Effect of substituting fine rutile of the flux with nano TiO$_2$ on the improvement of mass transfer efficiency and the reduction of welding fumes in the stainless steel SMAW electrode

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Abstract: This paper presents a novel method for reducing fume formation rate (FFR) and hexavalent chromium (Cr(VI)) concentration in welding fumes by substituting fine rutile in the flux of SMAW electrode with nano TiO$_2$. A maximum reduction of FFR up to 21% and Cr(VI) up to 42% was achieved in the experimental electrode. For the first time, the experimental study related the efficacy of mass transfer of specific elements to their percentage reduction in the emission. The results of the constituent analysis showed that Fe, Ni, Cr and Mn in the welding fumes were reduced up to 16%, 44%, 32% and 28% respectively due to the deoxidization property of the nano-Ti, which prevented the target elements to get oxidized.

Keywords: mass transfer, fume formation rate, hexavalent chromium concentration, nano-TiO$_2$

1 Introduction

Austenitic stainless steel SS316LN is the most extensively used base material in the nuclear power industry, boiler industry, petroleum industry etc. due to its excellent resistance property to corrosion and oxidation at high temperatures [1–3]. The welding consumable commonly employed for the fabrication of components having SS316LN as the base material is E316-L16, where the flux used is of rutile type. The electrode flux and core wire are two integral parts of welding electrodes, where flux ingredients decompose at high temperature to serve various functions during welding, while the elements in the core wire are transferred to the weldment [4–10].

The properties of the weldment like mechanical strength, deep penetration, smooth finish etc are dependent on the efficacy of metal transfer from electrode to weld pool during the welding process with minimum loss [11–15]. Nevertheless, welding fumes are formed during such processes by (i) evaporation, followed by the nucleation and rapid condensation of metal vapors and (ii) spatters, which are particles expelled from the agitated molten weld pool during welding [16–21]. The exposures of various welding fumes particulates (Fe, Mn, Ni, Cr etc) cause harmful diseases to the welders and other occupants [22–27]. Though, few investigations reported on the improvement of mass transfer efficiency by varying the flux compositions, its information on reduction of emissions were scarce [11–15]. Therefore, a systematic study on the effect of mass transfer efficiency of elements in the flux coated electrodes on fume emission reduction is required.

Various studies have focussed on the reduction and control strategies of hexavalent chromium Cr(VI) emission in welding fumes by process modification and consumable modification, of which the former was effective on the processes like GMAW, GTAW and the latter was effective on the SMAW process, due to the limitation of providing the factors like shielding gas flow rate, shielding gas compositions, welding speed, filler wire feed rate etc. [28–35]. Therefore, the consumable modification process was considered to be at the best possible strategy towards reduction of hazardous constituent emissions at source [5, 36–39].
Table 1: Chemical composition of base metal and Core wire

| Elements (wt%) | Base Metal | Core Wire |
|---------------|-----------|-----------|
| Fe            | Balance   | Balance   |
| Cr            | 16-18     | 15-19     |
| Ni            | 10-14     | 9-12      |
| Mo            | 2-3       | 2-5       |
| Mn            | 2         | 1.6       |
| Si            | 0.1-0.3   | 1.2       |
| N             | 0.045     | 0.2-0.4   |
| P             | 0.03      | 0.050     |
| C             | 0.03      | 0.02      |
| S             | 0.03      | 0.04      |

Table 2: Chemical composition of flux

| Chemical Ingredients                | Weight percentage |
|-------------------------------------|-------------------|
| Rutile sand coarse and fine         | 40-50             |
| Titanium Oxide                      | 1-15              |
| Nickel                              | 1-10              |
| Ferro Manganese                     | 1-3               |
| Chromium                            | 15-25             |
| Molybdenum                          | 0-4               |
| Calcium Flouride                    | 2-10              |
| Cryolite                            | 0-5               |
| Calcium Carbonate                   | 15-18             |
| Feldspar                            | 0-3               |
| Niobium                             | 0-3               |
| PottasiumTitanate                   | 0-3               |
| Chromium(III) Oxide                 | 0-0.5             |
| Pottasium Hydroxide                 | 0-0.5             |
| Pottasium Silicate                  | 1-5               |
| Ferro Silicon                       | 0.1-1             |
| Sodium Silicate                     | 1-5               |

In the present investigation, the fine rutile powder in the electrode flux was substituted by nano TiO$_2$ at various weight percentages and subsequently its effect on the Fume Formation Rate (FFR) and Cr (VI) concentration in the welding fumes was experimentally investigated. Even though the alteration in flux composition is a possible way to investigate the Cr(VI) emission, it will exhibit a vast deviation in the welding metallurgy. Therefore, modification of consumable with its respective nanoparticles without significantly altering the flux composition is the strategy adopted in the present work. Thus this way of consumable modification has the following advantages: a) the better deoxidizing property of titanium [40] compared to other elements in the flux would prevent the oxidation of other alloying elements, which leads to reduced emissions, b) the choice of nano sized TiO$_2$ in the flux would probably accelerate the deoxidization characteristics, c) no change in the composition of flux ingredients and c) substantial quantity of the element being replaced distributed uniformly throughout the flux due to its nano size.

2 Materials and Methods

The stainless steel SMAW electrode selected for study was E316L16 with SS316LN core wire of diameter 4mm and rutile type flux formulation. The 460 mm diameter and 10 mm thick SS316LN circular base plate was used for laying bead on plate weld deposit for the purpose of fume collection. The weight percentage of the major elements in the base plate and consumable core wire are listed in Table 1. The experimental electrodes were fabricated incorporating nano TiO$_2$ (50 nm) via substitution for fine rutile in various proportions of 20%, 40%, 60%, 80% and 100%, and the respective electrodes are denoted as E1, E2, E3, E4 and E5. The conventional E316L16 welding electrode is represented as C. Both experimental and conventional electrodes were manufactured with an unaltered flux formulation in an identical manufacturing conditions using the welding electrode extrusion setup (LOGOS EP 50). The flux composition for the tested electrodes is shown in Table 2.

Figure 1 shows the schematic diagram of the fume collection chamber, which is constructed as per the ISO 15011-1 standard for the analysis of FFR during welding [35, 41]. The base plate was cleaned to remove dirt, rust and other coatings present on it prior to the commencement of welding. The welding was carried out using a constant current...
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DC rectifier (ARC 400 - RILION). The current of 140 A was set during welding. The fumes were deposited on a whatman GF/A filter paper using an extraction blower, which runs at 900 litres per minute for the 150s duration. The professional welder was employed for all welding trials. The filter papers subjected to fume collection were pre weighed and post weighed using a precision weighing balance (Shimadzu AUW220D). Three experimental trials were carried out for measuring fumes from each test electrode.

The measurements of Cr (VI) in fumes were carried out according to the procedure stated in NIOSH (7604) using the Atomic Absorption Spectrometer (AAS) (GBC 902) [42]. The elements in fumes were analysed using the Inductively Coupled Plasma- Atomic Emission Spectroscopy (ICP-AES) (Perkin Elmer – OPTIMA - 5300DV) as per the procedure mentioned in NIOSH (7300) [43]. For welding all experimental electrodes, the major elements viz. Fe, Mn, Ni, Cr in the fumes were measured and compared with the conventional electrodes. The ozone concentrations were measured during the welding process in all experimental trials using an UV-absorption ozone analyzer (BMT 964).

2.1 Mass transfer, weld metal recovery and percentage reduction in constituent emission calculations

The mass transfer coefficient of specific element associated with the welding is defined as the percentage transfer of corresponding element from the consumable electrode towards the weld pool. The mass transfer coefficient denoted by ($\eta$) can be calculated from the following equation (1) [12–14].

$$\eta = \frac{C_{\text{deposit}}}{C_{\text{wire}} + K_b C_{\text{coat}}}$$

Where $C_{\text{deposit}}$, $C_{\text{wire}}$ and $C_{\text{coat}}$ represent the weight percentage of the specific element in the weld deposit, core wire and flux respectively, whereas $K_b$ represents the ratio of weight of the flux to the core wire of the welding electrode. Elemental compositions of the weld metal were measured at 5 different locations using the scanning electron microscopy (SEM) coupled with electron dispersion spectroscopy (EDS) (TESCAN VEGA).

The weld metal recovery (WMR) of elements in the weldment is evaluated with respect to the mass balance between the consumable and weldment. The weld beads were deposited on the 10mm SS316LN base plates and its geometrical parameters (depth, width and area) were measured using the Image J software. The WMR percentage for the elements were calculated from the following equations (2-6) [5, 10].

**Percentage weld metal recovery of the element**

$$E(\%) = \left( \frac{Z_{\text{deposited}}}{Z_{\text{wire}} + Z_{\text{bm}} + Z_{\text{coating}}} \right) \times 100$$  \hfill (2)

Where, the quantity of element present in weldment

$$Z_{\text{deposited}}(g) = (M_{\text{bm}} + M_{\text{wm}}) \times \frac{C_{\text{deposited}}}{100}$$  \hfill (3)

the quantity of element present in the core metal wire

$$Z_{\text{wire}}(g) = \left(1 - \frac{L_a}{L_b}\right) \times M_{\text{fm}} \times \frac{C_{\text{wire}}}{100}$$  \hfill (4)

the quantity of element present in the base plate

$$Z_{\text{bm}}(g) = M_{\text{bco}} \times \frac{C_{\text{bco}}}{100}, \quad M_{\text{bco}} = AP \times L \times \rho$$  \hfill (5)

the quantity of element present in the flux coating

$$Z_{\text{coating}}(g) = \left(1 - \frac{F_a}{F_b}\right) \times M_{\text{fc}} \times \frac{C_{\text{coating}}}{100}$$  \hfill (6)

Where, $L_b$ and $L_a$ represent the electrode length before and after welding in mm, $F_b$ and $F_a$ represent the flux coating length before and after welding in mm, $M_{\text{wm}}$ represents the mass of the weld laid on the base plate, $M_{\text{bco}}$ represents the mass of penetration attained in the base plate under the weldment, $M_{\text{fc}}$ and $M_{\text{fm}}$ represent the mass of flux and filler materials involved in the welding, $AP$, $L$, and $\rho$ represent the penetrated area, bead length and material density.

The percentage reduction of the constituent element ($E$) in welding fumes of experimental electrodes is given in the equation (7).

$$\%R_E = \left(\frac{E_S - E_C}{E_C} \times 100\right)\%$$  \hfill (7)

Where, $E_S$ and $E_C$ are the percentage of element present in fumes of experimental electrode and conventional electrodes respectively.

3 Results and Discussion

Figure 2 shows the variation of FFR and Cr(VI) concentration for conventional as well as experimental electrodes. The FFR of 0.14 g/min and Cr(VI) concentration of 0.036...
Table 3: Ozone concentration of fumes, mass transfer coefficient and weld metal recovery during welding

| Electrode | Oz (ppm) | Cr (%) | Fe (%) | Ni (%) | Mn (%) | Cr (%) | Fe (%) | Ni (%) | Mn (%) |
|-----------|---------|--------|--------|--------|--------|--------|--------|--------|--------|
| C         | 0.32    | 75.25  | 88.85  | 90.23  | 23.99  | 91.97  | 95.8   | 86.4   | 41.03  |
| E1        | 0.22    | 77.52  | 89.25  | 92.56  | 26.52  | 94.5   | 95.95  | 91     | 42.95  |
| E2        | 0.26    | 80.22  | 90.56  | 94.56  | 27.96  | 96     | 98.01  | 92.6   | 46     |
| E3        | 0.26    | 81.53  | 91.25  | 96.25  | 30     | 97.9   | 99     | 94.2   | 49     |
| E4        | 0.28    | 82.26  | 92.23  | 97.56  | 31.25  | 100    | 100    | 96.3   | 51.06  |
| E5        | 0.20    | 81.67  | 90.25  | 95.62  | 29.88  | 98.2   | 97.95  | 95     | 49.98  |

Figure 2: FFR and Cr(VI) concentration

Figure 2 shows the variation of mass transfer coefficient ($\eta$) and weld metal recovery (WMR) for the experimental and conventional electrodes. The $\eta$ and the WMR portrayed the same trend in their variations for nano TiO$_2$ additions to the welding electrode. The mass transfer coefficients of the elements Ni, Fe, Cr and Mn were in the range of 90-95%, 88-90%, 75-82% and 23-30% respectively. Whereas, the焊 metal recovery of the corresponding elements were in the range of 86-95%, 95-97%, 91-98% and 41-50%. The main factor guiding the transfer of element was the oxygen affinity of the element subjected to oxidation from the welding electrode [44]. Whereas the WMR was the percentage recovery of the elements in the weldment after welding, and the variation of percentage WMR among the elements was due to their melting and boiling points of the corresponding elements taken into consideration [5].

3.1 Mass Transfer and weld metal recovery

With an increase of nano TiO$_2$ content in the flux up to 80% (E4), the FFR decreased drastically, whereas the Cr(VI) concentrations increased. This was due to the fact that the decrease in fumes in the vicinity of the welding arc increased the exposure of UV rays favouring ozone enhanced oxidation of Cr to its higher valency. The ozone concentrations during welding of the electrodes are given in Table 3.

The final experimental electrode E5 showed an increase in FFR with decrease in Cr(VI) as different from the trend exhibited in E1 to E4. This was due to the fact that the higher quantity of nano TiO$_2$ present in the flux increased the reactivity during welding. Even though the improved deoxidization potential of nano sized Ti favoured the reduction of FFR from E1 to E4, it reached the maximum limit of fume suppression at E4 followed by emitting the element Ti in the welding fumes due to the excess reactivity at E5. This was confirmed by the constituent analysis of welding fumes, and the results are shown in Figure 2.
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Figure 3: Mass transfer coefficient and weld metal recovery

der decrease in $\eta$ and WMR were observed for E5 due to the excess reactivity offered by nano TiO$_2$ compared to E4, all the experimental electrodes showed better $\eta$ and WMR.

3.2 Mass transfer coefficient and the constituent emission in the welding fumes

The percentage reduction of various elements in the welding fumes with respect to their mass transfer efficiency for all experimental electrodes are shown in Figure 4. As the majority of the welding fumes in the range of 90-95% during welding process were emitted from the consumable electrode [45], it was indispensable to draw a relation between $\eta$ of the elements in the electrode and the percentage reduction of the corresponding elements in the fumes. The percentage reduction of the elements in the fumes and their corresponding mass transfer efficiency portrayed a same trend for the various combinations of the experimental electrodes. The percentage reductions of the constituents Fe, Ni, Cr and Mn in the welding fumes for the experimental electrodes were (4-16)%, (18-44)%, (8-32)% and (10-28)% respectively. The highest reduction percentage in emission was observed for Ni, which was due to its highest mass transfer efficiency resulting in efficient transfer of element towards weld. The next efficient $\eta$ was occurred for Fe. However, the percentage reduction of its welding fumes was the least. This was due to the presence of highest weight percentage of the Fe element in the base metal, core wire and flux. In addition, the majority of elements in the flux were in the form of ferro-mixed compounds like ferro silicon, ferro manganese etc.

The elements Mn and Cr showed the percentage reduction of welding fumes in the range of (8-32)%, which was due to low mass transfer efficiency of the elements. However, Cr showed a higher reduction percentage compared to Mn due to the inclusion of higher weight percentage in the range of (16-20) in the consumable as well as base metal compared to Mn which is a deoxidiser.

4 Conclusion

A novel welding electrode was developed by replacing the fine rutile particles in the flux with the substitution of TiO$_2$ nano compounds to investigate the mass transfer efficiency and its effect on FFR, Cr(VI) concentration in the welding fumes.
The experimental electrodes E4 (80% nano TiO$_2$ substitute) portrayed 21% reduction in FFR with 31% reduction in the Cr(VI) concentration which was the optimum combination of experimental electrodes. Even though, the combination E5 (100% nano substitute) showed the highest reduction of Cr(VI) accounting to 42%, the Ti emission in welding fumes was higher and hence increased the FFR.

The substitution of nano TiO$_2$ in the conventional welding electrodes had significantly increased mass transfer efficiency, favoured weld metal recovery by promoting better deposition/alloying of the major elements such as Fe, Cr, Ni and Mn in the weld metal rather than oxidizing/vaporizing to fumes. The mass transfer efficiencies of the elements were in direct proportions with their percentage reduction in fumes for various combinations of the experimental electrodes. For the experimental electrodes, the percentage reductions of the constituent elements Fe, Ni, Cr and Mn in the welding fumes were in the range of (4-16)%, (18-44)%, (8-32)% and (10-28)% respectively.

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