Composition of the Coatings Of Welding Electrodes

Summary. By means of some diagrams of simplified electrode coatings the connections and the differences between types of electrodes are shown. An important factor is the FeO content of the slag, which not only affects the mechanical properties but also strongly influences the weldability of the electrode.

Introduction

It is interesting that in the symbolization of welding-electrodes according to the I.S.O. standards, besides the various numbers an additional indication-showing the character of the coating as acid or basic, for example-has again been reverted to. Even more interesting is the possibility of speaking of a small number of types, despite the large numbers of electrode makes. This limited diversity can be accounted for if the similarities and differences in the composition of the coating are examined closely. If attention is paid to the most important chemical reaction taking place in arc welding, an insight into these similarities and differences can be obtained. From the nature of the examination this insight can be given only in a general way, but it shows that the possibilities existing as regards the development of weldingelectrodes are limited. The various factors governing the welding-process often lead to results that cannot be harmonized chemically and physically, and accordingly the best combination of properties will always prove to be a compromise.

The dominating reaction is the combustion reaction or, rather, the oxidation-reduction interaction

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between molten metal, slag and surrounding air. Since this reaction takes place in the presence of the main constituent iron, the equilibrium of the reactions of the various coating elements with the weldpool will be reflected in a certain iron-oxide content of the slag. With the other slag-formers the iron oxide forms compounds or mixtures in the slag and therefore strongly influences the slag properties, which are so important for welding. The iron oxide is then in equilibrium with the metal composition and thus determines the oxygen content of the deposited weld metal. How this content affects the mechanical properties is household knowledge.

Not so widely known, however, is the important part played by oxygen and, therefore, by iron oxide with regard to the surface tension and the fluidity of the metal. Not until 1956 were accurate tests carried out in this respect (See fig. 1) (1).



Fig. 1. Influence of C, N, S and O on surface tension of liquid iron.

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It is shown clearly that, in addition to sulphur, oxygen causes a sharp reduction in the surface tension — so sharp a reduction, in fact, that it is doubtful whether tests made before that time, to ascertain the influence of other alloying elements, This unfamiliarity with the role of are reliable. oxygen is remarkable, since in our circles this action had long ago been accepted as a working hypothesis, based on indirect observations. Important in this connection are the observations of Fast (2) in his experiments with molten pure iron in various gas atmospheres. The crucibles (ZrO_2) in which melting took place often cracked. The cracks sometimes became 1 mm wide. The molten pure iron did not run through the cracks, however. It did do so if a little oxygen was admitted. The molten iron has a convex meniscus : when a little oxygen is admitted, this becomes flat to concave.

When bare iron wires were melted in the oxyacetylene flame Tichodew (3) noted that if the oxygen content increased the droplets became 30 to 40% smaller.

The behaviour of the various electrode types reveals a clear line. The iron-oxide content in the slag and, therefore, the oxygen content of the metal decrease from the types with an "iron-oxide" coating (O), via the "acid" coating (A) and the rutile coating (R and T), to the "basic" coating (B). In equal measure it is seen that the profile of the weld bead in the fillet weld changes from decidedly concave for the "O" types, via less concave and flat, for acid and rutile coatings, to distinctly convex in the case of the low-hydrogen rods.

To the same extent the possible uses of the rods increase in positional welding and in penetration welding of the root run in a Vee groove. Verticalposition welding cannot be done with the "O" rods; the material does not remain in place and penetration welding is not possible, either. With the "A" rods vertical-position welding can be done, the root run sags less and only occasionally forms "pearls". In the case of the "R" rods there is a considerable improvement in this respect, and in that of the low-hydrogen rods the position is decidedly good.

The slag also plays a part, of course, and accordingly not only surface tension is concerned. Especially in vertical-position welding, however, in the case of which the slag, which solidifies much later, can give the solidifying metal little support, this influence is striking. So that this effect may be examined more fully for the various types, the coating compositions of the latter, arranged according to the iron-oxide content in the slag, will be discussed further.

General

With regard to the application of the various coating elements round the core wire, we shall proceed from the process most frequently employed—extrusion. This means that the components must be mixed with a moulding and a binding agent in a finely divided state, to work them into a plastic mass that can be extruded round the core wire and which, following drying, yields a solid and manageable substance. Suitable moulding agents are kaolin, bentonite, talc and—to a lesser extent—asbestos. These are all A1 or Mg silicates, which, owing to their chemically bound water, possess plastic properties. As a binding agent K or Na water glass can be used ; these, too, are water-bearing silicates.

If the chemical formulas of, say, kaolin (A1₂O₃, $2SiO_2.2H_2O$) and potassium waterglass (K₂O×SiO₂. 4H₂O) are considered, it is observed that these substances are built up out of oxygen compounds and so play their part in the oxidation-reduction interaction. The obvious substances to be taken as further constituents are those which are known to be added in the production of steel. If we start from three simple substances such as magnetite (Fe_3O_4), quartz (SiO₂) and calcareous spar (CaCO₃), then, in a three-substance diagram, we can show the mixture proportion at which a slag suitable for welding forms (fig.2). The diagram shows coating compositions and no slag composition. In the case of the slag it would be necessary to include the reaction products formed during welding. Moreover certain quantities of moulding and binding agents have been taken as a basis (Kaolin: 10; magnetite, quartz, calcareous spar: 90; potassium water glass: 10). For point A in the diagram this means a coating composition of 10% Kaolin, 36% magnetite, 27%



Fig. 2. Three-substance diagram of composition of "O" electrode coating.

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quartz, 27% calcareous spar and, of potassium water glass, 10% of this over-all weight.

The range suitable for welding is hatched and cannot be sharply defined. There is little point in doing so, as the following observation will show; it can only be determined empirically in the given conditions. The diagram was made for a core-wire diameter of 4 mm, with a coating thickness of $1.6 \times \text{core}$,, as were the following diagrams.

The range found indicates an oxidizing or ironoxide type of electrode, marked O in the I.S.O. symbolization.

Iron oxide coating ; indication O

Though electrodes with this type of coating are unimportant, we shall nevertheless dwell on them a little longer, since what can be said in general about them more or less applies to the other types as well. It has been found that there is no point in comparing this diagram, whether through conversion of the coating constituents or through conversion of the slag composition, with other diagrams known from silicate chemistry, to look for combinations, solutions, melting-points and viscosities. In the short time in which the melting and solidification processes take place in welding the equilibrium employed in silicate chemistry is by no means reached.

If iron silicate, for example, is added and corresponding amounts of iron oxide and quartz are omitted, nothing like the same result is obtained. In amounts that are not too large, magnetite, for example, can be replaced by iron silicate (fayalite), without compensation of the SiO_2 content; the same weldability range is nevertheless retained.

The fact that no equilibrium is reached is shown clearly by experiments carried out by Fast (4). who built up a certain coating composition through mixing of complicated and simple compounds, either melted or sintered or not. The more combination reactions had to take place for the slag composition sought to be obtained, the lower the degree of viscosity became. There is little point in carrying out viscosity measurements in respect of a welding-slag, since if a slag that has once solidified melts again it will present a different picture. Fortunately the same final state is always arrived at in welding, and the variations due to changed welding conditions therefore remain within SO

limited a range that this final state is affected very little. In the case of the tests referred to it was possible to arrive at a slag corresponding to a normal "acid" slag, but this did not wet. Accordingly the slag is useless as a welding-slag, for covering of the metal is not complete, with the result that the appearance becomes irregular and there is a risk of slag inclusions and porosity. The condition under which there is spreading of a droplet of slag on liquid iron is given by the relation :

$t F_e > t_{sl} + t F_e / slag.$

There is little sense, again, in trying to make a good slag on the basis of measurement of these tensions; this measurement is too complicated. Moreover, calculation must then be from the slag back to the coating. In addition this yields only one aspect of the slag. There are about 30 conditions that a slag must meet if it is to be usable for welding. It is possible to study the tendency, but the actual test, i.e., making a slag and welding immediately elucidates all the influences, and this has been found still to be the simplest way.

In order nevertheless to obtain an insight into the purpose of the changes in the coating, the aid of another investigation can be called in, viz. that of the build-up and composition of slags in general. With this a picture can be formed, which is indeed very simple but nevertheless has an illuminating effect. If we start from the SiO_2 corner in fig. 2 we are therefore concerned with a pure silicate slag. Most is known about the build-up of slags of this kind.

The building-element is the silicate tetrahedron (fig. 3), with one Si atom surrounded by four O atoms. Each corner has a residual valence, so that an SiO_4^4 group has four negative valences. These tetrahedra may have corners in common with one another. If all the corners are connected to each other, then the substance has the stoichiometric relation SiO_2 . Crystallized the groups are divided evenly and are seen in the flat plane as regular hexagons (fig. 3; on the left). In the vitreous or the molten state all, or nearly all, the corners are connected but irregular (fig. 3; on the right). A melt of this kind, with many connections, is very viscous.

If a metal oxide such as CaO, MgO or FeO is added, then the oxygen atoms of the oxide added join the SiO_4 tetrahedron, so that a connected corner is detached from its SiO_4 partners.

Expressed as a formula, the results will be, say :

Si-O-Si + FeO = $Si-O^-+O-Si$ + Fe²⁺₄

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Every oxygen atom in the fraction has a negative charge and can accordingly hold an F_e^{2+} or another positively charged metal ion in the neighbourhood of the corner, where it can also be placed in crevices of the lattice. The more metal oxide is added, the more the lattice is broken open and the viscosity decreases (fig. 4). Finally the structure of the liquid is that of a disorderly version of the crystal, as shown for MgSiO₄ in fig. 5. Further addition results in a melt with SiO₄⁴⁻ groups and O²⁻ ions, together with the equivalent number of positive metal ions.

For an iron-silicate slag this has the additional consequence that when enough Fe^{2+} ions are connected to the outside of the silicate groups this slag will wet the liquid iron; the iron ions are immersed, as it were, in the liquid metal.



Fig. 3 Diagram of the silicon-dioxide tetrahedron as crystalline and as vitreous silicic acid. a) Crystalline Silica b) Molten Silica

This can also be found in our diagram in fig. 2. In the extreme left hand corner the slag is very thick and vitreous. If the slag is "diluted" through the addition of CaCO₃, then through the heating of the coating the carbonate will yield carbonic acid, which has a favourable effect in the arc. The remaining CaO will join the silicate lattice according to the previous diagram. As a result the chains are broken open and the slag becomes thinner. Since Ca does not dissolve in iron, the Ca²⁺ ions connected at the edge will not be immersed in the liquid metal, and the slag will not wet ! The addition of Fe₃O₄, on the other hand, will likewise yield dilution of the slag, but will also result in wetting. Consequently we shift higher up in the triangle. The *limited* range obtained as usable



Fig. 4. Diagram of the solution of bivalent metal ions in molten silicic acid.

also depends, then, on the other required slag properties—mainly coming-off of the slag.

If we remain more on the side of CaO-FeO, then here, too, no wetting slag will form, since the iron is present as a ferrite ion $Fe_2O_5^{4-}$; it is therefore surrounded by O atoms as in Si in the SiO_4^4 —tetrahedron and accordingly it cannot be immersed in the metal. Not until an excess of FeO is present and there will be more Fe²⁺ beside O²⁻ does wetting occur again.

It is clear that fundamentally it makes little diffrence whether other metal atoms than the aforementioned Ca and Fe take part in the reaction—Mg and Mn, for example of magnesium no wetting will be obtained and in that of manganese there will be wetting. Therefore it is understandable that there is little change in the character of the slag and that in the case of an entirely different chemical composition one can still speak of the same type. A slight shift in the range of weldability will be obtained, but it will remain at approximately the same level and it is in every way justified to continue referring to an iron-oxide type.

In this system fluidity and wetting of the slag are accordingly found to be possible only with a high FeO content, and also, therefore, where there is a high burn-off of Si, Mn and C, with all the consequent effects on the mechanical properties of the weld metal. In the top we accordingly get such intense burning that transfer of the material is accompanied by a shower of sparks. The marked oxidizing character also entails susceptibility of this type to a high carbon content of the steel to be welded, since the carbon will react with the slag while gas forms, which leads to so-called boiling.



Fig. 5. Diagram of crystalline magnesium silicate.

To bring about an improvement we must add reducing constituents, and we then obtain the picture shown in fig. 6.

Acid coating ; indication A

The construction of fig. 6 is the same as that of fig. 2. As well as an extruding agent and a binding agent a certain quantity of ferromanganese has been added (Kaolin, 10; FeMn, 20; magnetite, quartz, calcareous spar, 70; potassium water glass, 10), and the same three components as in fig. 2 have been used.

The usable range is now lower. The slag has a higher degree of viscosity and is more vitreous. The reason is that we are now in a range with a higher SiO_2 content. The addition of FeMn to the coating causes the MnO content of the slag to increase to about 10%, on account of combustion. This MnO will be absorbed in the same way as FeO; a dilution can be expected. Unlike CaO, MnO has the character of a solvent; M_n^{2+} ions and F_e^{2+} ions will be immersed in the metal; accordingly the slag will wet more rapidly.

The lower FeO content of the slag results in a better chemical composition of the metal, which is reflected in better mechanical properties. If variations are introduced by means of various similar minerals, the character of the slag and the type of electrode will not change. The relatively small region shown in the diagram is retained, and here, too, it is therefore explicable that, despite many possible variations in the chemical composition of the coating, reference can be made to an acid type. In the case of this type the carbon content is approximately maintained, and so is the manganese content. The slag, however, still oxidizes to such an extent that it is difficult to increase the silicon content via the coating, in spite of the high SiO₂ content of the slag. Accordingly the addition of alloying elements in the coating, to improve the mechanical properties, is not a very economical practice. The composition remains a peculiar compromise between a quantity of oxidizing constituents and a large quantity of reducing constituents. Especially in welding in position the slag properties are not very attractive. When welding upwards one likes to have a slag that leaves the weldpool free and concentrates in the case of solidification to reduce the risk of slag inclusions at the edges. The acid slag has this property only to a limited extent.



Fig. 6. Three-substance diagram of composition of acid-type electrode coating.

On the other hand the reducing proportion is now such that the chemically-bound water can deliver hydrogen, which, combined with the acid character of the slag, causes a certain susceptibility to sulphur (5). Altogether, this is not a satisfactory situation. It has been possible to obtain an improvement of the bad properties through the use of a new material, rutile (TiO₂) (fig. 7). This is no longer an iron-oxygen compound, and therefore it no longer supplies FeO direct to the slag.

Rutile coating ; indication R & T

A study of the diagram in fig. 7 shows that really two usable ranges have formed, and that both ranges are larger—especially near the top. Accordingly this leads to difficulties in the description. This was also felt when the I.S.O. standard was drawn up, and a distinction was made between R and T types. N.E.N. 1062 (in Dutch standardization) likewise recognizes a difference and even divides the rutile group into three subgroups. With the available standard specifications it is nevertheless difficult to identify the various kinds. In the Anglo-Saxon countries, and also in the Netherlands, the type with a great deal of rutile was in use sooner.

Owing to the favourable slag properties (good covering, fluidity and easy coming-off), combined with the low FeO content (now obtained only through the combustion), it is possible to make the coating thinner and to retain good mechanical properties.

As a result the electrode becomes what is known as colder, has a coarser droplet and is more suitable for vertical-position welding and bridging. Because of an intensification in the flow of gas—addition of cellulose material—a better passage of droplets is ensured, but indirectly a protective gas atmosphere is formed, as well, which compensates for the thinner



Fig. 7. Three-substance diagram of composition of rutile-type electrode coating.

coating. This is found to be most marked in the case of the cellulose types (I.S.O. indication : C). These types—including the cellulose type, as regards its small amount of slag—belong in the part of the triangle with a higher TiO_2 content. The extent of this rage shows that more variation is possible here, and accordingly most firms make several versions of these types; they come more or less under the indications Ra and Rb of N.E.N. 1062.

From these types a more heavily coated type was developed, which is also characterized by a high TiO_2 content. Usually the cellulose content will remain less than 5%. This type is described in Holland

under Rc, and it is especially suitable for making large welding-lengths. It strongly suggests the iron-oxide type, on account of the handsome appearance of the bead and the fact that the slag comes off of its own accord. Owing to the low FeO content of the slag, about 6%, the mechanical properties are very good however. The concave shape of the weld bead in fillet welds is not so pronounced here as in the case of the O type and, particularly of late, it has been endeavoured to effect an improvement by making the coating extra heavy. This has been done without any increase in efficiency, however, and only with the object of obtaining more slag.

Not until later was an entirely different type added, which has a much lower TiO₂ content but needs no iron oxide in the coating. In Germany, where this type was used before the heavy-coated Rc type mentioned previously, reference is made to the "titansaure" type as opposed to the "erzsaure" (or, for us, the normal acid) type. This name is a very apt one. If the iron oxide in the acid types is replaced by rutile, then, strangely enough, a highly weldable electrode is obtained, which has changed but little in character. Only a few adjustments with the other materials are necessary to give the coating its optimum properties. As compared with the viscous slag of the acid types, the slag of this rutile rod is thinner, but it still has this character. In vertical-position welding this favourable property emerges much more clearly; the slag concentrates better and runs away better, while the metal remains in position better owing to the higher surface tension resulting from the lower oxygen content. On account of this low oxygen content the mechanical properties are slightly better, as well.

If the acid electrodes did not have a 5 to 10% shorter fusion time, they would disappear from the market altogether !

The higher the TiO_2 content in the coating, the slower the rod. Hence the O type of rutile rod has a 10 to 15% longer fusion time than the "rutile-acid" type.

Giving an explanation for the behaviour of the various constituents in these types is a more difficult matter.

It is curious—remaining in the bottom of fig. 7 —that Fe_3O_4 can be replaced by TiO_2 or ilmenite (FeO.TiO₂). All intermediate proportions can be realized. That TiO_2 would behave like FeO is improbable, although titanium, as Ti^{4+} , is found in glass at high temperatures. A study of the SiO₂. TiO₂ system (6) shows, that TiO₂ itself has glassy properties, through building-up of a lattice with TiO₆ octahedrons. The mutual connection between these octahedra is not as strong as that of the silicon tetrahedra, however, and accordingly the rutile slags are not as viscous. Moreover titanium can occur in the orthosilicate system SiO_4^{4-} with the configuration TiO_4^{4-} , in which case Si is replaced by Ti. This likewise means a thinning of the slag, since the mutual connection at the corners is not as strong any more. As a result the slag obtains a more crystalline character in the case of solidification, while owing to the presence of Fe²⁺ and Mn²⁺ and, possibly, Ti⁴⁺ the wetting properties remain safeguarded.

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In the higher range the formation of titanates must be accepted, possibly with the inclusion of silicon in the lattice. Here, too, FeO and MnO can be bound to the octahedron in the way described in the case of the SiO₄ tetrahedron, and therefore wetting can occur.

Despite the low FeO content of the slag, the desire for a still better deoxidized material remains. This wish has been fulfilled through the use of an entirely new material, fluorite or CaF_2 (fig. 8).

Low-hydrogen type ; indication B

Here an entirely different picture presents itself. So far as oxides play a part in the composition, these are so stable in relation to iron that the FeO content of the slag is only a few per cent. The chemical conditions have accordingly become so much more favourable that the reducing constituents can be drastically decreased and alloying through the coating becomes much simpler and more effective.

As "diluting" factor fluorite (or fluor spar) has been introduced here. A calcareous spar—fluorite ratio of about 1 to 1 is employed. Now a very thin slag forms, which has a strong tendency to sag.

Accordingly the addition of quartz or silicates and rutile to the mixture is aimed wholly at improvement of this slag property and is limited only to the extent that the chemical advantage obtained must not, of course, be nullified (Kaolin, 5; FeMn, 5; quartz, calcareous spar, fluorite, 90; potassium water glass, 15).

The exceptionally low FeO content is reflected in the excellent mechanical properties of the weld metal. As a result the surface tension is so high that in verticalposition welding and when a root-penetration weld is made the material remains in position.

Here too, however, an advantage immediately entails a drawback. The use of fluor spar introduces fluor ions in the arc, owing to which the ignition



Fig. 8. Three-substance diagram of composition of lowhydrogen-type electrode coating.

voltage is adversely affected and difficulties arise in respect of welding with alternating current.

The low FeO content places the $H_2O + Fe - FeO +$ H_2 equilibrium so strongly on the side of hydrogen that special measures have to be taken to make and keep the water content as low as possible! We do not wish to deal with these difficulties in this connection, but here too we shall try to give an explanation for the behaviour of the slag. The considerations given up to this point leave us completely in the lurch. In order nevertheless to be able to give an explanation of the wetting, use can be made of the hypothesis that Kozakewitch put forward in the "Revue de Metallurgie" of 1949 (7) with regard to his research as to emulsion formation of slag and steel. He points out the tendency of slags containing fluorite to form an emulsion of iron in slag, as opposed to that of silicate slags to form an emulsion of slag in iron.

In the case of iron-silicate slags large SiO_4 ions will retain small Fe ions at the iron/slag boundary plane. The Fe ions will repel each other, and the densest accumulation of these groups is possible only at a curved plane, with the Fe ions on the outside.

That means that there is a tendency towards formation of slag droplets, which leads to slag inclusions in metal.

Accordingly as the composition deviates more from iron silicate that tendency will decrease, so if other atoms or groups position themselves in between, the tendency towards slag inclusion will be less pronounced. Accordingly this property will occur less in the order in which the types of electrode have been discussed here.

In the case of fluorite slags, on the other hand, the molecule FeF₂ will form, which ensures wetting. However, at the slag/metal boundary plane there is now one small ion of Fe in the metal and there are two large ions of F in the slag. Hence, where this configuration is concerned, as well, there will be a tendency towards formation of a curved plane, reversed in this case, however. Therefore the curved plane, with Fe on the inside, will enclose metal and the tendency towards formation of metal inclusions in the slag will develop. The weld metal of low-hydrogen electrodes is indeed much purer than any other weld metal. And if the slag of a low-hydrogen electrode is pulverized, then, even if all the enclosed spatters, etc. have been removed, some movement can be observed with a magnet. The explanation is simple, perhaps, but it is interesting as a working hypothesis. At all events it has been crowned with success through the development of enclosed welding, as answer to this hypothesis. In enclosed welding, a gap between two parts to be connected, e.g. two pieces of rail, is filled up continuously by welding with electrodes of the "B"-type without slag removal. The weld metal is supported at the open ends of the gap by copper moulds, hence the name : "Enclosed Welding". If the copper moulds are placed in such a way that a small amount of the slag can flow away during welding, excessive slag does not hamper the building up of the weld metal. Anyway, with a proper "basic" slag there is no danger for slag inclusions, as long as the welding is performed in such a way that the slag is properly remolten at the next pass.

New developments

The foregoing rightly suggests that the possibilities for making various electrode types are only very limited. This does not alter the fact that development and improvement of electrode coatings are still possible. This is substantiated particularly by the appearance of a new type of coating, known as the zircon-basic coating (8).

This electrode too is a typical compromise solution to requirements in respect of welding. The convex appearance of the weld bead with a high surface tension, obtained with a basic coated electrode, can only be improved through the use of a "heavy" slag, which solidifies at a higher temperature as the normal basic slags.

On the other hand the low FeO content must be guaranteed to ensure the good mechanical properties. This can be obtained by addition of zirconium-oxyde instead of SiO_2 in figure 8, and shifting to a lower CaF₂ content.

It follows that this type cannot be employed for vertical-position welding, since the slag does not flow away easily. Hence the general purpose character of a normal low-hydrogen electrode must give way to the handsome appearance of the zircon-basic electrode.

To make the best of this limited character, namely the usability in the horizontal position only, this type of coating is usually found as a so-called high efficiency electrode.

The high efficiency of electrodes, where more metal is deposited than the weight of the core of the electrode, is obtained through the addition of iron powder in the coating.

In principle this addition of iron powder can be applied to all types of coating mentioned in this article.

The type of coating will not change by this addition, only the thickness of the coating must be increased to obtain the same amount of slag needed for the protection of the weld metal.

The amount of iron which will transfer from the coating to the weld metal, depends on the quantity added and on the type of coating. With an "O" type of coating a considerable amount will be burnt and will be found as FeO in the slag. Therefore "O" type high efficiency electrodes do not occur, whereas all other types can be found in a high efficiency version as well.

Writer's comment :

This article is not intended to be a guide to develop more and better electrodes; however, it is meant for the consumers to provide a better insight into the relation between welding performance and mechanical properties of the different types of electrodes. It is hoped that it will facilitate the correct choice of the proper electrode for the job. Moreover, if it contributes to a better understanding of the fact that mechanical quality of weld metal is related to operational weldability, it might help already in the design of the construction to ensure a high quality of the welded product.

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