Wetting the surface of the welded products with protective coatings during MAG welding

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Abstract. In this paper, theoretical and experimental studies of the kinetics of spreading (distribution) of protective coatings when welding MAG on a solid metal surface in the absence of extraneous (external) driving forces of hydrostatic pressure, gravity, etc. In the kinetic mode, wetting appears as the spreading of liquids on a solid surface.

1. Introduction

The interaction of molten metal droplets during welding of MAG with a solid metal surface is a complex physicochemical problem, the scientific and applied solution of which has greatly increased in recent years due to the continuously expanding application of this type of welding in industry. Prevention of the bond strength of molten metal droplets with a solid metal surface is provided by protective coatings that are applied to a solid metal surface during MAG welding [2–5].

Wetting the surface of the metal being welded (solid metal surface) with liquid material (protective coating) during MAG welding is an indispensable condition for its formation. In the kinetic mode, wetting is represented as the spreading of liquids over a surface. Wetting and spreading are spontaneous processes occurring due to a decrease in the Gibbs surface energy [1].

The appearance, continuity, adhesive strength and protective ability of coatings depend on how well the coating wets the substrate and spreads on it.

2. Main part

Ensuring the interaction of dissimilar materials requires contact between them [6–10]. Since the action of forces – orientational, induction, dispersion – manifests itself at a distance not exceeding 0.5 nm, contact can be considered only if the gap is not more than 0.5 nm. The speed at which a specific contact is reached depends on the nature of the surface and the properties of the contacting materials. The contact of solid surfaces with gases is easily achieved, but even when using liquids there are favorable conditions for contacting. The surface topography is important in providing contact. A rough surface can be considered as a multicapillary system. The depth of inflow (rise) of the liquid H into the pores of such a substrate is determined by the forces of capillary pressure:

$$H = \frac{K\sigma \cos \varphi}{\rho g},$$

where $K$ – is a constant;
$$\sigma$$ – is liquid surface tension;
$$\cos \phi$$ – is capillary inclination angle (wetting angle);
$$\rho$$ – is liquid density;
$$r$$ – is capillary (pore) radius;
$$g$$ – is gravity acceleration.

The rise time $$\tau$$ to establish the hydrostatic equilibrium of the liquid column can be calculated based on the Poiseuille equation:

$$\tau = \frac{2\eta l^2}{r\sigma \cos \phi},$$

where $$l$$ – is capillary (pore) length.

It follows from the foregoing, that the main factors determining the completeness of contact (filling of irregularities and pores of the surface of the substrate) are the viscosity, density and surface tension of the protective coating, the size, shape and location of the surface irregularities. It is important to note that the rate of absorption of protective coatings decreases, however, the possible depth of their penetration increases with a decrease in the diameter of capillaries and cavities. The viscosity of the protective coatings deposited on the substrate varies widely – from several units Pa·s (for solutions) to many thousands Pa·s (for melts). It does not remain constant but increases rapidly when the coating is cured. This makes it difficult to achieve full contact. The penetration of coatings into the recesses of the substrate (cavity) is also prevented by the air in them (figure 1).

![Figure 1. The penetration pattern of the protective coating in surface irregularities: 1 – substrate, 2 – air cavities, 3 – protective coating.](image)

Since the dimensions of the contact surface significantly affect the adhesion of the coatings, there is usually an interest in increasing it. Nevertheless, even on non-porous substrates with a low degree of surface roughness, contact is never absolutely complete.

The surface tension at the solid – liquid interface is indirectly judged by wetting $$\theta (C = \cos \theta)$$. It is believed that the liquids moisten the solid at $$\theta < 90^\circ$$, and at $$\theta > 90^\circ$$ they do not wet.

At a minimum contact angle $$\theta = f(\tau)$$, favorable conditions are created for producing defect-free films due to good spreadability of the material and, therefore, high protective characteristics of the coatings are achieved.

Wettability is determined by the height $$h$$ and radius $$r$$ of a drop of material deposited on a substrate and examined under a microscope.

The following is calculated $$\tan \theta$$:

For $$\theta < 90^\circ$$ (figure 2, a)

$$\tan \theta = \frac{2rh}{(r^2 - h^2)};$$

For $$\theta > 90^\circ$$ (figure 2, b)

$$\tan \theta = \frac{\sqrt{2rh - h^2}}{r - h}.$$
Figure 2. Scheme for determining the wetting angle $\theta$: a) $\theta<90^0$, b) $\theta>90^0$.

Using the table of trigonometric quantities, we can find $\theta$ and $C = \cos \theta$.

The wetting angle can also be determined by graphical construction. A graph is plotted on graph paper to do this, plotting the drop radius $r$ on the abscissa axis and height $h$ on the ordinate axis. From point $H$ and $P$, arcs are drawn with a radius of $HP$ (figure 3) until they cross each other through the points of intersection with the vertical $OA$ (point $A$). Then point $A$ is connected to point $P$ and at point $P$, the perpendicular $BP$ is restored to the straight line $AR$. The wetting angle $\theta$ is between the perpendicular $BP$ and the horizontal $OP$.

Figure 3. Determination of the wetting angle by graphical construction.

Thus, the wettability is determined by the wetting angle and is a characteristic of surface tension on the surface “coating – substrate” and can serve as an indirect characteristic of the spreadability of the protective coating.

Let us consider a drop of a protective coating with a contact angle $\theta$ placed on a solid horizontal surface in air. In the absence of external influences, the drop has the shape of a spherical segment (figure 4).
Figure 4. A drop of liquid on the surface of a solid.

If we denote the surface tension at the interface “solid body – gas”, “solid body – liquid” and “liquid – gas” by \(\sigma_{sg}\), \(\sigma_{sl}\), \(\sigma_{lg}\), and the surface area of the phases involved in wetting by \(\omega_{sg}\), \(\omega_{sl}\), \(\omega_{lg}\), respectively, we can evaluate the surface energy of the system as

\[
G_{surf} = \sigma_{sg} \omega_{sg} + \sigma_{sl} \omega_{sl} + \sigma_{lg} \omega_{lg}. \tag{5}
\]

It is always less than the sum of the surface energies of individual substances, since there is wetting of the surface, which is associated with a decrease in the surface energy of the system. To remove the droplet from the surface, work must be applied, which can be calculated as the product of the adhesion work \(W_a\) and the surface area of the liquid-solid contact \(\omega_{sl}\):

\[
W = W_a \omega_{sl}. \tag{6}
\]

In turn, the work of adhesion \(W_a\) can be determined from the well-known Young equation:

\[
\Sigma_{sg} - \sigma_{sl} = \sigma_{lg} \cos \theta; \tag{7}
\]

\[
W_a = \sigma_{lg} - \sigma_{sl} = \sigma_{lg}(1 + \cos \theta) \tag{8}
\]

The product \(\sigma_{lg} \cos \theta\) is often called the wetting energy or adhesive stress. The adhesion work is greater, the stronger the interaction of the contacting phases.

To characterize the wetting process, Schönborn introduced the spreading coefficient \(S\), the difference between the work of adhesion and the work of cohesion \(W_k\), numerically equal to \(2 \sigma_{lg}\):

\[
S = W_a - W_k = W_a - 2 \sigma_{lg} = \sigma_{lg}(\cos \theta - 1). \tag{9}
\]

When completely wetted, \(S \to 0\). In this case, it is necessary that the adhesion work is 2 times greater than the surface tension of the liquid at the interface with the environment. From equation (9) it also follows that the smaller the work of fluid cohesion (less than \(\sigma_{lg}\)), the easier this liquid wets various solids.

Another characteristic of wetting ability may be the relative work of adhesion:

\[
Z_a = \frac{W_a}{W_k} = \frac{1 + \cos \theta}{2}. \tag{10}
\]

Depending on the interaction at the interface, the values of \(Z_a\) can vary from 1 to 0.

The work of adhesion when wetting solids is usually positive, since forces of intermolecular attraction always act between bodies of any nature. Therefore, equilibrium contact angles, as a rule, are less than 1800 (absolute non-wetting is not realized).

The surface roughness positively affects the wetting of hydrophilic bodies (\(\theta\) decreases) and in most cases negatively affects the wetting of hydrophobic ones. Spreading processes are complicated in the case of highly viscous liquids. The angle \(\theta\) in this case, as a rule, is high (close to 900) and often a false impression is created that the liquid does not wet the surface well. It does not take into account the fact that the equilibrium state of the contact angle for such liquids is established slowly, over time. In
addition, the angle formed by spreading can easily change under the influence of mechanical influences. Spreading in a viscous regime, as well as swelling (restoring a forcefully deformed drop to its original state), is opposed by a certain mechanical force $f$, which is nothing but the strain force of the sample. It is not true thermodynamic equilibrium that intensifies, but false, inhibited:

$$\Sigma_{\text{sg}} - \sigma_{\text{sl}} = \sigma_{\text{lg}} \cos \theta + f. \quad (11)$$

If the force $f$ is large, then the spreading, despite its economic profitability, does not occur. Therefore, it is possible to lower the viscosity of the protective coatings to improve the spreading.

"Runaway", the collection of coatings in separate islands and drops are the signs of poor wetting of the surface. This phenomenon is often observed when applying aqueous protective coatings to poorly degreased surfaces.

The wetting of 9 types of coatings was studied (see table 1) [2, 9 and 10] with various types of substrates: steel in the delivery state, sandblasted and ground surfaces and a surface with a thin layer of lubricant. Measurements of droplet sizes were carried out using an MPB-2 microscope.

### Table 1. Compositions of common protective coatings.

| Coating | Composition of coating |
|---------|------------------------|
| MV      | Chalk – 35% (GOST 4415–75), water – 65% (GOST 2874–73) |
| KBZH    | Concentrate of sulphite-alcohol stillage bard – 190 g and water 1000 g |
| PZ-1    | Concentrate of sulphite-alcohol bard KBZH – 75 g, soap – 35 g, soda ash – 25 g and water – 1000 g |
| AD      | Aluminum powder PAK-1 (GOST 5494-71) – 100 g, dextrin (GOST 6034-74) – 100 g and water – 1000 g |
| MZHS    | Chalk – 30%, liquid glass – 65% |
| AZHS    | PAK-1 aluminum powder – 50 g, liquid glass – 1000 g |
| TSZHS   | Zircon (TSMTU 4469–54) – 30%, liquid glass – 70% |
| TSPR    | Zircon – 40%, polyvinyl butyral (GOST 9439–73) – 3%, solvent 646 (GOST 18188–72) – 57% |
| SC      | RTU Silicone Cream 322–57 |

The studied protective coating was applied to the sample using the pipette, the droplet size was determined according to the procedure shown in figure 1. Five drops of the test coating were applied to each sample to obtain more accurate research results. Then, according to formulas (3) and (4), the contact angle $\theta$ was calculated.

The results were processed according to the method of Ya.I. Frenkel to determine the error of the measurement results. Such processing of the results consists in assessing the value of the sample average (arithmetic mean) and determining its accuracy. The calculation was carried out according to the following formulas:

$$\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i, \quad (12)$$

where $\bar{x}$ – is a sample mean;

$n$ – the number of measurements;

$x_1, x_2, ..., x_n$ – are random variables.

Since the measurement errors are random, the resulting estimate of the result $\bar{x}$ is also random. The measure of its error is the so-called selective standard of the mean:
\[ S_x = \sqrt{\frac{S_x^2}{n}}, \]  

where \( S_x^2 \) – is a sample variance that can be calculated based on the same sample:

\[
S_x^2 = \frac{\sum_{i=1}^{n} (x_i - \overline{x})^2}{n-1} = \frac{\sum_{i=1}^{n} x_i^2 - \frac{1}{n} \left( \sum_{i=1}^{n} x_i \right)^2}{n-1}.
\]  

The error value of the found estimate \( \overline{x} \) is determined by the value of the so-called confidence interval \( \varepsilon_\beta \), which “covers” the true value \( \alpha \) with a given confidence probability, i.e.

\[
\alpha = \overline{x} \pm \varepsilon_\beta.
\]  

The value of the confidence interval for sufficiently large sample sizes \((n \geq 30 – 50)\) depends only on the accepted value \( \beta \), for example:

- For \( \beta = 0,68 \) \( \varepsilon_\beta = S_x \).
- For \( \beta = 0,95 \) \( \varepsilon_\beta = 2S_x \).
- For \( \beta = 0,99 \) \( \varepsilon_\beta = 3S_x \).

The dependence on the number of experiments \( \varepsilon_\beta \) is also significant for values of \( n < 30 \), which is most characteristic of the experiment. In this case, the tabular value of the \( t \)-criterion corresponding to the significance level \( p = 1 - \beta \) and the number of degrees of freedom of the sample variance \( f = n-1 \) is used as a coefficient for calculation of \( \varepsilon_\beta \):

\[
\varepsilon_\beta = t(p, f) \sqrt{\frac{S_x^2}{n}}.
\]  

If the values of the boundaries of the confidence interval \( \overline{x} - \varepsilon_\beta \) и \( \overline{x} + \varepsilon_\beta \) have different signs, the assessment of the result is insignificant and with probability \( \beta \) we can assume that \( \overline{x} \approx 0 \). Usually \( \beta \) equals 0.95, less often 0.99 and 0.999.

Let us give an example of calculating the error of the wetting angle for the PZ-1 coating deposited on a sandblasted surface. After coating the samples, the following contact angles were obtained: 51.1\(^{\circ}\); 56.9\(^{\circ}\); 40.0\(^{\circ}\); 38.9\(^{\circ}\); 47.5\(^{\circ}\). We define the measurement error according to the methodology above for \( \beta = 0.95 \). In this case, \( n=5; f=n-1=5-1=4 \). Using formulas (12) ... (14) we calculate the sample mean and variance:

\[
\overline{X} = \frac{51.1 + 56.9 + 40.0 + 38.9 + 47.5}{5} = 46.88^{\circ};
\]

\[
S_x^2 = \frac{(51.1 - 46.88)^2 + (56.9 - 46.88)^2 + (40.0 - 46.88)^2 + (38.9 - 46.88)^2 + (47.5 - 46.88)^2}{5} = 45.922.
\]
Next, according to the Student's distribution tables, we find the value \( t(pf) = t(0.05; 4) = 2.78 \) and by formula (17) we calculate the value of the confidence interval:

\[
\varepsilon_B = 2.78 \sqrt{\frac{45.922}{5}} = 8.42^\circ.
\]

Estimation of the wetting angle by the formula (15) is 46.88±8.420.

Next, \( C = \cos \theta \) and the relative work of adhesion \( Z_a \) were calculated. The obtained research results show that the aqueous solution of chalk (MV) and the aqueous solution of KBZH wet the steel in the delivery state satisfactorily (the average contact angle \( \theta_{av} \) for MV is 24 ... 32°, for KBZH – 23 ... 33°) and the ground surface (\( \theta_{av} \) for MV – 22 ... 33°, for KBZH – 35 ... 45°) and wet sandblasted surface worse (\( \theta_{av} \) at MV – 49 ... 58°, at KBZH – 48 ... 62°) and a surface with a thin layer of lubricant (\( \theta_{av} \) for MV – 34 ... 46°, for KBZH – 47 ... 53°).

Coatings MZHS and AZHS wet the steel in the delivery state satisfactorily (\( \theta_{av} \) for MZHS – 68 ... 870, for AZHS – 61 ... 680) and a ground surface (\( \theta_{av} \) for MZHS – 44 ... 640, for AZHS – 53 ... 64°), wet the sandblasted surface poorly (\( \theta_{av} \) for MZHS – 96 ... 124°, for AZHZ – 88 ... 92°), and wettability improves when these coatings are applied to a surface with a thin layer of lubricant (\( \theta_{av} \) for MZHS – 29 ... 39°, for AZHZ – 43 ... 51°), obviously, applying of the engine oil film on the surface reduces the surface tension of the coating droplet and improves its wetting. The coatings of TSZHS and SK wet the steel in the delivery state satisfactorily (\( \theta_{av} \) for TSZHS – 54 ... 88°, for SK – 46 ... 69°), sandblasted (\( \theta_{av} \) for TSZHS – 45 ... 87°, for SK – 61 ... 76°) and polished (\( \theta_{av} \) for TSZHs – 45 ... 87°, for SK – 61 ... 76°) surfaces and better wet the surface with a thin layer of lubricant (\( \theta_{av} \) for TsZhS – 17 ... 35°, for SK – 23 ... 35°).

AD coatings wet steel in the delivery state satisfactorily (\( \theta_{av} = 27 ... 39° \)), sandblasted (\( \theta_{av} = 23 ... 37° \)) and polished (\( \theta_{av} = 19 ... 27° \)) surfaces, and wet the surfaces with a thin layer of lubricant worse (\( \theta_{av} = 34 ... 86° \)). A coating PZ-1 has the best wetting results.

The average wetting angle of degreased surfaces does not have a large spread and is in the range of 35 ... 45°, when applying these coatings to the surface with a thin layer of lubricant, the wetting sharply improves, and the wetting angles are in the range of 16 ... 20°. It is obvious that the addition of surface-active substances (surfactants) to the protective coating (soap, soda ash) sharply reduces the surface tension and increases the wetting ability of the coatings. For example, the introduction of 0.1% oleic soap (sodium oleate) into water reduces its surface tension from 72 to 25 erg/cm².

3. Conclusion

As a result of studies for determining the wettability of the applied protective coatings on the surface of the welded products during MAG welding, it was found that satisfactory wetting is observed for the PZ-1 coating, which can be recommended for widespread use in welding production. It is possible to recommend protective coatings based on liquid glass (MZHS, AZHS, TSZHS) for introduction into production as lubricant for surfaces.

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