Development of a Portable Direct Reading Spectrometer to Monitor Oxygen-Hydrogen Containing Contaminants in Gas Tungsten-Arc Process Shields

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ABSTRACT. A small portable spectrometer was developed to monitor oxygen and hydrogen as the free or dissociated products in the gas tungsten-arc welding process. These components are detected if in the shielding gas, adsorbed on the metal surface or dissolved in the metal itself. The hydrogen, 6562.8 Å, and oxygen, 7771.9 Å, lines were monitored and the argon 8521.4 Å line was used for the internal standard. An internal standard was necessary because small variations in arc length, condition of metal surface and other excitation parameters produced decided differences in spectral response at these relatively high current levels. The instrument, a fixed Eagle mount, used a 76 x 50 mm, 60 cm focal length, concave grating with 610 grooves/mm blazed in the second order. The reciprocal dispersion at 6562 Å was 12 Å/mm. The oxygen triplet was resolved.

Optical design requirements included the use of very short arc lengths, as in the order of 0.5 mm, an optical plate of 65 to 75 deg with a large flat plate instead of the conventional 90 deg with respect to the electrodes, and an arc that does not remain in a fixed optical position in space. The focusing lens-limiting aperture assembly was mounted on the torch head with a fiber optic bundle transmitting the light to the spectrometer. The direct-ratio readout system using a Devar ratio computer on each analytical channel was essentially instantaneous and recorded only the signal above background, including the very high background caused by the introduction of the electrode tip in the optical path. This was accomplished by the use of an oscillating optical block placed after the entrance slit. This caused the emission line to oscillate across the exit which produced an a-c signal above the d-c signal from background radiation.

Introduction
Impurities in the shield gas of the gas tungsten-arc welding process of aluminum alloys as well as impurities on the surface of the work metal that yield hydrogen and oxygen species, reduce weld quality. Spectroscopic techniques not only see the impurities in the shield gas but also the impurities adsorbed on the metal surface as well as gases dissolved in the metal or trapped in inclusions.

In a previous study spectrographic techniques were developed to measure the concentrations of oxygen, hydrogen or hydrogen bearing compounds and nitrogen in the inert gas shield and surface contaminants at moderate level current arcs. In addition, some of the parameters that influenced the protective qualities of the arcs were investigated, such as flow velocity, air currents, moisture in the hose line, surface scale, etc.

This initial study was extended to the use of low ampere d-c arcs for oxygen, hydrogen and nitrogen, to gaseous halogens, and the influence of different gas mixtures, arc current, and some metal alloys on the spectra.

In this program, additional parameters involved in the spectral monitoring of atmospheric contaminants in the gas tungsten-arc welding process were studied and a direct reading spectrometer was developed and tested.

Evaluation of Analytical Parameters

Equipment and Materials

The welding equipment included a variable-speed (rate, 1 to 120 ipm) side-beam carriage and a heavy duty clamp-down fixture mounted on a 10 ft side beam. The clamp-down fixture was designed to hold plates 18 x 36 x 1 in. and larger. An automatic welding unit that maintains a constant arc length was mounted horizontally and at right angles to the front of the side arm fixture on a stationary column. An optical bench to support selected optics was designed and mounted on the welding unit, clamp-down fixture and spectrograph.

Fig. 1—Experimental layout showing welding unit, clamp-down fixture and spectrograph

Fig. 2—Side arm optical mount attached to torch head

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Experimental Studies and Discussion

The experiments for this study were performed by passing an aluminum alloy plate clamped in the clamp-down fixture, in front of the welding torch. The flow of the helium shielding gas and the quantities of argon, oxygen, hydrogen and nitrogen were measured by calibrated rotometers. A weld pass consisted of moving the metal plate past the welding torch during which the metal was melted and resolidified. Part of the time two plates were actually welded together during which time spectrographic measurements were made.

Internal Standard Studies

In the initial program, a 50% argon–50% helium mixture was used as the shielding gas and several argon lines in the 13.3 eV excitation potential range had been evaluated. However, in this program only high-grade welding helium was to be used. Relatively large variations in spectral response resulted from minute changes in arc length, current flow, nature of metal surface, etc. This required an internal standard.

Helium lines, non-dispersed and dispersed light were found to be unsatisfactory for an internal standard.

Analytical Line Response

The spectral response for both the oxygen 7771.9 Å and the hydrogen 6563 Å lines was linear in the 0–300 ppm range (Fig. 3); as to be expected, the response was greater at the higher current densities. The photomultiplier tube response for shield gas at 0 ppm added did not record 0 mv because, in addition to other sources for contaminants, even good commercial grade inert welding gases were found to contain from 25 to about 100, and on some occasions even greater than 1000 ppm contaminants. The signal for the oxygen 7771.9 Å line at constant concentration essen-
Position of Electrode Tip

The relative position of the electrode tip with respect to its image's position on the limiting aperture was noted to significantly influence the photomultiplier response. Therefore a 2X image magnification with a 1/4 mm limiting aperture was used to measure this effect more carefully. This permitted a 0.62 mm section of the 2 mm arc length to be viewed by the spectrometer. Measurements made with the tip of the electrode image at 0.2, 0.5, and 1.0 mm from the edge of the aperture resulted in slopes of 59, 50, and 42%, respectively, which indicates the greatest number of excited species to be in the cathode region.

In arc welding, very short arc lengths are used which leaves little space for variation. Therefore, a jig was designed in order to set the electrode at a constant position with respect to the nozzle and calibration lines were inscribed on the limiting aperture.

Calibration Curve Standard

Argon was evaluated at specific concentrations from 0.125 to 2%, with oxygen and hydrogen in the 0 to 500 ppm. This resulted in a parallel and relatively straight family of curves, the relative position being determined by the concentration of the argon. The precision of each series of six points, obtained by spectrographic densitometer measurements was quite good with respect to line formation.

The influence of the position of the electrode tip with respect to the limiting aperture for calculated values of

Oxygen 0/0.5% Argon using a 2 mm arc length with a 2X image magnification and a 1.25 mm limiting aperture is illustrated in Fig. 4. These results were also noted for hydrogen. For the required short arc lengths the 0.2 to 0.3 mm position was adopted.

The results with argon as the internal standard were satisfactory for a 0–500 ppm range for oxygen and hydrogen.

Points on calibration curves for both oxygen and hydrogen in the 0–100 ppm range were very erratic when 2024 aluminum alloy was used. Cleaned and prewarmed. These improved somewhat when the work metal was preheated to a higher temperature. When a weld pass was made with clean shield gas before each calibration pass, the points formed a good calibration curve. The heterogeneous concentration of contaminants (s) which apparently existed at the surface was reduced or evenly distributed by the weld pass. The calibration curves were curved at the lower concentrations indicating residual contaminants. It was found that using a 100 amp arc, starting with a room temperature 36 x 18 x 1 in. 2024 aluminum alloy plate, 13 minutes were required for the signal for the 6563 A hydrogen line to become approximately constant. Much less difficulty was experienced with aluminum alloy 2219.

Black Body Radiation

The optical axis cannot be at right angles to the electrodes because the work metal represents the lower electrode. It must be at some angle in which the optics are focused into or near the edge of the hot molten metal (puddle).

The level of radiation from the work metal can vary with the beam carriage rate of travel and the current which influences the size of the puddle, and, in turn, the level of radiation. Because of the very short arc requirement, the position of the tungsten electrode on the limiting aperture is critical and radiation from the puddle and other sources results in widely varying levels of black body radiation entering the spectrograph. This is the reason that both direct as well as internal standard responses show more variation with very short arc lengths.

Other factors that influence the amount of stray black body radiation are the reflection of the white hot electrode tip in the puddle, the alloy, and the cleanliness of the surface. Reflection of the electrode tip often was in the limiting aperture which resulted in relatively large changes in photomultiplier output. Background from these variations as well as possible misalignment by the welding operator would be too severe for practical operation and internal standard control.

A rotating wedge in the non-dispersed beam was used to eliminate the above effect by oscillating the diffracted light beam across the exit slit. The thermal background will be a varying d-c signal, but the oscillation of the signal line results in a short pulsing d-c or effectively an a-c output that can be separated from the d-c background and amplified. This principle is illustrated in Fig. 5.

Readout was with an electronic a-c voltmeter and an oscilloscope. The deviation of the wedge was adjusted to give a sinusoidal-like 10 cps output which indicated a symmetrical sweep of the analytical line on both sides of the exit slit. With a constant flow of hydrogen it was found that the influence of arc length was reduced. Even when the glow from the tip of the hot electrode entered the aperture there was essentially no difference in the signal from the selected analytical line. However, if the electrode tip was permitted to penetrate any appreciable distance into the aperture field, the analytical signal decreased because the actual arc area seen by the spectrograph had been decreased.

Development of the Spectrometer

Basic Design Requirements

The basic design for the instrument was dictated by the available spectral lines, simplicity of optical design for portability, arc lengths required, high level of stray radiation, and the required speed of the readout.

The spectral region was dictated by the 6562.8 A hydrogen line since this is the only sufficiently sensitive line in the air spectrum region, and the 7771.9 A oxygen line is the only available sensitive line close to the hydrogen line. In this region the strongest, though relatively weak, nitrogen line is the one at 8216.4 A. However, nitrogen was dropped from the list of elements to be monitored since it appeared to have no deleterious effects and since a Mg III line from the 2024 Mg-Al alloy interfered with the nitrogen line.

The argon 8521.4 A line was select.
ed from several useful lines as an internal standard because of space requirements. The concentration of argon was 2% or less.

Integration of line intensities, coupled with a time of discharge system, could not be used because immediate and continuous readings were required. The approach devised made use of multiplier-divider computer modules that continuously compute the output ratio of each analytical line to the argon internal standard line.

**Design of the Instrument**

**Optical Plan.** A scale drawing of the optical plan with the photomultiplier tubes in place are shown in Fig. 6. The design is essentially a fixed Eagle mount in which the slit, grating and focal curve are rigidly mounted in relation to each other. The use of a single optical element is an advantage because the introduction of another element introduces an additional source of instability. However, the relatively large angles of refraction increases the degree of aberrations. This is not serious since photomultiplier tubes were used, there were no close interfering lines.

The S-l response tube, available at that time only with the large photocathode, is the only phosphor to cover the required total region. These tubes, including the Mu-metal shield and brackets, were 1.88 in. in diameter and with the socket approximately 5 in. long, which created a serious deterrent in the attempt to develop compact-portable instrumentation (presently photoreceptors are available which are much smaller with respect to physical size). In order to meet the space requirements of these tubes on a focal curve, a minimum reciprocal dispersion of 15 Å/mm was required which is high for a relatively small instrument. This also resulted in a very long focal curve with respect to the suggested radius of curvature of...
about 60 cm.

Grating and Mount. A grating was designed that more than met the above requirements. It was a 610 grooves/mm (15,000 lines/in.) replica concave grating with a 60 cm radius of curvature and was blazed in the second order for the 6400 to 8500 Å region. Its effective surface was 76 by 50 mm so that the instrument had an effective aperture ratio of approximately \( f/8 \). At the angle of incidence of 19 deg, the reciprocal dispersion was calculated to be 12.4 Å/mm, 11.0 Å/mm and 9.9 Å/mm, and the distance \( r \) from the center of the grating to focus was 530.1, 476.2 and 430.2 mm for the hydrogen, oxygen and argon lines, respectively. Theoretical resolving power was 90,000; the oxygen 7771 Å triplet was resolved.

The grating block was borosilicate glass, 56 × 82 × 12 mm with a grooved face of 50 × 76 mm. An offset edge, 3 × 3 mm, was ground on each of the four sides of the blank so it was held behind a frame with the face projected in front of the mount in order to avoid any stray diffracted light. This provided a shock-resistant mount so that the grating could not become dislodged and damaged—Fig. 7.

Between the frame and the offset edge of the blank the tolerance was 0.13 mm (0.005 in.) and between the blank and walls of the mount, 0.25 mm (0.010 in.). Three flat 0.020 in. (0.51 mm) phosphor bronze springs held the grating against the front retaining frame. This provided equivalent pressure at all points and so avoided distortion resulting from pressure which could be the case if the grating was held against the back wall of the mount, especially when quite large temperature changes occurred.

Side Arm Mount-Entrance Optics. The work metal is the large lower electrode, so the optical system must be focused at some angle in which the optics is looking directly into or at the edge of hot molten metal. The heat produces warping; the constant arc length head follows this change in space, thus the entrance optics must be able to follow this change. Therefore a side-arm mount was designed to carry the entrance optics which included the condensing lens, a red filter and a three-axis movable stage which holds the combination, limiting aperture and entrance end of the fiber optic bundle. Details of this assembly are illustrated in Fig. 8. This side arm mount, \( \frac{1}{4} \) in. aluminum, was designed to be attached to a plate previously fitted to the side arm of a particular welding machine.

The condensing lens, with an effective aperture of 33 mm, gave an effective magnification of 3X with 1 mm (0.040 in.) entrance slit, theoretically, an arc gap of 0.35 mm (0.014 in.) can be viewed. The lens accepted a solid angle of light of 22 deg which gave an entrance and emergence angle of 9 deg for the fiber optics bundle. This slightly overfilled the grating with light which is necessary to avoid a fluctuating background signal which would have been recorded as part of the a-c signal. The angle of the optical axis with the work metal was 15 deg. These represented the best optical compromise.

If a larger lens had been used, a larger angle with the work metal would be required resulting in increased pickup of background. If the lens had been moved closer to the arc, more fogging would result from metal spatter and again a larger work angle with the metal would be necessary. An inexpensive Tiffen 1A series V filter, which removes the spectral emissions from the 2200 to 6000 Å region, fits into the lens holder directly in front of the lens. In addition, this inexpensive filter protects the lens from spatter.

The aluminum block mounted on the three-way stage holds the end of the fiber optic bundle and also acts as the diaphragm on which the position of the electrode tip and work metal can be observed. The three-axis movable stage permits the positioning and focusing of any portion of the arc on the aperture.

Fiber Optic Bundle. A nearly coherent fiber optic bundle was used to transmit the light from the arc to the spectrometer. The ends of this bundle were cemented into aluminum blocks and served as the entrance slit of the spectrometer and limiting aperture on
the side arm mount. Both ends of the bundle were the same size, 1 × 19.8 mm. Only the middle section carried light from the arc. The fibers used were 0.004 in. in diameter and were parallel so that the bundle was very nearly coherent. The core material was Shott F-2, \( N_p = 1.62 \), glass rod, and the coating was Kimble R-6 glass, \( N_D = 1.52 \). The bundle was protected with latex rubber tubing which, in turn, was covered with tinned copper tubular braid.

**Exit Slit System.** The exit slits, part of the photomultiplier tube shield assembly, were adjustable with the instrument in operation. Optimum adjustment with respect to line oscillation was determined by the shape of the sinusoidal-like output on the oscilloscope indicating a symmetrical sweep on both sides of the slit. Initially, a wide entrance slit, 1 mm, and exit slits, 2 mm, were planned because of the very small though intense section of usable arc, light losses along the fiber optic bundle, and the relatively low efficiency of the S-1 phosphor. A second reason was to provide a fiber optic bundle of sufficient strength to be relatively rugged. Wide slits were possible because no interfering lines were close and high resolution was not necessary.

The total system was far more sensitive than expected so the entrance and exit slits were reduced by one-half and load resistors for the PM tubes were changed.

**Optical Compartment.** The optical compartment was actually divided into two separate light-tight compartments—Fig. 6. This arrangement made it possible to adjust exit slits with the instrument in operation. Photomultiplier tubes can also be replaced without disturbing the optical alignment.

**Background-Optical Wedge Principle.** To avoid the influence of the high and varying background, the optical wedge principle combined with a-c amplification of the emission line signal was used.

A circular glass disc, ground 3.3 deg off parallel, was initially included in the design. However, it produced uneven illumination of the grating and a false readout signal resulted.

A rectangular crown glass prism, 1.25 in. wide × 1 in. thick × 1.75 in. high, encased in a metal frame and
mounted vertically between two bearings, produced the required even illumination. With the oscillating prism and a-c amplification, the actual readout signal was not influenced by the white hot electrode tip in the optical path.

**Electronic System**

The functional block diagram of the solid state electronic system is shown in Fig. 9. An approach was devised for immediate readout that used ratio computers and continuously recorded relative analytical line intensity.

The instrument operates from a 115 VAC line which feeds the synchronous motor, the regulated low-voltage d-c power supplies and alarm circuitry. The low voltage supplies, in turn, feed the amplifying and computing circuitry and the high-voltage regulated supply feeds the photomultiplier tubes. The individual channel calibration rheostats operate from the common high-voltage source. The 10 eps signals from each of the three photomultiplier tubes, as a result of the emission line oscillating across the exit slit, are amplified by a-c coupled amplifiers which are followed by full-wave rectifiers and single time constant filters. The resulting d-c signals are amplified by small operation amplifier modules to the level required to operate the ratio computers. The two ratio computers, the Devar-Kinetics type 19-302 multiplier-divider computer modules, continuously compute the output ratio of each analytical line to the argon internal standard. The resulting quotient signals are fed to miniature point-tracking Rustrak recorders.

The effect of temperature change on the sensitivity of the photomultipliers results only from a change in photomultiplier supply voltage. A temperature change of 40° C will produce about a 4% change in the output voltage of the converter. This change is the corona tube voltage 0.4% and, due to the eight-power exponential relationship of the photomultiplier, changes the gain about 32%. The Devar-Kinetics type 19-302 multiplier-divider computers are solid-state high-speed switching modules in which the computer function is

\[ X_0 = \left( \frac{A_1 X_1 + A_2 X_2}{X_3} \right) X_0 \]

where, \( A_1 \) and \( A_2 \) are constants, \( X_1 \) and \( X_2 \) are positive polarity values. A +10 v potential was used for \( X_1 \) and 40,000 ohm multiplying resistors were used for each of the \( A_1 \) and \( A_2 \) positions making these constants 0.5 and 2, respectively. Therefore the function becomes:

\[ X_0 = \left( \frac{0.5 X_1}{X_2} \times 10 \right) \times 2 \]

where \( X_3 \) is the internal standard signal and \( X_1 \) the analytical line signal.

**Calibration and Performance**

The nearly ideal calibration procedure is to have high purity gases, clean metal gas lines, work metal with a very low gas content, a very clean smooth surface and a hot torch from which gases have been desorbed, as well as a good family of calibrated flowmeters. The rheostats on the analytical channels are adjusted to obtain the deflection on the recorders corresponding to concentration and then locked.

The instrument responded closely to the added quantities of gases. The recorder reproduction for six runs in the concentration range from 0 to 100 ppm by volume is illustrated in Fig. 10. The curve at the lower concentration indicates the presence of residual impurities which peak largely from the helium. Several passes were made to heat the work metal to desorb surface moisture and to produce a clean bead before each gas addition was made. A massive block of aluminum alloy 2219 was the positive electrode or the work metal. Part of the variation (Fig. 10) is due to variation in the amounts of gas metered on each run.

The instrument was very sensitive and each channel essentially responds instantaneously to changes in contaminant levels. For example, a little oxide from a "stubbed" tungsten electrode, other oxide scale or a partly charred hydrocarbon such as a crayon mark, would cause a very wide fluctuation of response including off-scale in the 100 ppm range.

Cold metal with ordinary machined surfaces yielded large variation of response, i.e., usually 50% or more full scale (0-100 ppm calibration) as well as a continual variation of small fluctuations for both the oxygen and hydrogen channels. These gradually decrease to a reasonably stable response as the work metal becomes hot. The response further stabilizes as the arc passes over the smooth surface from a previous pass.

Both channels responded to off scale when a person's breath was blown gently across the arc which indicated the ease in which the helium shield was penetrated.

Arc length variation causes some variation in response of the analytical channels. A decrease from 1 mm to 0.5 mm (0.040 to 0.020 in.) resulted in approximately a 10% decrease in the oxygen response while an increase from 1 mm to 1.5 mm (0.040 to 0.060 in.) produced about a 5% increase. The response also varied slightly with gas flow rate and current, and was sensitive to rate of travel of the work metal, especially when cold or only warm on the first pass. With the other parameters constant, there was less variation in spectral response at the slower rates of travel so apparently the arc is actually volatilizing impurities which are swept away with the shield gas.

The hydrogen channel responded three to four scale divisions (0 to 100 ppm full scale calibration) when the arc with pure shield gas (no contaminants added) was passed over a previous weldment where 100 ppm hydrogen had been added to the shield gas. The variation at this time was less than ±0.5 scale division. The oxygen channel remained constant. The actual detection limits are not known. So far, no matter how clean the system and the gas is supposed to be, a signal or a photograph of the hydrogen 6562 A line was obtained.

**Summary**

The studies on the parameters involved in the spectroscopic monitoring of gas tungsten-arc shields and on applications of the concept indicated that such monitoring was feasible for both research and practical welding. A small portable spectrometer was designed to monitor hydrogen and oxygen or contaminants containing these elements using the arc as the excitation source. These components are detected if in the shielding gas, adsorbed on the metal surface or dissolved in the metal itself. The instrument was designed to operate under adverse optical conditions, i.e., the very short arc lengths, optical planes other than 90 deg and with a source that does not remain in a fixed optical position in space. The direct-ratio readout system was instantaneous and recorded only the signal above background including the very high background caused by introducing the electrode tip in the optical path.

**References**