Evaluation of the efficiency of solid-phase activation of modifying complexes

E N Eremin
Omsk State Technical University, 11 Mira ave., Omsk, 644050, Russia
weld_techn@mail.ru

Abstract. The efficiency of the solid-phase activation of modifying complexes has been evaluated. It is shown that such preliminary treatment of refractory particles leads to a significant increase in the diffusion coefficients in the matrix of the metal-ultrafine powder complex. The introduction of modifying complexes that have undergone solid-phase activation into liquid nickel increases the degree of supercooling of the melt and reduces the grain, which characterizes a high degree of intensity of the action of inoculators. In this case, the most intense effect is exerted by the addition of the TiCN-Ni and TiCN-Ti complexes that have undergone solid-phase activation.

1. Introduction
A significant increase in the service properties of the metal of workpieces obtained in the foundry can be achieved by the implementation of the modification technology. In this process, nucleation is carried out by introducing solid refractory particles into the molten metal [1-4]. Most often, ultradispersed powders of previously synthesized refractory compounds of a number of transition metals with a dispersion of 0.01-0.1 microns are used as solid particles - inoculators. However, commercially available powders are characterized by significant oxidation of surface particles, which worsens their wettability by the melt and significantly complicates the process of their direct introduction into the liquid metal. All this determines the low efficiency of the modification process.

2. Setting tasks
For the successful introduction of such particles-inoculators into liquid metal, their preliminary preparation is necessary, which consists in creating a metal shell - a protector on their surface, which ensures wetting with metal melts. Therefore, the efficiency of modification with such complex modifiers is largely determined by the presence on the surface of the particles of inoculators of an activated transition layer made of the tread metal [5]. In this respect, solid-phase activation (SPA) of the modifying complexes used is promising. In connection with the above, the work posed the task of assessing the effectiveness of the application of such processing of ultradispersed powders that have found wide application in the compositions of modifying complexes.

3. Investigation of the process of solid-phase activation
The objects of research were briquettes with a diameter of 30 mm and a height of 10 mm obtained by pressing a mixture of a powder of a cladding metal (protector) and ultrafine powder (UP). For the cladding of the particles of inoculators, sintering of briquettes in a vacuum using an SGV-2 unit was used.

The efficiency of solid-phase activation of modifying complexes is primarily determined by the diffusion of non-metals in the UP - metal system. In complex powder systems, the diffusion process is calculated relative to the effective diffusion coefficient $D_{ef}$, which is calculated by the formula [6]:

$$
D_{ef} = \sqrt{D_0 + \left(\delta_s / \bar{a}ight)} \sqrt{D_s},
$$

where $D_0$, $D_s$ - coefficients of volumetric and surface diffusion; $\bar{a}$ - average grain size; $\delta_s = 2a$; $a$ - is the interatomic distance.
To determine $D_{ef}$, H$_\mu$ polytherms were used in the interaction zone of the UP-Me sintered briquettes for different sintering temperatures ($T_{sp}$) (Fig. 1), assuming that equal H$_\mu$ values correspond to equal non-metal contents at the measurement point.

The concentration of a diffusing substance (diffusant) at a distance $x$ for the case of diffusion from a flat source of finite thickness can be found by the formula [7]:

$$C(x,t) = 2C_0h \sum_{n=1}^{\infty} \frac{\cos \lambda_n x - \lambda_n h \sin \lambda_n x}{1 + \lambda_n^2 h^2} e^{-\lambda_n^2 D t / h},$$  \hspace{1cm} (2)$$

where $C_0$ – is the initial concentration of diffusant in the source; $h$ – is the thickness of the diffusant source; $l$ – is the thickness of the plate with the final size.

The eigenvalues $\lambda_n$ are determined by the transcendental equation:

$$\cot \lambda_n l = \lambda_n h.$$  \hspace{1cm} (3)$$

In the calculations, it was assumed that $h$ and $l$ are constant values: $h = 3$ mm, $l = 10$ mm at $t = 1800$ sec. According to the polytherms H$_\mu$ for various $C_0$, it is possible to establish the values of the diffusant concentration when they are equal to a certain value of $C^*$ by the formula:

$$C_1(x_1, t) = C_2(x_2, t) = C_3(x_3, t) = C^*.$$  \hspace{1cm} (4)$$

To solve the system of nonlinear equations (2) - (4) and to determine the diffusion coefficients from the values $x_1$, $x_2$, $x_3$ ($D_1$, $D_2$, $D_3$), the following values are taken: $T_{sp 5} = 1200$ °C, $x_1 = 188$ µm, $T_{sp 4} = 1100$ °C, $x_2 = 82.2$ microns, $T_{sp 3} = 1000$ °C, $x_3 = 57.5$ microns.

The $D_{ef}$ values were calculated using the formula (1), taking $d_{Ti} = 2.92 \times 10^{-10}$ m; $d_{Ni} = 2.48 \times 10^{-10}$ m; $d = (2-4) \times 10^{-5}$ m. The calculation results are summarized in Table 1. In this case, it was assumed that $D_0$ in equation (1) determines the value $D_{ef}^D$, since $D_0$ is in the range of $10^{-4}$-$10^{-6}$, and $D_3$ for the selected temperatures is within $10^{-7}$-$10^{-8}$ and the change in the value of the coefficient will be $10^{-14}$-$10^{-16}$, which is negligible compared to $D_0$. 

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**Figure 1.** Polytherms of microhardness in the interaction zone in a two-layer briquette UP-Me:

1 – $T_{sp} = 800$ °C; 2 – 900 °C; 3 – 1000 °C; 4 – 1100 °C; 5 – 1200 °C.
To estimate the tabular value of $D_{ef}^T$ and the calculated $D_{ef}^P$, the value of $D_0$ was selected according to the data of [8]. The calculated values of the effective diffusion coefficients $D_{ef}^T$ are shown in Table 2.

**Table 1.** Calculated values of the effective diffusion coefficients $D_{ef}^P$ of non-metals in the matrix of a two-layer briquette of the Me-UP complex, m$^2$/s

| Complex   | 1000 °C         | 1100 °C         | 1200 °C         |
|-----------|-----------------|-----------------|-----------------|
| Ni-TiCN   | $3.7851 \cdot 10^{-8}$ | $3.79171 \cdot 10^{-8}$ | $3.8255 \cdot 10^{-8}$ |
| Ti-TiCN   | $2.1788 \cdot 10^{-9}$ | $2.2532 \cdot 10^{-9}$ | $2.4103 \cdot 10^{-9}$ |
| Cr-TiCN   | $3.7828 \cdot 10^{-8}$ | $3.8060 \cdot 10^{-8}$ | $4.2210 \cdot 10^{-8}$ |
| Fe-TiCN   | $3.8198 \cdot 10^{-8}$ | $3.8297 \cdot 10^{-8}$ | $3.8361 \cdot 10^{-8}$ |

**Table 2.** Tabular values of effective diffusion coefficients $D_{ef}^P$ non-metals in the complex, m$^2$/s

| Complex   | 1000 °C         | 1100 °C         | 1200 °C         |
|-----------|-----------------|-----------------|-----------------|
| Ti-C      | $2.8 \cdot 10^{-13}$ | $2.51 \cdot 10^{-13}$ | $2.3 \cdot 10^{-14}$ |
| Cr-C      | $2.3 \cdot 10^{-12}$ | $1.8 \cdot 10^{-11}$ | $5.7 \cdot 10^{-11}$ |
| Fe-C      | $3.6 \cdot 10^{-13}$ | $1.0 \cdot 10^{-12}$ | $1.0 \cdot 10^{-12}$ |
| Ni-C      | $1.23 \cdot 10^{-10}$ | $2.2 \cdot 10^{-10}$ | $4.9 \cdot 10^{-10}$ |

From the comparison $D_{ef}^T$ with $D_{ef}^C$ it can be seen that in systems with UP, the diffusion coefficients of non-metals are two to three orders of magnitude higher than the tabular values obtained for systems with coarse-grained powders of 40-200 microns, which are also used in a number of modification processes.

The results obtained are confirmed experimentally. Thus, microspectral analysis of the contact area of a two-layer briquette of the TiCN-Ni system passed through TPA showed the mutual diffusion of titanium into the nickel matrix and nickel into the UP matrix (Fig. 2).

**Figure 2.** Change in the content of Ti(C) and Ni(C) in the area of contact of UP TiCN with a nickel matrix at a distance $l$

In addition, fractograms of fractures of briquettes of the TiCN-Ti systems indicate that TiCN particles with a clear cut are clad with the matrix material after TPA and acquire a rounded shape (Fig. 3).
Study of the process of degassing briquettes in vacuum with a rarefaction \((1-4) \times 10^{-4}\) mm Hg. in the chamber of the EMAL-2 mass spectrometer showed that the composition of the evolved gases from TiCN-Ti includes \(\text{CO}_2\) (emission peak at 300 °C), \(\text{N}_2\) and \(\text{CO}\) (emission peak at 450 °C), atomic nitrogen (emission peak at 350 °C) and \(\text{H}_2\), which has a doublet release peak at 350 and 650 °C (Fig. 4) [9].

It was found that gas evolution for TiCN-Ti practically ceases after 30 min exposure at 800 °C, and for TiCN-Ni - at 950 °C. Therefore, for TiCN-Ti, the sintering time is assumed to be 30 min at a sintering temperature of 850-900 °C, and for TiCN-Ni, 30 min at 950-1000 °C.

Thus, the temperature and duration of TPA UP are determined by the kinetics of gas desorption during heating of the briquette of the modifying complex.

The effectiveness of the modes of TPA modifying complexes was checked by the thermograms of crystallization of cyclically superheated nickel, fixing the overcooling \(\Delta T\) as the degree of the intensity of the action of the inoculator. Five-fold cyclic overheating of Ni to 1800 °C with cooling to 1450 °C sequentially increases \(\Delta T\) to 55-60 °C (Fig. 5, a). The introduction of sintered briquettes from non-ultrafine Ni and Ti powders into the prepared liquid nickel reduces \(\Delta T\) by 30 °C, i.e. about twice.

![Figure 3. Fractograms of fractures of TiCN-Ti briquettes after TPA](image)

![Figure 4. Dynamics of desorption of gases (Q) during heating of the briquette of the modifying complex TiCN-Ti: Q is the signal of the mass spectrometer proportional to the partial pressure of the gas components](image)

![Figure 5. Influence of the number of remelts (I-V) on nickel overcooling (\(\Delta T\)) (a) and the effect of modifying complexes on nickel overcooling (\(\Delta T\)) after the V-th remelting (b): 1 – the base of the complex (nickel powder); 2 – TiCN](image)
The addition of UP to the briquette composition changes $\Delta T$ by an amount depending on the type of UP and its amount, as well as on the metal of the briquette matrix (Fig. 5, b). The most intense effect on the decrease in $\Delta T$ and the decrease in the Ni grain is exerted by the addition of the TiCN-Ni and TiCN-Ti complexes (Fig. 5 b, 6).

Figure 6. Influence of the amount of UP TiCN (K) on subcooling ($\Delta T$) and the number of grains (N) (per unit area of the nickel section): 1 – $\Delta T$; 2, 3 – N

It is noted that in the TiCN-Ni-Ti complex at a ratio of Ti:Ni = 1:3 and $T_{sp} > 950 \, ^\circ C$, an intermetallic compound is formed by the mechanism of self-propagating high-temperature synthesis (SHS-process), accompanied by an increase in the briquette temperature to 1180 $^\circ C$. The effectiveness of the influence of such a complex on $\Delta T$ decreases, apparently, due to the coagulation of UP particles and a decrease in the diffusion coefficients of Ti, Ni, C, and N in the Ni$_3$Ti compound.

Thus, the most intense modifying effect is exerted by ultrafine powders of the TiCN-Ti, TiCN-Ni and TiCN-(Ni+Ti) complexes that have undergone solid-phase activation.

4. Conclusion
The solid-phase activation of the particles of the modifying complexes leads to a significant increase in the diffusion coefficients in the matrix of the Me-UP complex. The introduction of modifying complexes that have undergone solid-phase activation into liquid nickel increases the degree of supercooling of the melt and decreases the grain, which characterizes the degree of intensity of the action of the inoculator, by half.

The most intense modifying effect is exerted by the addition of the TiCN-Ni and TiCN-Ti complexes.

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