INVESTIGATION OF PROCESSES TAKING PLACE DURING FORMATION OF Al - Cu COATINGS.

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ABSTRACT
In this paper, on the basis of analysis of the parameters of coating production by casting method, the author investigates the mechanism of their formation. However, the special consideration has been given to analysis of the theoretical and real distribution of the temperatures in active covering. The a.m. analysis and carried out experiments indicate that the formation of coatings in consequence of melting of covering ingredients and the diffusion in the system: liquid cast steel- liquid Al-Cu alloy is impossible. This conclusion is in contradiction with the suggestions of the other authors [4,5].

The carried out experiments indicate that the formation of coatings under discussion takes place only when the infiltration of liquid cast steel into porous powder mixture occurs at the initial stage of the contact between the reactive phases.

1. Introduction

The metal parts of installations (cast from Fe-Ni-Cr alloys) for petrochemical industry and some kinds of furnaces to thermochemical treatment undergo the high-temperature corrosion [1]. This type of corrosion takes place particularly intense when the unmachined surfaces of castings remain in direct contact with gaseous atmosphere exhibiting a high carburizing potential [2].

In order to reduce the disadvantageous effects of this process the author has worked out a method of production of Al-Cu protective coatings directly in a casting mould [3]. This method consists in applying on the inner surfaces of a mould the specially prepared powder mixture of metals (Al+Cu), which after pouring the liquid alloy into a mould and after solidification of a casting forms on its surface a suitable coating. W.Sakwa [4] distinguishes three various mechanisms of coatings’ formation, taking as a criterion the difference between the temperature of alloy being poured into a mould and the melting point of active mixture ingredients:
1. If the difference is significant, the coating forms by melting of the mixture, diffusion and solidification from liquid phase.
2. If the difference is slight, the coating forms by infiltration of the alloy into porous mixture, incipient melting of grains and solidification.
3. If in the mixture are present metals or alloys of high melting points, the coating forms exclusively by infiltration, and they are called “grainy” coatings.

J. Gawroński and co-authors [5] have investigated the production process of the composite coating (made of high-carbon FeCr) on low-carbon cast steel when the a.m. temperature difference was $\Delta T=350^\circ C$. On the basis of a computer stimulation and direct measurements of the temperature during the experiment, they have stated that alloy coatings form from liquid phase.

This paper is an attempt to explain the mechanism of coatings’ formation in the case when the active mixture consists of Al and Cu powders (plus binder and flux [3]), and the casting alloy is G-25NiCrSi3617 creep-resisting cast steel.

Taking W. Sakwa’s criterion we should believe that Al-Cu coatings form according to the first mechanism, because when the temperature of pouring of cast steel is about 1630$^\circ C$ the difference ($\Delta T$) is 550$^\circ C$ in relation to copper and is as big as 970$^\circ C$ in relation to Al. However, the author is going to prove that:
- the infiltration of liquid cast steel into porous material of active covering is the first stage of coating formation,
- the only part of active mixture which is mounted by liquid alloy would be present in the coating.

2. Experimental and results

The material used in the investigation was obtained during the casting experiment, which was planned and described in paper [3]. On the inner surface of a casting mould the specially prepared activating mixture was applied, which forms on a casting an appropriate coating after pouring the liquid alloy (in our case G-25NiCrSi3617 cast steel) into a mould.

During the experiment the following parameters of production have been changed:
- $X_1$ - Al/Cu ratio in mixture in the range of 1,5÷2,5,
- $X_2$ - density of covering of the mould surface with active mixture from 0,01 to 0,3 [g/cm$^2$], what corresponds to the zone thickness of 0,11÷2,5 [mm],
- $X_3$ - diameter of a casting from 20 to 50 [mm],
- $X_4$ - temperature of pouring of cast steel in the range of 1627÷1664 [°C],
- $X_5$ - rate of raising of metal in a mould from 2,9 to 7,8 [cm/s],
- $X_6$ - metallic pressure from 13,6 to 17,4 [cm],
- $X_7$ - max temperature of heating up of the centre of active covering in the range of 1073÷1335 [°C]. This value has been calculated from a simplified model of the heat exchange on the way: casting - active covering - casting mould. This model takes into account both the thermophysical properties of the active mixture and the thermal effects occurring during its heating up, and it omits the infiltration phenomenon of cast steel.
into porous powder mixture as well as the dynamics of filling in a mould [3]. This equation is as follows:

$$T_{\text{max}} = 832 - 221X_2 + 2,7X_2X_3 + 12,8X_2^2 + 10,9X_3 - 0,16X_3^2 + 0,2X_4$$  \hspace{1cm} (1)$$

where: $R = 0.972$, $F = 94.36$

As a result of carried out tests, 43 cylindrical sample castings have been obtained. In the process of further investigation the thickness and structural examinations have been carried out and their results are presented in papers [3,6]. The structure of coatings did not show the features characteristic for casting alloy. To determine the Al and Cu contents in investigated coatings the material for the chemical analysis has been obtained by slicing the sample material at the depth equal to the depth of the coatings. The next step comprised the calculation of a complete set of $T_{\text{max}}$ values for all carried out casting experiments. The obtained values have been taken as a variable parameter of production ($X_7$).

To check, if there are reliable dependencies between the chemical composition of the coatings and their thickness and the production parameters, the approximation calculations based on the publication of K. Mańczak has been used [7]. The obtained results are presented in Table 1.

<table>
<thead>
<tr>
<th>Table 1. The equations describing the mass transport (Al and Cu) in the process of formation of casting coatings on L25H17N36S cast steel.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equations</td>
</tr>
<tr>
<td>---------------------------------------------------------------</td>
</tr>
<tr>
<td>$Y_1 = \exp(9.39 - 9.047X_2 - 0.691X_3 + 4.413\ln X_2^2)$</td>
</tr>
<tr>
<td>$Y_2 = \exp(1.464 - 5.465X_2 + 0.586X_3 + 7.923\ln X_2)$</td>
</tr>
<tr>
<td>$Y_3 = \exp(4.14 - 2.25X_2 - 0.96X_7 + 0.43X_2X_7 - 1.2X_7^2 + 1.1\ln(X_7X_8))$</td>
</tr>
<tr>
<td>$Y_4 = \exp(1.59 - 5.88X_2 + 7.99\ln X_2 + 0.46\ln(X_2X_3))$</td>
</tr>
<tr>
<td>$Y_5 = \exp(0.928 + 5.713X_2 + 0.404X_3 + 3.678X_7^2)$</td>
</tr>
<tr>
<td>$Y_6 = \exp(1.516 - 5.092X_2 + 0.5X_3 + 3.786\ln X_2^2)$</td>
</tr>
<tr>
<td>$Y_7 = \exp(6.771 - 1.237X_2^2 + 0.905X_3 - 4.531\ln X_7)$</td>
</tr>
</tbody>
</table>

$Y_1$ - average content of Al in a coating [%], $Y_5$ - sum of contents of Al and Cu [g/cm$^2$], $Y_2$ - stream of Al [g/cm$^2$], $Y_6$ - sum of streams of Al and Cu [g/cm$^2$], $Y_3$ - average content of Cu in a coating [%], $Y_7$ - coating thickness [µm], $Y_4$ - stream of Cu [g/cm$^2$].
$X_1$-$X_7$ - variable technological parameters of casting in standardized form acc. to formula:

$$X_{\text{stand}} = (X_i - X_{\text{min}})(X_{\text{max}} - X_{\text{min}}) + 0.5$$

(2)

where: $X_i$, $X_{\text{min}}$, $X_{\text{max}}$ - real values, $R$ - multidimensional correlation coefficient, $S$ - unbiased variance estimator, $F$ - Snedecor's test value.

As it can be seen from Table 1, only for three equations ($Y_3$, $Y_4$, and $Y_5$) the variable values $X_4$ and $X_7$ are present. In Figure 1 the graphical illustrations of functions $Y_3$ and $Y_4$ made for the real values of variables $X$ are presented. These equations have been chosen because they show that the influence of the pouring temperature ($X_4$) on Cu transfer from the mixture to a casting has quite different character.

The presented above picture made the author to investigate the real temperature distribution in the active covering. The methodology and results of investigation have been presented in paper [9]. Herein, only the most important results are cited, and namely:

- the maximum temperature at the boundary cast steel - active covering exceeds the finish temperature of solidification of cast steel only in 5 cases (among 31 investigated cases), and in 5 cases it is even lower than the melting point of Cu; on average it is lower about 100°C than the temperature calculated with the use of a mathematical model of heat exchange,

- the real temperature of the covering centre is approximately equal to the calculated temperature ($X_7$),

Fig.1. Influence of pouring temperature ($X_4$), max temperature of heating up of active covering centre ($X_7$) and density of covering of a mould ($X_2$) on Cu content in a coating ($Y_3$) made for $X_6=17.4\text{cm}$ – a), rate of metal raising ($X_5$) on a total content of Al+Cu in a coating ($Y_5$) – b).

Rys.1. Wpływ temperatury zalewania ($X_4$) na zawartość Cu w powłoce ($X_7$) oraz: gęstości pokrycia formy ($X_2$) na zawartość Cu w powłoce ($Y_3$) sporządzony dla $X_6=17.4\text{cm}$ – a), szybkości podnoszenia metalu ($X_5$) na sumaryczną zawartość Al+Cu w powłoce ($Y_5$) – b).
- the real time, from the moment of finishing of pouring until the moment of reaching the maximum temperature at the boundary cast steel - active covering, is much longer than the calculated time and it changes in a wide range from 44 to 262 seconds,
- the values of calculated temperatures depend on: density of covering of a mould with active mixture (X₂), metallostatic pressure (X₆), and first of all a rate of metal raising in a mould (X₅).

During taking out of the castings with coatings from the moulds it has been stated that they exhibited a significant roughness (Rₐ = 40÷80µm), whereas the castings solidifying in a twin mould cavity (without active covering) had the roughness of Rₐ=20÷40µm. Moreover, it was noticed that the whole active mixture was stuck to castings.

The calculations of the process efficiency of the mass transfer on the way active covering - casting have proved that 23÷63% of Al and Cu powder mass contained in mixtures have not been transferred to castings [3]. The diffractometric examinations of the mixture residues have shown the presence of the following compounds: Al₂O₃, Al, CuO, Cu₂O, SiO₂ and complex compounds of sodium silicates and aluminosilicates with participation of copper. At the same time in ten cases (among 43 tests) the fact of partial melting of active covering ingredients has been noticed. The melted parts had the shape of lamellae bent concentrically in relation to the axis of a casting. These lamellae of 0,5÷10 cm² in area had the thickness of about 1 mm, and they were separated from a casting by unmelted active mixture or had with it only point contact. The chemical composition of the lamellae is as follows [wt%]: Cu 50,1; Al 44,7; Si 3,2; Fe 0,9; Ni 0,7; Cr and Na 0,2 each. The diffractometric examination has revealed the presence of only two-phase constituents: the solution of Cu in Al - α₉₆ and CuAl₂ phase.

A phenomenon of the local melting of active mixture (in most cases) takes place when the calculated values of the variable X₇ is low and is comprised in the range of 1060÷1170°C.

The observations described above have been the reason for repeating the calculations describing the mass transport, in which the thickness of active covering has also been taken into account. The volume density of surface covering of a mould X₂₅ has been calculated, and as a result the value which approximately is equal to an inverse of roughness of active mixture has been obtained (Fig.2). The similar procedure applied like in the case of equations presented in Table1 has resulted in obtaining of new equations, which are shown in Table 2.
Table 2. The new equations describing the mass transport in the investigated process.

<table>
<thead>
<tr>
<th>Equations</th>
<th>Statistical values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_1 = \exp(39.1-48.21X_{25}^{2}+10.4X_{25}^2+26.7lnX_{25}+0.33lnX_2X_5)$</td>
<td>R=0.977 S=0.154 F=77</td>
</tr>
<tr>
<td>$Y_2 = \exp(20-36X_{25}^2+7.6X_{25}^2+21.7lnX_{25})$</td>
<td>R=0.989 S=0.137 F=229</td>
</tr>
<tr>
<td>$Y_3 = 2.7+0.3X_4X_5-0.79X_{25}^2-0.61/X_{25}$</td>
<td>R=0.939 S=0.150 F=40</td>
</tr>
<tr>
<td>$Y_4 = \exp(-4.79-4.61X_{25}+0.73X_4X_5+7.21lnX_{25}-0.25lnX_1X_3)$</td>
<td>R=0.982 S=0.175 F=103</td>
</tr>
<tr>
<td>$Y_5 = \exp(37-46X_{25}+10X_{25}^2+25lnX_{25}+0.2lnX_1X_3)$</td>
<td>R=0.976 S=0.132 F=75</td>
</tr>
<tr>
<td>$Y_6 = \exp(-2.5-5.6X_{25}+0.32X_7+0.32X_3+8lnX_{25})$</td>
<td>R=0.992 S=0.119 F=223</td>
</tr>
<tr>
<td>$Y_7 = \exp(3.5-4.5X_{25}+0.65X_4X_7+6lnX_{25})$</td>
<td>R=0.905 S=0.339 F=24</td>
</tr>
</tbody>
</table>

$X_{25}$ - volume density of surface covering of a mould with mixture $[g\text{ Al+Cu}/mm^3]$. The other notations as in Table 1.

$X_{25}$ is linked with the covering density of a mould $X_2$ by a statistical formula:

$$X_{25} = 0.93\cdot10^{-3} + 0.88\cdot10^{-4}X_2^2$$

(3)

where: R = 0.992; S = 0.616; F = $\infty$.

A graphical form of formula (3) is shown in Figure 2. Analogically to Figure 2, in Figure 3 are presented the graphs of new functions $Y_3$ and $Y_5$.  

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**Fig.2.** Graphical form of formula (3).

**Rys.2.** Graficzna postać zależności (3).
Assuming (at the beginning) that the coatings form by melting, it has been decided to make the process easier by increasing the contact surface of grains of Al and Cu powders in the mixture. This effect has been achieved by:
- decreasing the granularity of Al and Cu powders from 71±100µm to 40±71µm (test C16),
- using powders of various granularity i.e. Al 71±100µm and Cu<40µm (test E16),
- using Al powder in the shape of flakes (test L16 and D16), whereas for other tests this shape has been changing from the shape of drop to the shape of cylinder.

The amount of flux has been increased from 5 to 9% because of an increase of the specific surface of grains, and for tests with Al having the shape of flakes an amount of binder has also been increased from 12 to 24% (water-glass R145).

Later on it has been checked if the change of the melting point of fluxes added to active mixtures, or the kind of alloy have the influence on mass transport from active covering to a casting. So, instead of the previously used flux (45% KCl + 45%NaCl + 10% NaF) having melting point of 550°C the following fluxes have been used:
- 50%KCl + 32%LiCl + 10%NaF + 8%ZnCl₂, T_{melt} = 440°C, (A16),
- 50%BaCl₂ + 25%KCl + 20%NaCl + 5%CaF₂, T_{melt} = 600°C, (B16).

In the both a.m. cases the amounts of added fluxes have been the same (5%), and neither the kind nor the amount of the binder have been changed (12%).

During the last experiment (Z16) in place of cast steel the cast iron containing 3,3% C, 2,1% Si and 0,48% P has been poured into a mould, and which later on has been verified as GG - 15.

The other conditions in which tests have been carried out are as follows: \( X_1=2,0 \); \( X_3=35 \) [mm]; \( X_2=0,16 \) [g/cm²] with the exception of D16 test where \( X_2 =0,03 \) [g/cm²].
The other parameters of production and obtained results are presented in Table 3, in which for comparison the 16.5 experiment carried out earlier is also presented [3]. The notations of variables $X_1\div X_7$ and $Y_1\div Y_7$ are identical as in Table 1.

Table 3. The parameters of production and results obtained for additional experiments.

<table>
<thead>
<tr>
<th>Test symbol</th>
<th>$X_4$ [°C]</th>
<th>$X_5$ [cm/s]</th>
<th>$X_7$ [°C]</th>
<th>$Y_1$ [%]</th>
<th>$Y_2$ [g/cm$^2$]</th>
<th>$Y_3$ [%]</th>
<th>$Y_4$ [g/cm$^2$]</th>
<th>$Y_7$ [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C16</td>
<td>1640</td>
<td>3.1</td>
<td>1180</td>
<td>1.45</td>
<td>0.019</td>
<td>0.60</td>
<td>0.005</td>
<td>912</td>
</tr>
<tr>
<td>E16</td>
<td>1630</td>
<td>5.7</td>
<td>1178</td>
<td>1.02</td>
<td>0.012</td>
<td>0.32</td>
<td>0.003</td>
<td>287</td>
</tr>
<tr>
<td>D16</td>
<td>1650</td>
<td>6.2</td>
<td>1311</td>
<td>trace</td>
<td>0</td>
<td>trace</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>L16</td>
<td>1670</td>
<td>5.2</td>
<td>1195</td>
<td>0.16</td>
<td>0.002</td>
<td>0.05</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>A16</td>
<td>1620</td>
<td>5.4</td>
<td>1176</td>
<td>4.02</td>
<td>0.037</td>
<td>2.13</td>
<td>0.019</td>
<td>1025</td>
</tr>
<tr>
<td>B16</td>
<td>1620</td>
<td>5.4</td>
<td>1176</td>
<td>3.68</td>
<td>0.025</td>
<td>1.80</td>
<td>0.014</td>
<td>554</td>
</tr>
<tr>
<td>Z16</td>
<td>1450</td>
<td>6.1</td>
<td>1142</td>
<td>5.54</td>
<td>0.063</td>
<td>3.49</td>
<td>0.032</td>
<td>1433</td>
</tr>
<tr>
<td>16.5</td>
<td>1645</td>
<td>5.7</td>
<td>1181</td>
<td>3.81</td>
<td>0.030</td>
<td>1.89</td>
<td>0.015</td>
<td>911</td>
</tr>
</tbody>
</table>

3. Discussion

On the basis of the equations presented in Tables 1 and 2 it can be stated that the biggest influence on the effectiveness of the formation of the investigated coatings have:
- superficial or volume density of covering of a mould with active mixture ($X_2$), ($X_3$),
- rate of metal raising in a mould ($X_5$),
- maximum temperature of heating up of the centre of covering ($X_7$), acc. to equation (1), which depends on the temperature of cast steel being poured into a mould only in slight degree ($X_4$).

The temperature of pouring, which acc. to W.Sakwa and J.Gawroński is a very important factor, in the investigated area is present only in two equations in Table 1 ($Y_3$ and $Y_5$) and three equations in Table 2 ($Y_3$, $Y_5$, $Y_7$). This parameter effects mainly Cu transport from covering to a casting. As it can be seen from Fig. 1, an increase of this temperature results in a slight increase of Cu and Al+Cu contents in a coating. On the other hand on the mass transfer much more significant influence has the temperature $X_7$; its increase results in reduction of Cu content in a coating (Fig. 1a), and for the temperatures higher than 1140°C, a total amount of Al+Cu also decreases (Fig.1b). It should be stated that the analysis of the data presented in Table 2 has not shown the similar contradictions. The explanations concerning the influence of temperatures on Cu transport in the investigated process were the subject of the separate publication of the author [8].

As it was shown in paper [9], the pouring temperature does not influence on real distribution of maximum temperatures in active covering. However, the highest temperatures at the boundary cast steel - active covering can be reached in most cases after about 120 s from the moment of filling up a mould with liquid alloy. Despite the
fact that this temperature is lower than the finish temperature of cast steel solidification, in all cases the presence of a coating on castings has been noticed. On the other hand, the melting of active mixture does not lead to an increase of the effectiveness of the mass transport to a casting because the melted parts do not remain in contact with casting material, what is proved by their chemical and phase composition. However, an increase of the temperature of the alloy being poured into a mould favours the mass transfer from active covering to a casting, as it can be seen from all equations shown in both tables. The advantageous effects on this process have also an increase of the rate of metal raising in a mould ($X_5$) and an increment of the metallostatic pressure ($X_6$). The significant values of these parameters ($X_4$, $X_5$, $X_6$) favour the infiltration process mainly by reducing the surface tension and the alloy viscosity, as well as by reducing the initial temperature of wettability and adhesive attraction of the ingredients, increasing at the same time the kinetics of the processes at the boundary liquid metal - solid body $[10-12]$.

The introduction to the calculations of the volume density of covering ($X_{25}$) has shown that an increase of the amount of mixture applied on the unit surface of a mould results in an increase of its density (the porosity has been reduced), what is shown in Fig.2. This effect significantly limits Al and Cu transport, if the volume density exceeds $1.05 \times 10^{-3}$ [gAl+Cu/mm$^3$]. This statement points out that the infiltration takes a significant part in the process of coatings’ formation. The credibility of this observation can be supported by the additional examinations presented in Table 3. When the size of grains in the mixture has been reduced and differentiated (tests C16 and E16), which resulted in lowering its porosity, the effects of the mass transfer have been significantly lessen, and the use of Al in the shape of flakes almost completely has led to retardation of this process.

The application of fluxes of various melting points and grey cast iron in a place of G - 25NiCrSi3617 cast steel (tests A16, B16 and Z16) show that the surface phenomena occurring at the very first moment of the contact between liquid alloy and mixture have the decisive influence on the whole process of casting coating formation.

CONCLUSIONS

1. The Al-Cu casting coatings on creep-resisting cast steel do not form as a result of melting of the part of the active covering and the diffusion in the system liquid-liquid (cast steel- Al-Cu alloy). The melting of the unidentified volumes of the mixture does not lead to an increase of Al and Cu on a casting.

2. An increase of the pouring temperature of cast steel does not result directly in intensification of the mass transfer, but only indirectly improves the ability of the alloy to infiltrate porous mixture. This conclusion remains in contradiction with the other authors’ statements $[4,5]$.

3. An increase of the porosity of the active mixture significantly limits the mass transfer on the way: active covering-casting.
4. At the first stage of the formation of the investigated coatings the infiltration of liquid alloy into porous powder mixture takes place, and the coating consists of the only parts of active covering, which would be infiltrated by the liquid alloy at the first stage of contact.

REFERENCES


Recenzował:
Prof. dr inż. Józef Gawroński