Oxygen and Nitrogen Contamination

During Arc Welding

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Abstract

The sources, mechanisms, and expected levels of oxygen and nitrogen contamination during gas tungsten arc, gas metal arc, shielded metal arc, self-shielded metal arc, and submerged arc welding are reviewed. Calculations indicating the importance of decomposition of SiO_2 into silicon monoxide and oxygen are presented, indicating that silicon transfer between the slag and metal occurs by a gas-metal rather than a slag-metal reaction mechanism. A model suggesting that arc stabilizing additions to fluxes should provide volatile subspecies upon heating is also discussed.

Introduction

Oxygen and nitrogen contamination of weld metal is of concern in that relatively small quantities of these elements may affect the cleanliness, toughness and/or porosity of the resulting weldment. Generally speaking, these elements should be maintained at as low a level as possible; except perhaps in the case of austenitic stainless steels, where the percentage of delta ferrite may be manipulated by changing the nitrogen content of the weld metal. In any case, the sources and mechanisms which control the oxygen and nitrogen contents during welding must be understood in order to provide control over the process and the resultant properties of the weldment.

Providing that high quality starting materials are used, there are basically only two sources of oxygen and nitrogen contamination of the weld metal; viz., absorption from the surrounding atmosphere and reaction with any flux which may be present. Absorption from the atmosphere depends largely on plasma jet phenomena;flow rate, composition,and ionization state of the shielding gas; and the absorption mechanisms at the molten metal-gas interface. Fluxes may contribute oxygen by decomposition of less stable oxides, while nitrogen contamination from the flux, which is of potential concern,[1] is not generally important. The purpose of the present paper is to discuss these sources and their relative importance in the various arc welding processes.

Arc Phenomena

Rein has described the oxygen and nitrogen levels to be expected when using several different arc welding processes.[2] His summary, reproduced in Figure 1, illustrates the wide variations in nitrogen and oxygen levels which may be found among arc welding processes generally, and within the individual processes specifically. In order to understand these differences, it is necessary to distinguish the basic differences between the processes. First, however, several fundamental aspects of arc welding should be reviewed.

Welding arcs consist of ionized gases conducting large electrical currents. The arc maintains a delicate balance between the heat generated by the electrical resistance of the plasma and the heat lost to the surrounding atmosphere, workpiece and/or electrodes by conduction, convection, and radiation. The size of the arc is determined by balancing the pressure of thermal expansion of the plasma and the pressure of electromagnetic constriction on the conducting ions. If either of these balances is upset, the arc becomes unstable, leading to wide variations in welding current and possible extinction of the arc.*

A simple calculation, using estimates of electron mobility, plasma density, and arc geometry,shows that it is only necessary for approximately 3 to 30% of the arc plasma to become ionized in order to conduct the welding current, hence relatively small additions of easily ionizable elements can lower the arc temperature and change the arc profile near the molten metal surface, where the contamination reaction is occurring. If these easily ionizable additions are not continuous or uniform, arc instabilities may occur. It is interesting to note that oxygen and nitrogen have lower ionization potentials than either Ar or He. Carbon dioxide has an ionization potential that lies between oxygen and nitrogen. Since atomic or ionized oxygen and nitrogen are chemically more active than the respective diatomic molecules, the choice of shielding gas can have a profound effect on the resultant contamination levels of these elements. An equimolar mixture of nitrogen-CO_2 should produce strongly ionized CO and O and weakly ionized N_2 near the molten metal surface, creating a plasma of lower temperature and lower nitrogen activity than an equimolar mixture of nitrogen-Ar, in which the N_2 near the surface must be strongly ionized. On this basis alone, the N_2-CO_2 mixture might be expected to produce lower nitrogen levels in the weld metal. Such an effect has, in fact, been noted.[3]

Another arc phenomenon that is of general importance is the formation of plasma jets. This phenomenon was described originally by Maecker[4] as originating from a difference in magnetic pressure caused by the divergence of electrical current traveling from the electrode to the workpiece. These jets attain velocities of up to 600 m/sec, causing the entrainment of large quantities of gases into the arc plasma. If insufficient inert shielding is available, atmospheric gases will be pulled into the plasma by these jets. Jet formation requires less than 50 microseconds, hence any arc fluctuations below approximately ten kilohertz will alter the jet behavior leading to instabilities and possible atmospheric contamination. Such fluctuations are to be expected in all consumable electrode welding processes.

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* It should be noted that the present discussion is concerned primarily with DC arcs. AC phenomena, while more complicated, follow the same basic principles.
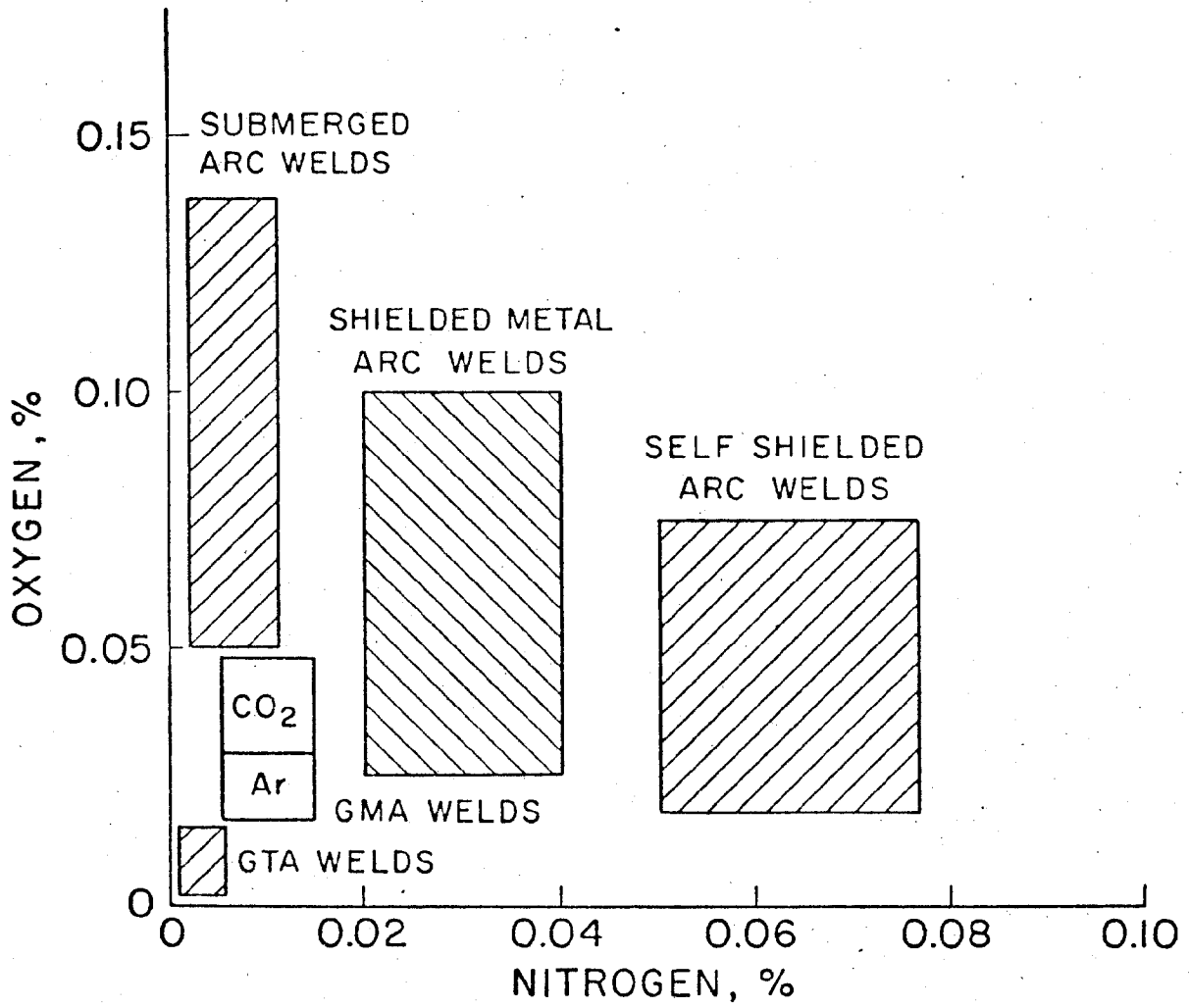
Figure 1. Oxygen and nitrogen levels expected from several arc welding processes. (After Rein.[2])

Welding Processes

Given the above brief discussion of shielding gas composition and plasma jet behavior, it is now worthwhile to review Figure 1 in more detail, describing the phenomena particular to each welding process.

1. Gas tungsten arc welding

The gas tungsten arc process produces the cleanest arc welds possible. The oxygen and nitrogen levels depicted in Figure 1 for GTA welding represent variations in initial base metal purity.

The cleanliness of GTA welding results from the absence of a flux, coupled with a short, very stable non-consumable arc. The stable arc provides smooth, uniform jet flow and the short arc length permits efficient shielding with gases that are required to be free of either oxygen or nitrogen.

2. Gas metal arc welding

The gas metal argon arc process differs from GTA welding only in the use of a consumable electrode. The shielding gas flow rate is increased to compensate for the longer arc length, however, oxygen and nitrogen contamination arises from plasma jet instabilities, which are inherent in any consumable electrode process. An oscilloscope trace of the current and voltage during GMA welding reveals arc interruptions lasting a few milliseconds. As noted previously, fluctuations on this time-scale may cause the plasma to be extinguished, upsetting local gas flow behavior in the arc. When the arc is reignited only milliseconds later, large amounts of gas are aspirated into the arc cavity. Often atmospheric gases are included and contamination results. The higher oxygen levels observed when using CO_2 gas shielding are obviously caused by creation of CO and O in the welding arc. At these temperatures, carbon monoxide is a reducing gas; however, the oxygen combines with the weld metal causing loss of carbon in steels, formation of additional CO gas, and a net increase in the weld metal oxygen content.

Neither GTA nor GMA welding processes utilize fluxes for molten metal protection, and hence any oxygen or nitrogen contamination must result from either decomposition of the shielding gas or incomplete atmospheric shielding. As shown in Figure 1, these processes produce the least contaminated deposits. It will be shown subsequently that the greater oxygen contamination levels of the remaining three processes, SAW, SMAW, and SSMAW, are partially due to inadequate atmospheric shielding, but also depend significantly upon the breakdown of less stable oxides in the flux.

3. Shielded metal arc welding

Due to extensive empirical flux formulation studies and a moderate level of heat input, shielded metal arc welds are capable of unusually high quality weld deposits. As such, this process continues to find favor in many applications; however, continued progress is likely to be extremely slow.

Shielded metal arc welding is an open arc process in that no external shielding gas is applied. Exclusion of atmospheric contaminants is dependent upon a slag cover over the solidifying weld pool as well as gas evolution from decomposing flux. Since this is a consumable electrode process, arc fluctuations are inherent in the process. Atmospheric contamination cannot be avoided; it can only be minimized by choosing

carbonate or cellulosic coatings which evolve copious amounts of carbon dioxide or hydrogen upon decomposition. As will be discussed later, part of the oxygen contamination in this process results from breakdown of less stable oxides in the flux.

4. Self-shielded arc welding

Self-shielded arc welding is very similar to shielded metal arc welding except for the addition of strong nitride forming elements (e.g., Al, Ti, Zr) to the welding wire. These nitride forming elements are also strong deoxidizers, which results in slightly lower oxygen levels than are found in SMA welding; however, this improved deoxidation leads to an increased rate of nitrogen absorption, as seen in Figure 1.

The rate of nitrogen absorption on iron surfaces is strongly dependent on the oxygen content of the iron, decreasing by a factor of six as the weld metal oxygen content increases from 100 ppm to 750 ppm.[5] Hence, any alloy additions which tend to lower the oxygen content of the weld metal will also increase the rate at which nitrogen is absorbed into the weld metal. Even modest bulk concentrations of oxygen cause saturation of the iron surface by oxygen atoms, presenting a barrier to nitrogen transfer from the gas to the metal phase.[6]

The competition of nitrogen and oxygen for surface active sites on iron provides an explanation of the observation made by Sis,[3] that carbonate self-shielded electrodes result in lower weld metal nitrogen levels than do basic (CaF_2) self-shielded electrodes. The carbonate electrode not only releases CO_2 shielding gas, but increases the oxygen content of the weld metal, significantly reducing the weld nitrogen content.

5. Submerged arc welding

Although commonly believed to provide complete exclusion of atmospheric contamination, the submerged arc welding process can be shown to achieve weld metal oxygen levels which are inexplicable in terms of flux decomposition reactions.[7] Evidence of this can be seen most readily in an analysis of weld metals produced with basic fluxes. These weld metals commonly are reduced in all deoxidizing elements: C, Mn, Si, Al, etc., compared with the base metal and wire analyses; yet the weld metal oxygen level is much higher than the starting materials. A mass balance on such a system requires a source of oxygen separate from the flux. Atmospheric entrainment due to arc fluctuations and instabilities in the slag cover is the most likely explanation.[7] Nonetheless, the very high oxygen levels associated with acidic flux submerged arc welding cannot be caused solely by atmospheric contamination. Such a large quantity of atmospheric oxygen would be expected to produce significant increases in the nitrogen content as well, producing an oxygen-nitrogen distribution similar to that observed in SMAW. The bulk of the oxygen contamination occurring during submerged arc welding must be related to decomposition of the oxide fluxes.

Flux Decomposition Reactions

The empirical fact that the oxygen content of commercial submerged arc welds can be related to a basicity index is well known,[8] if not appreciated. Several experts, failing to see any logical connection between flux basicity and expected oxygen content of the weld metal, have proposed instead that fluxes be classified according to their "oxygen potential." One of the difficulties with this proposal is that the concept of oxygen potential is ill-defined. In steelmaking slags, the oxygen potential is controlled by the FeO activity in the slag, although this is known to be

a complex function of the basicity.[7] In arc welding, however, much higher temperatures are attained and at these temperatures several other flux components may achieve higher oxygen potentials than FeO. Consider, for instance, the decomposition of silica liquid into silicon monoxide gas plus oxygen, as given in the reaction

$$SiO_2 \; (\ell) \rightarrow SiO \; (g) + 1/2 \; O_2 \; (g). \qquad\qquad (1)$$
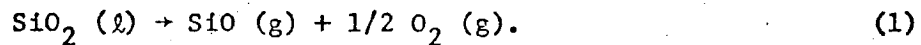
$$K = \frac{P_{SiO} \; P_{O_2}^{1/2}}{a_{SiO_2}}$$

At normal steelmaking temperatures this reaction is of little importance, although in the presence of carbon its importance in the blast furnace reaction has been suggested.[9] In arc welding systems, Heile and Hill have demonstrated that this reaction may be responsible for the generation of silica fumes.[10] As the temperature of interest increases above that required for steelmaking, many of the oxides which are normally considered to be most stable are actually among the least stable. North, et al., have claimed that CaO is chemically active in arc welding fluxes.[11]

An important consideration in reviewing reaction (1), is the fact that one oxygen atom is released for every silicon monoxide molecule formed, hence, the O_2 partial pressure for this reaction must be one-half the SiO partial pressure. This constraint permits the equilibrium constant for reaction (1) to be rewritten as

$$K = \frac{(0.5)^{1/2} \; (P_{SiO})^{3/2}}{a_{SiO_2}} = \frac{2P_{O_2}^{3/2}}{a_{SiO_2}} \; .$$

Choosing 2000°C as the temperature of interest for the silica reaction during arc welding,[7] and calculating an equilibrium oxygen potential for reaction (1) above, as well as the FeO reaction equilibrium in CaO-SiO₂-FeO slags with 1% and 5% FeO, results in the graph presented in Figure 2. This figure presents the oxygen pressure (or oxygen potential) as a function of basicity. Dashed reference lines are given for the oxygen potential of air and pure FeO at this temperature. In addition, the observed oxygen potential of the weld metal is shown by a dotted line. The fact that this dotted line does not correspond directly to any other line shown illustrates that the weld metal and slag cannot be considered to be in equilibrium at 2000°C.[11] It will be noted that, at 2000°C, the oxygen potentials of both FeO and SiO₂ are generally greater than the weld metal oxygen potential, implying that either compound is potentially oxidizing to the weld metal at this temperature. It will also be noted that the oxygen potential of the SiO₂ decomposition reaction is significantly greater than the FeO oxygen potential, hence it cannot be assumed that FeO controls the oxygen potential of complex oxide fluxes at the elevated temperatures occurring during arc welding. It is probable that the bulk of the oxygen found in submerged arc weld metal made with acidic fluxes results from the decomposition of SiO₂ rather than FeO. This is evidenced by the large increase in weld metal silicon content (up to one percent) when acid fluxes are used.[8] Furthermore, the extremely rapid kinetics observed for the SiO₂ decomposition reaction imply that it is a gas-metal, rather than slag-metal, reaction; which is again evidence that reaction (1), i.e., formation of silicon monoxide gas from the slag, is the first step in oxygen and silicon transfer to the weld metal when employing high silica
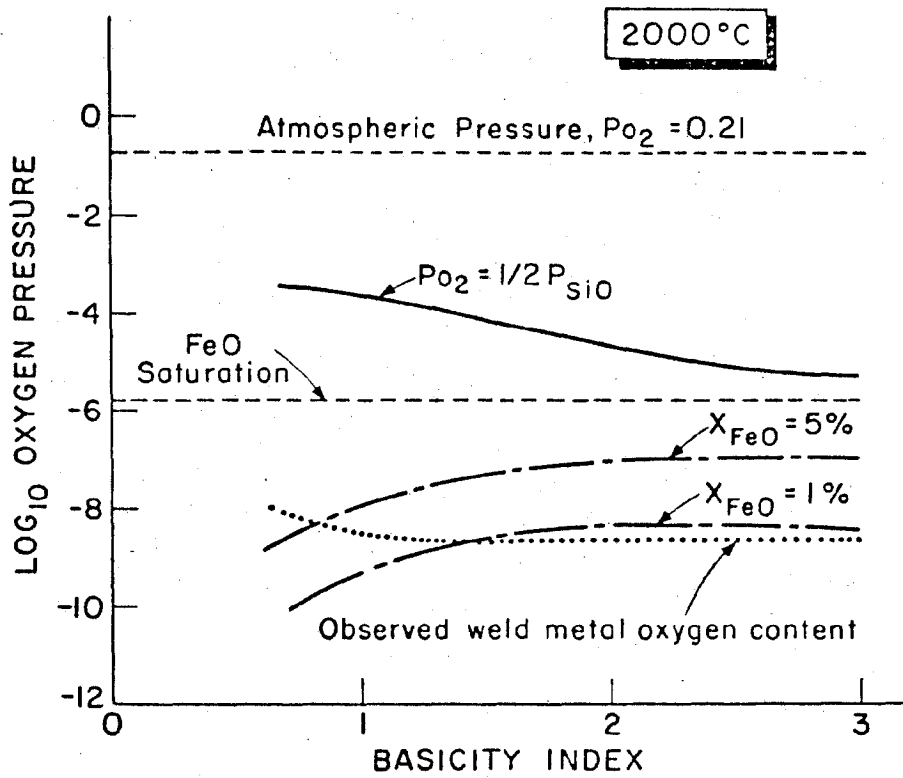
Figure 2. Oxygen potential as a function of basicity for SiO_2–CaO (solid line) and SiO_2–FeO (dashed lines) based slags at 2000°C.
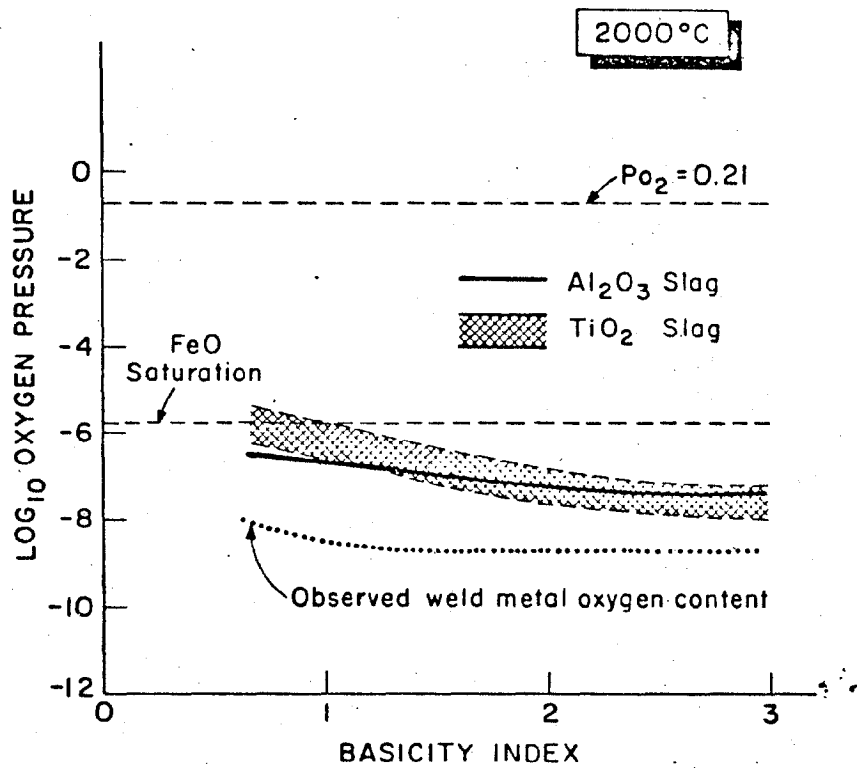

Figure 3. Oxygen potential as a function of basicity for TiO_2–CaO and Al_2O_3–CaO based slags at 2000°C.

activity (acid) fluxes.

It is possible to formulate acid fluxes which are low in silica, primarily by using TiO_2 or Al_2O_3 as major constituents. An analysis was performed for each of these components in a manner similar to that described above for SiO_2. The results of this calculation are shown in Figure 3.* It is readily apparent in comparing Figures 2 and 3 that Al_2O_3 and TiO_2 provide a significant reduction in the oxygen potential when compared with SiO_2; hence, either of these components would be expected to lower the oxygen content of the weld metal when used as a replacement for silica. This has been observed in rutile based slags by North, et al.[11] Furthermore, the gaseous suboxides TiO and AlO form much less readily than SiO, which implies that the kinetics of the TiO_2 and Al_2O_3 decomposition reactions will be much slower than the SiO_2 reaction.

The thermodynamic data for the preceding reactions have all been calculated at 2000°C for reasons discussed elsewhere[7]; however, the same general trends and conclusions would be applicable at any temperature above approximately 1800°C. The analysis presented in no way implies that 2000°C is the only temperature of interest. Extreme thermal gradients exist during arc welding, and the chosen temperature merely represents a convenient reference from which to evaluate the relative thermodynamic stability of the various oxides.

While the above discussion on flux decomposition during arc welding applies most directly to the submerged arc process, the conclusion that SiO is an important constituent in the arc atmosphere of any silica based flux welding process is a general one.[10] In fact, the realization that SiO_2 is capable of evolving large quantities of a gaseous suboxide aids one in rationalizing the relative arc stabilizing effect observed for various compounds by Hazlett, as reproduced in Table 1.[14]

Table 1.   Relative Arc Stability Produced by Various Compounds (from Hazlett[14])

Arc Stability Index	Compound
1	Commercial Flux
2	K_2CO_3
	$CaCO_3$
3	Fe_2O_3
	SiO_2
	Na_2CO_3
4	MnO_2
	$MgCO_3$
	MgO
	Al_2O_3
	CaF_2
5	Na_2SiO_3

* The thermodynamic data for Al_2O_3-CaO slags were taken from Rein and Chipman.[12] Activities for the TiO_2-CaO system are not available, although the data of Martin, et al.[13] suggest that the activity of TiO_2 in CaO is similar to that of SiO_2 in CaO. Hence, the calculation for TiO_2-CaO melts was done for unit activity and given the same slope as shown in Figure 2 for the SiO_2-CaO system.
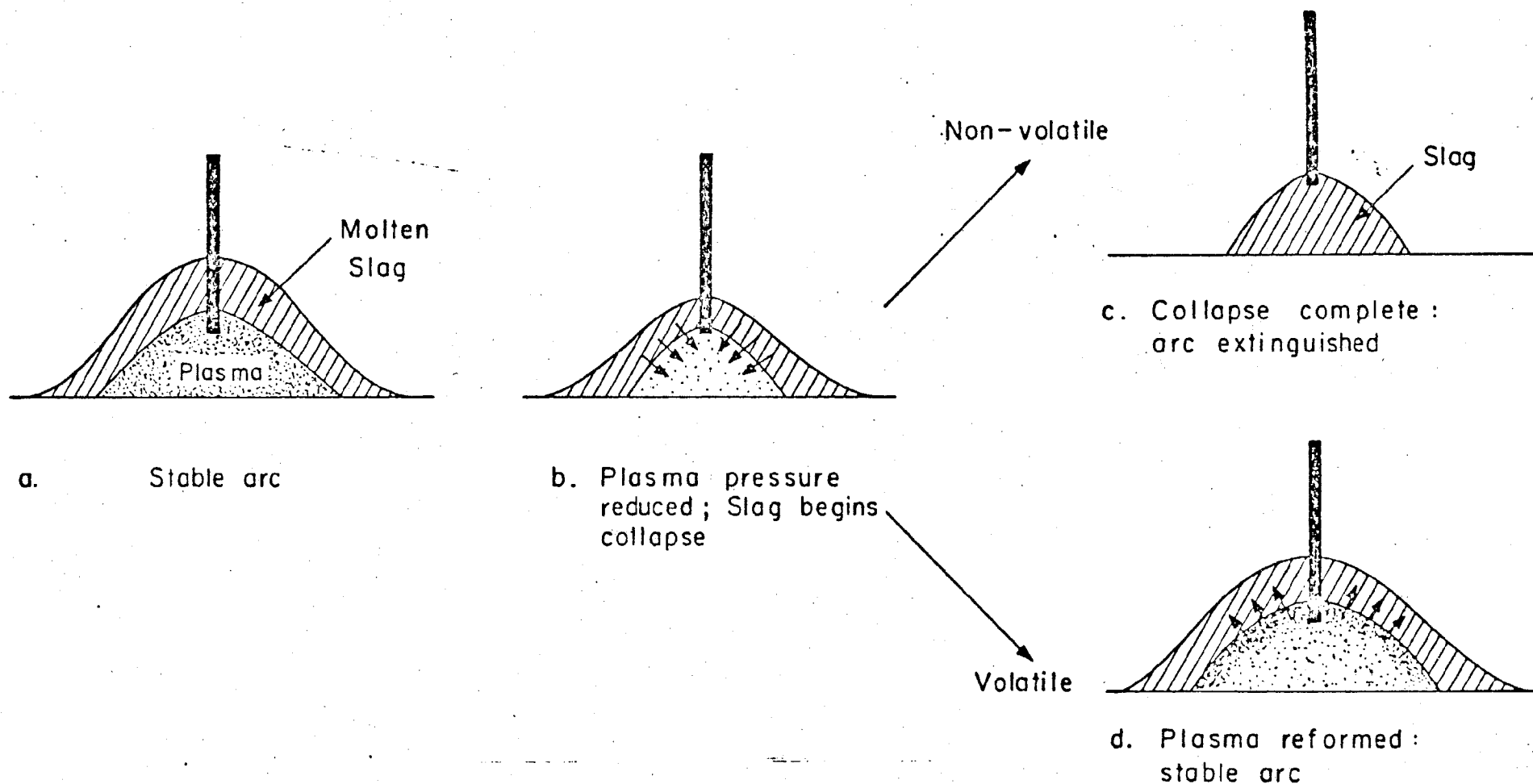
Figure 4. Schematic of the effect of volatile flux components on the stability of the submerged arc welding process.
a. Stable arc. b. Plasma begins to be consumed by reaction with the weld metal; slag begins to collapse. c. Flux without volatile components; plasma is consumed; slag collapses and arc is extinguished. d. Flux with volatile components; heated slag produces plasma ions; pressure increases, slag is pushed back to stable arc position.

Although arc stability is dependent upon numerous factors, the most stable submerged arc fluxes shown in Table 1 tend to produce a gaseous reaction product upon heating. It is thought that this gas evolution process provides a stabilizing effect on the possible extinction of the arc plasma by the molten slag cover. As depicted schematically in Figure 4, a flux which does not evolve gas upon heating would tend to swamp out the arc if any decrease in plasma pressure were encountered. A gas evolving flux, on the other hand, would rapidly heat up if more closely exposed to the arc, thereby evolving gas, increasing the local plasma pressure, and pushing back the molten slag. This latter process would provide a stable arc plasma free of extinction by collapse of the molten slag. The most stable compounds in Table 1 are generally carbonates which evolve CO_2 upon heating; but Fe_2O_3 and SiO_2, which are both greater stabilizers than several of the carbonates, may also evolve gases; the former by changes in stoichiometry and the latter by formation of a volatile suboxide. It is currently believed that a volatile flux component, essentially a source of plasma ions, is a requirement of stable submerged arc welding fluxes. Russian investigators have found it necessary to add chloride salts for improved arc stability when welding highly reactive titanium alloys under fluoride based fluxes.[15] Under these conditions, the titanium weld metal will consume any oxygen ions in the plasma. If a new source of ions is not provided, the plasma will be extinguished for lack of a carrier gas. Chlorides have much lower vapor pressures than fluorides, and hence, would provide a gaseous plasma which would not be consumed by the titanium.

Conclusions

The extent of oxygen and nitrogen contamination during arc welding is dependent upon the process employed. These differences can be rationalized in terms of plasma jet phenomena, shielding gas composition, surface absorption phenomena, alloy additions, arc stability, and flux chemistry. It has been shown that silicon monoxide formation from the flux may provide an explanation of the rapid transfer of silicon between the slag and the metal. Substitutions of TiO_2 and Al_2O_3, being more stable than SiO_2, have the potential of reducing oxygen contamination. One possible requirement of arc stabilizing elements in submerged arc welding is that they provide a source of gaseous ions upon heating.

Acknowledgements

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