Control of exposure to hexavalent chromium concentration in shielded metal arc welding fumes by nano-coating of electrodes

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ABSTRACT

Background: Cr(VI) is a suspected human carcinogen formed as a by-product of stainless steel welding. Nano-alumina and nano-titania coating of electrodes reduced the welding fume levels.

Objective: To investigate the effect of nano-coating of welding electrodes on Cr(VI) formation rate (Cr(VI) FR) from a shielded metal arc welding process.

Methods: The core welding wires were coated with nano-alumina and nano-titania using the sol-gel dip coating technique. Bead-on plate welds were deposited on SS 316 LN plates kept inside a fume test chamber. Cr(VI) analysis was done using an atomic absorption spectrometer (AAS).

Results: A reduction of 40% and 76%, respectively, in the Cr(VI) FR was observed from nano-alumina and nano-titania coated electrodes. Increase in the fume level decreased the Cr(VI) FR.

Discussion: Increase in fume levels blocked the UV radiation responsible for the formation of ozone thereby preventing the formation of Cr(VI).

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Introduction

Welding produces toxic fumes and gases, which are hazardous to both workers and environment [1,2]. The risk of exposure depends on the individual concentration of the metallic species in fumes which varies with the chemical composition of the electrode and the base plate.

To minimize exposure to the hazardous components in fume is a challenging task. For instance, stainless steel contains 10.5–20% by weight of Cr, inducing enhanced corrosion resistance. Thus, welding stainless steel imposes enhanced risk of exposure to hexavalent chromium (Cr(VI)). The evolution of Cr(VI) during welding is due to oxidation of metallic Cr and Cr(III) by ozone or presence of certain alkaline oxides in the shielded flux, which could form stable Cr(VI) compounds that are suspected carcinogens [3]. In order to comply with the limits imposed by the Occupational Safety and Health Administration (OSHA), to a stringent value of 5 µg/m³, intense efforts are being carried out to reduce (a) alkaline content of the electrode and (b) ozone concentrations by adding reactive metals to the electrode or by the use of a secondary reducing shield gas.

Earlier, it was found that potassium and sodium oxides could influence more in the formation of Cr(VI)

in fumes than lithium oxides [4]. Dennis et al. [5] replaced potassium in the flux of a tubular wire arc welding process with lithium and found a significant reduction in the concentration of Cr(VI). The authors were however concerned with the addition of lithium since it is a biologically active ion with a threshold limit value (TLV) similar to Cr(VI).

On the other hand, reduction of ozone concentration to reduce Cr(VI) formation appears to be quite promising strategy. Dennis and co-workers [5] found that addition of 1% Zn to a metal core arc welding wire enhanced the fume level thereby preventing the UV light from forming ozone and thus reduced the Cr(VI) concentration. However, there were concerns over the formation of ZnO and ZnCl during welding. Further, such a direct addition process hinders the usual production process of electrode. Later, Dennis et al. [6] used a secondary shield gas containing reducing agents like NO and C₂H₄ in a gas metal arc welding (GMAW) process to achieve a drastic reduction in ozone level. Nevertheless, its application is limited to automatic welding processes where there is a provision for changing the shield gases and not for other self shielded processes like SMAW.

Reports indicated that the properties of a conventional electrode could be improved with the help of

nanotechnology [7,8]. Recently, the authors coated the core mild steel welding wires with nano-titania and nano-alumina and achieved a significant reduction in fumes [9,10]. The fume concentration was found to vary with the crystallite size of the deposit. The fume level was found to be less for a homogeneous deposit with lower crystallite size and vice versa. However, studies on the effect of coating on emission of heavy metals like Cr(VI) during welding are still lacking and offer a scope for in-depth study.

Thus, in this paper, an attempt was made to find the effect of nano-coating of stainless steel electrodes on the concentration of Cr(VI) in fumes. Other objectives were to evaluate the effect of each coating process parameters on the concentration of Cr(VI) in fumes using the Taguchi methodology of Design of Experiments (DoE) and to analyze and compare the metallic constituents in the collected aerosol from coated and commercially available uncoated electrode using the Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES).

Materials and methods

Core welding wires were coated with nano- Al_2O_3 and nano- TiO_2 . The coating technique adopted was sol-gel dip coating which compared to other methods appears efficient and economical [11].

Experimental design

In the sol-gel method, the properties of a nano-alumina film depend on several process parameters such as: molar concentration of the sol, dipping time, and sintering temperature [10] while, the properties of a nano-titania film depends on the poly ethylene glycol (PEG) content too [9]. PEG act as a binder for the TiO_2 film [12]. After preliminary experimental trials in the laboratory, a workable range of these parameters was chosen, as shown in the Table 1.

The workable range indicates the lower and upper limit values of process parameters within which a uniform coating is obtained. For instance, in nano-alumina coating, no coating was observed for a molar concentration value less than 0.01 M and the coating was peeling off for a molar concentration value above 0.03 M and so on.

Since there are various process parameters each at different levels, the basic design requires conducting a large number of experimental trials which is not only time consuming but also expensive. To avoid this difficulty, the Taguchi methodology of Design of Experiments known for its capability in correlating input parameters and the output response by conducting the least number of experiments was employed in this work [13–15].

The design was based on the L9 orthogonal array which necessitated a total of 9 (nine) experiments to be carried out as shown in Tables 2 and 3.

Preparation of coated electrodes

The core stainless steel welding wire (SS 316 LN) of 3.15 mm diameter and 350 mm length purchased from a local electrode manufacturer was used as the coating substrate. The chemical composition of the wire is shown in Table 1s of the Electronic Supplementary Information (ESI). These were polished with different grades of emery paper and cleaned with acetone. Square pieces of dimension $10 \times 10 \times 5$ mm were cut from the same grade material for the structural and morphological characterization of the resultant coating. The procedure reported by Sivapirakasam et al. [10] was followed for nano-alumina coating while that reported by S. Mohan et al. [9] was followed for nano-titania coating. During the deposition, to avoid the possible formation of cracks, the sintering was carried out in 5 steps inside a muffle furnace equipped with a PID controller. The following steps were adopted for the sintering process: Initially, the temperature of the furnace was raised to 1/5th of the target temperature. Immediately after this temperature was attained, the controller was set to 2/5th of the target temperature and so on. Similarly, each target temperature was achieved at a minimal heating rate of $1^\circ\text{C}/\text{min}$. The specimen was kept at the target temperature for one hour and the furnace was turned OFF after that. To ensure gradual cooling, the specimen was removed from the furnace only after it attained the room temperature.

After coating, the core wires were taken to the electrode manufacturer for flux coating. The flux formulation used was of E 316L, the composition of which is shown in the Table 2s of ESI. The uncoated electrodes were also made at par with the coated electrodes to ensure minimum variation while comparison.

Table 1. Levels of process parameters.

Nano-Alumina film	Parameters	Unit	Level I	Level II	Level III
	Molar Concentration, M	M	0.01	0.02	0.03
	Dipping Time, D	min	60	120	180
	Sintering Temperature, S	$^\circ\text{C}$	300	400	500
Nano-Titania Film	Molar Concentration, M	M	0.45	0.55	0.65
	Amount of PEG, P	g	0.5	2.0	3.5
	Dipping Time, D	Min	60	120	180
	Sintering Temperature, S	$^\circ\text{C}$	500	600	700

Table 2. Design matrix, FFR, and Cr(VI) FR from nano-alumina coated electrodes.

Run No.	Molar Conc (M)	Dipping Time (min)	Sintering Temperature (°C)	FFR (g/min)	Cr(VI) (wt %)	Cr(VI) FR (mg/m ³)
1	0.01	60	300	0.037	0.99	0.41
2	0.01	120	400	0.042	0.13	0.06
3	0.01	180	500	0.051	0.05	0.03
4	0.02	60	400	0.021	1.50	0.35
5	0.02	120	500	0.029	1.15	0.37
6	0.02	180	300	0.011	4.01	0.55
7	0.03	60	500	0.025	1.43	0.39
8	0.03	120	300	0.033	1.04	0.38
9	0.03	180	400	0.078	0.030	0.026

Table 3. Design matrix, FFR, and Cr(VI) FR from nano-titania coated electrodes.

Run No.	Molar Concentration (M)	Dipping Time (min)	Amount of PEG (g)	Sintering Temperature (°C)	FFR (g/min)	Cr(VI) (wt %)	Cr(VI) FR (mg/m ³)
1	0.45	60	0.5	500	0.051	0.019	0.010
2	0.45	120	2	600	0.017	0.46	0.087
3	0.45	180	3.5	700	0.047	0.026	0.013
4	0.55	120	0.5	700	0.025	1.01	0.28
5	0.55	180	2	500	0.038	0.046	0.019
6	0.55	60	3.5	600	0.014	1.11	0.17
7	0.65	180	0.5	600	0.03	0.41	0.136
8	0.65	60	2	700	0.008	3.79	0.34
9	0.65	120	3.5	500	0.041	0.04	0.018

Coating characterization

The surface morphology of the coated specimens was examined using the Scanning Electron Microscope (TESCAN, VEGA SBH). From the SEM images, the porosity of the coated surface was estimated using the image analysis software, imageJ. The phase analysis of the coating was carried out by the X-ray Diffraction Analysis using a computer controlled X-ray Diffractometer (Rigaku Ultima III) under Cu-K α radiation ($\lambda = 1.54$ Å). The peaks obtained were compared with the JCPDS (Joint Committee on Powder Diffraction Standards) database to confirm the presence of alumina and titania in the coating. The average crystallite size of the coating was found out from the XRD graphs using the following Scherrer's equation [9,10,14]:

$$T = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where T is the mean crystallite size, λ is the X-ray wavelength; β is the Full Width at Half Maxima (FWHM) of the peak corresponding to the diffraction angle, θ .

Measurement of fume formation rate (FFR)

The measurement of Fume Formation Rate (FFR) conformed to the ISO 15011-1 standard [16,17]. A fume collection chamber of similar construction as recommended by the American Welding Society was used in this study (Figure 1).

The weld was laid on SS 316 LN plates fixed on a variable speed rotating plate inside the chamber. The authors have chosen SS 316 LN instead of SS 316 L since it is potentially being used as the major structural material in

fast breeder reactors in the nuclear industry [18]. Though the low carbon content in SS 316 L reduces the tendency of carbide precipitation and localized corrosion in the weld, it has a detrimental effect on the strength of the weld thereby limiting its use. The addition of Nitrogen in SS 316 L will enhance the strength of the weldments both at room and elevated temperature, imparts additional resistance to corrosion, and enhances properties like tensile, creep, fatigue, impact toughness etc. which are prerequisites for the aforementioned application [19]. Further, due to the superior properties, SS 316 LN also finds its applications in other industries like cryogenic and automotive.

The chemical composition of the base plate is shown in Table 1s of ESI. The emitted fumes were collected on a Whatman GF/A filter paper (253 × 204 mm, 1.6 μ pore size) at a flow rate of 900 l/min. The welding lasted 60 s and the extractor fan was left running for another 90 s to ensure maximum fume collection. The difference in weight of the filter paper before and after fume collection was divided by the arcing time to calculate the FFR.

Cr(VI) analysis

For the analysis of Cr(VI) content in the collected fume, the filter paper was processed as per the extraction procedure detailed in the NIOSH method 7600 [20]. The fume samples were leached in the basic carbonate solution (2% NaOH/3% Na₂CO₃) which has been demonstrated by Pederson et al. [21] as an effective method to separate Cr(VI) from other compounds. The detailed steps involved in the extraction are as follows: The fume samples of ~25 mg were placed in 150 ml conical

Figure 1. Fume test chamber.

flasks. To this 40 ml of basic carbonate solution along with 10 ml of deionized water was added and simmered for 20 min. It was then filtered, cooled, and transferred into 50 ml volumetric flasks. The resultant samples were then analyzed for the Cr(VI) concentration by employing an Atomic Absorption Spectrometer (AAS) (Make GBC Model 902) at 359.7 nm [5,6,22]. Even though, the NIOSH 7600 standard specifies measurement of Cr(VI) by Visible Absorption Spectrophotometry, AAS was employed in this work as it permits a relatively simple determination of Cr(VI) content in welding fume [21].

Ozone measurement

Ozone concentrations were measured at a fixed sampling position relative to the welding arc at an angle of 60° from the horizontal and at a horizontal distance of 75 mm from the weld pool [5]. The sampling probe was connected to a precalibrated UV-absorption ozone analyzer (Make Ecotech Model EC 9810B) via a PTFE tube. The analyzer was capable of measuring ozone concentrations in the range 0–20 ppm with a sensitivity range of 0.005 ppm. A 5 micron PTFE filter was inserted in the connecting tube to prevent welding fume from entering the analyzer. Before undertaking any measurements on welding emissions the sampling probe, PTFE tubing and the filter were conditioned to prevent subsequent absorption of ozone. This was done by the passage of 10 ppm ozone from an ozone generator for 10 min. Ozone measurements were averaged over a 60 s period after first welding for 60 s. This is to allow for the establishment of the welding regime. All experiments were performed in triplicate.

Constituent analysis

The fume samples were analyzed for Fe, Mn, Cr, Ni, and Mo using the Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) (Perkin Elmer model OPTIMA 5300DV) as per the standard method enclosed in NIOSH 7300 [23]. In addition to the above elements the concentrations of Al and Ti in fume were also measured.

SEM-EDS and oxygen analysis

Energy dispersive X-ray spectroscopy (EDS) (JEOL model JED 2300) was carried out using a high magnification scanning electron microscope (SEM) (JEOL model 6390 LV) for the local elemental chemical analysis of the weld. For this, weld samples were cut into 1 cu.cm size, ultrasonically cleaned in acetone for 10 min and then subjected to EDS spot scanning analysis at 3 different points across the weld bead [9].

The oxygen content in the weld was analyzed by employing an oxygen analyzer (Make Eltra, Model ONH-2000) [9].

Statistical analysis of the output data

In Taguchi method, any repetitive data in an experiment can be transformed into a consolidated value called the Signal-to-Noise (S/N) ratio, which represents the amount of variation present in the output response. The equation for S/N ratio depends on the criterion of the performance parameter to be analyzed, Cr(VI) concentration in this case. Since a lower value of Cr(VI) concentration was desirable, the following equation for “lower the better” type of S/N ratio was applied [9,14].

$$\eta = 10 \log \left[\frac{1}{n} \sum_{i=1}^n y_i^2 \right] \quad (2)$$

where η is the S/N ratio y_i is the measured output value for the i th repetition and n is the number of repetitions in a trial.

To carry out Analysis of Variance (ANOVA), the total variability of S/N ratios was divided into contributions by each process parameter and the error. The total sum of the squared deviations $(SS)_T$ and the sum of squared deviation due to each process parameter $(SS)_p$ were found out using the following equations:

$$(SS)_T = \sum_{i=1}^m \eta_i^2 - m \bar{\eta}^2 \quad (3)$$

$$(SS)_p = \sum_{j=1}^t \frac{(s \eta_j)^2}{t} - \frac{1}{m} \left[\sum_{i=1}^m \eta_i \right]^2 \quad (4)$$

where m represents the number of experiments in an orthogonal array, η_i the mean S/N ratio for the i th experiment, η_m the total mean of S/N ratio, j the level number of the process parameter p , t the repetition of each level of the parameter p , and $s\eta_j$ the sum of the S/N ratio involving the parameter p at level j . The variance of the process parameters (V_p) was calculated as per the following equation:

$$V_p = \frac{(SS)_p}{(df)_p} \quad (5)$$

where $(df)_p$ is the degree of freedom of the process parameter given by $t-1$. Since it is a saturated design where all columns were assigned with factors, the variations due to error were estimated by pooling the estimates of factors having the least variance. The corrected sum of squares $(\hat{S})_p$ for each process parameter was calculated as:

$$(\hat{S})_p = (SS)_p - (df)_p V_e \quad (6)$$

Finally, the percentage contribution ρ was found out using the following relation:

$$\rho = \frac{(\hat{S})_p}{(SS)_T} \quad (7)$$

Results and discussion

Tables 2 and 3 shows the FFR and Cr(VI) concentration in fume of nano-alumina and -titania coated electrodes, respectively. The data presented is the average of three replicates of FFR and Cr(VI) concentration. The data were within $\pm 3\%$ variation.

Cr(VI) formation rates [Cr(VI) FR] were calculated from the resultant value of FFR and Cr(VI) concentration in fume [6]. The FFR, Cr(VI) concentration in fume and the Cr(VI) FR for the uncoated electrode were obtained as 0.030 g/min, 1.25%, and 0.043 mg/m³, respectively. As seen from the Tables 2 and 3, the Cr(VI) FR varied from 0.026 to 0.55 mg/m³ for nano-alumina and 0.010–0.34 mg/m³ for nano-titania coated electrodes with changes in the process parameter combination. The variation in Cr(VI) FR is indicative of the significant influence of coating process parameters. Besides, it is interesting to note that in most experimental runs, an increase in FFR, reduced the formation of Cr(VI). The following sections give a detailed discussion on the effect of each coating process parameter on the Cr(VI) FR.

Effect of nano-alumina coating process parameters on Cr(VI) FR

The main effect plot of coating process parameters on the Cr(VI) FR from the nano-alumina coated electrodes is shown in Figure 2.

The variation of Cr(VI) FR with molar concentration of alumina sol is depicted in the first row of the Figure 2. The Cr(VI) FR first increased and then decreased with the molar concentration of the sol. In order to understand this trend, three critical runs were selected from the Table 2 based on the values of Cr(VI) FR viz; run 9 with the lowest Cr(VI) FR, run 6 with the highest Cr(VI) FR and run 1 with a medium Cr(VI) FR. The coated square pieces corresponding to these critical runs were then subjected to SEM and XRD analysis, the results of which are given in the Figures 3 and 4. From the SEM images, the percentage porosity, an estimate of the number of pores, was measured using the image analysis technique and shown in Table 4.

A close examination of the Figure 3 and Table 4 indicate an increase in homogeneity (Figure 3(b)–(a)) and decrease in porosity (43–32%) of the coating with an increase in molar concentration of the sol which might have resulted in increased Cr(VI) FR. However, with further increase in molar concentration, the homogeneity of the coating has decreased (Figure 3(c)), however with an increase in porosity from 32 to 75% resulting in a decrease in Cr(VI) FR. Also, from the XRD graphs (Figure 4), it was observed that, the coating corresponding to run 9 (with 0.03 M molar concentration) exhibited an intense peak for alumina suggesting a higher crystallite size. Similarly, the peak with the least intensity was noted in run 6 (molar concentration 0.02 M) indicating a lower crystallite size. Further, the average crystallite size estimated from the XRD graphs was found to be 95 nm for run 9 and 33 nm for run 6 (Table 4).

The second row of Figure 2 shows the effect of dipping time on the Cr(VI) FR. A gradual decrease in Cr(VI) FR was seen with an increase in dipping time. With an increase in dipping time, the coating became non-uniform (Figure 3(c)) and porous. As shown in Figure 2 (third row), the Cr(VI) FR decreased with an increase in the sintering temperature to a medium value (400 °C) and then increased. The following reasons may be assigned to the above behavior. As the sintering temperature increased, the coating became non-homogeneous with large number of pores (Figure 3(c)). With the further increase in sintering temperature, the coating became more uniform with fewer pores causing an increase in Cr(VI) FR.

Effect of nano-titania coating process parameters on Cr(VI) FR

Figure 5 shows the main effect plot of process parameters on the Cr(VI) FR for the nano-titania coated electrode. The Cr(VI) FR increased with an increase in the molar concentration of the sol as seen in the first row of Figure 5. Similar to the case of nano-alumina coated electrodes, three critical runs were selected from Table 3, viz; run 1 with the lowest Cr(VI) FR, run 8 with the highest, and run 6 an intermediary.

Figure 2. Main effect plot showing the variation of Cr(VI) FR with: (a) Molar concentration of the sol, (b) Dipping time, and (c) Sintering temperature for the nano-alumina coated electrode.

The SEM micrographs and the XRD spectra of the coated square pieces corresponding to these critical runs are shown in Figures 6 and 7.

As seen from Figure 6 and Table 4, there was an increase in homogeneity (Figure 6(c)–(a)) and decrease in number of pores of deposit (porosity decreased from 80% through 38–25%) with an increase in the molar concentration of the sol. The effect of dipping time on the Cr(VI) FR is depicted in the second row of Figure 5. There was a linear decrease in Cr(VI) FR with an increase in dipping time. With an increase in dipping time, the coating became non-homogeneous with larger number of pores and contributed to decreased Cr(VI) formation.

As shown in the third row of Figure 5, there was a slight increase in the Cr(VI) FR with the PEG content up to a medium level (i.e. 2 g) followed by a sharp decrease. This may be attributed to the following; with an initial increase in the PEG content (i.e. from 0.5 g–2 g),

there was an increase in the homogeneity of the deposit (Figure 6(a)). With the further increase in the PEG content, the uniformity of the coating was found to deteriorate with large number of pores, resulting in a decrease in Cr(VI) FR (Figure 6(b)).

As seen in the fourth row of Figure 5, the Cr(VI) FR increased with the sintering temperature. The homogeneity of the deposit exhibited a visible increase with the sintering temperature as shown in Figure 6(c)–(a).

Thus, in summary, the morphology and crystallite size of the deposit has been shown to influence both the quantity of fumes produced and the Cr(VI) FR. The Cr(VI) FR showed an inverse relationship with FFR in which the former decreased with an increase in the latter. A mechanism for the increase in fume levels with a decrease in homogeneity of the deposit has been proposed by Mohan et al. [9] and Sivapirakasam et al. [10]. On this basis, the reason for decreased Cr(VI) FR due to the coating of nano-alumina and nano-titania can

Figure 3. SEM images of nano-alumina coated specimens [(a) Run 6, (b) Run 1, and (c) Run 9].

be well explained. The high temperature of the welding arc plasma causes dissociation of nano-alumina and nano-titania into their respective ions as per the following equation:

where M represents either Al or Ti and n represents its valency (3 for Al and 4 for Ti). The M^{n+} ions so formed might ionize the shielding gas molecules like CO_2 by the mechanism of collision.

The resultant M (i.e. Al from nano-alumina coated electrode or Ti from nano-titania coated electrode) goes and deposit in the weld pool. To confirm the presence of M in the weld deposit, its SEM/EDS analysis was carried out, the results of which are shown in Figures 1 and 2 of ESI and Table 5.

It was observed that nano-alumina electrode corresponding to run 9 exhibited lower concentrations of Al in the weld deposit. Similarly, a low concentration of Ti in the weld deposit was noted for nano-titania electrode

corresponding to run 1. In both cases, the coating was non-homogeneous with a higher crystallite size. This is an indication of the lower rate of the preceding reactions (Equations (8) and (9)) for run Nos. 9 (nano-alumina coated electrode) and 1 (nano-titania coated electrode). The decrease in the rate of reaction results in more M^{n+} ions remaining unreacted in the arc atmosphere (Equation (8)). Since, further removal of electrons from M^{n+} require much higher voltages, the overall ionization potential of the arc atmosphere increases leading to higher fume levels. Higher fume level physically obstructs the UV radiation responsible for the formation of ozone. Table 4 gives the ozone concentrations near the arc measured for three critical runs of nano-alumina and nano-titania coated electrodes. The ozone concentration obtained from the uncoated electrode was 0.90 ppm. It was evident from the Table 4 that the coated electrodes corresponding to run 9 (nano-alumina coated electrode) and run 1 (nano-titania coated electrode) exhibited lower ozone concentrations compared to the uncoated electrode. The decrease in ozone levels retards the oxidation of metallic Cr and Cr(III) to Cr(VI) leading to lower Cr(VI) FR.

Figure 4. XRD patterns of nano-alumina coated specimens [(a) Run 6, (b) Run 1, and (c) Run 9. Symbols Δ and Θ represent the peaks of alumina and substrate].

Table 4. Average crystallite size, porosity, and ozone concentration (three critical runs).

Run No.	Molar Concentration (M)	Dipping Time (min)	Sintering Temperature (°C)		Crystallite Size (nm)	Porosity (%)	Ozone (ppm)
Nano-alumina coated electrode							
1	0.01	60	300		40	43	0.75
6	0.02	180	300		33	32	1.00
9	0.03	180	400		95	75	0.10
Run No.	Molar Concentration (M)	Dipping Time (min)	PEG (g)	Sintering Temperature (°C)	Crystallite Size (nm)	Porosity (%)	Ozone (ppm)
Nano-titania coated electrode							
1	0.45	0.5	60	500	105	80	0.05
6	0.55	3.5	60	600	45	38	0.25
8	0.65	2	60	700	20	25	0.55

However, a homogenous deposit with a lower crystallite size (run 6 of nano-alumina coated electrodes and run 8 of nano-titania coated electrodes) result in a higher rate of the aforesaid reactions as indicated by higher Al and Ti level in the weld deposit. This leads to increased CO_2^{n+} level in the arc atmosphere (as noted from Equation (9)) implying better ionization of the arc atmosphere. Thus, the effective voltage required for a stable arc may be less resulting in lower fume levels. Lower fume levels lead to increased ozone concentration in the vicinity of the arc (as seen from Table 4) due to which the Cr(VI) FR increases.

Statistical analysis

Statistical analysis of the Cr(VI) FR was carried out in order to find out the optimum parameter settings and analyze the contribution of each factor to the output

response. While the S/N ratio was helpful in optimizing process parameter settings, the significance of each factor was analyzed using analysis of variance (ANOVA).

The S/N ratio calculated with the experimental results and the mean S/N ratio at three levels of process parameters for the output response (viz., Cr(VI) FR) for the nano-alumina and nano-titania coated electrodes are presented in Tables 6 and 7, respectively.

Regardless of the type of performance characteristics desired, i.e. higher the better, lower the better or nominal the better, a large S/N ratio implied better performance characteristics. In other words, the largest S/N ratio yields the most optimal level of the process parameters.

Hence it was inferred from the Table 6 that, for a nano-alumina coated electrode, a lower value of molar concentration, higher value of dipping time, and medium value of sintering temperature were optimal in reducing the formation of Cr(VI). Alternatively, a lower molar

Figure 5. Main effect plot showing the variation of Cr(VI) FR with: (a) Molar Concentration of the sol, (b) Dipping time, (c) PEG content, and (d) Sintering temperature for the nano-titania coated electrode.

concentration and sintering temperature, a medium dipping time, and a higher amount of PEG were favorable in reducing Cr(VI) FR from a nano-titania coated electrode (Table 7). The difference between the maximum and minimum S/N ratio for each process parameter was noted. For nano-alumina coated electrode, the highest difference was with the molar concentration implying its highest influence on Cr(VI) FR and the lowest value was for dipping time reflecting its lowest influence. Likewise, for the nano-titania coated electrode, the highest influence on Cr(VI) FR was by the molar concentration of the sol while the lowest influence was by the amount of PEG.

The ANOVA results for the output response are presented in Tables 8 and 9 from where the contribution of each process parameter to the Cr(VI) FR can be observed.

For the nano-alumina coated electrodes, the molar concentration of the sol has the highest influence (50.79%) in reducing the Cr(VI) FR and the lowest influence is by dipping time (16.81%). Similarly, for the nano-titania coated electrodes, the molar concentration

of the sol contributed 63.90% toward reducing the Cr(VI) FR while the PEG content influence was only 3.05%.

Constituent analysis of fume

The constituent analysis results of the collected aerosol are shown in the Figures 8 and 9. Figure 8 shows the variation in concentration of metallic constituents at the three critical runs of nano-alumina coated electrodes. The horizontal line represents the concentration of metallic constituent from the uncoated electrode.

The results indicated a reduction in the concentration of metallic constituents for run no. 6 (corresponding to a homogenous deposit with lower crystallite size) and an increase in concentration of metallic constituents for run no. 9 (corresponding to a non-homogeneous deposit with higher crystallite size).

The variation in concentration of metallic constituents for nano-titania coated electrodes is shown in Figure 9, where the horizontal line stands for the concentration

Figure 6. SEM images of nano-titania coated specimens [(a) Run 8, (b) Run 6, and (c) Run 1].

values from the conventional uncoated electrode. The highest concentration of metallic constituents was noted for run 1 (corresponding to a non-homogenous deposit with higher crystallite size) while the lowest was for run 8 (corresponding to a homogenous deposit with lower crystallite size).

In order to understand the reason behind this variation, the weld specimens corresponding to the three critical runs of nano-alumina and -titania were subjected to oxygen analysis. The results of the analysis are shown in Table 10.

It was evident that the oxygen level in the weld for the nano-alumina coated electrode corresponding to run 6 was much higher than that for the other two runs (run 9 and run 1) and the uncoated electrode. Similarly, for the nano-titania coated electrode, run 8 exhibited the highest oxygen content and run 1 exhibited the lowest.

The percentage of alloying elements in the weld pool from both nano-alumina and nano-titania coated electrodes were identified using the SEM/EDS analysis (Table 5). It was found that the nano-alumina coated electrodes corresponding to run 6 and nano-titania

coated electrodes corresponding to run 8 yielded higher depositions of alloying elements in the weld compared to that of the uncoated electrode. On the contrary, run No. 9 (nano-alumina coated electrode) and run No. 1 (nano-titania coated electrode) exhibited lower concentrations of alloying elements in the weld pool.

The above findings indicated that a homogeneous deposit with a lower crystallite size result in an increased oxygen level in the weld pool. An increase in oxygen level enhanced the stirring effect of the weld pool and facilitated the deposition of alloying elements in it. This prevented the evolution of the constituent elements as fumes. In the same way, for a non-homogeneous with a higher crystallite size, as seen in run no. 9 (nano-alumina coated electrode) and run 1 (nano-titania coated electrode), the oxygen level in the weld pool is less which result in its low stirring effect. This retards the deposition of alloying elements in the weld pool resulting in its evolution as fumes.

Nevertheless it could be noticed that, though the concentration of alloying elements were higher in some experimental runs (run no. 9 of nano-alumina coated electrode

Figure 7. XRD patterns of nano-titania coated specimens [(a) Run 8, (b) Run 6, and (c) Run 1. Symbols Δ and Θ represent the peaks of titania and substrate].

Table 5. Chemical composition of weld metal for the uncoated and coated electrodes.

Designation/ Elements		Composition, (wt %)							
		Fe	Cr	Mn	Ni	Mo	Al	Ti	Others
Uncoated		67.9	18.06	0.93	10.56	1.84	0.07	0.09	0.55
Nano-alumina Coated	Run 1	67.6	18.09	0.9	10.58	1.82	0.08	0.08	0.85
	Run 6	68.01	18.14	0.95	10.61	1.86	0.09	0.11	0.23
	Run 9	67.3	17.8	0.87	10.45	1.81	0.05	0.06	1.66
Nano-titania coated	Run 1	67.1	17.9	0.85	10.41	1.8	0.05	0.06	1.83
	Run 6	67.5	18.05	0.91	10.54	1.82	0.06	0.07	1.05
	Run 8	68.05	18.09	0.96	10.59	1.86	0.08	0.1	0.27

Table 6. S/N ratios for Cr(VI) FR from nano-alumina coated electrode.

Factor	Level I	Level II	Level III	Max-Min
M	-1.59	-4.58	-2.66	2.99
D	-3.64	-2.77	-2.45	1.19
S	-4.00	-1.99	-3.15	2.01

Table 7. S/N ratios for Cr(VI) FR from nano-titania coated electrode.

Factor	Level I	Level II	Level III	Max-Min
M	-1.71	-7.64	-7.14	5.93
D	-6.16	-5.51	-6.80	1.30
S	-1.98	-6.83	-6.54	4.85
P	-7.56	-7.10	-6.23	0.46

Table 8. ANOVA table for Cr(VI) FR from nano-alumina coated electrode.

Source	Df	SS	V	$\bar{S}$	% Contribution
M	2	1.59	0.79	1.28	50.79
S	2	0.74	0.37	0.43	32.15
D	2	0.31	0.15		16.81
Error	2	0.004	0.002		0.25
Total	8	2.644			

Table 9. ANOVA table for Cr(VI) FR from nano-titania coated electrode.

Source	Df	SS	V	$\bar{S}$	% Contribution
M	2	4.41	2.21	3.89	63.90
D	2	0.73	0.37	0.21	12.50
S	2	1.50	0.75	0.98	20.10
P*	2	0.52	0.26		3.50
Total	8	7.16			

and run no. 1 of nano-titania coated electrode), the values were less than their corresponding TLV's.

Toxicological aspects of coated electrodes

The findings of the present study indicated that nano-titania and nano-alumina are potential candidates in retarding the formation of Cr(VI) during welding. The reduction percentage was much higher for the latter (76%) compared with the former (40%). However, for the commercial exploitation of these materials in the welding industry, its toxicological and health aspects were also analyzed.

Figure 8. Variation of metallic constituents' concentration with the three critical runs for nano-alumina coated electrode.

Figure 9. Variation of metallic constituents' concentration with the three critical runs for nano-titania coated electrode.

Table 10. Weld metal oxygen content (ppm).

Designation		Weld metal oxygen Content (ppm)
Uncoated		480.3
Nano-alumina coated electrode	Run 1	450.6
	Run 6	501.1
	Run 9	410.4
Nano-titania coated electrode	Run 1	397.2
	Run 6	467.7
	Run 8	522.3

Table 11. Comparison of previous reports with the coated electrodes.

Literature	Additive used	TLV of the additive (mg/m ³)	Additive Concentration in fume (mg/m ³)
Kimura et al. [4]	Li	0.05	4.73
Dennis et al. [5]	Zn	5	Not reported
Coated electrodes	Al ₂ O ₃	10	4.2
	TiO ₂	15	0.6

Firstly, the method of coating selected here did not require the direct use of nanoparticles. As an alternative, the coatings were achieved from their respective precursors, Aluminum Iso-Propoxide and Titanium-Tetra Butoxide, where its exposure risk is minimized compared to direct handling of nanoparticles.

Secondly, since fume is composed of several metallic constituents, any method focusing on the reduction of Cr(VI) concentration should not neglect its impact on other metallic constituents. In the present method, a higher reduction of Cr(VI) FR up to a level of 0.02 mg/m³ and 0.01 mg/m³ was achieved at run 9 of nano-alumina and run 1 of nano-titania coated electrodes, respectively. Consequently, other metallic constituents exhibited an increase in their concentration. Even so, they are still within their respective TLV's. Thus, there is no concern regarding the overall exposure risk associated with the present method.

Lastly, any material used for the reduction of Cr(VI) should not impose a threat of exposure in fumes. Similar to the present work, there were two reported literatures on the reduction of Cr(VI) at the source by using additives. In Table 11, a brief description of these works and its comparison with the present method is given.

Kimura et al. [4] used Li in place of Na and K in a SMAW process and found a significant reduction in Cr(VI) concentration. However, the authors noted an excess amount of Li in the fume. Since Li is classified as a biologically active ion with a TLV same as that of Cr(VI), its usage leads to further complication. Dennis et al. [5] reported the use of metal cored wire containing 1% Zn in a GMAW process as a way to reduce Cr(VI). However, the authors raised concern over the formation of ZnCl and ZnO while welding. The nano-alumina and

nano-titania used in the current study have relatively higher exposure limits. Further, their concentrations in fume were seen much lesser compared to their respective TLV's. Thus, there is a considerable scope for recommending the coated electrodes as a promising solution to control Cr(VI) emission.

Conclusions

This work highlighted the favorable influence of nano-coating stainless steel SMAW electrodes in the reduction of Cr(VI) formation while welding. The core welding wires were coated with nano-structured alumina and titania using the sol-gel dip coating method prior to its flux coating. The experiments were designed and the results analyzed using the Taguchi methodology. Following were the major findings evolved from this study:

- The respective reduction percentages obtained in the concentration of Cr(VI) from nano-alumina and nano-titania coated electrodes were 40% and 76%.
- The FFR and Cr(VI) FR had an inverse relationship with each other in that the latter decreased with an increase in the former. A non-homogenous deposit with a higher crystallite size provided a better reduction in the Cr(VI) FR and vice versa. This was attributed to the decrease in ozone levels in the vicinity of the arc due to which oxidation of metallic Cr and Cr(III) to Cr(VI) was prevented.
- The constituent analysis of the collected aerosol revealed lower concentrations of metallic constituents for a homogenous deposit with lower crystallite size and higher concentrations for a non-homogenous deposit with higher crystallite size. All concentration values were, however, within their respective TLV's.
- The proportionate contribution of each process parameter in reducing the Cr(VI) FR from both nano-alumina and nano-titania coated electrodes were analyzed using ANOVA. For both coated electrodes, the molar concentration of the sol contributed the highest of 50.79 and 63.90%. For nano-alumina coated electrodes the lowest influence was by dipping time (16.81%) while for the nano-titania coated electrodes, quantity of PEG had the least influence (3.05%) in reducing the Cr(VI) FR.
- The process of coating employed here has hardly any potential toxicological and health effects. The methodology adopted in this work can hence be recommended for large-scale commercial production of welding electrodes with reduced Cr(VI) formation in fumes.

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