Investigation of the influence of tungsten carbide nanopowder WC and the mixture of tungsten carbides and titanium carbides (WC, TiC) on the change of concrete performance properties

V.Gavrish¹, T.Chayka¹, G.Baranov¹, A.Y. Oleynik¹, Y.O.Shagova¹

¹Scientific and educational center "Advanced technologies and materials", Sevastopol State University, 33 Universitetskaya Str.,299053, Sevastopol, Russian Federation
E-mail: vmgavrish@sevsu.ru

Abstract. The paper deals with the possibility of changing the operational properties of concrete (strength, water absorption, corrosion resistance) by adding WC tungsten carbide nanopowders and a mixture of WC tungsten carbide and TiC titanium carbides obtained from hard-alloy waste to the initial composition. As a result of the research, the concentrations of nanopowders were determined, at which the maximum change in strength is observed. Changes in water absorption at different time intervals and corrosion resistance of concrete samples at optimal concentrations were studied. The paper shows a positive effect on the performance of concrete mixture of WC, WC and TiC nanomodifiers.

1. Introduction

Today in the world requirements to construction materials, including concrete, are constantly increasing, traditional methods and materials for their preparation are not enough. The most effective way to change the properties of concrete is to introduce special additives depending on the application (plasticizing, water reducing, increasing strength, etc. [1-3].

Scientists in many countries are interested in research in the field of obtaining and using nanosize admixtures in the concrete mixture, because the introduction of nanostructure modifiers leads to significant changes in the properties of all composites [4-5]. The most widely used nanoparticles in the construction sector are carbon nanotubes, Cu, SiO₂, Al₂O₃, Fe₂O₃, TiO₂ nanoparticles [6-7]. However, the commercial success of nanoparticles depends on the ability to produce these materials in large quantities using low-cost technologies.

Scientists [8] have proposed the use of refractory metal nanopowders and their compounds as an additive to concrete, from carbide wastes and production products. This technology allows producing nanopowders in industrial volumes and at relatively low cost. Researches have shown [9], that at introduction of nanomodificators there is a considerable increase in strength properties of concrete.

2. Experimental part

In the study of the effect of nanoparticles obtained from carbide wastes on the properties of concrete, portland cement PC500-DO (CEM I) (JSC "Novoroscemment", Russia, GOST 10178-85, GOST 30515-97) was used as a binder. The choice of this brand of portland cement is due to its availability and high demand in the domestic market of Russia. As a fine aggregate we used gray sea sand, 1.5 - 2 mm fraction, coarse aggregate - crushed stone of dense rocks, 5-10 mm fraction. Powders produced by...
technology [8] from titanium tungsten alloys - nanopowder of WC and TiC mixture and from tungsten-cobalt alloys - WC tungsten carbide powder were used as nanodificators. The shape of the powder particles is nanoplates of 20-300 nm, these particles can form agglomerates up to 1.8 microns in size. The number of agglomerates does not exceed 13-15%.

Adhering to the ratio of the working solution (cement : sand : gravel : water = 1 : 2.4 : 4.3 : 0.6), mixtures with modifiers of different concentrations of 1, 2, 3, 4% of the mass of the binder were prepared. Also a control mixture without modifiers was prepared. The received concrete mixture was filled in standard forms with the size 100x100x100 mm (GOST 22685-89). Compressive strength test of tested concrete samples was carried out at the age of 28 days on the testing machine IP-500-1. Optimal concentration of concrete admixture was determined by maximum strength of the sample.

Water absorption of control samples (without additive) and for samples with optimal concentrations was tested after reaching the age of 28 days. Water absorption of samples was determined in accordance with GOST 12730.3-78, by immersing them in a container filled with water. The samples were weighed every 24 hours until the results of two consecutive weighs differed by more than 0.1%.

The corrosion resistance tests were carried out on concrete samples after 28 days of strength gain. On the side surfaces and the bottom edge of concrete samples with a brush applied bituminous waterproofing mastic (MBG) Opti Lux (Russia) with a thickness of at least 0.3 mm. After drying the coating during the day, unprotected working surfaces of samples cleaned with sandpaper to remove traces of coating and film of cement stone. Then the samples were placed in a container filled with corrosive media, and the distance from the sample surface to the surface of the liquid should be at least 2 cm. When studying the corrosion process, distilled water GOST 6709-72 was used as an corrosive medium. The ratio of solution volume in cubic centimeters to 1 cm of the sample surface 50:1. Hydrogen index of distilled water is pH=7.3. To determine the content of calcium cations in water the complexonometric method of volume analysis was used.

3. Analysis of results obtained

The results of studies of the influence of nanomodifiers on the strength properties of concrete are presented in Fig. 1.

![Figure 1](image.png)

**Figure 1.** Change in the strength of concrete (%) depending on the content of nanomodifiers in concrete.

The obtained results (Fig. 1) show positive influence of nanomodifiers obtained from carbide scrap on concrete strength characteristics. Changes in strength as a result of increased content of additives are wave-like. Concentrations of nanopowders, at which the maximum effect from the action of nanomodifiers is observed, are optimally accepted. Changes in strength, more than 50% is achieved by using a modifier mixture of WC and TiC at its concentration of 2% of the mass of the binder. When using a nanomodifier WC maximum change in strength is more than 45% at its
concentration of 3% of the mass of the binder. Further study of water absorption (Tables 1–2) and corrosion (Fig.2) of samples was carried out with samples at appropriate optimal concentrations. Table 1. Results of the study of water absorption by mass (Wm) and volume (Wv) of tested concrete samples during 65 days.

| Day | Reference Sample (without modifier) | Sample With modifier WC, TiC (2 %) | Sample With modifier WC (3%) |
|-----|------------------------------------|------------------------------------|-------------------------------|
|     | Wm | Wv | Wm | Wv | Wm | Wv |
| 1   | 5.52 | 12.00 | 4.25 | 9.50 | 4.95 | 11.12 |
| 2   | 5.64 | 12.25 | 4.47 | 10.00 | 5.04 | 11.31 |
| 3   | 5.64 | 12.25 | 4.47 | 10.00 | 5.15 | 11.56 |
| 4   | 5.75 | 12.50 | 4.70 | 10.50 | 5.15 | 11.56 |
| 5   | 5.75 | 12.50 | 4.70 | 10.50 | 5.15 | 11.56 |
| 7   | 5.75 | 12.50 | 4.70 | 10.50 | 5.15 | 11.56 |

The data obtained from the test results of water-saturated samples at various times indicate a significant reduction of water absorption in compositions containing nano additives. Samples with the addition of nanopowder consisting of a mixture of tungsten carbide, titanium - reduced water absorption by more than 18%, with the use of tungsten carbide nanopowder - reduced by more than 10% compared to the control sample without adding a nanomodifier. Reduction of water absorption of the modified samples is due to the fact that nanoparticles act as crystallization centers of hydrate phases, while filling the space between cement grains. This leads to a decrease in porosity and compaction of the composite structure.

Table 2. Results of the study of water resistance of concrete samples.

| Concrete samples | Dry strength, R, MPa | Strength in water saturated state, Rw, MPa | Softening Coefficient, Kp |
|-----------------|----------------------|------------------------------------------|--------------------------|
| Reference Sample (without modifier) | 13,185 | 11,105 | 0,842 |
| Sample With modifier WC, TiC (2 %) | 20,342 | 18,081 | 0,889 |
| Sample With modifier WC (3%) | 16,264 | 14,051 | 0,863 |

The calculated softening coefficient in all investigated samples, which characterizes the property of materials to keep their strength in the water-saturated state, is above 0.8, which characterizes them as water-resistant.

As shown by the results of the study of changes in strength of modified and control samples after a long period of hydration (Table 2), the strength of the control sample (without the modifier) decreased by 15.7%, the strength of the sample with the addition of tungsten carbide modifier decreased by 13%, concrete sample with the addition of a mixture of WC and TiC, the strength decreased by 11%.

The results of the study of leaching corrosion of concrete samples by determining the concentrations of calcium cations in liquid at different stages of the experiment are shown in Figure 2.
The concentration of calcium hydroxide in the liquid at different times characterizes the kinetics of the leaching process. Based on the data presented, we can assume that the first three days the mechanism of corrosion destruction is the same for all samples. Starting from the third day, the amount of hydroxides in the solution starts to grow. Maximum release of hydroxides is observed in the control sample, slightly lower - in samples modified with tungsten carbide. As a result of the study of corrosion resistance of concrete samples, it was found that the use of WC, TiC modifier decreases the leaching of calcium from the concrete sample by more than 44%, when using WC modifier by more than 14% compared with control concrete (without the use of modifier).

4. Conclusions
It has been found that tungsten carbide nanopowder and a mixture of tungsten carbide and titanium carbide contribute to a denser structure of the concrete composite:
- increasing specimen strength by more than 50% (when using WC nanopowder, TiC 2% of the binder mass), more than 45% (when using WC nanopowder 3% of the binder mass)
- by preventing the penetration of moisture, reducing water saturation of samples - softening coefficient in all investigated samples is above 0.8, which characterizes them as water resistant. Adding tungsten carbide nanopowder to concrete mixture leads to 10% decrease in water absorption of the sample, adding tungsten carbide and titanium carbide nanopowder mixture reduces water absorption by more than 18% compared to the control sample.
- increasing the corrosion resistance of concrete samples, it was found that the use of WC, TiC modifier reduces the degree of leaching of calcium from the concrete sample by more than 44%, when using WC modifier by more than 14% compared with the control concrete (without the use of modifier) by 80 days.

Thus, tungsten carbide nanopowders WC and the mixture of tungsten carbide and titanium WC, TiC, have a positive effect on the performance of the concrete mixture and can be used for the manufacture of products in civil and industrial construction, as well as in the construction of hydraulic structures.

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