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STUDY ON THE EFFECT OF NANOSIZED PARTICLES OF TiN AND SiC ON THE WEAR RESISTANCE, MICROSTRUCTURE AND CORROSION BEHAVIOR OF OVERLAY WELD METAL

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ABSTRACT

The paper presents a comparative study on the effect of TiN, SiC, and TiN+Cr nanosized particles (NP) on the wear resistance, microstructure and corrosion behaviour of specimens of overlay weld metal. The specimens are obtained by manual arc overlay welding. Coated electrodes E300 containing nanosized particles in the coating and base electrodes without any nanomodification are used. The effect of nanomodifying on wear resistance is determined by comparing the wear resistance of overlay welds produced with electrodes containing nanosized particles and overlay welds produced with base electrode under the same test conditions. The corrosion behaviour is studied using the method of cyclic immersion in 3.5% NaCl for 720 hours. Obtained data on the effect of the type and concentration of nanosized particles on wear resistance and corrosion behaviour of the weld metal are discussed in connection with the microstructure changes induced by the nanomodifiers added in the electrode coating.

Keywords: nanomodified overlay weld metal, nanoparticles TiN, SiC, TiN+Cr, wear resistance, microstructure, corrosion resistance.

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AIMS AND BACKGROUND

The metallic materials modified with nanosized particles (NP) show improved mechanical and physical characteristics, due to the reduced grain size and the increased relative part of grain boundaries. Considerable progress in the manufacture of nanomaterials is achieved over the last decades by implementation of various methods. The focus of research is aimed at present towards the production of nanostructures and coatings with higher wear- and corrosion resistance.

The industrial steel constructions corrode easily during service period due to the high sensitivity of steel to aggressive environments. One of the main problems in many industries is the corrosion of welded constructions in acidic aqueous solutions. Corrosion inhibitors are usually added to the base and the weld metal in order to prevent their degradation. The most well-known acid inhibitors are organic compounds containing nitrogen, sulfur, and oxygen atoms. Their inhibitory effect is due to their adsorption on the metal surface. Besides the high inhibitory efficacy, the high inhibitor quality means low cost, low toxicity and easy manufacture. Usually, to improve the wear resistance of the surfaces, after the overlay welding and machining, the parts are subjected to a suitable heat treatment.

The application of nanotechnology over the last two decades plays an important role in the corrosion protection of metals[1,2]. Although scarce, some data on the effect of nanosized particles (NP) (basically introduced in order to improve the mechanical properties of the metal) on the corrosion resistance are reported in the scientific literature. It was found out later that NP act as corrosion rate inhibitors also[3÷6]. The effect of nanomodifiers proved similar to that of organic inhibitors but without their negative effect on the environment, so nanomodifiers can be an effective alternative to the dangerous and toxic compounds.

A lot of investigations considering different surfacing techniques were carried out in order to improve the surface properties of materials[7]. There are data about the production of nanomodified overlay weld material of increased hardness and wear resistance by manual arc welding using electrodes with nanosized particles introduced in their coating[8÷10]. No such data are available on the influence of nanomodified welding electrodes on the structure and corrosion rate of the produced overlay weld metal.

In order to improve the wear resistance of the surfaces, the parts are usually subjected to an adequate heat treatment after welding and machining. The idea of adding nanomodifier in the electrode coating is to increase the wear resistance of the overlay weld attaining the needed operational properties without any subsequent heat treatment and thus to improve the efficiency of the process.

This study is aimed to investigate the influence of TiN, SiC and SiC+Cr nanosized particles introduced in the coating of a basic IZA E300 welding electrode on the microstructure, wear resistance and corrosion behavior of overlay weld metal.

EXPERIMENTAL PART

Tested materials. Base electrode IZA E 300 was selected to develop test series electrodes by addition of NP to the coating. IZA E 300 electrode is designed for producing overlay weldings on worn surfaces or for preventive welding. The chemical composition of the overlay weld metal obtained with this electrode is shown in Table 1.

Table 1. Chemical composition of the overlay weld metal

C [mass %]	Mn [mass %]	Si [mass %]	Cr [mass %]
0.1 – 0.15	1.6 – 1.8	0.4 – 0.8	0.8 – 1.2

Three surface layers were overlay welded with electrode IZA E 300 on a plate of low-alloy low-carbon steel S235JR. The hardness of obtained overlay weld layers allowed for subsequent machining.

Usually, in order to increase the wear resistance of surfaces, after overlay welding and machining the parts are subject to a suitable heat treatment. The adding of NP in the coating of electrode IZA E 300 aims to increase the wear resistance of the overlay weld layer and to reach the needed operational properties without any subsequent heat treatment, i.e. to improve the process effectiveness.

The nanomodification of test electrodes coatings was carried out by adding different quantities of nanosized TiN, SiC, and TiN+Cr powders using the described technology[9].

The coating materials were delivered and graded in accordance with their technical requirements. According to the manufacturer's data, the size of TiN particles was (50±5) nm and the size of SiC particles was (60±5) nm. The quantity of the added nanomaterials supplemented the total iron powder content.

Before being added to the coating the NP powders were mechanically activated in a ball mill in order to increase their efficiency and wetting. Potassium water glass was used as a binding agent for the coating. The diameter of electrode wire was 3.25 mm, the length was 450 mm. The technological properties of the produced test electrodes were reported[9].

Test specimens. Cylindrical test specimens with diameter of 8 mm and height of 20 mm were water cut from the overlay weld plate. Their hardness, microhardness and wear resistance were studied and reported in [10÷14]. Ultrasonic comparative assessment of the internal incompleteness of the overlay weld layers was conducted [15].

The overlay weld specimens suitable for microstructure and corrosion tests were selected on the basis of the registered deviations of hardness and wear resistance of overlay welds made with modified test electrodes from the weld made with the base electrode IZA E300.

The microstructure and corrosion resistance specimens were cut out from the top layer of the overlay weld metal. Three discs about 1 mm thick were cut out from each specimen: one disc for metallographic analysis and two for corrosion tests.

The designations of test specimens and the contents of NP in the used test electrodes coating are given in Table 2. The overlay weld obtained without nano-modification is marked as E300.

Table 2. Content and type of nanomodifier in the coating of the test electrodes

Specimen No	E300	1.1	1.2	1.3	2.1	2.2	3.1
Amount of nano-modifier in the coating [mass %]	--	0.1%TiN	0,4%TiN	3.0%TiN	0.4%SiC	1.5%SiC	1.5% TiN+Cr

Test methods. The wear resistance assessment was performed according to a method developed by the authors [16,17]. A specialized device based on the kinematic circuit „pawl-disk" was developed for the purpose[10]. The mass loss of the tested samples for a certain number of cycles was measured and the wear intensity and wear resistance were calculated on the basis of friction track length. The wear resistance of samples made with nanomodified electrodes was compared with that of the overlay weld made with base electrode under the same testing conditions.

The metallographic specimens were polished and etched with 4%HNO_3 to develop the microstructure. The microstructure of the overlay weld metal was analyzed by the method of light microscopy (LM) using JENAVERT Carl Zeiss metallographic microscope.

The corrosion resistance of the overlay weld metal was investigated by the method of periodic immersion in 3.5% aqueous NaCl solution followed by drying. The overall duration of the testing was 720 hours, the ratio of the total immersion time to the total drying time was 1:1. The corrosion products were removed after the test completion, the mass was measured before and after the test and the mass loss indicator Δm [g] was calculated. The corrosion rate K was determined as $K=\Delta m/S.h$ [g/m^2h], where S is the specimen area, h – the test duration.

RESULTS ANS DISCUSSION

Wear resistance test. The results on the effect of nanomodifying on wear resistance of the tested overlay welds are represented in Table 3. The index "Relative wear resistance" was derived from the mean value of wear resistance of two simultaneously tested modified samples with the same NP type and content (the

Table 3. Relative wear resistance

	Highest relative wear resistance						**Lowest relative wear resistance**
Specimen No	**1.2**	**2.1**	**2.2**	**3.1**	**1.3**	**E300**	**1.1**
NP [%]	0.4% TiN	0.4% SiC	1.5% SiC	1.5%TiN+Cr	3.0% TiN	-	0.1% TiN
Relative wear resistance	2.66	2.57	2.09	1.74	1.14	1.0	0.77

sample with maximum of deviation is excluded) related to the wear resistance of the sample made with the base electrode (without NP in the coating).

The highest values of relative wear resistance were observed in the specimens with 0.4% TiN and 0.4% SiC (No.2.1 and No.1.2). The obtained relative wear resistance values for the two electrodes are close to one another and show an increase of wear resistance respectively of 2.57 and 2.66 times compared to the base electrode. The increase in NP content up to 1.5% resulted in some decrease in the relative wear resistance, the value remaining higher up to 2.09 times for the specimen with 1.5 % SiC (No. 2.2). The adding of 3.0% TiN (No.1.3) caused further decrease but the relative resistance still remained 1.14 times higher than that of the base specimen.

The lowest value of wear resistance was obtained for the specimen with 0,1% TiN (No. 1.1) - 0.77 of that of the base electrode.

Microstructure test. The metallographic investigation showed ferrite-perlite microstructure of Widmanstatten's type in all tested specimens. The ferrite was acircular, with widely varying sizes of the needles. Fig.1 displays the microstructures of all tested specimens weld with modified electrodes containing different types and concentrations of NP in the coatings. The microstructure of non-modified specimen E300 is shown also (Figure 1a).

Most coarse-grain structure was observed in specimen No.1.2 (Figure 1c) and specimen No.2.1 (Figure 1d) obtained with electrodes containing respectively 0.4%TiN and 0.4%SiC in the coating. The microstructure of the specimen with SiC was slightly coarser than with TiN. The length of Widmanstatten's needles in both cases was between 25÷30µm, the width 4÷5µm. The grain size in both 0.4% specimens was about 20 times larger than in the specimen obtained with the base electrode (Figure 1a).

No preferred microstructure orientation was observed in the specimens with 0.4%TiN and 0.4%SiC, in contrast to the base electrode E300, in which preferred

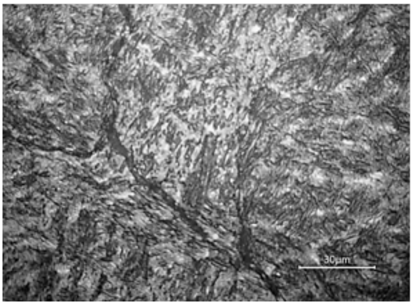

Fig. 1a. Specimen E300 – base electrode

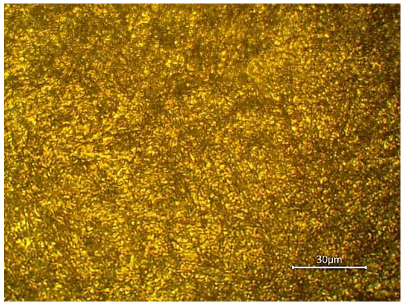

Fig. 1b. Specimen **1.1** (0.1% TiN)

Fig. 1c. Specimen **2.2** (1.5%SiC)

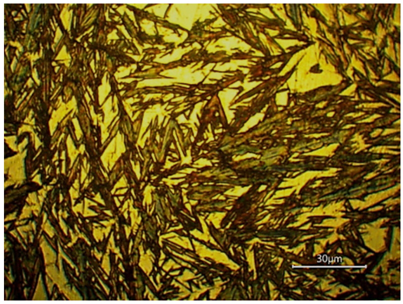

Fig. 1d. Specimen **2.1** (0.4% SiC)

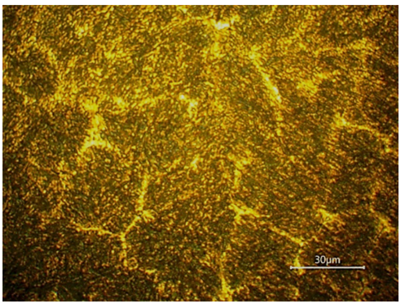

Fig. 1e. Specimen **2.2** (1.5%SiC)

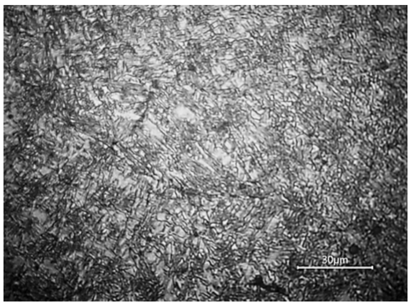

Fig. 1f. Specimen **3.1** (1.5% (TiN+Cr))

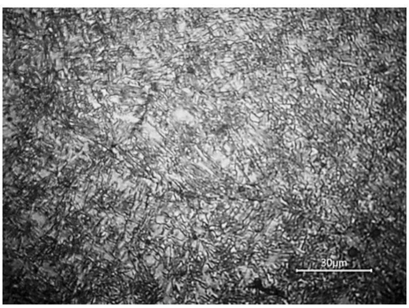

Fig. 1g. Specimen **1.3** (3% TiN)

Fig 1. Microstructure of the overlay weld metal orientation of ferrite needles in different crystallographic directions was observed (Figure 1a).

Preferred orientation was recorded also in specimens with 1.5% and 3% NP (specimens No. 3.1, 1.3 and 2.2), but not in the specimen with the finest structure No. 1.1 (0.1% TiN) (Figure 1b).

The trend of grain size change, depending on the type and content of nanomodifiers in the tested specimens, is represented on Table 4.

Table 4. Change of the grain size of overlay weld metal depending on the type and on content of nanoparticles

	Most coarse-grain structure	→					Most fine-grain structure
Specimen No, total [%] NP	**2.1** 0.4% SiC	**1.2** 0.4% TiN	**E300**	**3.1** 1,5% (TiN + Cr)	**1.3** 3.0 % TiN	**2.2** 1.5% SiC	**1.1** 0.1 % TiN
Specimen No, [%] TiN		**1.2** 0.4% TiN	**E300**		**1.3** 3.0 % TiN		**1.1** 0.1 % TiN
Specimen No, [%] SiC	**2.1** 0.4% SiC		**E300**			**2.2** 1.5% SiC	
Specimen No, [%], (TiN+Cr)			**E300**	**3.1** 1.5% (TiN+Cr)			

No clear dependence of grain size on the type or the content of nanomodifier could be seen in Table 4 data. The grain size of specimens obtained with electrodes containing 3% or 0.1% TiN is smaller than of the specimen obtained with reference electrode E300. The increase in the total NP content from 0.4% to 1.5 or 3.0% ensured some refinement of the structure, but not the smallest grain size – it was obtained with 0.1%TiN.

Corrosion test. The corrosion rate values obtained from the performed corrosion tests are represented in Table 5. All data are the average of the results of two specimens tested in parallel.

Depending on the calculated corrosion rate K, the test specimens could be divided in four groups:

Group I: specimen 3.1 (1.5% TiN+Cr) – lowest corrosion rate

Group II: specimens 2.1 (0.4% SiC) and 2.2 (1.5% SiC)

Group III: specimen 1.3 (3.0% TiN)

Group IV: specimens E300, 1.2 (0.4% TiN), 1.1 (0.1% TiN) – highest corrosion rate.

Table 5. Corrosion rate of overlay weld metal with different types and contents of nanoparticles

	Highest corrosion rate K	→					Lowest corrosion rate K
Specimen	**1.1**	**E300**	**1.2**	**1.3**	**2.2**	**2.1**	**3.1**
NP [%]	0.1% TiN	-	0.4% TiN	3.0% TiN	1.5% SiC	0.4% SiC	1.5% (TiN+Cr)
K [g/m^2h]	1.69537	1.67880	1.63424	1.55262	1.33520	1.29664	1.21834
Group	IV			III	II		I

The division into groups was made based on the following assumption: when the difference of K values of two neighbor specimens was less than 5%, the specimens were classified in the same group; when the difference of K exceeded 5% the specimens belonged to different groups. The differences of K values of specimens belonging to groups II or IV layed within test uncertainty limits, the uncertainty resulting from the specimen size and weight measurement before and after removal of the corrosion products.

Group I contained only the specimen 3.1, which showed the lowest corrosion rate, even lower than the rate of the base electrode E300. This result could be explained by the presence of Cr in the composition of the nano-modifier. Evidences for the beneficial effect of Cr as corrosion inhibitor of metal coatings modified with nanosized particles are given in [5].

The modification of electrodes with 0.4% TiN did not significantly influence the corrosion resistance of the overlay weld metal, the corrosion rate K of 0.4% specimen remained close to K of the non-modified specimen (group IV). A slight increase in the corrosion resistance was observed at 3.0% TiN (group III), and the best corrosion resistance was obtained at 1.5% (TiN+Cr) (group I).

The values of K of the overlay metal, obtained with electrodes with 0.4% SiC or 1.5% SiC (group II), were close but significantly lower than the values of K for the base electrode E300 or the values obtained with the 0.4% TiN modifier. This means that the nano-modifier SiC is more effective as a corrosion inhibitor than TiN.

CONCLUSIONS

- The effect of addition of TiN, SiC, and TiN+Cr nanosized particles to the coating of the E300 base electrode on the microstructure, wear and corrosion resistance of overlay weld metal was studied.
- It was found out that the wear resistance of the overlay weld metal depended on the content of nanoparticles in the electrode coating. The highest wear

resistance was observed at concentration of 0.4% SiC and 0.4% TiN. The values of relative wear resistances were close to one another in both cases, respectively 2.57 and 2.66 times higher compared to the non-modified base specimen E300. In this case the role of the type of used NP was negligible.

• The microstructure, obtained with nanomodified electrodes containing 0.4% TiN or 0.4% SiC, was much coarser than the microstructure obtained with the reference electrode E300. Most significant grain refinement was observed in the overlay weld, obtained with electrode containing 0.1% TiN.

• The metallographic study showed Widmanstatten's ferrite-pearlite microstructure in all tested specimens. No clear dependence of the grain size on the type or content of the used nano-modifiers was observed.

• It was not possible to identify the exact dependence between the grains size and the modifier content through metallographic analysis, hence additional electron backscatter diffraction (EBSD) analysis is needed. The EBSD analysis could allow to perform a quantitative analysis in terms of the grain size depending on grains' number in a particular crystallographic plane.

• The specimens, modified with 0.4% NP, showed most coarse grain microstructure but highest relative wear resistance.

• The corrosion resistance of the overlay metal depended both on the type and on the concentration of the nano-modifier. The highest corrosion resistance was achieved after introduction of 1.5% (TiN+Cr) nano-particles in electrode coating.

• The modification with SiC proved more favourable for corrosion resistance compared to TiN.

• No correlation was identified between the corrosion resistance and the grain size of the overlay weld metal.

• To obtain more accurate dependences of the corrosion rates on the type and on the amount of nano-modifiers, it is envisaged to extend the scope of the investigation by increasing the concentration levels of the modifier. To reduce the relative share of the test uncertainty in the final result for corrosion rate, it is planned to increase the number and the size of the tested specimens in each series.

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