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THE INFLUENCE OF METAL OXIDE NANOPARTICLES ON PROPERTIES OF WATER GLASS

Determination of the influence of the colloidal nanoparticles of zinc oxide additions on the properties of water glass, a binder of moulding and core sands - is the subject of the paper. The nanoparticles of zinc oxide in various suspensions were introduced into water glass and the adhesive properties were examined by measuring the quartz wettability by the binder. The binder-matrix interactions were verified by strength tests of loose self-setting sands with modified binders. The most efficient quality improvement of moulding sands with water glass can be achieved by the binder modification. Multimolecular components such as polyphosphate, polyacrylamide, carboxymethylcellulose, and polyvinyl alcohol have been used up to now as modifiers. They differed in: their polymerisation degree, molecular mass, kind and number of functional groups. The performed investigations of water glass modification by the suspension of ZnO nanoparticles in ethanol and in propanol indicated that strength R_m^u of loose self-setting sands with water glass modified by the suspension of ZnO nanoparticles in ethanol and in propanol (without a chemical hardener) increases when the modifier is added. In the case of adding the modifier in the form of a suspension of ZnO nanoparticles in propanol - sand strength R_m^u increases by approx. 8% (when modifier addition equals 3 mass %) and by approx. 26% (when this addition equals 5 mass %), whereas when the modification is carried out by the suspension of ZnO in ethanol - sand strength R_m^u increases by approx. 18% (when modifier addition equals 3 mass %) and by approx. 12% (when this addition equals 5 mass %).

Keywords: **modification, water glass, nanoparticles**

WPŁYW NANOCZĄSTEK TLENKU METALU NA WŁAŚCIWOŚCI SZKŁA WODNEGO

Przedmiotem badań jest określenie wpływu dodatku zawiesin koloidalnych nanoczastek tlenku cynku na właściwości szkła wodnego - spoiwa mas formierskich i rdzeniowych. Do szkła wodnego wprowadzano nanoczastki tlenku cynku w różnych zawiesinach i określano jego właściwości adhezyjne poprzez pomiar zwilżalności kwarcu przez spoiwo. Oddziaływania spoiwo-osnowa zweryfikowano poprzez pomiary wytrzymałościowe sypkich mas samoutwardzalnych z udziałem spoiw modyfikowanych. Jak wykazały badania, najbardziej efektywną poprawę jakości mas ze szkłem wodnym można osiągnąć poprzez modyfikację spoiwa. Dotychczas jako modyfikatory zastosowano wielomolekularne komponenty różniące się: stopniem polimeryzacji, masą molekularną, rodzajem i ilością grup funkcyjnych, takie jak np. polifosforan, poliakrylamid, karboksymetyloceluloza, alkohol poliwinylowy. Przeprowadzone badania modyfikacji szkła wodnego zawiesiną nanocząstek ZnO w etanolu oraz w propanolu wykazały, że wytrzymałość R_m^u sypkich mas samoutwardzalnych ze szkłem wodnym zmodyfikowanym zawiesinami nanocząstek ZnO w etanolu i w propanolu (bez chemicznego utwardzacza) wzrasta przy dodatku modyfikatora. W przypadku dodatku modyfikatora w postaci zawiesiny nanocząstek ZnO w propanolu wytrzymałość R_m^u mas wzrasta o ok. 8% (dodatek modyfikatora 3% mas.) i o ok. 26% (dodatek modyfikatora 5% mas.), natomiast przy modyfikacji zawiesiną ZnO w etanolu wytrzymałość R_m^u mas wzrasta o ok. 18% (dodatek modyfikatora 3% mas.) i o ok. 12% (dodatek modyfikatora 5% mas.).

Słowa kluczowe: **modyfikacja, szkło wodne, nanocząstki**

INTRODUCTION

Moulding sands with organic binding agents, hardened by acids, are strongly toxic. This situation requires - on the one hand - investments providing safe and proper work conditions in foundry plants, while - on the other hand - the costs of moulding sands are high (especially sands with furfuryl alcohol based binders). The above inconveniences have motivated researchers to look for binders without such disadvantageous properties.

One of such binders is water glass; cheap, easily accessible and not toxic. However, the unfavourable properties of sands with water glass are: brittleness, worse shakeout of moulds and worse reclaimability. Simultaneously the possibilities of water glass as a moulding and core sands binding agent are not fully utilised.

Regarding the technological aspect, the following requirements should be simultaneously fulfilled:

- Ensure optimal conditions for core and mould hardening, as well as ensure the required level of mechanical, physical and chemical properties (strength, hygroscopicity, brittleness etc.)
- Ensure decreased retained strength of cores and moulds in a wide temperature range (300÷1200°C), which will improve their knocking out ability
- Improvement of moulding and core sands reclaiming ability.

An analysis of model: matrix-binder combinations [1, 2] indicated that the final moulding sand strength depends on the geometry of the formed connections, the adhesive strength (δ_A) of the: matrix-binder and the cohesive strength (δ_K) of the binder.

The adhesive strength is related to the matrix wettability by water glass. Water glass wettability is 2-4 times smaller than the matrix wettability by organic binders [1]. The main reason for this property is a lack of functional groups in the water glass structure. Thus, in order to improve it, certain functional groups should be introduced into this binder structure (e.g. -NH=, $-NH_2$=, -COOH, OH- etc.)

The water glass cohesive strength, while retaining the module, depends on the geometrical dimensions of the bonding bridge and the stresses related to them [3].

The most efficient quality improvement of moulding sands with water glass can be achieved by binder modification. Multimolecular components as polyphosphate, polyacrylamide, carboxymethylcellulose, and polyvinyl alcohol have been used up to now as modifiers. They differed in their: polymerisation degree, molecular mass, kind and number of functional groups.

The last decades have witnessed the development of a new material group, so-called nanoparticles [4-7], among others, the nanoparticles of ceramic materials: SiO_2, Al_2O_3, $CaSiO_3$, ZnO etc.

Nanoparticles introduced into the matrix (binder) form new systems so-called nanocomposites. Nanoparticles can change the initial binder properties by physical or chemical influences. A majority of investigations concerning water glass modification has focused on the application of organic compounds. The few results, presented in references, indicate a favourable influence of the micro- and nanoparticles of MgO and Cr_2O_3 on the retained strength, which is related to improvement of the shakeout of moulds property [8].

The literature data concerning water glass modification by the nanoparticles of inorganic compounds are fragmentary and rather of a qualitative character [9]. There are no systematic investigations, which would connect the way of modification with the kind of influence in the: water glass - modifier system and with the structure of the formed nanobinder (nanocomposite) and its properties.

An attempt to modify water glass with a zinc oxide nanoparticles colloidal suspension (ZnO) in organic suspensions was undertaken in the study, as well as the impact of the kind of influence: binder-modifier, matrix - modified binder, were determined.

EXPERIMENTAL PROCEDURE

Materials and testing methodology

Binder modification was performed with water glass:

- "R 145" of a module M = 2.5 and density d_{20} = = 1470 kg/m^3, pH = 11.2.

The modifier applied was:

- colloidal suspension of ZnO nanoparticles of dimensions < 10÷100 nm > in ethanol or propanol: concentration of suspension: 0.3 M.

Water glass modification was performed by introducing a 3 or 5 mass % of an alcoholic suspension of ZnO nanoparticles and them homogenising the mixture.

In order to determine the interactions between: the matrix and the - modified binder, the wettability in the system: quartz-binder was measured [10]. The measurements were carried out by means of a prototype apparatus.

The influence of water glass modification on the moulding sand properties was verified by checking the tensile strength $R_m{}^u$ of loose self-setting sand after 24 h of hardening.

Results and their discussion

Figures 1a and b illustrate the quartz wettability by unmodified water glass (curve 1) and that modified by the suspension of ZnO nanoparticles in ethanol (curve 2) and in propanol (curve 3). As is generally known, the quartz wettability by water glass is low. The wetting angle equals approx. 66 degrees directly after the binder application (θ_0) and approx. 50 degrees when the: quartz-binder system reached a steady state (θ_r). The performed wettability tests with modified water glass indicate that the applied modifier influences not only the angle values of θ_0 and θ_r but also the time of reaching a stationary state τ_r. This influence depends on the amount of modifier and the applied suspension. The addition of a 3 mass % of modifier in the form of an ethanolic or propanolic suspension causes a rather small decrease in angles θ_0 and θ_r and shortening of the time ($\tau_{r.}$) of reaching a stationary state (Fig.1a).

An increase in the modifier part by mass (ZnO nanoparticles in both suspensions) to 5 mass % (Fig. 1b) significantly decreases wetting angles θ_o, θ_r and time τ_r. The binder with the addition of a 5 mass % of the ZnO nanoparticles suspension in propanol had the lowest values of contact angles (36 and 20 degrees) had. This significant decrease indicates a stronger adhesive influence of the quartz-binder, in the case of applying a solvent of a longer carbon chain. The shortening of the time needed to obtain a stationary state by the quartz-binder system indicates the modifier influence on the wetting process kinetics.

Figures 2 and 3 illustrate the changes in strength of moulding sands with unmodified water glass and that modified by suspensions of ZnO nanoparticles in in various alcohols.

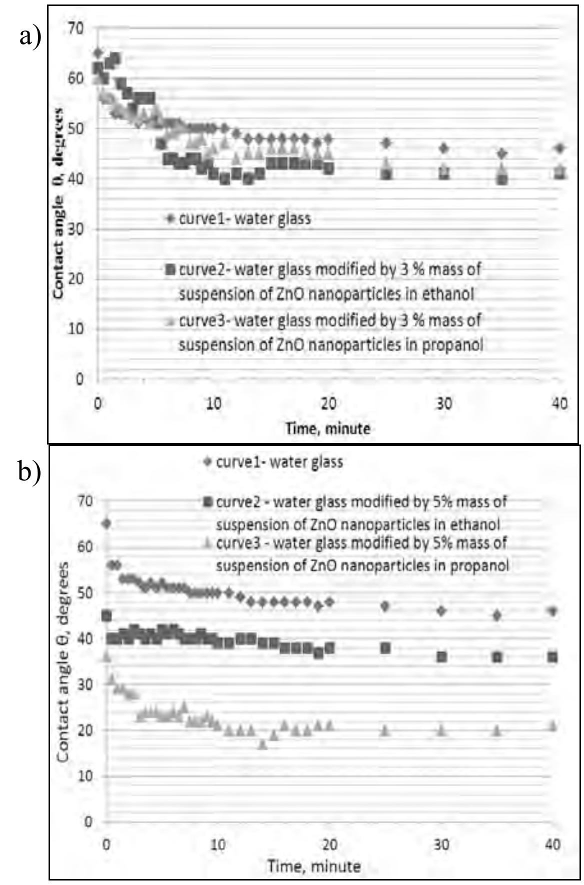

Fig. 1. Changes of wetting angle of quartz by water glass modified by addition of 3 mass % (a) and 5 mass % (b) of colloidal ZnO suspension in alcohols

Rys. 1 Zmiany kąta zwilżania kwarcu przez szkło wodne modyfikowane dodatkiem w ilości 3% mas. (a) i dodatkiem 5% mas. (b) zawiesiny koloidalnej ZnO w alkoholach

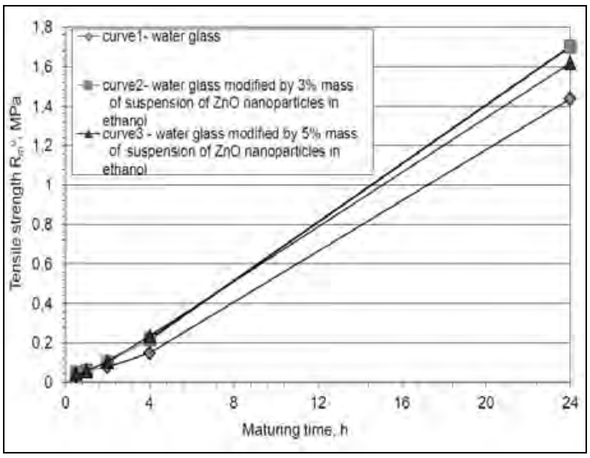

Fig. 2. Strength of moulding sands with water glass, unmodified and modified. Sand composition (in part by mass) curve 1: sand - 100, water glass - 3; curve 2: sand - 100, water glass - 3, suspension of ZnO nanoparticles in ethanol - 3 mass %; curve 3: sand - 100, water glass - 3, suspension of ZnO nanoparticles in ethanol - 5 mass %. Hardening conditions: t_{ot} = 23.5°C, moisture content - 39%

Rys.2. Wytrzymałość mas ze szkłem wodnym niemodyfikowanym i modyfikowanym. Skład masy (w cz. mas.) krzywa 1: piasek - 100; szkło wodne - 3; krzywa 2: piasek-100; szkło wodne - 3; zawiesina nanocząstek ZnO w etanolu - 3% mas.; krzywa 3: piasek - 100; szkło wodne - 3; zawiesina nanocząstek ZnO w etanolu - 5% mas. Warunki utwardzania: t_{ot} = 23,5°C, wilgotność względna - 39%

The obtained tensile strength R_m^u results of loose self-setting sands with unmodified water glass and that modified by the colloidal ZnO suspension in ethanol (Fig. 2) and in propanol (Fig. 3) after various sand maturing times, are presented. Curves 2 and 3 in these figures are related to the 3 and 5 mass % of the added modifier - respectively. As results from the performed tests, a significant increase in R_m^u is seen after 4 hours of sand maturing time in the air and obtains its maximum value not earlier than after 24 hours.

Sand strength R_m^u (after 24 h of hardening) of sands, in which the binder was modified by the ZnO suspension in ethanol was similar regarding both additions of the modifier (3 and 5 mass %) and was equal to 1.70 and 1.62 MPa - respectively. Larger differences in the R_m^u of sands (after 24 h of hardening) were found for binders modified by the ZnO suspension in propanol (Fig. 3; curves 2 and 3).

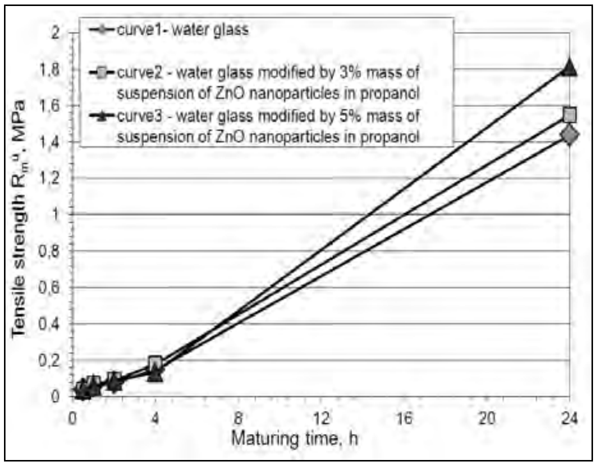

Fig. 3. Strength of moulding sands with water glass, unmodified and modified. Sand composition (in part by mass) curve 1: sand - 100, water glass - 3; curve 2: sand - 100, water glass - 3, suspension of ZnO nanoparticles in propanol - 3 mass %; curve 3: sand - 100, water glass - 3, suspension of ZnO nanoparticles in propanol - 5 mass %. Hardening conditions: t_{ot} = 23.5°C, moisture content - 39%

Rys. 3. Wytrzymałość mas ze szkłem wodnym niemodyfikowanym i modyfikowanym. Skład masy (w cz. mas.) krzywa 1: piasek - 100; szkło wodne - 3; krzywa 2: piasek - 100; szkło wodne - 3; zawiesina nanocząstek ZnO w propanolu - 3% mas.; krzywa 3: piasek - 100; szkło wodne - 3; zawiesina nanocząstek ZnO w propanolu - 5% mas. Warunki utwardzania: t_{ot} = 23,5°C, wilgotność względna - 39%

The investigations of the interactions between: quartz-water glass and quartz-modified water glass correlate well with the strength tests of loose self-setting sands with water glass. The correlation concerns both the amount of introduced modifier and hardening time.

CONCLUSION

The performed investigations of water glass modification by the suspension of ZnO nanoparticles in ethanol and in propanol indicated:

- Influence of introduced modifier on quartz wettability (interphase interactions: quartz-binder).
- Strength R_m^u of loose self-setting sands with water glass modified by suspension of ZnO nanoparticles in ethanol and in propanol (without chemical hardener) increases when modifier is added. In the case of adding modifier in form of suspension of ZnO nanoparticles in propanol - sand strength R_m^u increases by approx. 8% (when modifier addition equals 3 mass %) and by approx. 26% (when addition equals 5 mass %), while when modification is carried out by suspension of ZnO in ethanol - sand strength R_m^u increases by approx. 18% (when modifier addition equals 3 mass %) and by approx. 12% (when addition equals 5 mass %),
- Wettability tests correlate well with strength investigations.

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REFERENCES

[1] Kuckui P., Nowe kierunki rozwoju mas ze szkłem wodnym oraz elektrolitycznych metod i mokrej regeneracji. Tłumaczenie artykułu zamieszczone w Przeglądzie Odlewnictwa 6/90, s. 195-200.

[2] Hutera B., The boundary cases of bonds formation and models of their destruction, Zeszyty Naukowe AGH, ser. Metallurgy and Foundry Engineering 1995, 21, 3, 225-232.

[3] Hutera B., Lewandowski J.L., Smyksy K., Wytrzymałość kohezyjna szkła wodnego, Archiwum Technologii Maszyn i Automatyzacji 2001, 21, 87-94.

[4] Stypuła B., Banaś J., Habdank-Wojewódzki T., Krawiec H., Starowicz M., PATENT: P-369 320, "Sposób otrzymywania mikro- i nanocząstek tlenków metali", reported: 28.07.2004, grantem: 07.10.2009.

[5] Avella M., Bondioli F., Cannillo V., Errico M.E., Ferrari A.M., Focher B., Malinconico M., Manfredini T., Montorsi M., Preparation, characterisation and computational study of poly (ε-caprolactone) based nanocomposites, Materials Science and Technology 2004, 20, 1340-1344.

[6] Kacperski M., Wstępne badania nad wpływem rodzaju modyfikatora na właściwości nanokompozytów epoksydowych, Kompozyty (Composites) 2004, 4, 9, 28-32.

[7] Haiying Wang, Yilong Bai, Sheng Liu, Jiali Wu, C.P. Wong: Acta Materialia 2002, 50, 4369-4377.

[8] Wang Ji-Na, Fan Zi-Tian, Wang Hua-Feng, Dong Xuan-Pu, Huang Nai-Yu, An improved sodium silicate binder modified by ultra-fine powder materials, China Foundry 2007, 4, 1, 26-30.

[9] Zhu Chun-Xi, Recent advances in water glass sand technologies, China Foundry 2007, 4, 1, 13-17.

[10] Hutera B., Smyksy K., Lewandowski J.L., Drożyński D., Wybrane aspekty oznaczania zwilżalności osnowy przez materiały wiążące stosowane w masach formierskich, Archiwum Technologii i Automatyzacji 2003, 23, 1, 63-70.

