Metal Vapors in Gas Tungsten Arcs: Part II. Theoretical Calculations of Transport Properties

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Theoretical calculations of gas tungsten arc transport properties have revealed that small amounts of low ionization potential elements such as aluminum or calcium do not have as great an effect on the electrical and thermal conductivities as has been previously reported, if the presence of other metal vapors such as iron or manganese is also considered. It is therefore concluded that the effects of minor elements on arc properties may be less important than has previously been believed in explaining the variable penetration often associated with minor element additions to the base metal, and that weld pool convection effects such as surface tension modifications are probably more important. However, the effects of vapors emitted by the tungsten electrode may have a great effect on arc properties, as the shielding gas is otherwise free of contaminants in the upper regions of the arc.

I. INTRODUCTION

The calculation of plasma transport properties can provide valuable information concerning the behavior of the gas tungsten welding arc. The electrical and thermal conductivities of the plasma will determine the arc configuration and, subsequently, the transport of energy to the weldment.\textsuperscript{1,2}

The thermal and electrical conductivities of argon and helium plasmas containing small amounts of iron, calcium, and aluminum vapors were calculated from established plasma physics formulae. Qualitative analysis of the results can lead to a fundamental understanding of the effects of metal vapors on the welding arc. A more rigorous study will involve the solution of the Elenbaas-Heller equation in cylindrical coordinates by the finite element method, with the calculated conductivities as input data. Such an investigation is beyond the scope of this work but will be presented elsewhere.\textsuperscript{3}

Theoretical calculations of plasma transport properties are very approximate due to the complex nature of plasma behavior and inexact knowledge of collision cross-section values. The calculations of various investigators are often in marked disagreement with experimental data and with each other.\textsuperscript{4} However, such calculations can be very helpful in determining the relative effects of compositional variations on the plasma properties, and subsequently on the transport of energy to the weldment.

II. PREVIOUS WORK

A large number of investigators have reported theoretical and experimental data for the transport properties of pure argon or pure helium plasmas.\textsuperscript{5} Investigations regarding mixtures of gases are less numerous.

Glickstein\textsuperscript{1} calculated the thermal and electrical conductivities of argon and helium plasmas with small additions of aluminum vapor. He found that even concentrations as small as 0.01 pct Al will significantly increase the electrical conductivities of the inert gases at low temperatures, particularly in the case of helium. This was attributed to the low ionization potential of aluminum, which results in an increase in the electron density at lower temperatures. The changes in thermal conductivity were less significant, with small increases at low temperatures for that of argon, and little change in that of helium, except at high concentrations and temperatures.

Glickstein substituted these calculated values into a one-dimensional model of the welding arc in order to explain the effects of aluminum on stainless steel welds reported in the literature.\textsuperscript{5} However, Glickstein’s model is inadequate in that it considers only the addition of aluminum to a pure inert gas. This is not the true nature of the welding arc. In practice, an arc on stainless steel will contain not only argon or helium, but also a mixture of iron, manganese, chromium, and other metal vapors.\textsuperscript{5} These elements have ionization potentials which, while not as low as that of aluminum, are much lower than those of the inert gases (see Table I of Part I\textsuperscript{6}). Therefore, it can be expected that the addition of a small amount of Al vapor to the welding arc plasma will have a less noticeable effect than that of aluminum added to the pure inert gas.

Gvozdetskii and Rublevskii\textsuperscript{7,8} calculated the electrical conductivities of helium plasmas containing small amounts of lanthanum and aluminum vapors. Again, it was found that small amounts of these low ionization potential elements produced significant increases in the electrical conductivity. Neither this investigation nor Glickstein’s, however, is revolutionary in its findings. It has long been known that small amounts of low ionization potential material will greatly increase the conductivities of inert gases. The seeding of inert gases with cesium and other alkali metals has been the subject of extensive research in the field of magnetohydrodynamics for many years.\textsuperscript{9} The effects of copper additions to nitrogen have also been investigated in the area of circuit breaker technology.\textsuperscript{10–13}

To the best of the authors’ knowledge, this is the first investigation involving a plasma model which closely approaches the actual environment of the welding arc: an inert gas of high ionization potential containing a small amount of metal vapor of intermediate ionization potential, and the possibility of a smaller amount of low ionization potential material such as aluminum or calcium.
III. THEORY

A. Species Densities

The first step in calculating plasma transport properties is the determination of the plasma composition. The densities of ions, electrons, and neutral atoms are given by Saha's equation:

\[ \frac{n_e n_i}{n_a} = \frac{Z Z_i (2\pi m_k T)^{3/2}}{Z_a \hbar^3} e^{-\frac{V_i}{kT}} \]  

where \( n_e, n_i, \) and \( n_a \) are particle volume densities (m\(^{-3}\)) of electrons, ions, and neutral atoms, respectively.

\( T \) = absolute temperature (K)
\( V \) = ionization potential (J)
\( m_e \) = rest mass of electrons (kg)
\( k \) = Boltzmann's constant (J/K)
\( \hbar \) = Planck's constant (J s)

The internal partition functions, \( Z_e, Z_i, \) and \( Z_a \), are given by:

\[ Z = \sum g_i e^{-\overline{w}_i/RT} \]  

where \( g_i \) is the degeneracy or statistical weight corresponding to the energy level \( u_i \) (in J). For a monatomic gas:

\[ g = 2S + 1 \]

where \( \overline{S} \) is the vector sum of the spin numbers \( S \).

Partition functions were calculated from data given in the NBS tables of atomic energy levels compiled by Moore.18 The degeneracy of electrons is 2.

In calculating the particle densities from Saha's equation the assumptions of quasi-neutrality \( n_e = n_i \), kinetic equilibrium \( T_e = T_i = T_a \), and ideal gas behavior were made. Finkelburg and MacKee16 and Olsen27 have shown these assumptions to be valid for the arc column. For units of \( T \) in K and \( n \) in cm\(^{-3}\), the ideal gas law can be applied thus:

\[ n_e + n_i + n_a = 7.34 \times 10^{21} / T \]  

Total particle densities of binary and ternary component plasmas were calculated by simply combining proportions of the pure plasmas, e.g.,

\[ n_e^T = n_e^{10\text{Fe}} + 0.1n_e^{1\text{Al}} + 0.01n_e^{10\text{Al}} \]  

for an Ar + 10 pct Fe + 1 pct Al plasma, where \( n_e^{10\text{Fe}} \) is the electron density for the pure argon plasma, \( n_e^{1\text{Al}} \) for the pure iron plasma, and \( n_e^{10\text{Al}} \) for the pure aluminum plasma, and \( n_e^T \) is the total electron density of the mixed plasma.

This is a fairly crude approximation. However, our results for binary gas mixtures indicate changes in electrical and thermal conductivities comparable to those reported by Glickstein, particularly in the case of helium. Lieberman performed these calculations for Glickstein using an elegant method of minimizing Gibbs free energy with geometric programming.18 This process is justifiable for plasmas such as SF\(_6\) (for which Liebermann's methods were originally devised) for which stoichiometric relationships exist, but for the welding plasma, for which the metal vapor content can only be estimated, such complications are unnecessary. The goal of this study was to determine the effect of a small amount of aluminum or calcium on the properties of a plasma containing a greater amount of other metal vapors such as iron. For such a purpose, this simple method is adequate. Similar simplifications were adopted by Abdelhakim et al., Shayler and Fang, and Gvozdetskii and Rublevskii.

The calculations were carried out over a temperature range of 500 to 20,000 K. The 20,000 K upper limit was chosen because higher temperatures are not likely to occur in the welding arc, and in order to allow the simplification of disregarding second ionization. Second ionization in argon \( (V_2 = 27.6 \text{ eV}) \) becomes appreciable above this temperature. Since rough calculations show that less than 30 pct of a welding arc plasma need to be ionized in order to conduct the applied current, such second ionization levels are expected to be very rare in welding arcs. Indeed, spectrosopic results confirm this.

B. Electrical Conductivity

The electrical conductivity of the plasma was calculated using a simple formula given by Cambel9 from original work by Chapman and Cowling:

\[ \sigma = \frac{0.532 e^2}{(m_e kT)^{1/2}} \frac{n_e}{n_e Q_e + \sum n_i Q_i} \]

where \( e \) is the electron charge, \( Q_e \) is the momentum transfer cross-section for electron-ion interactions,20 and \( Q_i \) is the momentum transfer cross-section for electron-neutral atom interactions and is dependent upon the species of atom. Values of these cross-sections have been experimentally determined.21-25 However, available data can be assumed accurate only to within an order of magnitude, and therefore negate the relevance of more complex expressions for the transport properties.

For \( T \) in Kelvins, \( Q_e \) and \( Q_i \) in cm\(^2\), and \( n_e \) and \( n_i \) in cm\(^{-3}\), \( \sigma \) in mhos cm\(^{-1}\) is given by:

\[ \sigma = \frac{3.85 \times 10^{-10}}{T^{1/2}} \frac{n_e}{n_e Q_e + \sum n_i Q_i} \]

C. Thermal Conductivity

The thermal conductivity of a mixture of monatomic gases \( \lambda_{\text{mol}} \) can be expressed as the sum of two contributions:

\[ \lambda_{\text{mol}} = \lambda_T + \lambda_R \]

\( \lambda_T \) is known as the translational thermal conductivity and is due to the elastic collisions of particles which allow transfer of kinetic energy.26 \( \lambda_R \) is the reactive thermal conductivity, and accounts for the diffusion of ionization reaction enthalpy.27

1. Translational thermal conductivity

Devoto28 gives a simplified expression for the translational conductivity:

\[ \lambda_T = \lambda_H + \lambda_e \]

where \( \lambda_H \) is the conductivity due to heavy species interactions and \( \lambda_e \) is due to electron-heavy species interactions. Neglecting the contribution of ions, \( \lambda_H \) can be expressed as \( x_i \lambda_A \), where \( x_i \) is the mole fraction of ions and \( \lambda_A \) is the thermal conductivity due to neutral atoms alone. Devoto28
has shown that for an argon plasma such an approximation yields values within a few percent of those produced by more rigorous calculations.

For this study the contribution due to neutral atoms (in units of W/m-K) has been calculated according to a solution of the Boltzmann equation:  

$$\lambda_n = 8.32 \times 10^{-2} \frac{(T/M)^{1/2}}{\sigma^2 \Omega^{2.34_e(T^*)}}$$  \[9\]  

where $M$ = molecular weight (amu)  
\$\sigma = \text{a characteristic diameter in Å}\$  
\$\Omega^{2.34_e(T^*)} = \text{collision integral (dimensionless)}\$  
\$T^* = kT/\epsilon = \text{reduced temperature (dimensionless)}\$  
\$\epsilon = \text{interaction potential (eV)}\$

Jin\(^{30}\) has shown the above formula to be consistent with experimental data to within a few percent for argon and other noble gases.

Values of $\epsilon/k$ and $\sigma$ for argon and helium are given by Hirschfelder, et al.\(^{29}\) Values for the metal vapors are not available in the literature and had to be approximated. The parameter $\epsilon/k$ was calculated according to:  

$$\frac{\epsilon}{k} = 1.157k_{b}$$  \[10\]  
where $T_b$ is the boiling point temperature. $\sigma$ was approximated as the atomic diameter of the element in solid form.\(^{31,32,33}\) In this study, the effects of metal atom interactions on the total thermal conductivity of the plasma are very small. Therefore, the above approximations will suffice.

The neutral atom translational thermal conductivity of a mixture of monatomic gases ($\lambda_{\text{mix}}$) was calculated with an equation given by Ulybin:\(^{34}\)  

$$\lambda_{\text{mix}} = \frac{\sum_{i=1}^{n} x_i M_i^{1/2}}{\left[ \sum_{i=1}^{n} \frac{x_i}{M_i^{1/4} \lambda_i^{1/2}} \right]^2}$$  \[11\]  
where $x_i$ is the molar fraction of species $i$.

The electron-heavy species interactions will dominate Eq. [11] at higher temperatures.\(^{35}\) These are accounted for by the Spitzer-H"{a}rm equation:  

$$\lambda_e = \left[ 1 - \frac{3\delta_g \gamma_r}{5\delta_r \gamma_g} \frac{20(4\pi \epsilon_0)^{2} k^{7/2} T^{5/2}}{c^6 m_e^{1/2} \ln(qC^2)} \right] \frac{2}{\pi} \delta_T$$  \[12\]  
where for singly charged particles:  
\$\gamma_e = 0.5816\$
\$\gamma_r = 0.2727\$
\$\delta_g = 0.4652\$
\$\delta_r = 0.2252\$
\$qC^2 = h/b_0\$
\$b_0 = c^2/(12\pi \epsilon_0 kT) = \text{impact parameter}\$
\$h^2 = e \delta_g T/(2\pi n_e^2) = \text{Debye length}\$
\$\epsilon_0 = \text{the permittivity of free space.}\$

Substitution of constants yields:  

$$\lambda_e = \frac{4.42 \times 10^{-10} T^{5/2}}{\ln(8.77 \times 10^{10} T^{3/2}/n_e^{1/2})}$$  \[13\]  
for $\lambda_e$ in W/m-K, $n_e$ in cm$^{-3}$, and $T$ in K.

Goldstein and Sekiguchi\(^{39}\) and Sekiguchi and Herndon\(^{40}\) have presented experimental data which are consistent with this simple theoretical expression.

2. Reactive thermal conductivity

An expression for the reactive thermal conductivity of any mixture of reacting gases and inert diluents has been derived by Brokaw.\(^{41,42,43}\) Brokaw’s equation was used in a form presented by Liebermann and Chen:\(^{35}\)  

$$\lambda_r = \frac{-3k}{8} \left[ \frac{\pi k T \Lambda_0}{2} \right]^{1/2} \frac{R_{ij} \Delta H_{ij}}{|R_{ij}|}$$  \[14\]  
for $\lambda$ in W/mK,  
where $\Lambda_0 = \text{Avogadro’s number}$  
i = 1, 2, ..., $N$  
j = 1, 2, ..., $N$  
$N = \text{number of reactions that occur}$  
k = Boltzmann’s constant (joules/K)  
$\Delta H_{ij} = \text{normalized heats of reaction (dimensionless)}$

The $R_{ij}$ elements are given by:  

$$R_{ij} = \sum_{k=1}^{N} \sum_{l=1}^{N} B_{kl} \Omega_{kl}^{(i,j)} \frac{1}{x_i \lambda_k} \left( \alpha_{jk} X_j - \alpha_{ik} X_i \right) \left( \alpha_{jk} X_j - \alpha_{ik} X_i \right)$$  \[15\]  
where $X_i$ = species mole fraction  
$\alpha_{jk}$ = stoichiometric coefficient for species $k$ in the $i^\text{th}$ reaction  
$Q_{kl}$ = collision cross-section (in m$^2$) for interaction between species $k$ and $l$  
$B_{kl}$ = the reduced mass and is given by:  

$$B_{kl} = \left[ \frac{M_k M_l}{M_k + M_l} \right]^{1/2}$$  \[16\]  

The above calculations were carried out for a wide variety of gas compositions from $T = 500$ K to 20,000 K at 500 K intervals. A PDP-11/23 computer was used to run RT-11 FORTRAN IV programs.

IV. RESULTS

A. Species Densities

The calculated electron densities of atmospheric pressure argon, helium, iron, aluminum, and calcium plasmas are plotted together in Figure 1. Helium has the highest ionization potential, and therefore exhibits the lowest values of $n_e$. As temperature increases, each gas becomes completely ionized. Thus, the curves will all merge at $n_e/2$. The consideration of second ionization would alter these curves.

It is interesting to note that, although calcium has a slightly greater ionization potential than aluminum, it clearly exhibits a higher degree of ionization at low temperatures. This illustrates the importance of considering partition functions in the calculation of species densities by Saha’s equation, a factor often disregarded in the literature.

B. Electrical Conductivity

The calculated electrical conductivities of binary mixtures of argon and helium with 10 pct iron, calcium, and aluminum additions are plotted in Figures 2 and 3. These graphs illustrate the dramatic effects of small additions of low ion-
Fig. 1—Densities of electrons in pure plasmas of various elements.

Fig. 2—Effects of 10 pct Fe, Ca, or Al vapor additions on the electrical conductivity of Ar.

Fig. 3—Effects of 10 pct Fe, Ca, or Al vapor additions on the electrical conductivity of He.

Fig. 6 and 7 compare the effects of 10 pct aluminum, iron, and calcium additions on the thermal conductivities of the inert gases, as found by other researchers.¹⁷⁻¹³. Note that iron has as great an effect as aluminum.

The conductivities of ternary gas mixtures are plotted in Figures 4 and 5. These mixtures are intended as a simplification of the gas composition in the welding arc, and the effect of a small addition of aluminum or calcium to an argon or helium plasma containing only iron vapor is considered. Iron vapor is intended to represent all of the intermediate ionization potential elements which are expected to vaporize from a stainless steel baseplate (Fe, Cr, Ni, Mn, etc.). Such a model will predict the effects of low ionization potential elements on the welding arc.

As the figures show, the effects of these additions are far less dramatic than Glickstein’s simple binary model predicts.¹ The addition of 1 pct Al or Ca to a 10 pct Fe + Ar/He plasma produces a negligible increase in the electrical conductivity. Even a 5 pct addition has little effect. Furthermore, bearing in mind that, in this model, iron represents the sum of all intermediate ionization potential base metal constituents, such high Al or Ca to Fe ratios are unlikely to occur in arcs on stainless steel. More plausible figures would be 0.1 pct or even 0.01 pct Al or Ca at 10 pct Fe concentrations.⁴⁴ The effects of such small additions would be completely negligible.

C. Thermal Conductivity

Figures 6 and 7 compare the effects of 10 pct aluminum, iron, and calcium additions on the thermal conductivities of
Fig. 4—Effects of 10 pct Fe and 1 pct Ca or Al vapor additions on the electrical conductivity of Ar.

Fig. 5—Effects of 10 pct Fe and 1 pct Ca or Al vapor additions on the electrical conductivity of He.

Fig. 6—Effects of 10 pct Fe, Ca, or Al vapor additions on the thermal conductivity of Ar.

Fig. 7—Effects of 10 pct Fe, Ca, or Al vapor additions on the thermal conductivity of He.
Ar and He. As in the case of electrical conductivity, it can be seen that aluminum has only a slightly greater effect than iron on the plasma transport properties.

The thermal conductivities of ternary gas compositions are illustrated in Figures 8 and 9. It can be seen that the addition of 1 pct Al or Ca to a 10 pct Fe + Ar/He mixture produces a negligible change in the thermal conductivity. It is therefore reasonable to conclude that the presence of low ionization potential elements in the welding arc will have little effect on arc transport properties, and that arc physics-based explanations of the effects of these elements on weld penetration are unfounded.

V. DISCUSSION

The calculations presented here have shown that small amounts of low ionization potential metal vapors will have little effect on the transport properties of the arc in the anode region, where the inert gas is already significantly contaminated with other metal vapors from the basemetal. However, it is interesting to recall some of the experimental findings presented in Part I and to assess their relevance in light of these calculations.

Firstly, the dramatic increase in the concentration of tungsten vapor in the arc upon the addition of oxygen to the shielding gas presents a situation in which the binary gas mixture model is valid: in the upper regions of the arc the shielding gas is virtually free of contaminants. The introduction of tungsten vapor from the electrode will result in the dramatic increases in electrical conductivity which the simple binary model predicts. However, these plasma effects may be secondary in importance to the effects of the oxygen on weld pool surface tension via the preferential oxidation of surface active elements. Nonetheless, one must recognize that oxygen enhanced metal vaporization may play a role in the upper regions of the arc where metal vapor concentrations are otherwise very small.

Secondly, the sudden increase in thorium vapor in the arc noted in Part I and the findings of Ivanova present a similar situation. The emission of thorium vapor from the electrode would also have a significant effect on the transport properties of the plasma in the upper regions of the welding arc. Ivanova found substantial emissions of thorium from the electrode during initial burning, decreasing to a background level after approximately twenty minutes. This can be correlated with the 15 to 20-minute electrode “burn-in” period required for stable arc performance. Due to its low ionization potential relative to argon (see Table 1 of Part I), thorium may distort the current distribution near the electrode. If the thorium is emitted from a new electrode in “bursts”, this would promote arc instability.

Finally, it is interesting to recall the findings of the authors concerning the emission of aluminum and calcium from the tungsten electrode. It was concluded that a significant part, but not all, of the calcium and aluminum detected in the arc may originate from the tungsten electrode. Again, metal vapors emitted by the electrode will enter a relatively pure inert gas in the upper region of the arc. The effects of
these vapors on arc transport properties will therefore be far more significant than those of similar vapors originating at the anode.

It is therefore concluded that, although the effects of minor elements in the base metal on weld penetration are more likely due to weld pool convection phenomena, the emission of metal vapors from the tungsten cathode may have a significant effect on arc properties, and may therefore affect weld penetration.

VI. CONCLUSIONS

The effects of small additions of aluminum and calcium vapors on the electrical and thermal conductivities of argon and helium plasmas containing iron vapor have been calculated. It has been shown that, when an inert gas containing other metal vapors is considered rather than a pure inert gas, the effects of low ionization potential elements are far less significant than previous reports have suggested. It is therefore concluded that the effects of these minor elements on arc properties are probably of secondary importance in explaining variable weld penetration. Other effects, such as changes in the surface tension coefficient of the weld pool may be more important in explaining the poor penetration observed in base metals containing these elements.

However, the effects of elements emitted by the tungsten electrode may be very significant, as the inert gas is otherwise free of contaminants in the upper region of the arc. In this case, the simple binary composition plasma model is valid, and the dramatic effects of even very small amounts of metal vapor on the arc transport properties may significantly alter the transport of energy to the weldment.

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