SURFACE CLEANLINESS VERIFICATION BY DIRECT OXIDATION CARBON COULOMETRY

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INTRODUCTION

The cleanliness of a metal surface is an issue in many industrial processes. The quality of adhesive bonding, electroplating and corrosion resistance after painting is adversely affected by contaminates on the surface of a metal. The need to assure and improve quality, while phasing out environmentally harmful cleaning solvents, has forced industry to face the challenge of abandoning many of its traditional cleaning methods and evaluating alternate cleaning processes.

An ideal method for cleanliness verification would provide a quick, direct quantitative measurement of the surface contamination while at the same time being inexpensive and easy to use. Many of the methods currently in use trade off cost and the ease of operation with the quality of analytical information. Surface techniques, such as Secondary Ion Mass Spectrometry (SIMS), provide a wealth of qualitative and quantitative information about contamination at a surface but these techniques are expensive and difficult to perform routinely. Other methods, such as the water break test, contact angle measurement or solvent extraction techniques, are inexpensive and easier to run than the surface techniques but their results can be classified as either non-quantitative, non-specific or indirect.

The method presented in this poster, Direct Oxidation Carbon Coulometry (DOCC), offer a better balance between cost, ease of use and quality of information than methods currently in use for cleanliness verification. Since most common surface contaminants are carbonaceous in nature, the measurement of surface carbon gives a direct indication of surface cleanliness. In DOCC, surface carbon on a sample is oxidized to CO_2 by combustion and then measured quantitatively by an automatic coulometric titration.

METHOD

Figure 1 shows a schematic representation of the combustion system. The system consists of a packed quartz combustion tube and two furnaces. The first furnace is set to 420° C for the determination of *organic* surface contaminates. The second furnace is set to 590° C for the determination of *inorganic* surface carbon. A single furnace set at 590° C is used if only the determination of *total* surface carbon is desired.

Samples are first inserted into the cool end of the combustion tube. The breech block is closed and the system is purged of atmospheric CO_2 with the oxygen carrier gas. The sample is then moved into the appropriate heating zone where the surface carbon reacts to form CO_2. Combustion gases are swept from the combustion tube into a coulometric cell where is it titrated with electrochemically generated hydroxide ion.

Since coulometry is a primary technique based on Faraday's law, no chemical calibration of the coulometer is required. Results of the analysis are calculated from the integration of the titration current and displayed directly as μg C. Time required for analysis is approximately 5 minutes for each form of carbon determined. Final results are generally reported as either mg C / ft^2, mg C / m^2 or mg C per part.

RESULTS AND DISCUSSION

Comparison of DOCC Results to other methods of Surface Cleanliness Verification

- Contact Angle Measurement compared to DOCC

  Surface wettability, as determined by measuring the contact angle between a water drop and the surface of a test piece, can be used to assess surface cleanliness. Large contact angles are associated with poor wettability and contaminated surfaces. Small angles are associated with good wettability and clean surfaces.

  Figure 2 shows the correlation between contact angle measurements and the results of DOCC. Samples exhibiting larger contact angles have a corresponding higher value of surface carbon. Samples with smaller contact angles, implying a cleaner surface, are associated with lower values of surface carbon.

- SIMS surface analysis compared to DOCC

  Three samples of steel were analyzed by Secondary Ion Mass Spectrometry (SIMS) to determine the distribution of carbon near the surface of the samples. The results of these analyses are shown in Figure 3. In this figure, the amount of carbon present is represented by the signal intensity of C^+ ions sputtered from the sample and the depth of the analysis is represented by the sputter time. For each of the samples, the signal for carbon is highest near the surface of the sample and decreases with depth until a constant level of carbon is reached. The differences in carbon level between early and late sampling distinguishes the amount of surface carbon on the sample from the bulk carbon in the steel. A qualitative comparison of the results show Sample 3 to have the highest level of surface carbon followed by Sample 2, and then, Sample 1.

  Surface carbon on these samples were also measured by DOCC and shown in Figure 3. The results of DOCC surface analysis correlate well to and follow the same trend as SIMS analysis.

Applications

- Evaluation of Cleaning Procedures

  In an effort to evaluate alternatives to vapor degreasing with 1,1,1-trichloroethane (TCE), sets of stainless steel union fittings were analyzed by DOCC after being subjected to different cleaning procedures. Figure 4 ranks and compares the results of the surface carbon analysis of different cleaning protocols along with the results of the fittings analyzed "as received". The best cleaning procedure, revealing the lowest surface carbon results with least variability, was spray impingement with an aqueous alkaline cleaning solution.

- Evaluation of Manufacturing Processes

  Table 1 shows surface carbon results obtained by DOCC analysis on two sets of steel samples produced by different manufacturing processes. Process B exhibited more than three-and one-half times as much organic surface carbon than Process A and twice as much inorganic carbon. The origins of the surface carbon in the manufacturing process were determined and kept under control by incorporating DOCC as an in-plant statistical process control tool.

CONCLUSION

The results of DOCC correlate well with both the results from simple empirical methods for the verification of surface cleanliness and the results of sophisticated surface techniques while retaining the best features of both.

The advantage of DOCC are

- Direct, quantitative measure of surface cleanliness through the determination of surface carbon
- Response independent of the type of carbon contamination
- No Chemical calibration required
- Ease of use
- Rapid analysis time (5 minutes)
- Low instrument and operation cost

Figure 1. Schematic Representation of DOCC Sample Handling System and Combustion Process

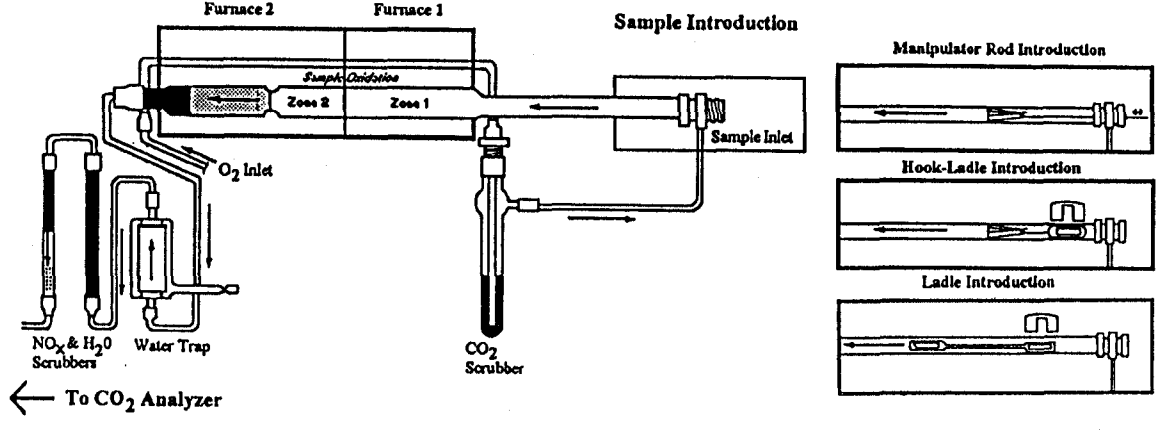

Figure 2. Cleaning's Effect on (A) Contact Angle and (B) Surface Carbon

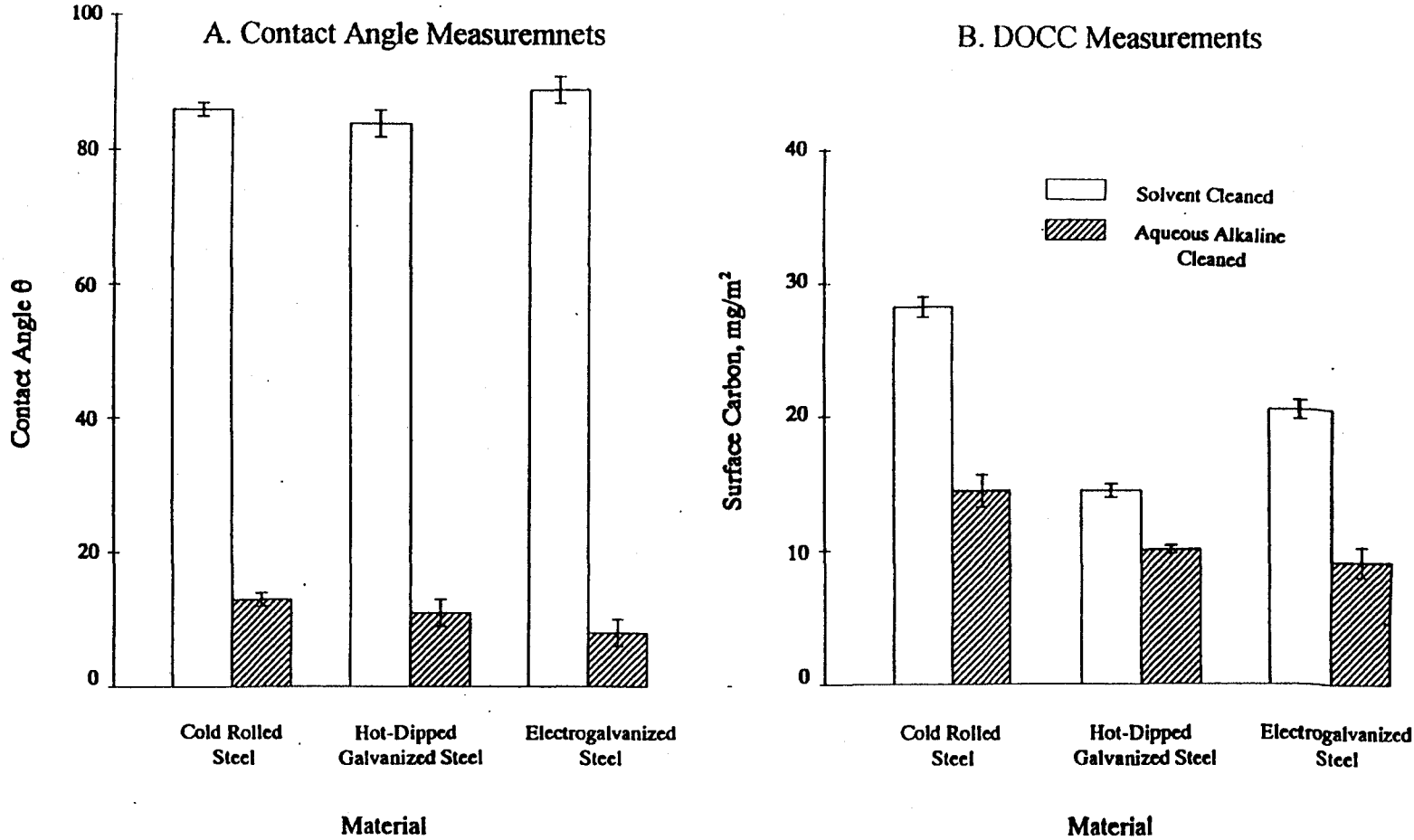

Figure 3. Comparative SIMS C^+ Depth Profile Analysis and DOCC Surface Carbon Measurements

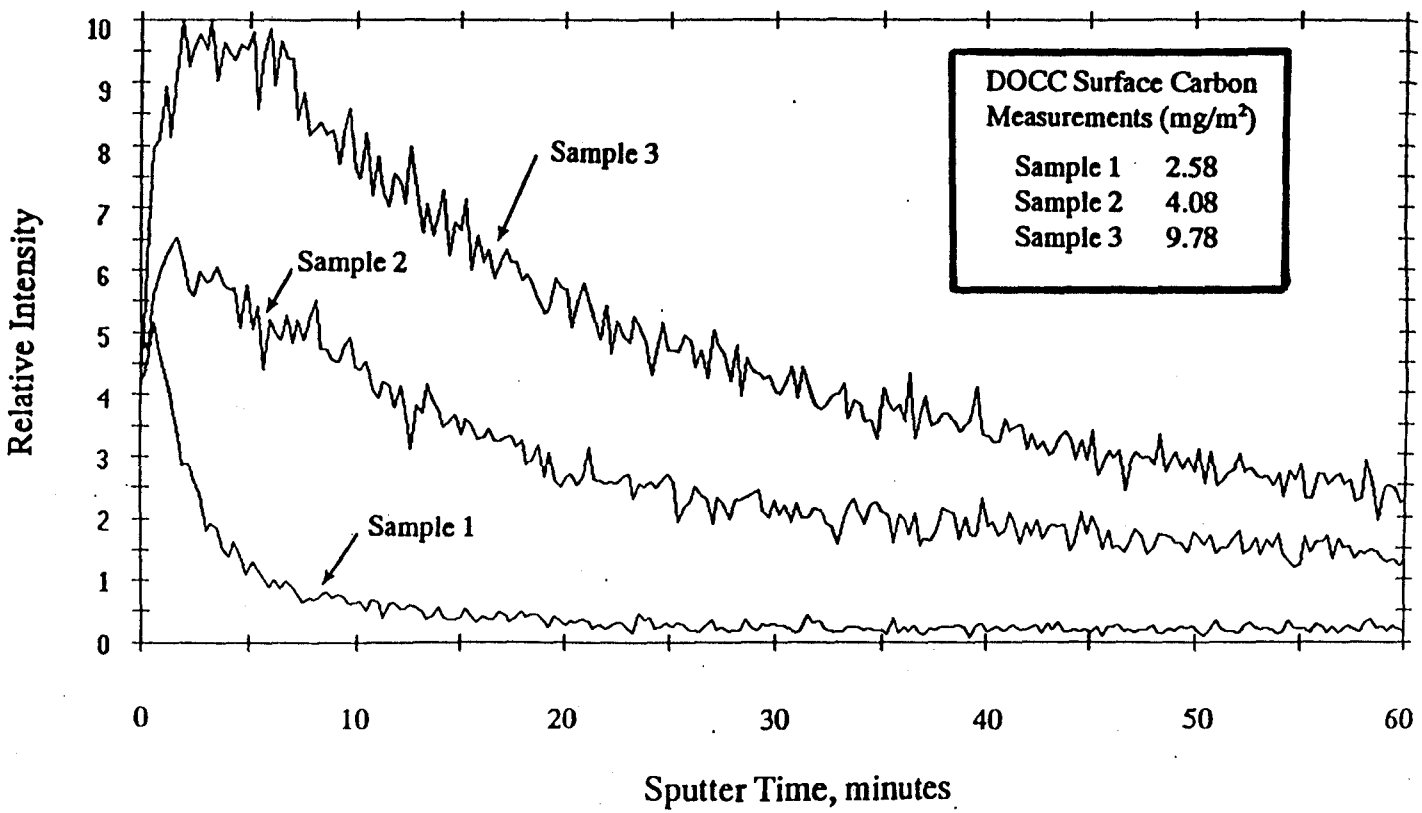

Figure 4. DOCC Results for Surface Carbon on Stainless Steel Union Fittings