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Welding consumables with lower emission of Cr^{VI}

Abstract: The article provides information about new filler metals used in the welding of popular stainless steel grades and discusses the formation of Cr^{6+} in dusts as well as alkaline metals connected with the process. Newly developed covered electrodes and flux-cored wires are characterised by the reduced emission of dust during welding and by the lower content of carcinogenic hexavalent chromium in dust. One of the major difficulties, i.e. the obtainment of required properties of the electrode cover, was solved by using a two-layer cover. New grades of electrodes and flux-cored wires were subjected to tests, among others at the British TWI, to compare the emission of dust and that of Cr^{6+} with those generated by standard materials. The above-named tests revealed that the at-the-source emission of Cr^{6+} was 4 times lower in terms of the electrodes and 3 times lower as regards the flux-cored wires than emissions accompanying the use of standard materials.

Keywords: welding consumables, filler metals, emission of Cr^{VI}, covered electrodes, flux-cored wires

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Introduction

The present paper summarizes the development of a new range of welding consumables, 308L-309L-316L stick electrodes and flux cored wires grades, which provides a significant reduction of fume emission rate and decreased content of hexavalent chromium in the fumes. Such consumables will contribute to improved welders' working conditions. The new range of stick electrodes can be produced in industrial conditions and electrode coating shows stable mechanical resistance and good adherence to the electrode core.

It is believed that presented new MMA and FCW electrodes, delivering reliable welding performances, are the first products of such type on the market.

Welding consumables with reduced emission of CrVI

Health and safety state agencies and organisations have imposed Occupational Exposure Limits (OELs) for total airborne particles, OEL varies from 1 mg/m³ in Netherlands to 5 mg/m³ in the UK, Australia and South Africa. Additionally, individual limits are applied for carcinogenic Cr^{VI}. French decree No. 2012-746 limits values for occupational exposure and more strict regimes have been imposed in France starting from the 1st of July 2014. The eight hour OEL limit of Cr^{VI} changed from 50 µg/m³ to the new limit of 1.0 µg/m³.

As hexavalent chromium may be present in the welding fume generated by stainless steel welding consumables, users of stainless steel

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welding consumables should assess the potential exposure to Cr^{VI} in their workplace, appropriate welding fume control solutions needed to reduce exposures to levels below applicable OELs. Most popular fume control solutions include personal protection equipment (PPE) and fume extraction systems. Nowadays, welders and welding engineers have also a chance to consider latest generation of welding electrodes to reduce the risk to a minimum.

Cr^{VI} fume generation principles

The 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.

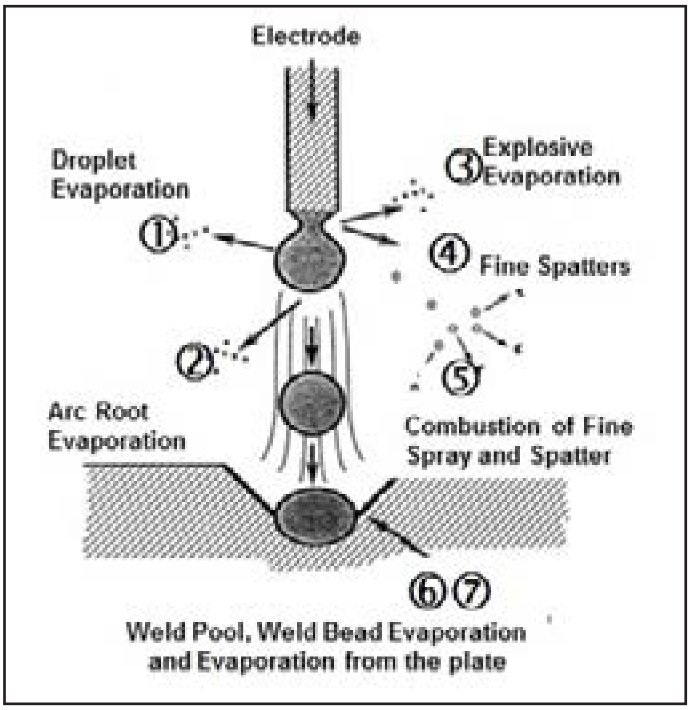

Fig.1- Fume generation sources during arc welding.

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 contain non-toxic Chromium, non-toxic trivalent (+3) chromium, and problematic hexavalent chromium (Cr^{VI}).

Relatively few components containing Cr^{VI} can be formed in fume and its formation principle is illustrated by equations [a] and [b] below.

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

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

The main issue lies in the formation of certain noxious compounds containing Cr^{VI}, such as Na_2CrO_4, K_2CrO_4, $K_2Cr_2O_7$, NaK3 $(CrO_4)_2$, NaK_3 $(Cr_2O_7)_2$ generated by vaporized Sodium (Na) and Potassium (K). Both elements are present in welding consumable composition or with chromium (Cr).

Development of welding consumables.

S. Kimura [1] proposed to eliminate ingredients containing Na and K from the coating with following substitution with equivalent ingredients to reduce the contents of compounds containing Cr^{VI} in the fume. 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 help to obtain good operative performance. Na and K compounds have positive influence on welding features like arc stability, bead appearance, slag detachability and arc elasticity. Elimination or even reduction of Na and K compounds may deteriorate those factors. In case of stick electrodes, application of a lithium-based binders as a replacement of Sodium- and/or Potassium-based compounds binders may results in low mechanical stability of coatings. MMA electrodes having fragile or even highly friable coating cannot be applied in industrial environment, where the electrodes are often accidentally knocked or roughly handled. The key is challenge was to reduce Na and K content in the electrode coating and to deliver new coating with the same mechanical stability and adherence to the core.

Clearinox E (MMA) and Clearinox F (FCAW).

Welding industry calls for development of new consumables designed for stainless steel with significantly lower fume emission rate and low concentration of Cr^{VI} in fumes. At the same time such electrodes should show equal or even superior welding behaviour as standard rutile consumables. Long term tests demonstrated that the reduction of FER and Cr^{VI} is achievable only through the suppression or significant reduction of Na and K compounds, however presence of such elements in electrode' flux/coating is beneficial for weldability.

In case of MMA electrodes, it is assumed that Na and K compounds in extremely small percentages would still provide both very good welding behaviour and robust coating if they won't be uniformly dispersed in the coating and localized only if specific areas. This lead to double-coated type of coating, for which suitable inner and outer coating formulations were developed. In addition, other raw materials containing alkaline elements were also replaced with similar powders instead of using Lithium silicate as the binder, for example Lithium feldspar instead of Na/K feldspar was used to compensate lack of Na and K with other ionizing agents to ensure good arc stability.

Regarding the flux-cored wires, the main challenge was also to achieve excellent operational performance similar to standard wires, even when the wires are used at low welding current. For the standard wires, the K and Na compounds, existing in the flux, are the key ingredients responsible for good welding characteristics. In this case new ionizing compounds were introduced to the flux to compensate their reduction.

Fume emission rate, test results

Tests were carried out by both internally 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'. In term of FER, three grades of coated electrodes (308L, 309L and 316L) were tested in diameters of 2.5, 3.2 and 4.0 mm. For the flux-cored range, the 316L and 309L grades were evaluated; 1.2 mm in diameter, M21 shielding gas.

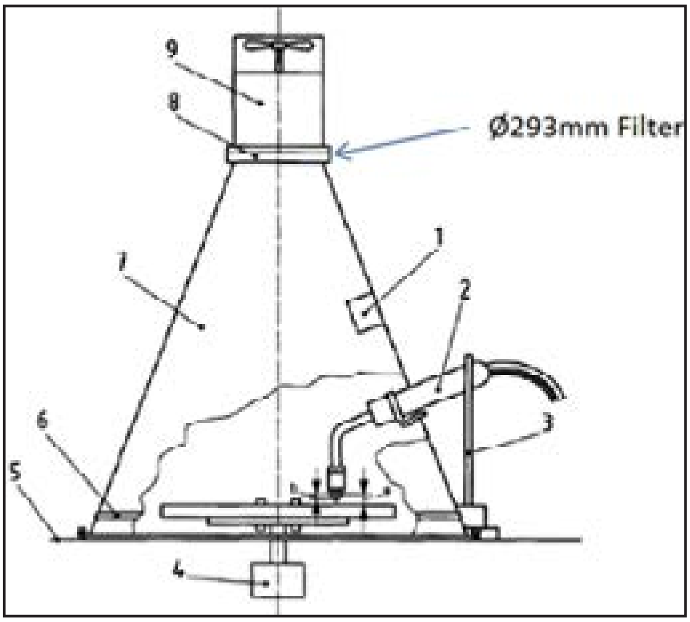

Fig. 2. Fume collecting installation: 1- view window, 2 - welding torch, 3 - torch support, 4 - plate rotation engine, 5 - support table, 6 – reinforcement, 7 - installation body, 8 - filter support, 9 – extractor.

Several determinations confirmed that fume emission rate is significantly lower for stick electrodes. Reduction of FER of new Clearinox/Clearosta electrodes reaches 30% to 40% comparing to standard grades. Data is given Table 1, visual comparison of solid particles emitted during welding is illustrated on Figure 3.

In case of flux cored wires FER is strongly affected by several factors such as transfer mode, amperage, voltage, and CO_2 content in Argon-based shielding gas.

Table 1. Fume emission rate of MMA electrodes.

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

Despite of this, reduction in emission of welding fumes is between 4% and 15% at specified tests conditions (Table 2).

Fig. 3. Macroscopic presentation of solid particles emitted in the fumes. 1 and 3 – standard consumables, 2 and 4 – new Clearinox electrodes with reduced FER.

Fume analysis

The chemical analysis of fume was done following the international standard too. Fume for MMA and FCW electrodes were collected after welding with 3.2 mm and 1.2 mm diameters respectfully.

The reduction in concentration of Cr^{VI} in the fume is up to 60% comparing to standard products for both MMA and FCW consumables as shown in Table 3. Described in the literature influence of Na and K on reduction Cr^{VI} has been confirmed. Variances in concentration of alkaline compounds in fumes were also observed, examples are indicated in Table 4.

The results of the analysis demonstrate that new 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 (Fig. 5) for Clearinox/Clearosta MMA electrodes and 3 times less for FCW wires comparing to standard products

Welding performance

Welding performances of 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

Table 2. Fume emission rate of FCW.

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/Clearosta F308L PF	1.2	Ar-$18\%CO_2$	385	4
Standard 309L	1.2	Ar-$18\%CO_2$	397	-
Clearinox/ Clearosta F309L PF	1.2	Ar-$18\%CO_2$	336	15
Standard 316L	1.2	Ar-$18\%CO_2$	312	-
Clearinox/ Clearosta F316L PF	1.2	Ar-$18\%CO_2$	294	6

Table 3. Chemical composition of fumes

Type	Product	Concentration in fumes (%m/m)					% reduction
		Fe	Mn	Ni	Cr total	Cr^{VI}	
MMA	Standard MMA308L	4.7	3.6	0.3	4.6	4.07	-
	Clearinox/Clearosta 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/Clearosta F309L PF	18.3	4.1	3.0	13.3	0.49	63
	Standard FCW 316L	11.4	7.9	1.3	7.2	0.52	-
	Clearinox/Clearosta 316L PF	18.0	10.1	2.6	10.2	0.19	63

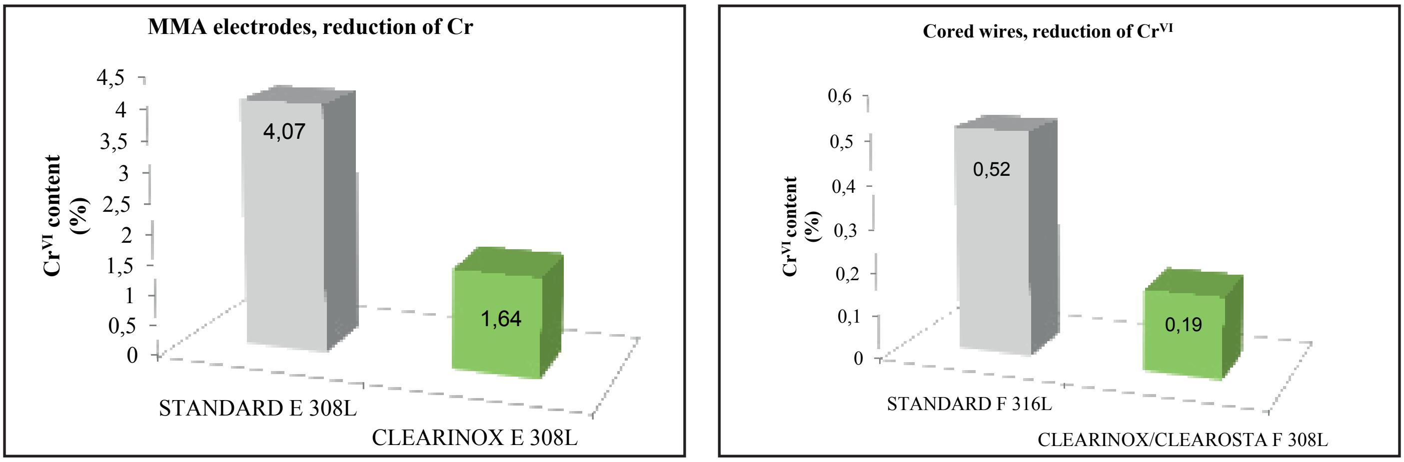

Fig. 4. Concentration of Cr^{VI} in welding fumes. MMA – electrode diameter 3.2mm; FCW – electrode diameter 1.2mm, M21 shielding gas.

material 304L plate thickness and values of welding current are given in Table 6.

Clearinox/Clearosta electrodes deliver very stable, spatter-free and smooth arc metal transfer. The strike and cold re-strike arc actions are very good. The weld bead is almost flat, it shows preferred silver colour with fine and regular ripples (Fig. 5 and 6). The weld pool is clearly visible during welding, it enables easy control of the weld pool. Self-releasing type of slag removal is observed. In addition, lower amounts of fumes were macroscopically observed during welding with new range of consumables.

Coating resistance was tested with respect to bending, falling and vibration. These tests demonstrated that the negative effect on coating resistance given by the various Li-based binder compounds was compensated through

Table 4. Concentration of K and Na in fumes.

Type	Produc	K (%m/m)	Na (%m/m)	Li (%m/m)
MMA	Standard 308L	28.8	1.9	0.4
	Clearinox/ Clearosta 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 5. Welding tests, main parameters

Electrode diameter (mm)	Plate thickness (mm)	Current (A)
2.5	3	75-80
3.2	5	110-115
4.0	10	150
5.0	10	200

Table 6. Welding tests, main parameters.

Electrode diameter (mm)	Plate thickness (mm)	Current (A)
2.5	3	75-80
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4.0	10	150
5.0	10	200

Fig. 5. Welding appearance and slag detachability, Clearinox/Clearosta E MMA electrodes

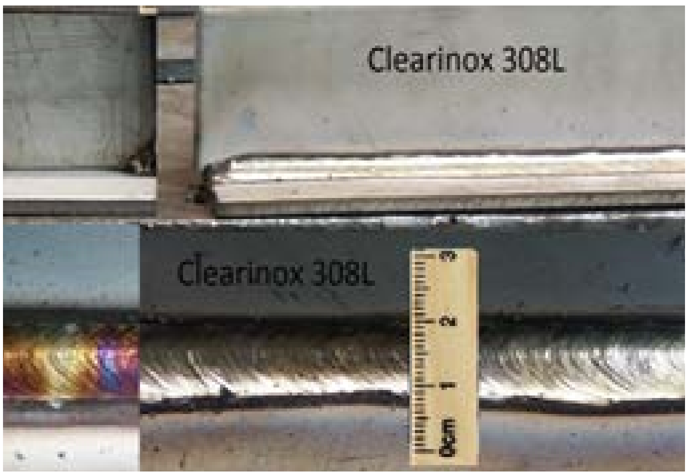

Figure 6. Bead appearance of welds made with standard and Clearinox/Clearosta electrodes

a particular coatings' formulation. The coating of Clearinox/Clearosta electrodes were found to be robust when abrasion or bending stresses were applied. Adherence of the coating to the wire rod is reliable When subjected to shock (falling), though slightly inferior compared to standard types.

Conclusions.

The first and unique range of stainless MMA and FCW electrodes has been developed. Composite nature of the coating is one of the bases of the solution in case of manual electrodes. In this case, when compared to standard stainless MMA electrodes, the fume emission rate is 30 to 40% lower and the concentration of hexavalent chromium Cr^{VI} in fumes reduced by up to 60%. Clearinox/Clearosta F range of flux cored wires poses FER reduced by up to 15% and, at the same time, content of hexavalent Cr^{VI} in the fumes is up to 60% lower.

Clearinox/Clearosta E manual electrodes for welding of most popular austenitic stainless steels are characterized by the same resistance of the coating and similar or better welding performance when compared to standard products.

References

[1] Griffiths T, and Stevenson A.C. "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.