Effect of Arc Welding Electrode Temperature on Vapor and Fume Composition

N. T. Jenkins, Ph.D.
Massachusetts General Hospital, Charlestown, Massachusetts, USA

P. F. Mendez, Ph.D.
Colorado School of Mines, Golden, Colorado, USA

T. W. Eagar, Sc.D.
Massachusetts Institute of Technology, Cambridge, Massachusetts, USA

Abstract

Welder exposure to potentially toxic compounds in fume can be reduced through the control of the welding process. Such efforts can be improved by better understanding how process parameters affect the elemental composition of welding fume. The vapor emitted from a consumable electrode is the dominant source of arc welding fume; for bare wire electrodes, the metal content of arc welding fume is essentially the same as that of the vapor. Many researchers have measured fume composition by many methods, but only a few have tried to use thermodynamic equilibrium calculations to predict the composition of the vapor that forms the fume. Attempts to do so have been flawed by assumptions that the temperature of the electrode droplet does not vary throughout the droplet, or with welding parameters. The temperature of the droplet surface, not of its bulk, determines the elemental composition of the vapor. Because evaporation is strongly dependent on temperature, a small change in surface temperature will cause a large change in vapor composition. This can be illustrated with a vapor-liquid binary phase diagram. Thus the vapor composition and therefore the fume composition are affected by changes in welding parameters that control droplet surface temperature. For example, because the surface temperature of the electrode droplet during spray mode is less than it is during globular mode, fume generated during spray mode has a greater fraction of volatile metals than fume formed during globular mode.

Fume Composition

Welder exposure to potentially toxic compounds in fume can be reduced through the control of the welding process. Such efforts can be improved by better understanding how process parameters affect the elemental composition of welding fume. Researchers have measured welding fume chemistry by many methods, but only a few have tried to predict the composition of the original vapor from thermodynamic calculations (1). The results of such modeling have been mixed, primarily because of incomplete assumptions about the temperature. The temperature is the primary factor that determines vapor composition (2).

Most fume researchers have assumed a single value for the gas metal arc welding (GMAW) droplet temperature to use in their thermodynamic calculations. Gray, et al., (3) and Podgaetski et al., (4) reported thermodynamic equilibria without explicitly stating the temperature they used. Hewitt & Hirst (5) considered fluxes in their calculations and Buki & Feldman (6) included oxides, but they too did not report the temperature. McAllister & Bosworth (7) assumed droplet temperatures were 1800–2200 K and were the first to include the effect of various shielding gases. Eagar, et al. (8) calculated gaseous equilibria for hexavalent chromium using varied shielding gases, at 2673 K.

None of these researchers considered the change in droplet temperature with time or how it changes with welding parameters. They also equated the surface temperature, which determines the composition of the evolved vapor and the fume formation rate, to the average temperature across the entire electrode droplet. They also did not consider that the surface temperature of the welding droplet during globular transfer was substantially different from that of a droplet during spray transfer (9). This can lead to misleading conclusions.

Electrode Temperature

Fume researchers have used simple approximations for the electrode temperature probably because determining the temperature of a material while welding is difficult. The transitory nature and extreme heat of welding prevents the use of thermocouples; calorimetric methods are also complicated to set up in situ. The use of pyrometric techniques is problematic because the intense radiation from the arc overwhelms the infrared emissions of heated surfaces. Therefore many welding researchers rely on calculations of the weld metal temperatures.

The weld pool temperature is relatively simple to calculate. This has been performed several times, notably by Block-Bolten & Eagar (10) who found that because of evaporative heat losses, an upper limit of 2300K to 2800K exists for the temperature of the weld pool of steel gas tungsten arc welding (GTAW). However, for consumable electrodes in GMAW, the temperature of the welding droplet is more complicated to determine, because of an input of higher energy density, because of a more transitory nature (droplet detachment), and because measurements with which to compare the calculations are harder to obtain. Generally, values for the bulk temperature of the electrode are reported close to 2900K (11).

(It should be noted that for GMAW, welding fume is dominated by evaporation from the electrode rather than from the weld pool. Heile & Hill (12) and Srekanthan (13) both compared the composition of fume collected while GMA welding with an...
Figure 1: Heat transfer through GMAW electrodes is controlled by electrode droplet size (17). Shadowgraphs are from 2%O₂-Ar shielded GMAW mild steel electrode (19).
electrode of a different composition than that of the base plate and both found that the fume composition was determined almost entirely by the electrode. The authors performed a similar study of hexavalent chromium. GMAW fume was collected while welding under spray conditions with E308L stainless steel welding wire on mild steel pipe and on stainless steel pipe at 31V, 175A with a 2%O₂-Ar shielding gas. ER70S-6 mild steel wire, which does not contain chromium, was used to weld at 33 V, 215A on a 304 stainless steel plate, also with spray transfer and with the same shielding gas. Fume was collected at 2.25 L/min for 30 seconds. The concentration of hexavalent chromium in fume created from the mild steel electrode was < 0.001 wt%. For the stainless steel electrode, it was 0.1 wt%, regardless of which base plate was used. Because mild steel does not contain chromium, the source of the hexavalent chromium in the fume must have been the electrode. It is clear that GMAW fume composition is dominated by vaporization from the electrode, not from the weld pool. The reason for this is because the weld pool is much cooler than the electrode.)

Haidar (14–16), using a Cray supercomputer, performed a complete fundamental calculation of electrode droplet temperature and how it changes with time and welding parameters. The use of a supercomputer can be avoided if the droplet size is measured and a semi-empirical model created, like those in papers by Mendez, et al., (17) and Bosworth & Deam (18). A summary of such models can be seen in Figure 1.

Smaller droplets, such as those formed during spray or pulsed transfer, have cooler surface temperatures than do larger droplets, like those from globular transfer, because there is a smaller barrier to heat transfer from the arc spot to the liquid-solid interface of the electrode. (However, smaller droplets may have greater bulk temperatures.) Therefore vapor of a composition enriched in the more volatile elements is evolved and further, less vapor forms. This can be observed in the change in fume composition with welding parameters, such as shielding gas oxidation potential (Figure 2 to Figure 5) or current (Figure 6). Both of these welding parameters change the size of the welding droplet and therefore its vaporization rate. Conditions that create fume containing the greatest fractions of volatile metals (e.g., manganese) are the same that create the smallest electrode droplet. Such conditions also minimize total fume formation. (Thus, efforts to decrease fume formation rates may also increase the fraction of manganese in the fume. Manganese emission rates therefore may or may not change significantly.)

Superheat

Based on an energy balance of a GMAW electrode, the surface temperature of the electrode droplet may exceed the boiling point (17). Haidar (16) also calculated the surface temperature of a mild steel 1.2 mm GMAW electrode at 183A and compared it with the value measured pyrometrically by Villemirot (23) at 160A. Both found that the surface temperature at the tip of the electrode droplet was approximately 3100K. This is very close to, if not above, the boiling point of pure iron (values in the literature include 3025K (16), 3273K (24), 3121K (25)); it is certainly above the vapor-liquid transition for a typical iron alloy used in welding (see Figure 7).

Like other phase changes, boiling can occur through nucleation. Vapor bubbles usually form heterogeneously in crevices of the container that holds the boiling liquid. (Consider a boiling pot of water on a kitchen stove; the bubbles form on the bottom of the pan.) For bubbles to form, superheating must be present in order to overcome the activation energy required to create new surfaces. Because heat is usually added at the solid-liquid interface and lost at the gas-liquid interface, the amount of superheating depends on crevice size where vapor bubbles heterogeneously nucleate (26).

However, when heat is added by a high-energy-density source, i.e. electron condensation in arc welding or laser radiation, the heat input is at the gas-liquid interface. (For an experimental study of surface superheats from laser processing, see Craciun & Craciun (27).) The solid-liquid interface is where heat is lost and is therefore the coolest part of liquid. Thus vapor bubbles will not nucleate at any solid crevices. Instead, the vapor phase must form bubbles completely in the liquid. Another difficulty for forming bubbles when intense heat is introduced at the liquid surface is that only a slender boundary layer will be hot enough for bubbles to nucleate in it. Under globular conditions, a 1.2 mm GMAW electrode droplet will have a thermal boundary layer approximately the size of 1/3 of the droplet (17). If the convective core of the droplet were at the boiling point, the surface temperature of a steel electrode droplet would have to be near 3300K for a bubble smaller than 0.1 mm in diameter to form, according to classical nucleation theory. The surface temperature would naturally have to be much greater than 3300K for even smaller bubbles to form.

Richardson (28) states that classical nucleation predicts homogeneous superheats much greater than what is observed, but this is probably because the experimental measurements were made in liquids heated through the solid-liquid interface where crevices caused heterogeneous nucleation. This is also probably the case for molten steel where vapor bubbles can presumably nucleate heterogeneously at pre-existing bubbles of gas, like carbon monoxide, coming out of solution. If this were the case, it would explain why lower carbon content in steel electrodes is linked with lower fume formation rates (29-32).

When gas-liquid interfaces are heated, cooling by non-nucleate surface evaporation normally prevents superheating. However, with high-energy-density heat sources and where heat loss is physically limited (like with the thin GMAW electrodes), it is possible to inject energy into the system faster than it can be removed by evaporation, as calculated by the Langmuir equation with even the most conservative estimates (33). Note that the Langmuir rate is for evaporation into a vacuum. When surrounded by an inert gas at atmospheric pressure, metal surfaces evaporate more slowly than the Langmuir rate, because the metal vapor must diffuse away from the evaporating surface. Thus evaporative cooling during welding is limited even more than that predicted by the Langmuir rate. If an energy balance is to be maintained, the surface temperature, which controls
Figure 2: Oxidation potential effect on composition (ICPMS) of fume from single-pulse (100 amps for 500 ms without droplet detachment) GMAW of ER308 stainless steel. GTAW fume composition also plotted. (Silicon is minutely present, but not measurable by ICPMS, so molar fractions of smaller magnitude, i.e. nickel, may have error)

Figure 3: Fume composition versus shielding gas oxidation potential in GMAW with 1.2 mm E308 stainless electrode (13).

Figure 4: Electrode droplet period / droplet size versus shielding gas composition in 1.6mm mild steel GMAW for various currents (20).

Figure 5: Fume formation rate versus shielding gas with 1.2 mm mild steel GMAW at 250 amp (12, 21).

Figure 6a: Fume generation rate and the nickel : manganese ratio versus current for argon shielded GMAW with 1.2 mm AWS ER307 Si electrode (22).

Figure 6b: Fume generation rate and the nickel : manganese ratio versus current for argon shielded GMAW with 1.2 mm ER308L Si electrode (22).
vaporization and thus evaporative cooling, must increase until the conditions for balance are met. If the surface temperature exceeds the boiling point, superheating occurs. This causes the formation of vapor bubbles that burst.

The superheat, or amount by which the boiling point is exceeded, will determine the chemical composition of a multicomponent vapor, similar to how the supercooling determines the composition of a condensate of an alloy. See Figure 7, the iron-manganese phase diagram at 0.3 atmospheres (the approximate partial pressure of metal vapor in a GMAW arc (1)). One can see that even a small change in superheat will effect a large change in vapor composition, given the same initial composition of the liquid. This explains how researchers have calculated that the vapor in a mild steel gas metal arc welding arc may be much as half manganese, even though the wire contains less than 2 wt% Mn (30). In Figure 7 it is shown how an increase of a mere 20K causes the vapor composition to decrease from 0.18 mole fraction of manganese to 0.08 when the liquid is initially at 0.015 mole fraction. The difference in droplet surface temperature between spray and globular transfer, or between pulsing and straight current can easily be greater than 100K (16).

![Figure 7: Iron-manganese vapor-liquid phase diagram at 0.3 atmosphere, adapted to show the effect of superheat on vapor composition (25).](image)

This is naturally a simple example of what can become complicated if one considers multicomponent alloys, the effect of halides on metal volatility (34), the presence of surface active elements (35), the effect of a plasma on vaporization (36), or mixing of the metal vapor with the surrounding gas (37).

**Conclusion**

It has been found that GMAW fume created during globular transfer contains less volatile metals than fume created during spray transfer. This is what prompted the proposal of the existence of welding fume that did not form from vapor, but from ejected liquid microdroplets, which would be similar in composition to that of the electrode (38). It has been claimed that globular fume has a greater portion of these coarse “unfractionated” particles and because of this, had a composition closer to the original electrode composition. Although such particles have been found to exist in GMAW fume, they do not form at a rate that significantly affects the overall composition of the fume, which is dominated by particles that condense from vapor (39). In addition, although overall fume formation rates increase, the fraction of coarse particles found in welding fume does not change from spray transfer to globular transfer, meaning the change in composition between the two modes is not caused by the existence of more coarse particles (1). Instead it must be due to a change in the vapor composition, which is caused by a change in surface temperature. Other welding process parameters that change droplet size and temperature, such as pulsing, will presumably also change fume composition accordingly.

It has been shown how sensitive vapor composition is to temperature. Therefore, it is important to use appropriate values for the surface temperature of the liquid metal vapor source that one is trying to model. In this way, welding fume composition can be linked with welding parameters, thus granting welding manufacturers and users predictive capability.

**Acknowledgements**

The funding for this project was provided by a grant from the U.S. Navy, Office of Naval Research.

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