liquid metal is sufficient, vaporization of the metal will occur. If this metal vapor condenses in the presence of oxygen then primary metal oxides can form, the composition of which depends on the metal composition. This type of fume formation is referred to as unfractionated (Gray et al, 1982). In some cases volatile elements within the liquid metal can cause selective evaporation of these elements. Selective evaporation occurs in elements that have the highest vapor pressure and the lowest vaporization temperatures. Elements with higher vapor pressure are more prevalent in fume, and thus produce higher amounts of fume (Kobayashi et al, 1983). High vapor pressures for manganese and iron explain why oxides that contain these two elements are formed by the vaporization method of fume formation. The main steps or phases in fume formation are listed below:

- Metal droplet expulsion
- Vaporization
- Condensation
- Oxidation (fractionated and unfractionated)
- Agglomeration

These aerosols are formed primarily through the nucleation of vapors followed by competing growth mechanisms such as condensation and coagulation. High temperature metal vapors transform into primary particles via homogeneous nucleation. Condensation increases particle growth due to added metal vapors. Coagulation then results in agglomeration through particle collisions. (Zimmer, 2002).

2.7 Fume characterization

Fume characterization is generally utilized to determine the composition, structure, size, and distribution of welding fume so that permissible exposure levels can be determined. It is also used to determine how the welding fume behaves in the industrial environment. Since the chemical composition of the welding consumable controls what kinds of materials and compounds are released in the fume particles, it is sometimes possible to predict whether hexavalent chromium will form in any appreciable amount, or whether certain oxides will form that may form that could be deleterious to the welder's health. Figure 2 shows how Mn and Cr content in fume varies with consumable composition. The characterization of welding fume depends on what the investigator hopes to determine. Some forms of characterization are rudimentary and require a fume hood and glass fiber filters, as with fume generation rate collections, while others may require precision collection techniques

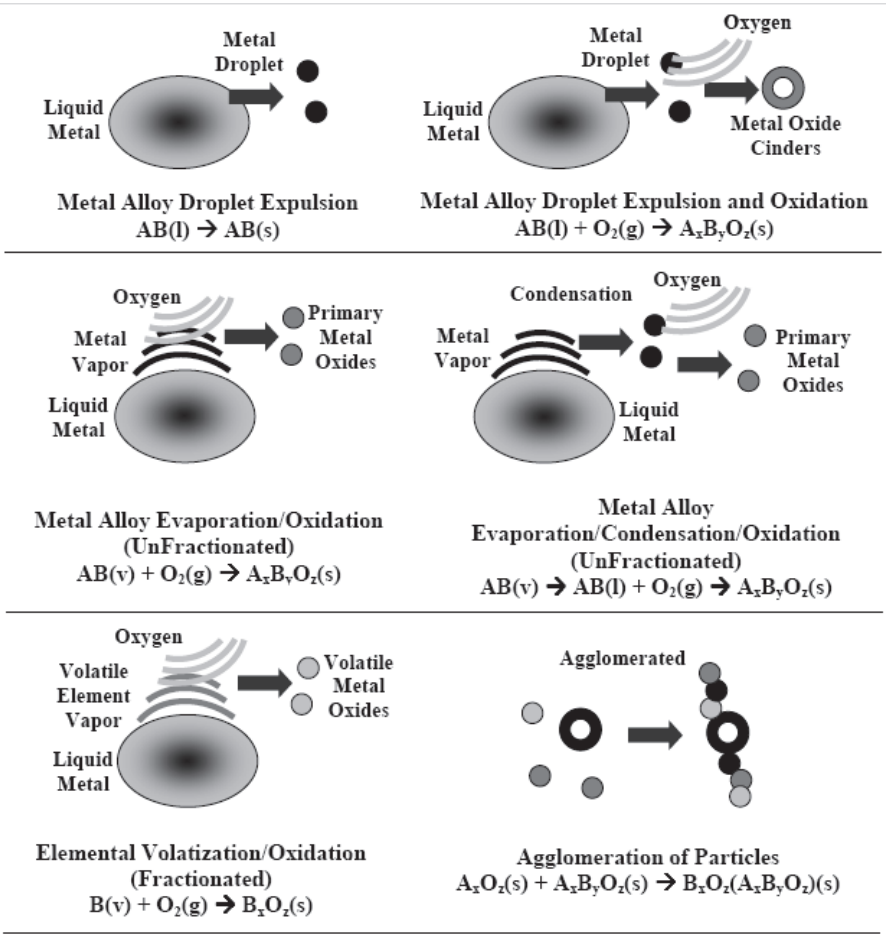

Fig. 1. Fume formation mechanisms. (Gray et al, 1982).

in concert with the latest in advanced characterization technology, such as electrical low pressure impactors and secondary ion mass spectrometers, respectively. Fume characterization can be broken down into two main categories: physical and chemical characterization. Due to the complexity and wide range of fume particles present in a typical weld plume, several techniques may be required to fully characterize the fume, as indicated in Table 2. This may, in turn, require several different fume collection techniques in order to identify different particles based on their size and morphology.

2.7.1 Physical characterization

The physical aspect of fume characterization includes such metrics as mass and number distribution and fume generation rate, which is also referred to as fume formation rate. Mass and number distributions can be quantified using cascading impactors or electrical low pressure impactors. The goal of physical characterization is to determine mass, number, weight, and fume generation rate. Also, the morphology of the fume, which is quantified by analyzing the size and shape of the fume particles, is included in this category.

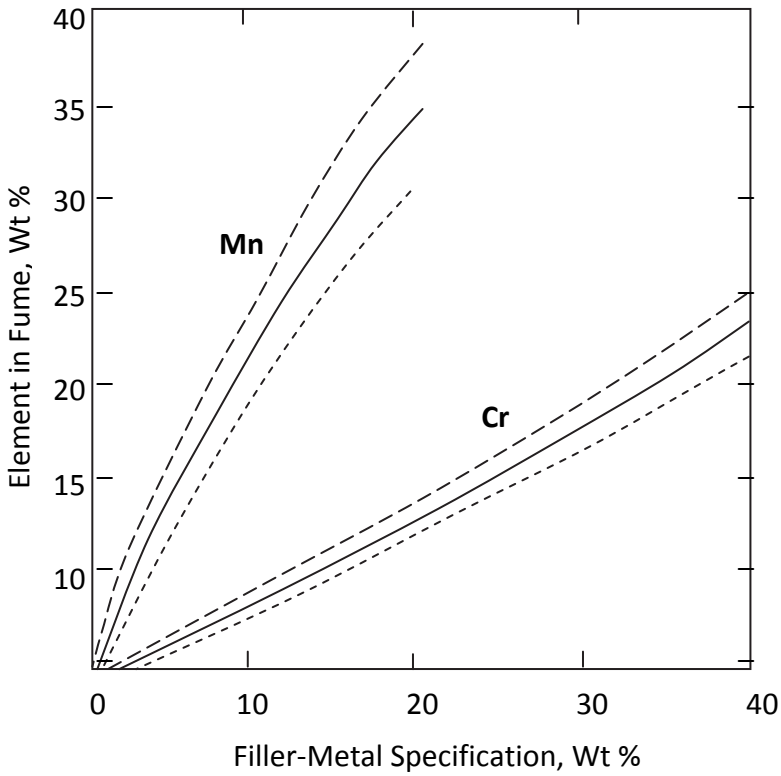

Fig. 2. Mn and Cr content in SMAW fume as a function of consumable composition (ACGIH, 2002).

The fume generation rate (FGR), sometimes referred to as fume formation rate (FFR), of a consumable is measured by collecting fume inside a fume hood, such as those designed by AWS standards. The total weight of the fume is determined by subtracting the weight of the filter from the final weight (with fume attached to the filter). Fume generation rate is generally determined using ANSI/AWS F1.2 method. The basic design of the fume hood used in this method is shown in Figure 3. Transfer mode can have an effect on fume formation rate. It has been demonstrated, using FCAW, that the surface tension transfer (STT) mode reduced the fume generation rate by 40-50% compared to continuous wave current mode. This reduction in fume formation was directly related to the amount of heat input in the electrode. The fume generation rate rises gradually as voltage and wire feed speed increased as the transfer mode changes from short-circuit to globular (Srinivasan & Balasubramanian, 2011).

Different shielding gas mixtures can be used with the GMAW process, which in turn, has an effect on fume generation rate. In Ar-based mixtures, increasing CO_2 had a greater impact than raising O_2. When O_2 was increased in ternary mixtures, the fume generation rate increased for Ar-5%CO_2, but not with Ar-12%CO_2. CO_2 additions in Ar-based shielding gases. A 100%CO_2 mixture produced the highest fume generation rate due to the globular transfer mode and increased spatter. Shielding gas mixture does not seem to have an effect on fume particle composition as the particles in all cases were characterized as $(Fe,Mn)_3O_4$ (Carpenter et al, 2009).

Fume generation rates rise as power is increased when the short-circuit transfer mode is implemented. Fume generation rates peak during the globular transfer mode and then drop as the transfer mode shifts to the spray type. Streaming transfer causes FGR to increase further (Quimby & Ulrich, 1999). Fume generation rates tend to increase with heat input for a given electrode. Fume generation rates also increase as the cross-sectional area of the electrode increases. Fume generation rates (FGR) and concentrations of total chromium and hexavalent chromium have been quantified for stainless steel FCAW electrodes using methods recommended by the American Welding Society, ICP-MS (NIOSH Method 7300) and ion chromatography (modified NIOSH Method 7604), respectively. The FGRs ranged from 189-344, 389-698, and 682-1157 mg/min at low, optimal, and high heat input, respectively. The ranges of total chromium FGR were 3.83-8.27, 12.75-37.25, and 38.79-76.46 mg/min at low, optimal, and high heat input, respectively. The hexavalent chromium range was 0.46-2.89, 0.76-6.28, and 1.70-11.21 mg/min at low, optimal, and high heat input, respectively. FGR, total chromium, and hexavalent chromium all increase with weld heat input (Yoon et al, 2003).

Gravimetric impactors and low pressure impactors can be used to collect fume used to quantify the mass distribution of the fume. The mass distribution of fume generated by a welding consumable is typically determined by collecting fume on an aluminum or polymeric substrate, whereby the weight of the fume is determined by weighing the substrate before and after the collection process. The mass of the fume is determined by subtracting the initial weight of the substrate or filter. Similarly to mass distribution an impactor is used to collect the fume used for the quantification of the number distribution. The impactors used can be gravimetric or low pressure, but they will generally have some sort of particle counting system incorporated into the design. In an electrical low pressure impactor, or ELPI, the particles drawn into the unit by suction are positively charged by the instrument. As these particles contact the electrometers, the system counts each individual particle so that a number distribution, from the ultrafines to the coarse particles, can be counted.

Characterization Method	Size Range (micron)	Detection Limit	Comments
Size Distributions			
Impactors	0.1 - 20		
Aerodyamic Particle Sizer	0.1 - 25		
SEM	0.5 - 50		
TEM	0.001 - 1		
Elemental Composition			
X-ray fluorescence (XRF)	bulk	100 ppm	*z > 10
Atomic absorption spectroscopy	bulk	10 ppm	z > 10
SEM-XEDS	1 - 50	0.10%	z > 10
Wavelength dispersive spectroscopy (WDS)	1 - 50	0.10%	z > 4
TEM-XEDS	0.01 - 0.5	0.10%	z > 5
Secondary ion mass spectroscopy (SIMS)	> 5	10 ppm	light elements
Auger electron spectroscopy (AES)	> 0.1	0.10%	z > 3
X-ray photoelectron spectroscopy (XPS)	> 5	0.10%	
Chemical Speciation			
X-ray diffraction (XRD)	bulk		
X-ray photoelectron spectroscopy (XPS)	bulk		
TEM Selected area diffraction (SAD)	0.3		

Table 2. Characterization methods used for analyzing welding fume particles (Jenkins & Eager, 2005b).

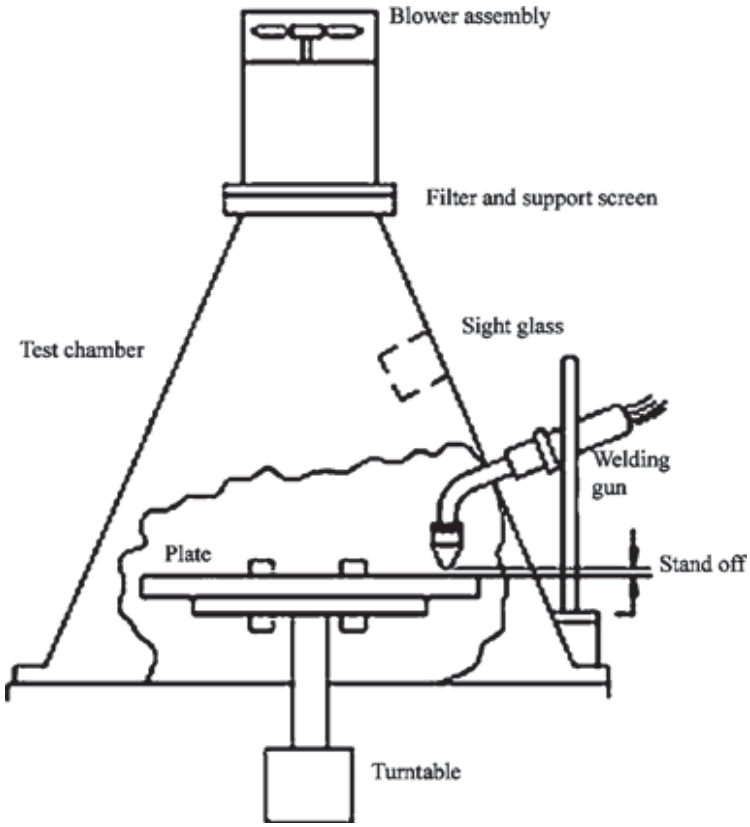

Fig. 3. Fume Hood Assembly (Srinivasan & Balasubramanian, 2011).

Cascade impactors, as shown in Figure 4, can be used to separate fume particles so as to determine their size distribution. The particle size distribution of GMAW fume typically consists of particle agglomerates smaller than one micrometer, meaning most of the fume is respirable. Less than 10% of the fume by weight can be microspatter. FCAW fume containes about 30% by weight of microspatter. This suggests that a smaller fraction of the FCAW fume is respirable compared to GMAW fume (Jenkins et al, 2005). There is a link between spatter and fume in arc welding. Spatter does not significantly contribute to the total amount of fume formed during arc welding. It is postulated that the proportional increase of fume and spatter formation is caused by the welding process variables (Jenkins & Eager, 2005a). Fume particle size distributions ($dN/dlogd_p$) can aslo be measured using a scanning mobility particle sizer (Zimmer, 2002).

Particle number distributions showed that E6010 and E7018 consumables produced fume where 95% of the particles were smaller in diameter than 0.3 um. For E308-16, 95% of the fume consisted of particles that were less than 0.6 µm in diameter. Most of the mass of the fume particles was larger than the respirable size range (>0.1 um). The mass of particles in the ultrafine range represented less than 2% of the total mass of the fume (Sowards et al,

2008). The number and mass distributions are shown for a series of FCAW consumables in Figure 5. Morphological analysis of particles via Scanning Electron Microscopy (SEM) can be used to reveal particle structures: spherical, irregular, and agglomerate (Figure 6). Another type of particle, rectangular, is generally present when magnesium is present. It is inferred that, based on X-Ray diffraction (XRD) results, the particles are MgO.

Exposure to welding fume can be quantified based on surface area and number concentration. Different measurement equipment can be used to characterize the total particle number concentration. These may consist of condensation particle counters or CPC, scanning mobility particle size or SMPS, and electrical low pressure impactor or ELPI. The CPC device can identify particle emission sources. The range of ultrafine particle number concentration can be detected by SMPS and ELPI. The ELPI is useful in that ultrafine sizes can be collected for further chemical analysis techniques. The specific surface area of the aerosols can be calculated using gas adsorption analysis, however ultrafine particles cannot be distinguished from particles with non-ultrafine sizes (Brouwer et al, 2004).

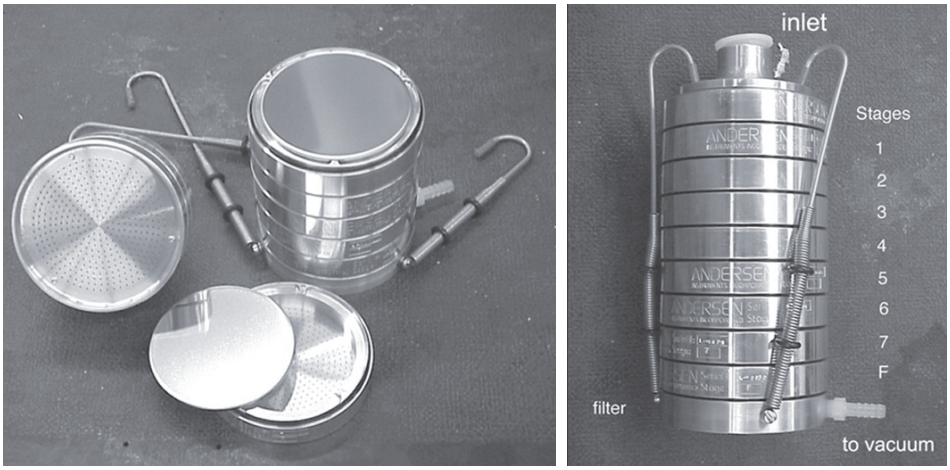

Fig. 4. Andersen Impactor as used by Jenkins. (Jenkins et al, 2005).

2.7.2 Chemical characterization

The other category of fume characterization is chemical and structural analysis. These include analysis of the chemical composition and crystal structure of fume particles. It is also concerned with the variation in composition with depth from the outer surfaces of the particles, as in X-Ray Photoelectron Spectroscopy or with Secondary Ion Mass Spectrometry. The crystalline phases present in fume can be identified with X-Ray diffraction (XRD) for fume collected in bulk, as in a fume hood. To identify crystalline compounds in individual particles, Transmission Electron Microscopy is generally performed. Particles are collected on a carbon-coated copper or gold grid and analyzed individually by selected area diffraction (SAD). Chemical composition can also be estimated in the TEM using X-Ray energy dispersive spectroscopy (XEDS).

X-Ray Flourescence and Wavelength Dispersive Spectroscopy can be used to determine stoichiometry and light elements, respectively. To determine elemental composition and stoichiometry, X-Ray Fluorescence can be implemented. This technique uses high-energy X-

rays to bombard a material. Upon bombardment, the material emits fluorescent X-rays. The characteristic X-ray radiation is detected by a Si(Li) detector. The amount of soluble hexavalent chromium, or Cr(VI), can be measured using ISO3613. Total chromium is determined using Inductively coupled plasma mass spectrometry or ICP-MS. This technique can also be used to determine the concentration of metals and non-metals in fume.

Various chemical analysis techniques can be implemented to characterize welding fume particles. The typical method of analyzing the elemental composition of welding fume is by the molar fraction of the metal cations, which can be done with SEM-XEDS and TEM-XEDS techniques. XRD is well suited for determining the phase composition of the welding fume. Welding fume collected from the GMAW process was predominately magnetite where approximately 10% of the cations were Mn. Welding fume collected from the SMAW process contains both a complex alkali-alkali earth fluoride phase and an oxide spinel phase. The metal cation fraction of the SMAW fume was 27% Fe, 10% Mn, 10% S, 28% K, and 25% Ca (Jenkins & Eager, 2005b).

Chemical analysis can be conducted with multiple techniques, which include energy-dispersive X-ray fluorescence spectroscopy (EDXRF), micro-Raman spectroscopy (MRS), and electron probe microanalysis (EPMA). In the fine fractions (0.25-0.5 µm), particles of irregular shape are rich in Fe, Si, Na, and C. In the 0.5-2.0um fractions, the particles are spherical with various types of Fe-rich particles that contain either Si, Mn, or both. MRS showed the presence of Fe-containing compounds such as hematite and goethite in all size fractions (Worobiec et al, 2007).

Changes in composition can have a drastic effect on fume composition. Fume from wires containing 1% Zn contained far less Cr(VI) than those produced by the wires that had no Zn. In addition, the use of 18V as opposed to 21V reduced the amount of Cr(VI) in the fume, most likely due to the lower FGR associated with a lower voltage (Dennis et al, 1996).

Previous work showed that reduction of sodium and potassium in SMAW led to reductions in Cr(VI) concentrations in fume as well as a reduction in fume generation rate. Lithium was used to replace potassium in a self-shielded FCAW electrode. This resulted in the reduction of Cr(VI) and fume generation rate. Another wire was made with 1% Zn resulted in reduction in Cr(VI). This wire resulted in greater than 98% reduction in Cr(VI) compared to the control wire when the shielding gas contained no oxygen. In the presence of oxygen, the 1% Zn increased the Cr(VI) generation rate higher than the control electrode. This study really underlined the importance of proper shielding gas usage (Dennis et al, 2002).

A colorimetric method for extracting and measuring manganese in welding fume was developed. It utilized ultrasonic extraction with an acidic hydrogen peroxide solution to extract welding fume collected on polyvinyl chloride filters. Absorbance measurements were made using a portable spectrophotometer. The method detection limit was 5.2 ug filter-1, while the limit of quantification was 17 ug filter-1. When the results are above the limit of quantification, the manganese masses are equivalent to those measured by the International Organization for Standardization Method 15202-2, which uses a strong acid digestion along with analysis by inductively coupled plasma optical emission spectrometry (Marcy & Drake).

One study utilized several characterization techniques to quantify number distribution, mass distribution, composition, structure, and morphology. FGR was dependent on heat input. XRD showed that flux composition had a profound effect on the phase structure of the fume. XRD results for common consumables include the following: E6010 (Fe_3O_4 or

magnetite. Peak shifts suggest that Mn and Si substituted for Fe in the Fe_3O_4 structure. E7018: contained additional peaks for NaF and CaF_2. XRD of E308-16 showed Fe_3O_4 and K_2MO_4, where M accounts for Fe, Mn, Ni, and Cr, and NaF. (Sowards et al, 2008)

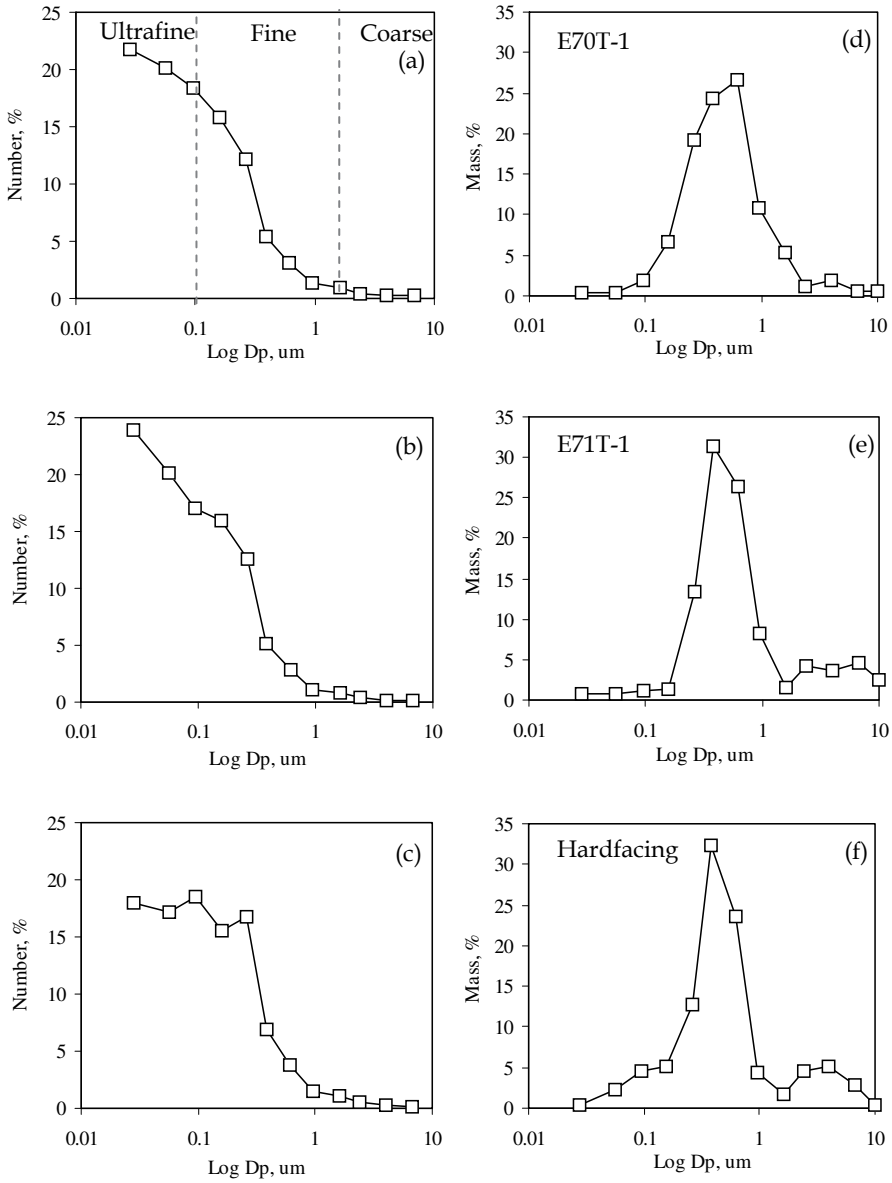

Fig. 5. Number (left) and Mass (right) distributions for FCAW fume.

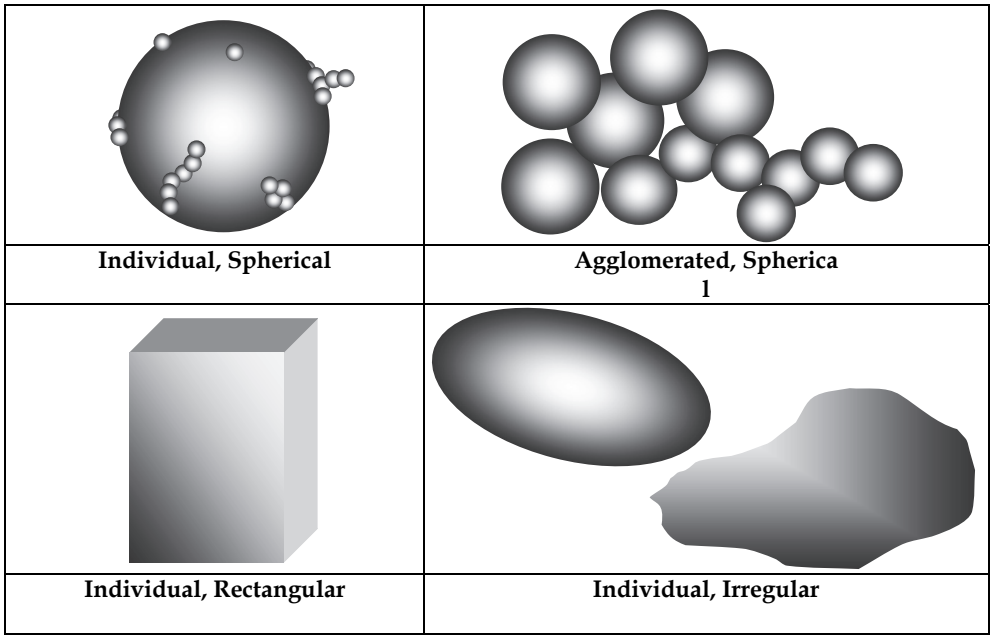

Fig. 6. General forms of fume morphology found in welding plumes.

Fume particles generated by SMAW can range in size from several nm to several µm. Therefore, multiple imaging and chemical analysis techniques were used to characterize them. SEM, TEM, and HR-TEM were used to characterize individual and bulk fume on each ELPI stage. SEM was used to characterize fume particles larger than 0.3 µm. The largest percentage of particles on all stages of the ELPI were agglomerates of spherical particles. Fume particles agglomerate together due to either charging or sintering. TEM and HR-TEM were used to characterize nano-sized particles. Most of the ultrafine particles had a crystalline structure with some having a core-shell morphology. Chemical analysis was done mainly with XEDS (both SEM and TEM) and XPS techniques. SEM-XEDS was used to analyze particles larger than 0.3 µm, while TEM-XEDS was used to analyze particles lower than 0.3 µm. TEM SAD showed that the ultrafine particles were predominantly meta oxides of the $(M,Fe)_3O_4$ type, where M stands for metals such as Mn and Cr that may substitute in the magnetite lattice. XPS confirmed the core-shell morphology by partial depth profiling and revealed the valence states for Fe and Mn as +2 and +3 as they are found mainly in the $(M,Fe)_3O_4$ compound. (Sowards et al, 2010) An XRD spectrum for E70T1-1 is shown in Figure 7. The XRD spectrum is used to show all of the crystalline phases or compounds present I the fume. TEM results show phase identification of individual particles and agglomerates in Table 3 for a series of FCAW consumables.

Secondary Ion Mass Spectrometry can be used to determine the elemental, isotopic, or molecular composition at the surface of the fume particles. Welding fume particles can be analyzed using low energy ion erosion. This can expose differences in fume particle structure and morphology. Fume particles can exhibit a core-shell morphology, which can be revealed using the low energy ion erosion technique (Figure 8). Differences in the process can have an effect on the chemical structure of the particles. For instance, particles

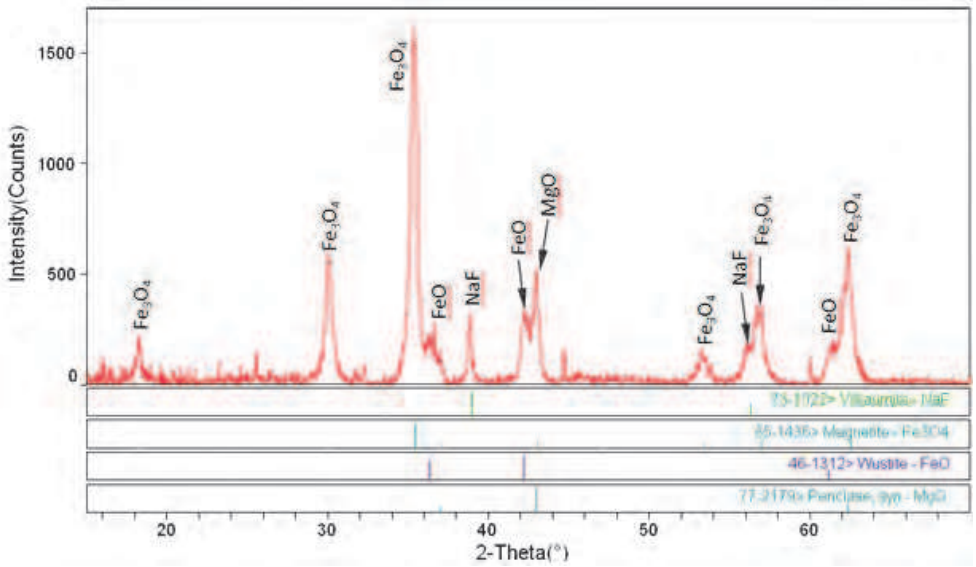

Fig. 7. XRD spectrum for E71T-1 fume.

formed during EBW contain a shell that is enriched in oxygen, fluorine, chlorine, and potassium, where the core is composed mainly of iron, chromium, and manganese. The GTAW particles are more oxidized than the EBW particles. The shells of the GTAW particles are composed mainly of fluorine and chlorine. The SMAW particles are more heavily oxidized than the other two processes. The shells of the particles produced with SMAW are rich in chlorides, fluorides, and potassium while the core is composed of iron, chromium, and manganese oxides. The differences in the shell composition are attributed to differences in atmosphere. Where the EBW process uses low pressure gases, the GTAW process uses an argon shield, and SMAW uses TiO_2 flux vapors (Konarski et al, 2003).

Sequential leaching is a method used to extract Ni and Mn species from welding fumes. Welding fumes were sampled with fixed-point sampling and the use of Higgins-Dewell cyclones. Ammonium citrate was used to dissolve soluble Ni, while a 50:1 methanol-bromine solution was used to dissolve metallic Ni. A 0.01 M ammonium acetate was used for soluble Mn, while a 25% acetic acid was used to dissolve Mn^0 and Mn^{2+}. A 0.5% hydroxylammonium chloride in 25% acetic acid was used for Mn^{3+} and Mn^{4+}. Insoluble Ni and Mn were determined after microwave-assisted digestion with concentrated HNO_3, HCl, and HF. Samples were analyzed by ICP quadruple mass spectrometry and ICP atomic emission spectrometry. Different welding processes and consumables were tested using the aforementioned techniques. The highest quantity of Mn in GMAW fumes was insoluble Mn where corrosion resistant steel was 46% and unalloyed steel was 35%. MMAW fumes contained mainly soluble Mn, Mn^0, and Mn^{2+}, while corrosion resistant steel contained Mn^{3+} and unalloyed steel contained Mn4+. GMAW fumes were rich in oxidic Ni, while the Ni compounds generated by MMAW are of soluble form. XRD was conducted and revealed that GMAW fumes were magnetite ($FeFe_2O_4$). MMAW fume contained $KCaF_3$-CaF_2 with some magnetite and jakobsite ($MnFe_2O_4$). (Berlinger et al, 2009)

MMAW of chromium nickel steel or high-alloyed steel generate chromium (VI) compounds such as chromium trioxide and chromates. Nickel oxides are generated when welding nickel and nickel base alloys during MIG welding. These include NiO, NiO_2, and Ni_2O_3. (Fachausschuss, 2008) Most aluminum welding operations involve the use of unalloyed or partially alloyed aluminum consumables. Ozone is produced by the effect of UV light emanated by the arc on the air. The use of these consumables produces fume that is mostly comprised of aluminum oxide. Aluminum-silicon and aluminum-magnesium alloys are the most commonly used aluminum alloy consumables.

Consumable	**Type**	**Size Range, nm**	**Compounds**
E70T-1	Agglomerates, spherical	30-230	$(Fe,Mn)_3O_4$ and SiO_2
E71T-1	Spherical, some square MgO	30-120	$(Mn,Fe)_3O_4$; MgO; small MgO particles
Hardfacing	Agglomerates, spherical	a) 30-70 b) 70-150	a) Al_2O_3, MgO and CaF_2 b) MgO and $(Mn,Fe)_3O_4$

Table 3. TEM results for fume particle type, size range, and compound as identified by SAD.

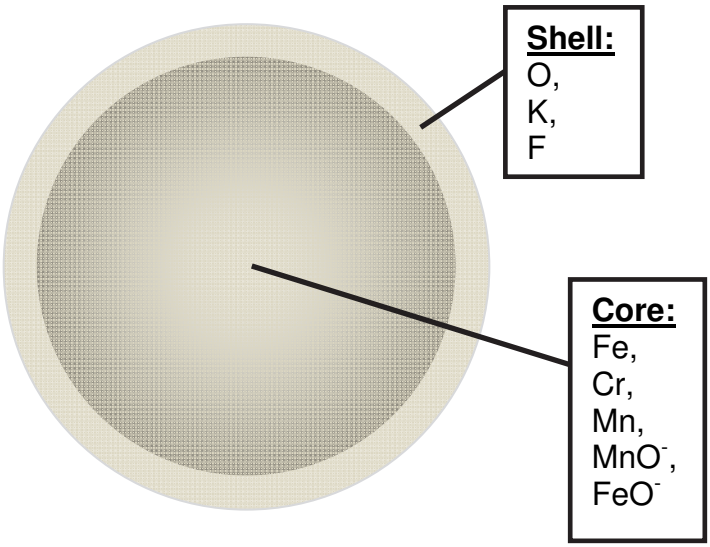

Fig. 8. Core-shell morphology of SMAW fume particles. (Konarski et al, 2003).

Proper ventilation systems: hoods, roof vents, high-speed intake and exhaust fans are used to capture fumes and gases in the direct vicinity of the welder. To capture welding fumes in large areas, using downdraft worktables is used. Outdoor fans can be used to direct plumes away from field workers. Working upwind from the welding operation can also decrease exposure. Respirators can be used to further protect the welder from exposure. These devices should be certified by NIOSH and practice or use of said device should adhere to OSHA's Respiratory Protection Standard. Proper training should be implemented to teach

welders and non-welders alike of the dangers of welding fume exposure. The correct use of respirators, avoidance of weld plumes, implementation of engineering controls that minimize exposure, and other safety practices that mitigate exposure levels should be implemented in any workplace. In addition, posting warnings in welding areas is a good way to inform employees and visitors of the potential dangers. Familiarity with ANSI Z49.1, Safety in Welding, Cutting, and Allied Processes should be readily available at the facility. Industrial hygiene monitoring plans, such as area monitors and personnel should be in place or available in all welding work areas and industrial hygienists should be present to monitor welders for exposures and potential exposures. To reduce welding fumes it is advisable to sue low-fume welding rodes and alternative welding methods, such as SMAW, which generates lower amounts of fume than FCAW.

3. Conclusion

Based on the review of the literature, the health effects associated with welding warrant the thorough analysis of aerosol particles that are produced as a byproduct of the process. Many techniques, both physical and chemical in scope, are available that adequately characterize the fume particles. Physical characterization methods, such as mass or number distributions, as well as particle sizers, can be used to determine how much of the welding fume is in the respirable range. Chemical analysis can be used to determine how electrode composition affects fume composition. One of the more complex welding fumes, that which is generated by FCAW consumables, shows that over fifty percent of the fume, by number, is in the respirable range. By mass, nearly ninety percent of the fume is respirable. Fume particle produced via FCAW are typically magnetite, with some manganese substituting in the magnetite lattice. Other compounds form depending on the elements present in the flux.

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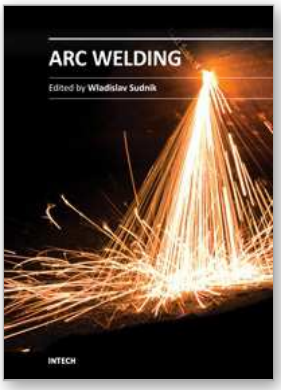

Arc Welding

Edited by Prof. Wladislav Sudnik

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Ever since the invention of arc technology in 1870s and its early use for welding lead during the manufacture of lead-acid batteries, advances in arc welding throughout the twentieth and twenty-first centuries have seen this form of processing applied to a range of industries and progress to become one of the most effective techniques in metals and alloys joining. The objective of this book is to introduce relatively established methodologies and techniques which have been studied, developed and applied in industries or researches. State-of-the-art development aimed at improving technologies will be presented covering topics such as weldability, technology, automation, modelling, and measurement. This book also seeks to provide effective solutions to various applications for engineers and researchers who are interested in arc material processing. This book is divided into 4 independent sections corresponding to recent advances in this field.

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