INVESTIGATION OF THE INFLUENCE OF MODIFYING NANOPOWDERS ON THE CHARACTERISTICS OF METAL ALLOYS

ИССЛЕДОВАНИЕ ВЛИЯНИЯ МОДИФИЦИРУЮЩИХ НАНОПОРОШКОВ НА ХАРАКТЕРИСТИКИ МЕТАЛЛИЧЕСКИХ СПЛАВОВ

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Abstract: *Nanopowders of TiCN and TiC prepared by Self-spreading High-temperature Synthesis (SHS) and Plasma-chemical synthesis (PCS) were investigated using HR SEM and EDS X-ray Microanalysis System. Castings of P265GH steel and AlSi7Mg aluminum alloy are modified with TiCN, TiC, TiN and AlN powders. They act as nucleus of crystallization in the molten metal. The results from laboratory experiments show that the microstructure is refined, the microhardness and some plastic properties are increased in comparison with the non modified castings.*
KEYWORDS: NANOMODIFIERS, NANOMODIFIED STEEL AND ALUMINUM CASTINGS, STRUCTURE AND PROPERTIES

1. Introduction

In order to improve the quality of cast metals and alloys - the refining of their microstructure, the increasing of their mechanical properties, their corrosion and abrasive resistance, the modifying with nano particles is used [1-2]. The nano modifiers which present high temperature melting compounds (nitrides, carbides, borides etc.) are obtained by means of plasma chemical synthesis and are covered with metal protector. They feature by high melting temperature (2273-3273 K) and dimensions from 4 to 100 nm. These particles posses unique physical and chemical properties and could be utilized for new materials designing as well as for conventional ones improving.
Some results from laboratory experiments with steel P265GH (DIN) and Al-Si castings modified with different types of nano particles are presented in the present paper.

2. Experimental

The chemical composition of the investigated steel is presented in *table 1*. The molten metal is obtained in induction furnace "Leibold Hareus" with capacity 10 kg. Additions of 0.0125-0.6 wt. % TiCN, TiC, TiN (clad with Cr) are introduced in the melt before pouring. Two types of castings with same configuration and different weight – 2.5 and 5 kg are developed.

Table 1. Chemical composition of P265GH steel.

Chemical composition of P265GH steel, wt. %						
C	Si	Mn	Cr	Ni	S	P
0.17-0.23	0.17-0.37	0.50-1.5	≤ 0.30	≤ 0.30	≤ 0.045	≤ 0.045

The chemical composition of the investigated AlSi7Mg alloy is presented in *table 2*.

Table 2. Chemical composition of AlSi7Mg alloy

Chemical composition of AlSi7Mg alloy, wt. %				
Si	Mg	Ti	Fe	Al
7-7.2	0.3-0.4	0.02	0,3-0,4	the rest

The alloy is melted in electric-resistance furnace with capacity of the crucible 0.5 kg for aluminum. Nanomodifiers TiN (clad with Al) and AlN (clad with Al+Cu) are added in the melt in quantity of 0.03-0.35 wt. %. Experimental castings of 0.250 kg weight are produced in metal mold.
The metallographic analysis is carried out by means of metallographic microscopes Reichert MeF2 and PolyvarMet up to 1000x magnifications. The quantitative metallographic analysis is carried out by means of automatic system Olympus MicroImage. The mean grain diameter is determined. The microhardness is measured by means of device MicroDuromat 4000 with load of 10g for 10s.
The investigated samples are mechanically tested using standard method. The tensile strength, the yield strength, the specific elongation and relative reduction are determined.

3. Results and discussions

3.1. Investigation of nanopowders TiCN and TiC by SEM

High melting point powders (carbides, borides, nitrides etc.) are produced by Self-spreading High-temperature Synthesis (SHS) or by Plasmo-chemical Synthesis (PCS). These powders are highly disperssed and posess widely developed surface, which interracts actively with the absorbed gases, forming oxides. As a consequence, the possibility of particles "wetting" from the molten metal is redused and this is the reason powders to be processed innitially for degasing as well as cladding of their surface.
Secondary Electron Microscopy (SEM) is used for characterization of the powders (Hitachi S-4800 High Resolution Field Emission SEM, 1 nm resolution at 15 kV and Hitachi S-4700 High Resolution Low Voltage Imaging with cold field emission gun: 1.5 nm resolution at 15 kV, the latter equipped with Oxford Instruments ISIS EDS X-ray Microanalysis System).
Images from the TiCN powder, obtained by SHS method are presented in *fig. 1.* The particles size is in the submicrom region, some of them reaching 1-2 μm. The particles are with irregular but smoothly formed shape. The EDS spectra, taken from the TiCN powder, show presence of titanium, carbon and nitrogen, the last two being clearly distinguished.
Images from TiN powder by PCS are presented in *fig. 2*. The particles posses relatively equalized size about 50 nm, as

well as mostly cubic shape. Again, single representatives reach micron size. The content of the powder exhibits availability of titanium and significant quantity of nitrogen, however slight peak of carbon is registered, which may be due to contamination.

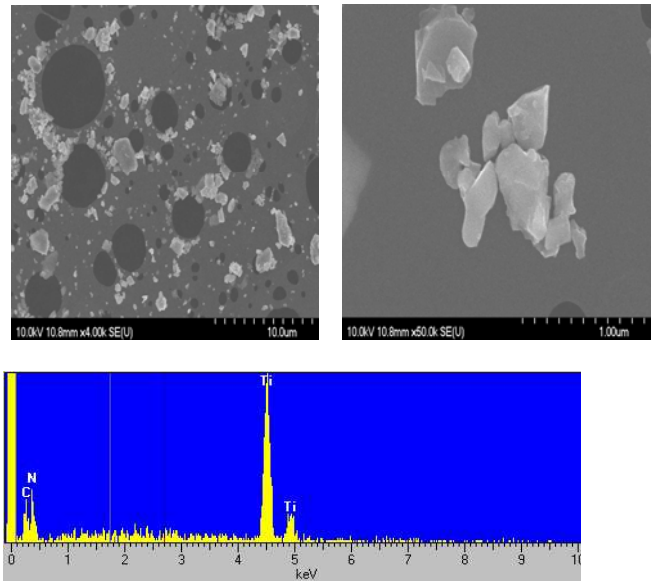


Fig.1.SEM images and EDS spectrum of TiCN, obtained by SHS method.

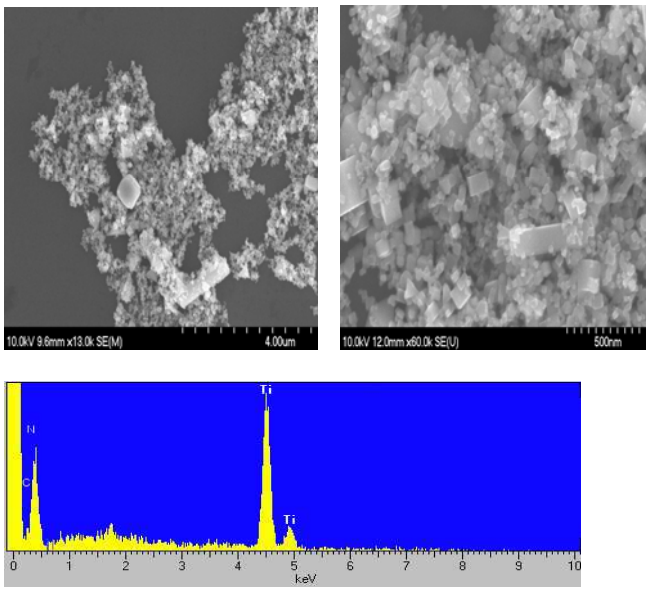
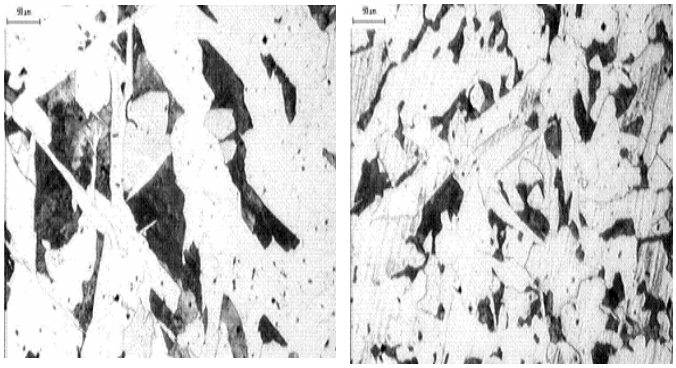


Fig.2. SEM images and EDS spectrum of TiN, obtained by PCS method.

Comparison of the powders obtained by the different mentioned above methods reveals that powder with better quality is produced by PCS method. Usage of nano-dispersed powders for modification in the production of metal alloys with improved properties requires searching of an optimal variant between their beneficial characteristics and economic effectiveness, taking into account the processing simplicity and significantly lower cost of SHS method.

3.2. Investigation of P265GH steel castings

The micro photos (*fig. 3*) and the results presented in *table 3* show that minimal quantity of 0.025% of TiCN and 0.0125% of TiC leads to a significant steel grain refinement - 31.01 and 27.6% respectively. The next concentration increasing of nanomodifier causes grain refinement but it is not significant. The difference between the mean grain diameter of unmodified steel and the mean grain diameter of modified steel in the all investigated modifier concentration range increases from 23 to 42 %. The microhardness of nanomodified samples is higher then the microhardness of unmodified sample. It is evident that the nanomodifying influence on the microstructure and microhardness. The graphical view of this influence is presented on *fig. 4*.



a b

Fig.3. Microstructures of P265GH steel samples
a) sample №1 unmodified; b) sample №4 modified with 0.0125 TiC.

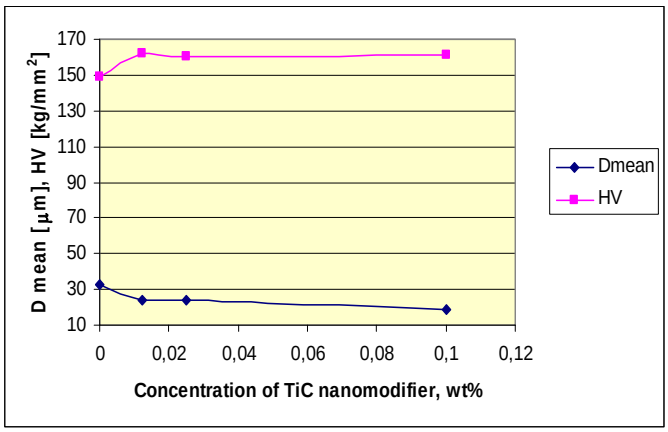


Fig. 4. Mean grain diameter and microhardness in dependence of the concentration of TCN nano modifier.

The microhardness increases with 7-18% and some of the samples improve their plastic characteristics with 19-27% *(table 3).* It could be concluded that after adding of 0.025 wt. % TiC in the melt the specific elongation increases with 18.8% and the relative reduction with 27%. The adding of 0.1 wt. % TiC leads to 10.7% yield strength increase.

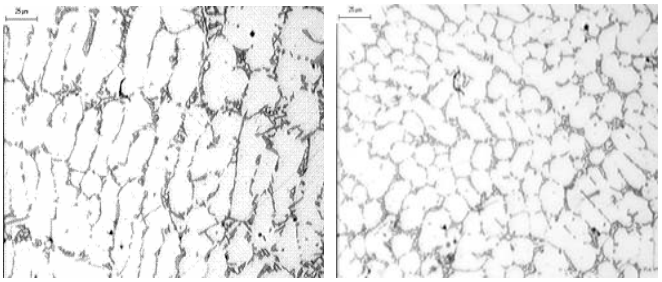
Table 3. Mean grain diameter, microharness and mechanical characteristics of modified with TiCN, TiN and TiC nanomodifiers P265GH steels samples

Sample №	Nano modifier wt [%]	D mean [μm]	Δ_D [%]	HV [kg/mm^2]	Δ_{HV} [%]	$R_{0,2}$ MPa	R_m MPa	A_5 %	Z %
1	-	32.93	-	149	-	223.0	451.5	29.7	45.5
2	0.025 TiCN	22.72	-31.01	176	18.12				
3	0.6 TiN	25.06	- 23.9	164	10.07				
4	0.0125 TiC	23.84	- 27.6	162	8.73				
5	0.025 TiC	23.64	- 28.21	160	7.38	227.5	449.0	35.3	57.8
6	0.1 TiC	18.98	- 42.36	161	8.05	247.0	454.0	28.7	32.2

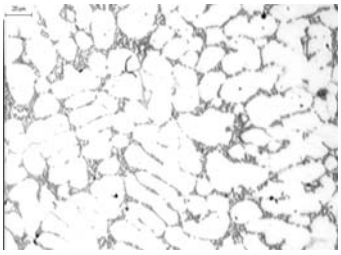
3.3. Investigation of AlSi7Mg castings

The microstructure and mechanical characteristics of the AlSi7Mg castings are shown in *table 2*. The microstructure is illustrated in *fig. 5 and 6*. The modified with TiN+Al and AlN+Cu+Al castings are featured with significant quantity of aluminum cells, then the modified has a dendritic structure – *fig. 5*. The volume fracture of the spherical α-cells in the modified castings is nearly two times bigger then the volume fracture in non modified one. The mean diameter decreases up to 26-28 %. The DAS- values decrease up to 15 % - *table 4 and fig. 5*. Except casting 6, a tendency of microhardness increasing is seen in all castings when TiN+Al is introduced. The increasing is 14.3 % in casting 4. In the investigated concentration range higher modifying effect for TiN+Al appears at 0.3 wt. % and for AlN+Al+Cu – at 0.05 wt. %.

From visual observation of the microstructure a refinement of Si and intermetal crystals, including Fe-containing ones, is established as well *(fig. 6).* That is due to their increased crystallization in small inter dendrite volumes - DAS values decrease up to 13-15 % (*table 4).*



a) unmodified b) 0.3% TiN+Al

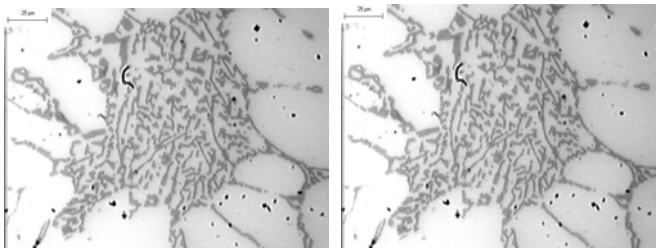


c) 0,05 % AlN+Al+Cu

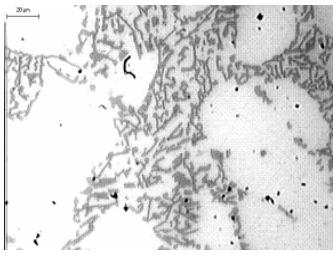
Fig. 5. Microstructure of unmodified (a) and modified by TiN+Al (b) and AlN+Al+Cu (c) castings.

Table 4. Microstructural and mechanical characteristics of unmodified and modified AlSi7Mg castings.

Casting №	Casting Treatment	D_{mean} [μm]	DAS [μm]	HV [kg/mm$^{2]}$	$R_{P0,2}$ [MPa]	R_m [MPa]	A_5 [%]
1	**unmodified**	**17.93**	**13.74**	**58.2**	**112**	**198**	**4.9**
2	**0.03 % TiN+Al**	**13.15**	**12.03**	**62.8**	**111**	**216**	**9.2**
	Alteration in %	*- 26.7*	*-12.4*	*7.9*	*-0.9*	*9.1*	*87.8*
3	**0.15 % TiN+Al**	**13.20**	**12.78**	**62.4**	**112**	**211**	**7.8**
	Alteration in %	*-26.4*	*-7.0*	*7.2*	*0*	*6.6*	*59.2*
4	**0.3 % TiN+Al**	**13.20**	**11.95**	**66.5**	**110**	**219**	**10.8**
	Alteration in %	*- 26.4*	*-13.0*	*14.3*	*-1.8*	*10.6*	*120.4*
5	**0.35 % TiN+Al**	**15.75**	**12.28**	**58.3**	**111**	**200**	**5.3**
	Alteration in %	*- 12.2*	*-10.6*	*0.2*	*-0.9*	*1.0*	*8.2*
6	**0.05 % AlN+Cu+Al**	**12.95**	**11.6**	**57.4**	**109**	**210**	**9.7**
	Alteration in %	*- 27.8*	*- 15.6*	*- 1.4*	*- 2.7*	*6.1*	*98.0*
7	**0.1% AlN+Cu+Al**	**16.67**	**13.26**	**60.7**	**111**	**209**	**8.5**
	Alteration in %	*- 7.0*	*- 3.5*	*4.2*	*-0.9*	*5.6*	*73.5*



a) unmodified b) 0.3% TiN+Al



c) 0.05 % AlN+Al+Cu

Fig. 6. Eutectic in unmodified (a) and modified by TiN+Al (b) and AlN+Al+Cu (c) AlSi7Mg alloy.

It is obvious that all mentioned above changes for the modified alloy are due to addition of the nanomodifier in the melt. The alternation of the form and refinement of the aluminum grains together with the fragmentation of the silicon and intermetal phases leads to improvement of the tensile strength and elongation *(table 4).* The yield strength values in practice do not alter. Experimental results of the mechanical tests are in agreement with the observations of the microstructure. The highest effect takes place in case of casting 4 (0.3 wt. % TiN+Al) – the tensile strength increases with 10.6 % and elongation – 2.2 times. In comparison with AlN+Al+Cu (casting 6 - 0.05 wt. %) addition of 0.3 wt. % TiN+Al has a higher influence, but the concentration of the latter is 6 times higher, what is not profitable. The increasing of the modifiers quantity (castings 5 and 7) does not lead to additional modifying effect. The established possibility for modification both grains and eutectic in Al-Si alloys is an advantage of the nanomodifiers in comparision with applied standard methods of double treatment - with master alloys AlTi or AlTiB for grain refinement and with AlSr – for eutectic modifying.

4. Conclusions

1. The treatment of molten metal with nanopowders has a significant modifying effect on the structure and mechanical properties of steel and Al-Si castings.
2. In nanomodified by TiCN, TiC and TiN P265GH steel castings the mean grain size decreases in the range 24-42%, the microhardness increases in the rage 7-18% and in some samples the plastic characteristics improve with 19-27%.
3. In nanomodified by TiN and AlN AlSi7Mg castings the mean grain size decreases up to 26-28 %, DAS - up to 15 %. The microhardness increases up to 14%, the tensile strength – up to 10.6 % and the elongation – more than 2 times.

5. References

1. Saburov V., A. Cherepanov, M. Zhukov at el. Plasmachemical syntesis of ultrafine powders and their application for modificaion of metals and alloys. – Novosibirsk, Nauka, 1995, 334 p. (in Russian).
2. Vissokov G. Plasma nanotechnologies, nanopowders – preparation, properties and application. – Publishing house of University of mining and geology, Sofia, 2005, 303 p.

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