THE USE OF COLLOIDAL SOLUTIONS OF ZINC OXIDE NANOPARTICLES IN INVESTMENT CASTING TECHNOLOGY

Studies presented here are relevant to the investment casting technology. The wettability of wax by the colloidal solutions of ZnO nanoparticles was tested in the following environments: esters, heptyl acetate (OH), butyl acetate (OB) and in alcohols: methanol (M), ethanol (E) and propanol (P). All colloidal solutions of ZnO showed very high effectiveness in wetting of the unmodified wax surface.

Next, onto the surface modified with colloidal solutions of ZnO, a liquid ceramic slurry was applied (CMC). The wettability of the modified wax surface by the ceramic slurry is strongly dependent on the structure of organic solvents (the number of the functional groups of -OH, -COOH and the length of carbon chains). As regards the modifier (ZnO), the best wax wettability by CMC was achieved applying previously onto the surface of the wax a colloidal solution of ZnO nanoparticles in butyl acetate (OB). The contact angle amounted to about 38 deg.

Studies using scanning electron microscopy (SEM) and X-ray microanalysis (XRD) allowed an assessment of the effect of colloidal solutions of ZnO nanoparticles on the wax -- CMC interface morphology.

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bromide (BCMA), or Rokatefenol. Besides the modification of a ceramic material, sometimes, also the surface of a wax pattern is modified [5]. For this purpose, in [6], the surface of a wax pattern was coated with polyvinyl alcohol dissolved in hot water, with polyvinylbutyral dissolved in ethanol, or with sodium carboxymethyl cellulose dissolved in water.

Studies conducted by the authors in recent years [7-9] have shown that colloidal solutions of ZnO nanoparticles in organic solvents are very effective in wetting of the wax pattern surface and fully applicable in the investment casting process. This paper presents the results of studies of the wettability of foundry wax patterns by selected colloidal. This paper presents the results of studies of the wettability of foundry wax patterns by selected colloidal solutions of nanoparticles of zinc oxide (ZnO) in organic solvents. Based on the results obtained, a modifier was selected to enhance the wetting of a hydrophobic surface of the wax pattern by ceramic slurry.

2. Research part

2.1. Test materials and methods of measurement

Studies of the wax wettability by colloidal suspensions of nanoparticles of metal oxides and ceramic slurry were carried out on the following test materials: -“red” wax, type - 405 supplied by REMET UK, -colloidal solutions of ZnO nanoparticles (nanoparticles with a diameter $d = 10 \text{ nm}$) electrochemically synthesised in: methanol (M), ethanol (E), propanol (P), butyl acetate (OB) and heptyl acetate (OH), at a concentration of $c = 0.3 \text{ M}$, prepared by electrochemical method [6,7,11]. The ceramic slurry contained: alumina (with the main grain fraction of 24 microns) and 30% aqueous solution of colloidal silica SiO$_2$ (trade name LUDOX -AS -30) in the ratio of Al$_2$O$_3$ : SiO$_2 = 1:1$.

The wettability of wax was determined measuring the size of the contact angle in time for the following systems: wax-nanoparticles suspension and slurry. Colloidal solution of ZnO in an organic solvent, it was left exposed to the air for about 24 h, and after the lapse of this time, liquid ceramic slurry was applied onto thus prepared surface of the wax and contact angle was measured again. For analysis, the initial values of the contact angle were adopted. The morphology of the modified wax surface was examined by SEM and XRD microanalysis.

2.2. Results and discussion

Figure 1 compares the values of the contact angle $\Theta$ obtained for the wax wetted by colloidal solutions of zinc oxide nanoparticles (ZnO nanoparticles with a fixed size) in various organic solvents. With constant diameter of the nanoparticles maintained ($d = 10 \text{ nm}$), the colloidal solutions in organic solvents are characterised by a very good wettability ($\Theta < 4-20 \text{ deg}$). It was confirmed that the wettability of wax by the colloidal solutions of ZnO is determined by the presence in the solvent of the functional groups of - OH, -COOH, - COOR, = C = O, and depends on the length of carbon chains in the solvent. The best wettability of wax was provided by heptyl acetate having the longest carbon chain and an ester functional group (-COOR). Excellent wetting of the wax by ZnO in (OH) is associated with the Lewis acid – base reaction (ZnO - solvent) [10, in press] and with the formation of hydrogen bridges between the wax components and the solvent functional groups.

Figure 2 shows the contact angle $\Theta$ obtained when the liquid ceramic slurry is wetting the wax surface previously modified with colloidal solutions of ZnO. The obtained results show that the examined solvents improve the wax wettability by the ceramic slurry. The best wetting effect was achieved when the wax surface was modified with the ZnO colloidal solution in butyl acetate. On the other hand, the use of a suspension in heptyl acetate resulted in total non-wettability of the wax surface by ceramic slurry.

It is interesting to note that the colloidal solution of ZnO in heptyl acetate, while being the best in wetting the wax surface ($\Theta \approx 4 \text{ deg}$), proves totally incapable of improving the wetting characteristics of the wax surface when the ceramic slurry is applied. This is in contrast with the best effect which, among all the modifiers tested, gave the use of butyl acetate. The contact angle of the ceramic slurry on the wax surface coated with a colloidal solution of ZnO in (OB) has reached the value of 38 deg.
wax modified with this agent is practically totally resistant to wetting by the ceramic slurry (84 deg). This behaviour of the system suggests that the long chains of heptyl acetate are “lying” flat on the wax surface and block the active sites of adsorption, making chemisorption in the next layer (ceramic slurry) very difficult.

In the case of ZnO - (OB) colloid, different orientation and alignment of the solvent particles on the wax surface are likely to take place, but the mechanism of this process is not known and requires more detailed studies.

The positive impact of the colloidal solution of ZnO in OB on an improvement of the wax wettability by ceramic slurry was further confirmed by SEM images of the wax-ceramic slurry interface cross-section (with and without the addition of modifier).

Figures 3-8 present the results of SEM examinations. Figure 3 shows the morphology of the applied ZnO nanoparticles in (OB). The diameter of the nanoparticles of a spherical structure is approximately 10 nm. Figure 4 shows a topographic image of the free surface of pure wax unmodified, i.e. not coated with a layer of ZnO suspension, and with visible traces of blowholes. Figure 5 shows a topographic image of the wax surface coated with a suspension of zinc nanoxide ZnO in (OB).

Fig. 3. SEM image of the ZnO colloidal suspension in butyl acetate

Fig. 4. SEM image of the unmodified wax surface

Figure 6 shows a topographic image of the ceramic slurry (Al₂O₃: SiO₂ = 1:1) with visible cracks characteristic of this material, generated during the drying process.

Fig. 6. SEM image of the ceramic slurry

Fig. 7. SEM image of the fracture surface: wax (with unmodified surface) – ceramic slurry

Fig. 5. SEM image of the wax surface modified by colloidal suspension of ZnO in butyl acetate

Figures 7 and 8 show SEM images of the fracture surface in samples of the wax-ceramic slurry system and wax-modifier ceramic- system, respectively, after application onto the wax surface of a colloidal solution of ZnO in OB followed by the application of ceramic slurry. The raw (unmodified) wax-ceramic slurry interface shows poor adhesion of the ceramic material to pure wax. In contrast, the image of the wax surface with the applied ZnO suspension in (OB) shows the wax-ceramic slurry interface with an obviously improved adhesion of the ceramic slurry to the wax surface.
The X-ray spectrum shown in Figure 9 as well as Figures 10 a-e illustrate, respectively, the fluorescent images of individual elements, showing also their distribution at the wax-ceramic slurry interface and confirming thereby the presence in the examined area (wax-ceramic slurry interface) of carbon (C) – the component of wax and solvent, aluminium (Al), silicon (Si) and oxygen (O) – the components of ceramic slurry, and zinc (Zn) – the colloidal component of modifier. It is interesting to note zinc concentration at the interface and traces of its diffusion in the direction of both the ceramic slurry and wax.
3. Summary

The conducted studies proved an effect of the wax surface modification with colloidal solutions of zinc oxide ZnO in organic solvents on the wax wettability by ceramic slurry. Keeping the size of ZnO nanoparticles (d = 10 nm) constant, this effect is conditioned by the presence of functional groups and the length of the carbon chain in a solvent. The most effective wetting of the wax surface was obtained in the case of heptyl acetate solutions (OH) − θ = 4 deg (the longest hydrocarbon chain), slightly inferior in the case of butyl acetate (θ = 16 deg). The wettability of the modified wax surface by ceramic slurry depends on the presence of functional groups on the wax surface necessary for the formation of hydrogen bridges with the components of this slurry. ZnO nanoparticles are involved in the acid-base reaction (Lewis acids) [10, in press] and in the formation of hydrogen bridges improving the wettability of waxes. Excellent wettability of wax by the ZnO - heptyl acetate colloid in practically total absence of the wettability by ceramic slurry of the wax surface modified with this colloid is most likely associated with the arrangement of carbon chains “lying” flat on the wax surface. This arrangement of the ester group blocks the sites active in the process of interaction with the ceramic slurry, thereby decreasing its ability to wet the modified wax surface (θ = 84 deg). In contrast, butyl acetate with a carbon chain shorter and of different orientation leaves free active centres of adsorption allowing good wetting of the wax by ceramic slurry (θ = 38 deg).

The studies using scanning electron microscopy (SEM) revealed the presence of an intermediate layer of the ZnO nanoparticles on the wax-ceramic slurry interface.

REFERENCES


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