Stainless welding consumables with low Cr^{VI} emissions

Oerlikon has developed new range of stick electrodes and flux-cored wires for Grades 308L, 309L and 316L stainless steel. These welding consumables significantly reduce fume emission rate (FER), by up to 40%, and Cr^{VI} emissions by up to 60%; which can help create a better working environment for welders.

Local and regional governments have imposed occupational exposure limits (OELs) or total airborne particle limits that vary from 1.0 mg/m^3 in Netherlands to 5.0 mg/m^3 in the UK, Australia and South Africa. But welding fumes can contain chemical elements such as Cr^{VI} with their own OEL values.

French decree No. 2012-746 limits values for occupational exposure and more restrictive values were applied in France from 1st of July 2014. The eight-hour OEL limit of Cr^{VI}, for example, changed from 50 µg/m^3 to the new limit of 1.0 µg/m^3 OEL with a 15-minute short-term limit of less than 5.0 µg/m^3.

As hexavalent chromium may be present in the welding fume generated by stainless steel welding consumables, users and employers of stainless steel welding consumables should assess the potential exposure to Cr^{VI} in their workplace, and the appropriate welding fume control solutions needed to keep exposures to levels below applicable OELs. When assessing the welding fume control solutions to use, in addition to considering personal protection equipment (PPE) and fume extraction systems, users and employers should also consider changing the welding consumable itself, which could reduce hexavalent chromium generation at the outset and lead to a positive impact on working conditions and environment.

The formation mechanism and Cr^{VI} reduction techniques are well known [ref.1], but the weldability of consumable products designed to reduce Cr^{VI} from welding consumables has previously proven inferior to those currently used in the field. Also, in the case of stick electrodes, poor extrusion behaviour and poor adherence and coating resistance during manufacture has prevented these consumables from reaching general market acceptance.

To meet this Cr^{VI} OELs and prevent risks for users and their environment, many methods for reducing airborne levels of Cr^{VI} are available, but when welding stainless steel, it may only be possible to stay below these levels by combining several available fume control solutions.

Welding consumables such as stick electrodes and cored wires with low Cr^{VI} source emission levels will, therefore, be a very valuable new tool to users and employers working to meet the new safety limits.

Cr^{VI} fume generation principles

Fumes emitted during welding result from complex processes of evaporation, condensation and oxidation mechanisms and their combination. These phenomena, as shown by Figure 1, generate fume at droplet level: inside the arc column; during spatter formation; or in the molten weld pool.

During stainless steel welding, the presence of high levels of chromium in the welding consumables leads to the formation of high chromium-bearing particles in the fumes. These chromium-bearing compounds feature non-toxic chromium in its elemental state; trivalent (+3) chromium, which is also non-toxic; and hexavalent chromium (Cr^{VI}).

Photo1: Nice welding appearance and easy slag detachability for Clearinox.

Relatively few components containing Cr^{VI} can be formed in fume and its formation principle is illustrated by equations [a] and [b] below. The problem lies in the formation, during welding, of certain noxious compounds containing Cr^{VI}, such as Na_2CrO_4, K_2CrO_4, $K_2Cr_2O_7$, $NaK_3(CrO_4)_2$, $NaK_3(Cr_2O_7)_2$. These result from the reaction of vaporised sodium (Na) and potassium (K), which are both present in welding consumable composition or with chromium (Cr).

$$2Na+Cr+2O_2 \rightarrow Na_2CrO_4 \quad [a]$$

$$2K+Cr+2O_2 \rightarrow K_2CrO_4 \quad [b]$$

A new consumable development route

To reduce the contents of compounds containing Cr^{VI} in the fume, the document by S. Kimura [11] proposed the elimination, in electrode coating formulations, of all ingredients containing the elements Na and K and their substitution with equivalent ingredients based on lithium (Li). However, this solution has always been difficult to implement and has never become an established industrial practice.

Compounds based on Na and K, either in the form of powders and/or liquid silicates, are conventionally used almost automatically in the coatings of stick electrodes since they play a vital role in obtaining good performances: good arc stability; suitable weld bead aspect; easily detachable slag; and friendly arc characteristics. By eliminating or even reducing the Na and K compounds, all these welding performance positives deteriorate quickly.

Particularly for Stick electrodes, the use of lithium-based binders as replacements for sodium- and/or potassium-based binders, but also other Li based powders, result in electrodes having a fragile, or even highly friable coating, making the electrodes thus formulated unusable in an industrial environment where the electrodes are often accidentally knocked or roughly handled, leading to their rapid deterioration.

In practice, the operating properties (weldability) of these lithium-based electrodes have proven to be inferior to standard rutile-types and consequently the market has rejected them. No electrode of this type has appeared on the stainless steel electrode market and the situation has been similar for flux-cored wires.

Clearinox E (MMA) and Clearinox F (FCAW)

Oerlikon's goal was to develop a new range of consumables for stainless steel welding – Clearinox E (MMA) and Clearinox F (FCAW) – that displayed low fume emission rates and significantly lower Cr^{VI} concentrations in welding fume than standard rutile-type consumables. In addition, equal or superior welding behaviour and characteristics were targeted compared to standard rutile-type consumables.

Trials demonstrated that the reduction of FER and Cr^{VI} is achievable only through the suppression or significant reduction of Na and K compounds, but welding characteristics require high levels of Na and K percentages in MMA coating formulations and filling flux for flux-cored wires.

In the case of MMA electrodes, the solution that emerged was based on the idea that the Na and K compounds in extremely small percentages would still provide both very good welding behaviour and a robust coating if such compounds are not uniformly dispersed in the entire coating, but limited to certain areas. The practical outcome of this solution is a double-coated electrode concept, for which suitable inner and outer coating formulations have been developed, along with optimal outer/inner coatings ratio in terms of mass.

In addition, instead of using lithium silicate as the binder, other raw materials containing alkaline elements were also replaced with similar powders, such as lithium feldspar instead of Na, K Feldspar, with compensation for the lack of Na and K with other ionising agents to ensure good arc stability.

Regarding the flux-cored wires, the main challenge was also to preserve the excellent operational performances of the standard wires, especially the spray-arc transfer characteristics, even when the wires are used at low amperages, for positional welding, for example. For the standard wires, the K and Na compounds existing in the filling flux are the key ingredients responsible for good welding characteristics. In order to compensate for their reduction, therefore, special ionising compounds were introduced in suitable percentages in the flux formulation.

Tests were carried out by both Oerlikon and The Welding Institute (TWI) in Cambridge, UK, based on the official international standard for the fume welding application, that is, ISO 15011: *'Health and safety in welding and allied processes: Laboratory method for sampling fume and gases'*.

Fume emission results

In term of FER, all three grades of Clearinox E (308L, 309L and 316L) were characterised, in diameters of 2.5, 3.2 and 4.0 mm. For the flux-cored Clearinox F range, the 316L and 309L grades were evaluated for 1.2 diameter in M21 shielding gas. The FER was also measured when using pure CO_2 shielding gas.

For the stick electrodes, several determinations confirmed that the fume emission rate is significantly lower – 30% to 40% reduction according to the type and diameter for Clearinox range compared to the standard rutile consumables tested. Some examples are indicated in Table 1. The difference is easily seen visually when long welding times are involved (Figure 3). It is also worth highlighting the agreement between the TWI and ALW results.

The fume reduction is lower for FCW than stick electrodes (5%-15% according to the type of product), but still show a significant improvement (Table 2). As stated in previous published studies, in the case of FCW, the FER is strongly

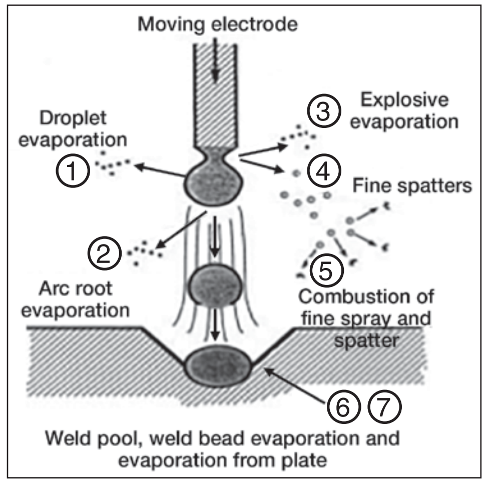

Figure 1: The source of fume generation during arc welding.

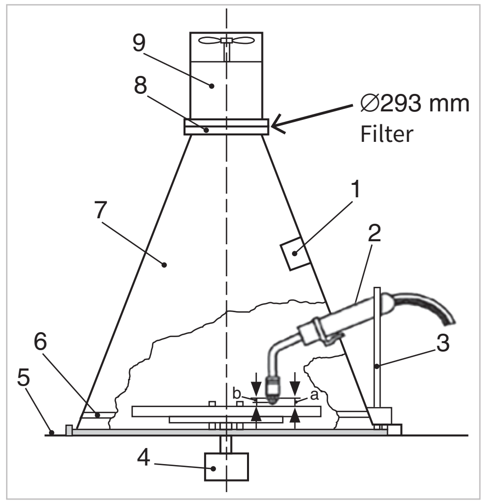

Figure 2: Fume collecting installation. 1: View window. 2: Welding torch. 3: Torch support. 4: Plate rotation engine. 5: Support table. 6: Reinforcement. 7: Installation body. 8: Filter support. 9: Extractor.

MMA electrode type	Diameter (mm)	Polarity	F.E.R (mg/min)	F.E.R Reduction (%)
Standard 308L	3.2	DC+	300	-
Clearinox E308L	3.2	DC+	198	34
Standard 309L	3.2	DC+	278	-
Clearinox E309L	3.2	DC+	190	32
Standard 316L	3.2	DC+	260	-
Clearinox E316L	3.2	DC+	180	31

Table 1: Fume emission rate – MMA electrodes.

FCW type	Diameter (mm)	Shielding gas M21 (18%CO_2)	F.E.R (mg/min)	F.E.R Reduction (%)
Standard 308L	1.2	Ar-18% CO_2	400	-
Clearinox F308L PF	1.2	Ar-18% CO_2	385	4
Standard 309L	1.2	Ar-18% CO_2	397	-
Clearinox F309L PF	1.2	Ar-18% CO_2	336	15
Standard 316L	1.2	Ar-18% CO_2	312	-
Clearinox F316L PF	1.2	Ar-18% CO_2	294	6

Table 2: Fume emission rate - FCW

affected by several factors such as transfer mode, amperage, voltage, and CO_2 content in Argon-based shielding gas.

Consequently, welding conditions have to be set up carefully according to the applications and workplace.

Fume analysis

The chemical analysis of fume has been done as indicated in section 4.3 following the international standard. Fume for MMA electrodes has been collected using diameter 3.2 mm and diameter 1.2 mm for FCW.

The reduction of concentration of Cr^{VI} in the fume is very significant for Clearinox range versus standard products (up to 60%) for both MMA and FCW as shown in Table 3.

The effect of Na, K reduction vs. Li addition in coating and in flux composition for FCW has been demonstrated by the high reduction of hexavalent chromium in fume.

We have also confirmed by consequence the different balance in concentration of alkaline into the chemical composition of the fume. Some examples are indicated in the Table 4.

The results of the analysis demonstrate that under laboratory conditions, the new Clearinox consumables produce less particulate welding fume containing less hexavalent Chromium than standard products.

Consequently, based on the data generated, the Cr^{VI} emission at the source is 4 times less (Table 4) for Clearinox MMA and 3 times less for Clearinox FCAW versus standard products.

Welding performance

The operative performances (weldability) of the new Clearinox range was compared to the current standard range. Clearinox E 308L, 309L and 316L electrodes were all tested in flat (PA) and horizontal fillet (PB) welding positions, with DC+ polarity. The base material 304L plate's thickness and amperages involved are indicated in Table 6.

The new Clearinox range displays a very stable, spatter-free and smooth arc metal transfer. The strike and cold re-strike are very good. The weld bead is almost flat, having a preferred silver colour with fine and regular ripples. The weld pool is very clear and visible during welding, enabling the electrode to be easily controlled. Slag removal is very good, sometimes self-releasing.

Even during the comparative welding session, visually lower quantities of fumes were noticed across the new range.

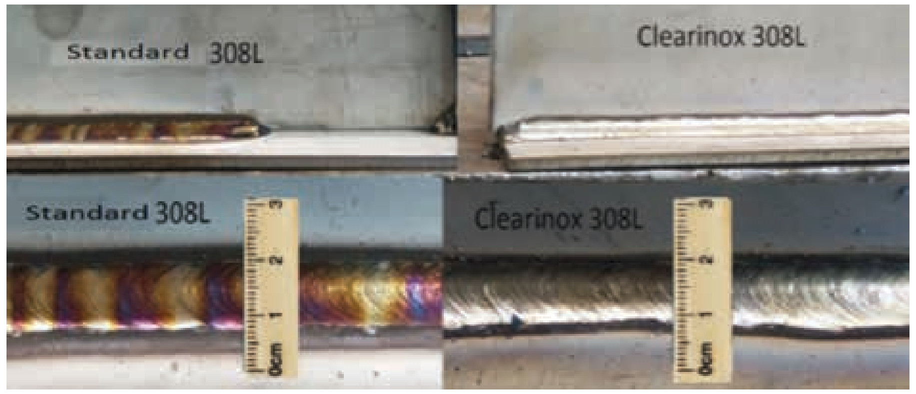

Photo 2: Nice weld bead appearance for Clearinox; lower fume emission vs. Standard (black area surrounding the bead).

Type	Product	Concentration in fumes (%m/m)					
		Fe	Mn	Ni	Cr Total	Cr^{VI}	% reduction
MMA	Standard MMA308L	4.7	3.6	0.3	4.6	4.07	-
	Clearinox E308L	6.7	4.6	0.5	5.2	1.64	60
FCW	Standard FCW309L	11.6	3.3	1.6	9.1	1.32	-
	Clearinox F309L PF	18.3	4.1	3.0	13.3	0.49	63
	Standard FCW316L	11.4	7.9	1.3	7.2	0.52	-
	Clearinox 316L PF	18.0	10.1	2.6	10.2	0.19	63

Table 3: Chemical composition of fumes.

Type	Product	K element (%m/m)	Na element (%m/m)	Li element (%m/m)
MMA	Standard 308L	28.8	1.9	0.4
	Clearinox E308L	2.7	1.3	4.1
FCW	Standard 316L	10.5	5.8	< 0.1
	Clearinox 316L PF	1.1	3.6	1.2

Table 4: Alkaline concentration in fume.

The coating resistance was also tested with respect to: falling; bending; and vibration. These tests demonstrated that the negative effect on coating resistance given by the various Li-based binder compounds were overcome by using the new Clearinox coating formulation. The coating of Clearinox electrodes was found to be robust when abrasion or bending stresses are applied. When subjected to shock (falling), though slightly inferior compared to standard types, the coating adherence on the wire rod is still very good.

Conclusions

Based on the double-coated concept, a new range of stainless MMA electrodes has been developed. When compared to standard stainless MMA electrodes, the fume emission rate of the new products is 30 to 40% lower and the concentration of hexavalent chromium Cr^{VI} in fumes is strongly reduced by up to 60% less. Expressed in mg/minute of fume emission, the new Clearinox E electrode range displays four-times lower hexavalent chromium (CrVI) levels.

A new range of flux-cored wires has also been developed. The fume emission rate for Clearinox F range is slightly reduced compared to standard flux-cored stainless steel wire(10-15%) while hexavalent Cr^{VI} levels in fume is significantly reduced (60%). Expressed in mg/minute of fume emission, the new Clearinox F range generates three-times less hexavalent chromium Cr^{VI}.

These new of welding consumables all display physical, operational and mechanical performances at the same level and sometimes superior levels when compared to standard products presently used on the market.

Ref : Griffiths T, and Stevenson AC: Development of stainless steel welding electrodes having a low level of toxic chromium in the fume; The 5th International Symposium of the Japan Welding Society, Advanced Technology in Welding, Materials Processing and Evaluation, 5JWS-IV-3, Tokyo, April 1990.