The Surface Chemistry of the Mild Steel and Glass Substrates for Thermal Spray

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Abstract. The surface chemical condition of substrates plays a key role in single splats formation. Single splats are the foundation of thermal spray coatings. In this study, the surface chemistry of the mild steel and glass substrates were investigated. The result indicated that the 100 °C heat treatment released the absorbents of mild steel substrates. The adsorbed water disappears from the surface of the mild steel sample after one hour of heat treatment at 100 °C; there is no adsorbed water on the surface of the glass sample.

Keywords: surface chemistry; xps; adsorbates; thermal spray; single splat.

1. Introduction
The surface chemistry of the substrates plays a significant role in splat morphology. The volatiles of adsorbents produce bubbles to the splats, achieve splashed splats and even fragmented splats. Many metals exhibit oxide layers of different thickness and composition as a result of their manufacture procedures. The preheating of metals gives off volatiles from the metal surface and alters the oxide thickness and composition [1]. Thermal energy can introduce surface separation of components because the oxides formation free energies are varying [2]. Hence, a different explanation for the transition temperature and surface chemicals possibly due to the volatiles of the substrates after heat treatment. Substrate heat treatment can get rid of the adsorbates or condensates [3]. However, most substrates are impossible to be polluted with xylene, glycol or glycerol. Hence the issue is what are “adsorbates or condensates” on mild steel and glass substrates? The mild steel substrates were heated at 100 ºC, hypothesized that the adsorbates were water.

Besides of remitting adsorbates or condensates, heat treatment of substrates also alternates the surface oxide thickness and composition. Chromium oxide at the inner layer and iron oxide at the outer layer was introduced by heat treatment of stainless steel, which was found by McDonald et al. [4]. The thickness of chromium oxide and iron oxide on the substrate heated at 350 ºC was 124 nm and 56 nm respectively, however their thickness on the substrate heated at 650 ºC was 204 nm and 84 nm respectively. But there was no difference in surface roughness between these samples [5]. Tran’s [6] research identified that the input heat from particles at impact can generate gas release from the surface of stainless steel and aluminum substrates. It can be assumed that mild steel substrates should react similarly because it can be easily oxidized and absorb adsorbates. While splat morphology on gold substrates had almost no difference with and without heat treatment, founded by Fukumoto et al. [7]. The effect of surface chemicals on splat morphology was not apparent, as gold is metallic materials which is not oxidized under these circumstances. Hence it can be presumed that...
glass substrates should perform similarly and that the splat morphology on glass substrates with and without heat treatment should not modify significantly.
To prove the above hypothesis, the X-ray photoelectron spectrometer (XPS) experiment was conducted on unheated mild steel, heated mild steel and glass samples. Mild steel and glass substrates were chosen because they are common materials. The surface of mild steel substrates is covered by oxides and adsorbents. The preheating amends the relative amount of these components. Such modifications can be identified by high resolution XPS.

2. Experimental Procedure
The X-ray photoelectron spectrometer (XPS) experiment was conducted with unheated mild steel, heated mild steel and glass samples. The mild steel substrates were polished. The composition of the mild steel substrates was 0.05–0.35 at%, 0.42–0.48 at%, 0.6%–0.9 at% for Si, C and Mn respectively, less than 0.06 at% for S and P totally. The glass substrates were chosen with the microscope glass slides. The composition was 72.20 at%, 14.30 at%, 1.20 at%, 6.40 at%, 4.30 at%, 1.20 at% and 0.03 at% for SiO2, Na2O, K2O, CaO, MgO, Al2O3, Fe2O3 respectively. The samples were cleansed respectively in each of the following solutions: dichloromethane, hexane, acetone and methanol and sonicated for 5 minutes at the mean time; followed by rinsing with distilled water. The samples then were dehydrated with hot air and all the glass samples and half of the mild steel samples placed in a desiccator. Half of the mild steel samples were put in an oven at 100 °C for 1 hour to get rid of any adsorbed water, then left at room temperature for half an hour and then put into the desiccator. All the samples remained in the desiccator for one day. They were exposed to air for one hour prior to the XPS experiment.

The XPS instrument used in this study was Kratos AXIS UltraDLD, manufactured by Kratos Analytical Ltd, Manchester, UK. The X-ray source was monochromatic Al Kα (1486.6 eV). The analysis software was CasaXPS. High resolution scans of Fe2p, O1s and C1s were gathered to investigate oxide/oxyhydroxide components on the surface of samples. The narrow scans were curve fitted using CasaXPS software with combination of Gaussian (G) and Lorentzian (L) (GL30) for the peak profile.

3. Results and Discussion
3.1. Survey of Glass, Unheated and Heated Mild Steel Substrates
The XPS wide scan of the unheated mild steel, heated mild steel and glass samples are shown in Figure 1. The atomic compositions of the sample from this scan are calculated and presented in Table 1. The spectra from the unheated steel and the heated steel samples reveal the peaks of Fe 2p, O 1s and C 1s. The spectrum from the glass sample demonstrates the peaks of O 1s, C 1s and Si 2s. However the carbon composition analysed by XPS is 40.3 at% for unheated mild steel sample and 41.2 at% for heated mild steel sample. Interestingly the carbon composition of the glass sample is 41.1 at% and similar to the unheated and heated mild steel substrate, indicating that the samples were contaminated by adventitious carbon when they were exposed to air. The peaks of Zn 2p, N 1s, Ca 2p and Si 2s from both unheated and heated mild steel samples have lower intensities than Fe 2p, O 1s and C 1s peaks. The peaks of Na 1s, Zn 2p, N 1s, Ca 2p, Sn 3d and K 2s from glass samples also have lower intensities than O1s, C 1s and Si 2s peaks. The existence of these remnant elements is ascribed to pollution from tap water during the cleansing process.
The difference in the XPS narrow scan normalized spectra of O 1s peaks, Fe 2p peaks and C 1s peaks of unheated and heated mild steel samples is indicated in Figure 2. There was no difference.
Figure 1. XPS wide scan of (a) unheated mild steel sample, (b) heated mild steel sample and (c) glass sample between the Fe 2p peaks in the unheated and heated mild steel samples. There was a difference between the O 1s peak from unheated and heated mild steel samples; as also indicated by the C 1s peak. This indicated that the chemicals on the surface of the heated mild steel did change after the 100 °C heat treatment.

Table 1. XPS composition of unheated, heated mild steel and glass samples (at %)

| Peak Area         | C 1s | N 1s | O 1s | Fe 2p | Ca 2p | Zn 2p | Si 2s |
|-------------------|------|------|------|-------|-------|-------|-------|
| Untreated Steel 1 | 39.8 | 0.8  | 42.1 | 15.7  | 0.3   | 0.3   | 1     |
| Untreated Steel 2 | 40.2 | 0.8  | 42.5 | 14.7  | 0.4   | 0.2   | 1.2   |
| Untreated Steel 3 | 41   | 0.5  | 42.2 | 15    | 0.3   | 0     | 1     |
| Average           | 40.3 | 0.7  | 42.3 | 15.1  | 0.3   | 0.1   | 1.0   |
| Heated Steel 1    | 41   | 0.7  | 43.5 | 13.3  | 0.3   | 0.3   | 0.9   |
| Heated Steel 2    | 39.3 | 0.8  | 42.7 | 16.1  | 0.2   | 0.2   | 0.7   |
| Heated Steel 3    | 43.3 | 0.5  | 42.8 | 11.6  | 0.2   | 0.4   | 1.1   |
| Average           | 41.2 | 0.7  | 43   | 13.7  | 0.2   | 0.3   | 0.9   |
| Peak area         | O 1s | C 1s | N 1s | Ca 2p | Na 1s | Sn 3d | Si 2p | Zn 2p | K 2 |
| Glass 1           | 40.8 | 40.6 | 1.6  | 0.9   | 1     | 1.7   | 12.4  | 0.2   | 0.7 |
| Glass 2           | 41.6 | 39.3 | 1.1  | 1     | 1.2   | 1.9   | 12.6  | 0.3   | 1   |
| Glass 3           | 40.9 | 40.5 | 1.4  | 1     | 1     | 1.7   | 12.2  | 0.3   | 0.9 |
| Average           | 41.1 | 40.1 | 1.4  | 1.0   | 1.1   | 1.8   | 12.4  | 0.3   | 0.9 |

Figure 2. Differences in the XPS narrow scan normalized spectrum of (a) O 1s peak, (b) Fe 2p peak and (c) C 1s peak

3.2. Curve Fitting of Narrow Scan of O 1s and C 1s Peaks
The curve fitted narrow scans of O 1s peaks for both unheated and heated mild steel samples are depicted in Figure 3. The O 1s line shapes for oxidation were quite different from unheated and heated mild steel samples. The O 1s envelope of unheated mild steel sample was fitted with 6 components assigned as lattice O\(^{2-}\) from Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\) at a banding energy (BE) of 529.9 ± 0.1eV, lattice OH\(^-\) from Fe(OH)\(_2\), and FeOOH at BE of 531 ± 0.1eV, adsorbed O\(^{\delta}\) (adsorbed atomic oxygen) at BE of 531.8 ±
0.1 eV, adsorbed OH at BE of 532.8 ± 0.1 eV, adsorbed OH⁻ at BE of 533.7 ± 0.3 eV and adsorbed H₂O at BE of 534.9 ± 0.3 eV [6]. The O 1s envelope of the heated mild steel sample was fitted with 5 components assigned as lattice O²⁻ at BE of 529.9 ± 0.1 eV, lattice OH⁻ at BE of 531.1 ± 0.1 eV, adsorbed O° at BE of 531.8 ± 0.1 eV, adsorbed OH⁻ at BE of 532.8 ± 0.1 eV, adsorbed OH⁻ at BE of 533.9 ± 0.1 eV. The adsorbed H₂O disappeared from the surface of the mild steel sample after one hour of heat treatment at 100 °C. It can be predicted that there will be less bubbles between the EMAA single splat and the mild steel substrate after one hour of heat treatment of mild steel substrates at 100 °C than substrates without heat treatment. Hence heat treatment of mild steel substrates can improve the EMAA coating properties, especially the mechanical properties.

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Figure 3. Curve fitted narrow scan of O 1s peak of (a) unheated mild steel, (b) heated mild steel samples

The high-resolution C 1s spectra are fitted with four components for both unheated and heated mild steel samples as shown in Figure 4. The most intense peak at 285.0 eV is produced from hydrocarbon groups (C–C/C–H) such as those in the mineral oil, the propyl chain in APS and the hydrocarbon contamination [8]. The BE at 286.5, 287.9-288.2, and 289.1 eV are assigned to C–OH, C=O, and COOH or O–C=O groups (carbonyl/Ester) respectively, which are the contaminants from the cleansing process [8]. Hence the C–OH and COOH species from the C 1s envelop are from the trace of acetone during the sample cleansing process.

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Figure 4. Curve fitted narrow scan of C 1s peak of (a) unheated mild steel and (b) heated mild steel samples

The Curve fitted narrow scan of the O 1s peak and the C 1s peak glass sample are shown in Figure 5. The O 1s envelope of heated mild steel sample was fitted with 4 components assigned as lattice OH⁻ at BE of 530.8 ± 0.1 eV, adsorbed O° at BE of 531.8 ± 0.1 eV, adsorbed OH⁻ at BE of 532.6 ± 0.1 eV, adsorbed OH⁻ at BE of 533.4 ± 0.3 eV [6].
Figure 5. Curve fitted narrow scan of glass sample of (a) O 1s peak and (b) C 1s peak

There was no adsorbed water on the surface of the glass sample which was proved by lack of bubbles between the EMAA single splat and the glass substrate which has been reported by Wei et al [9]. The C 1s peak at BE of 285.0 eV was assigned as (C–C/C–H) from hydrocarbon groups such as those in the propyl chain in any hydrocarbon, the mineral oil, and APS contamination [10]. The BE at 286.6, 288.2, and 289.2 eV were assigned to C–OH, C=O, and COOH or O–C=O groups (carbonyl/Ester) respectively which were the contaminants from the cleaning regime [11]. C–OH and COOH component from the C 1s envelope was from the residue of acetone residue that evolved during sample cleaning.

4. Conclusion

The heat treatment at 100 °C has an apparent effect on the chemistry of mild steel surface. The adsorbed atomic oxygen and COOH concentration were reduced. The adsorbed H2O was disappeared from the surface of the mild steel sample after one hour of preheating at 100 °C. There was no adsorbed water on the surface of the unheated glass sample. C–OH and COOH component from the C 1s envelope was from the residue of acetone residue. These findings are new to this area of thermal spray technology and provide a fundamental understanding to what is often assumed within common industrial practice concerning substrate heating effects.

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