DETACHABILITY OF SLAG CRUST IN ARC WELDING (Review)

Part 1. Mechanism of Chemical Adhesion of Slag Crust to Weld Metal

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The review is dedicated to analysis of existing notions about the mechanism of chemical adhesion of the slag crust to the weld metal in arc welding. An attempt has been made to detail this mechanism, allowing for the available data on the effect on it by phase composition of the slag crust. It is noted that elimination of chemical adhesion of the slag crust to the weld metal can be achieved by selecting the optimal combination of chemical composition of the slag and its oxidising potential.

Keywords: *automatic submerged-arc welding, multipass welding, narrow groove, alloyed steels, slag crust, detachability, chemical adhesion, phase composition, oxidising potential*

In development of welding technologies, welding consumables are chosen on the basis of a set of welding-operational properties, among which detachability of the slag crust is a key one.

Poor detachability of the slag crust decreases the productivity of welding operations and increases the probability of formation of exogenous non-metallic inclusions in the multipass weld metal. The character of detachability of the slag crust sometimes determines practicability of a welding technology and, in particular, the possibility of producing thick-walled narrow-groove butt welded joints. In this connection, investigations of the causes of poor detachability of the slag crust and search for the methods to improve this process have been the subject of fundamental research efforts conducted in the last sixty years.

This review is aimed at choosing the baseline approach to development of the flux for welding thick-walled narrow-groove butt joints on alloyed steels, the use of which could provide satisfactory detachability of the slag crust.

Some studies [1, 2] consider chemical bond of slag to the weld metal to be one of the causes of difficulties in removal of the slag crust from the surface of a welded joint. The mechanism of this phenomenon is described in study [1], which suggests that is it identical to the known mechanism of adhesion of oxide systems to metal, e.g. in enamelling of vessels or formation of burn-on on the surface of ingots cast into ceramic moulds. One of the characteristic peculiarities of the said mechanism is formation of a thin film of oxides of elements of the metal phase on the metal surface [1, 3–5]. Another process that is often considered to cause adhesion of the slag crust to the weld metal in welding is epitaxial crystallisation of slag phases on the oxide film as a substrate, these slag phases fitting the principle of structural, orientation and size correspondence (SOSC) to the oxide film [1, 6, 7]. SOSC of crystalline materials is ensured by the same type of their crystalline lattice, providing that the unit cell sizes differ but insignificantly. Therefore, according to [1, 6, 7], chemical bond of the slag crust to the weld metal in welding of steels can be eliminated by using a slag having the minimal oxidising ability and containing no compounds that fit the SOSC principle with respect to oxides on the surface of the weld metal made on steel (e.g. spinels).

Numerous investigations were carried out to determine the presence of correlation between phase (chemical) composition of the slag crust and character of its detachability [8–12]. It follows from the above studies that in the cases of unsatisfactory detachability of the slag crust its phase components do not fit the SOSC principle with respect to the most typical oxides forming on the surface of the weld metal. And vice versa, if detachability is good, it is almost always possible to determine which phases in the slag crust fit the SOSC principle. The data of study [13] on the effect of the rutile content of slag of the $CaO-CaF_2-SiO_2-TiO_2$ system on detachability of the slag crust contradict the obtained results [9]. Analysis of the results of studies [9–13] shows that it is by no means always possible to establish the clear relationship between phase composition of the slag crust and its detachability from the weld metal.

One of the conditions for epitaxial growth of oxides on the surface of the weld metal is a very low rate of reaction [14], as well as peculiarities of the diffusion and relaxation processes occurring in subsurface contact layers of the metal and slag [15]. The epitaxial growth of oxides is caused by chemical transformation taking place on the surface of the weld metal at insignificant changes in configuration of ions in a new (oxide) phase, compared to the initial (metal) phase [14]. Some mismatch of sizes of their lattices is compensated for by elastic alignment of the spliced crystal faces, or by formation of misfit dislocations within the contact zone [15], which, as a rule, is a cause of adhesion of thin oxide films to metals. However, it can be assumed that it is the diversity of the oxidation conditions in welding [8] and welding parameters [1] that leads to formation of higher oxides with different types of lattices in composition of the oxide film, as well as to a substantial change in thickness of the oxide film. All of these factors promote cleavage of the film and improvement of detachability of the slag crust. Hence, the similarity of metal and conjugate oxides in the SOSC principle is not always a sufficient precondition for deterioration of detachability of the slag crust in welding.

The authors of study [16] consider formation of mostly coordination-covalent chemical bonds on the surface of contacting materials to be the necessary condition for joining metallic materials to oxide systems. In this case both basic and acid oxides can serve as reagents. The technology for joining metal to glass [17, 18] provides for formation of a film of basic oxides that are reactive with respect to the key component of glass, i.e. covar SiO_2, on the metal surface. Joining of glass to covar takes place at $T \cong 873$–1473 K, at which the glass grows soft. Basic oxides reacting with SiO_2 form iron from the covar components. As follows from study [17], a strong joint between the glass and covar is provided by the following chemical reactions:

$$\frac{2}{3}\,Fe_3O_4 + SiO_2 \rightleftarrows 2FeO{\cdot}SiO_2 + \frac{1}{3}\,O_2;$$

$$2FeO + SiO_2 \rightleftarrows 2FeO{\cdot}SiO_2.$$

Based on the similarity of physical-chemical conditions for formation of the high-quality glass-metal joints and conditions taking place on the surface of contact of the weld metal with the softened slag in arc welding, it can be assumed that chemical bond of the slag crust to the weld metal can cause, to a large degree, the reactions identical to the above ones. As a rule, fluxes contain, in addition to SiO_2, also other components that enter into reaction with Fe_2O_3 and FeO to form complex oxides of the type of $Al_2O_3{\cdot}FeO$, $MgO{\cdot}Fe_2O_3$, etc.

In case of poor detachability of the slag crust, the weld surface in contact with the slag was found to acquire a characteristic microrelief [10, 19]. Peaks are formed from grains of the weld metal, and valleys correspond to the grain boundaries. The grain-boundary regions of metal are rich in elements that are present in the form of oxides only in the flux. These are aluminium, calcium, magnesium and sodium. An increased content of reactive elements that transferred from the weld metal (titanium, chromium, niobium and vanadium) was also detected. When using slags that provide good detachability of the slag crust no enrichment of grain boundaries with elements contained only in the slag, no segregation of alloying elements of the weld, and no presence of microrelief on the weld surface were observed. Based on these facts, the authors of study [19] assume that the slag crust chemically bonded to the metal surface is fixed locally: its main mass has the non-metallic material branches «rooted» at some depth into the boundaries of the sub-surface grains (Figure 1). In this case there is no adhesion between the slag and grain body (at a distance from the boundary).

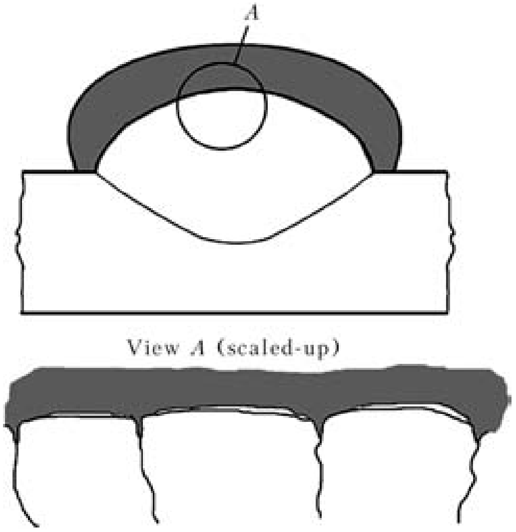

Figure 1. Schematic of adhesion of the slag crust to the weld metal caused by leading oxidation of the grain-boundary phase of metal with «rooting» of a non-metallic material into the grain boundaries

Properties of the oxide film are determined by the ratio of a volume of oxide to a volume of metal consumed for formation of the oxide, V_o / V_m [3–5, 14]. $V_o / V_m = 1.5$–2.0 or more for many metals that can be components of steel [3]. Therefore, as the oxide film grows thicker, it may separate because of increase in shear stresses. Steels that undergo $\alpha \rightleftarrows \gamma$ transformations have substantially changing crystalline lattice parameters. For example, the value of parameter a of unalloyed γ-Fe at 900 °C is 0.3645 nm, whereas this parameter of α-Fe at room temperature is equal to 0.28606. It seems that these and other factors do not favour increase in physical bond of the oxide film to the weld metal.

It is a known fact that the grain boundaries are characterised by abnormally high diffusion permeability of materials. The ratio of diffusion coefficients at the grain boundary and in the bulk of grain, Δ' / Δ, amounts to $1{\cdot}10^3$–$1{\cdot}10^5$, and increases with a decrease in temperature. For α- and γ-Fe a substantial excess of Δ' over Δ persists at a temperature of up to 1200 °C. Also, it is well-known that the thermal etching grooves form at the grain boundaries because of surface tension and diffusion [20, 21]. Considering the above facts and experimental results [11], the hypothesis of a local character of sticking of the slag crust to the weld metal [19] seems highly probable.

Examination of the slag–weld metal contact surface by the X-ray microanalysis and electron diffraction analysis methods showed that a thin (0.2 μm) intermediate oxide layer forming between the weld metal and slag crust at its poor detachability may consist of TiO, (Fe, Mn)O·Cr_2O_3, (Fe, Mn)O·V_2O_3, (Fe, Mn, Ni)]O·(Cr, Fe)$_2O_3$, etc. At good detachability of the slag crust the presence of the oxidised interlayer on the metal surface was not detected [7, 8].

Similar examinations performed by the secondary ion emission mass-spectrometry method in submerged arc welding with flux AN-348A of steel with a considerable content of vanadium revealed that the interlayer consisted of VO. A very high intensity of a flow of such ions as MnO^+, Mn^+, Fe^+ and FeO^+ is related to a defective structure of this interlayer and «lack of vanadium cations» [22]. The intensity of the flow of ions Si^+, FeO^+ and Mn^+ is 1.8, 3.7 and 9.7 times higher on the surface of the slag crust in contact with the weld metal than on its external surface, respectively. This suggests that the interlayer contains complex oxide compounds of the type of vanadates, manganates, silicates, spinels, etc.

If the weld is alloyed with elements having a higher affinity for oxygen (manganese, chromium, vanadium and titanium) than iron, the oxide film within the zone of contact of the softened slag with the solidified metal forms as a result of preferential oxidation of the most reactive of alloying elements with the slag, this being accompanied by formation of a relatively wide zone with a low content of this element near the surface of the weld metal [23]. In the weld on carbon steel, oxidation with slag causes appearance of the zones depleted in carbon, manganese and silicon [1].

Based on the above investigation results, the mechanism of formation of a strong joint between the slag and deposited metal seems to be as follows. The reaction of preferential oxidation of the most reactive alloying elements of an alloy takes place on the surface of contact of the softened slag with the solidified weld metal (region *ED* in Figure 2) due to the excessive content of ions O^{2-}. The rate of diffusion flows of metal cations and oxygen ions at the grain boundaries is much higher than in the bulk of grain with a relatively perfect structure, this causing the leading oxidation of exactly the grain-boundary phase of metal to form the «roots» of a non-metallic material at some depth in the grain boundaries. The process of formation of oxides is accompanied by diffusion of the most reactive alloying elements from the central volumes to an interface of the weld metal with slag, as well as by formation of the zone with a decreased concentration of these elements in metal. The surface grains are characterised by the presence of diffusion flows from the bulk of grain to its boundary. And it is this fact that explains the final distribution of a reactive alloying element described in study [10].

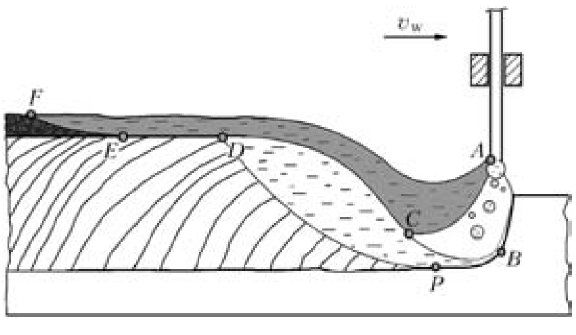

Figure 2. Schematic of the slag to weld metal interaction zones: *ABPC* — zone of high-temperature chemical reactions between slag and metal; *ABC* — zone of arcing and reactions between slag and metal at the stage of a droplet; *DPC* — zone of low-temperature reactions at the stage of the weld pool; *DP* — weld pool crystallisation front; *FE* — weld pool solidification front; *DC* — surface of contact between the molten slag and molten metal; *ED* — surface of contact between the molten slag and solidified metal

Simultaneously with their formation, oxides interact with other excessive ions of the slag phase. The products of interaction are complex oxide compounds (e.g. MeO·Me_2O_3 and MeO·MeO_2). The fist constituent of such a complex belongs to the oxide film on the weld metal, and the second contains a component of the slag phase. In turn, the main mass of the slag crust strongly fixed to this component forms on the surface of the interlayer consisting of complex oxide compounds.

Of undoubted interest is the bond between the newly formed interlayer of complex oxides and the weld metal. It can be assumed that the strength of this bond is determined to a large degree by the SOSC principle.

In phases that substantially differ in the SOSC principle from the steel weld metal (e.g. titanates MeO·MeO_2) the bond with the latter is violated or becomes weaker immediately after formation of oxides, i.e. at a temperature of about 1100 °C.

Many of the above factors work during the process of cooling of the weld metal, leading to separation of the complex oxide interlayer. Therefore, violation or substantial weakening of the bond between the slag crust and weld metal takes place on the considerable surface area of grains (at a distance from their boundaries). In particular, this applies to the interlayer containing a large amount of phases which differ in their structure from the weld metal. However, the «roots» of the oxide material may be reliably fixed in the grain-boundary valleys as the volume of oxide is always larger than the volume of metal consumed for formation of the oxide, $V_o/V_m > 1$. It is likely that this character of fixation of the slag crust on the surface of the weld metal (practically due to mechanical jamming of the «roots» of an oxide material in the grain-boundary valleys) is an additional cause of poor detachability of the slag crust in welding, independently of the relationship of structural-physical parameters of the metal and complex oxide interlayer.

In a case when the newly formed phase is similar to the weld metal in structure (e.g. spinel

$MeO{\cdot}Me_2O_3$), the strength of its bond to the metal hardly changes, compared to the strength of the thin oxide film, and remains high. Some mismatch between lattices of the γ-phase and spinels at high temperature can be compensated for with no damage to the bond strength by increase in the degree of imperfection of lattices of both phase within the contact zone.

If the energy of bond of the interlayer to the weld metal is higher than the energy required for the misfit dislocations to occur in the surface metal layer, increase in the dislocation density in a thin layer of the weld metal near the surface of its contact with the slag crust will take place during cooling of this metal layer (as well as during $\alpha \rightarrow \gamma$ transformation) [15]. It is likely that this process compensates for a difference in contraction of the metal and interlayer, as well as for a dramatic change in the lattice parameters in the course of the $\gamma \rightarrow \alpha$ transformation, thus resulting in persistence of the bond between the interlayer and weld metal and causing poor detachability of the crust.

It appears that in the last case the certain combination of peculiarities of a defective structure of the complex oxide film, diffusion and activity of oxygen in the slag and alloying elements in the weld metal, mutual solubility of oxides, and other factors may promote development of the processes competing with formation of spinels at the interface between the slag and weld metal. For example, such a process may be formation of higher oxides of the type of Me_2O_3, the lattice of which differs in the SOSC principle from the weld metal. The latter leads to violation of the initially strong bond of the spinel interlayer to the weld metal, thus improving detachability of the slag crust.

CONCLUSIONS

1. Poor detachability of the slag crust cannot be always explained by using the generally accepted interpretation of the mechanism of chemical adhesion of the slag crust to the weld metal. In particular, the value of structural-size correspondence of the slag and oxide film phases in the weld metal, as well as conditions and role of epitaxial crystallisation of the slag phases require further investigation and clarification.

2. The phase composition of slag may be heterogeneous in height of the slag crust. When comparing the slag and weld metal phases by the SOSC principle, it is necessary to account not for the integrated phase composition of the slag, but for its phase composition on the surface of the slag crust in contact with the weld metal.

3. The mechanism of adhesion of the slag crust to the weld metal can be controlled in the required way by changing strength of the chemical bond between the interlayer and weld metal, thickness and phase composition of the interlayer, which can be achieved by changing chemical composition of the slag and its oxidising potential.

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