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J. GÓRKA[1*], T. KIK[1], M. BURDA[2]

ATTEMPTS TO MODIFY AUSTENITIC STEEL WITH CARBON NANOTUBES

In this work, research on influence of multiwalled carbon nanotubes (MWCNTs), produced in Catalic Chemical Carbon Vapor Deposition, NANOCYLTM NC7000CNTs on a structure and properties of AISI 301 steel remelted by TIG arc. In the assessment of influence a type of carbon on properties and structure of austenitic steel, as a carbon filler was use also carburizer. In the specimens (AISI 301 plates) with dimensions 155×60×7 [mm] were drilled holes with 1.3 mm diameter and placed 0.5 mm under specimen surface. Next, to the drilled holes was implemented CNTs, carburizer and mixture of these both powders. Prepared specimens were remelted by TIG method on the CASTOTIG 2200 power source with 2.4 mm tungsten thoriated electrode with parameters sets for obtain 3.0 mm penetration depth. Remelted specimens were cut into the half of the welds distance and prepared for metallographic examinations. Cross sections of the specimens were tested on classical metallography microscopes, hardness tests, SEM analyses (on JEOL 5800 LV SEM EDX equipment) and phase identification by X-ray phase analysis on Philips APD X'Pert PW 3020 diffractometer. Hardness analysis indicates about 25% increase of hardness in the remelted area when the CTNs are used. In the specimens with carburizer there is no significant changes. SEM analyses of remelted areas on AISI 301 specimens modificated with CNTs, indicates that dark areas, initially interpret as one of the phase (based on optical microscope) is finally densely packed bladders with dimensions from 50 nm up to a few µm. These bladders are not present in the specimens with carburizer filler. High resolution scanning microscopy allow to observe in the this area protruding, longitudinal particles with 100-300 nm length. For identification of this phase, X-ray analysis was done. But very small dimensions of used CNTs (diameters about 9,5 nm), random orientation and small weight amount can make difficult or impossible to CNTs detection during XRD tests. It means that it is not possible to clearly determine nature of particles filling the cavities, it is only possible to suppose that they are CNTs beams with nanoparticles comes from their disintegration. Results of the researches indicates, that fill in the weld pool with different form of carbon (CNTs and carburizer) it is possible to achieve remelted beads with different structure and hardness distribution. It confirms validity of the research continuation with CNTs as a modifier of steels and also other metals and theirs alloys.

Keywords: multiwalled carbon nanotubes; carburizer; austenitic steel; TIG remelting; structure modification

1. Introduction

The unusual physicochemical characteristics of carbon nanotubes create prospects for their use in many fields of science and technology. In the field of materials engineering major studies on the application of carbon nanotubes include creating composite materials with polymer or metal matrix. Metal matrix nanocomposites have been produced so far mainly by powder metallurgy. Only some work has used welding techniques to produce coatings of special properties using carbon nanotubes [1-10]. There is no known work with the application of carbon nanotubes as a component having an effect on the structure of metals and metal alloys. Thus, there are reasons to do research in this field and the development of metal matrix nanocomposites using various means of remelting, including welding methods (arc remelting, plasma, laser, etc.). So far, there have not been systematic studies on the impact of nanostructured carbon materials on the crystallization and structure of metals and metal alloys. Metal matrix – carbon nanotube composites (MM-CNT) can be designed in order to obtain materials characterized by low density, high strength, low thermal expansion coefficients and high thermal conductivity. Lightweight and resistant structural materials constitute the basis for future, energy-efficient and, as a result, environmentally friendly and economical technological solutions for the aviation and automotive industries [11-23]. In recent years sharp increase in interest in nanocomposites. In this composites at least one of components has one or more dimensions in nanometric scale. This causes interaction on atomic

1 SILESIAN UNIVERSITY OF TECHNOLOGY, MECHANICAL ENGINEERING FACULTY, DEPARTMENT OF WELDING, 18 A KONARSKIEGO STR., 44-100 GLIWICE, POLAND
2 CAMETICS LTD, NANOTECHNOLOGY, CAMBRIDGE, CAMBRIDGESHIRE, UNITED KINGDOM

* Corresponding author: jacek.gorka@polsl.pl

or molecular level to influence macroscopic material properties. Most widespread nanocomposites with polymer matrix. Metal matrix nanocomposites are mainly fabricated by means of powder metallurgy. In both of this nanocomposite varieties positive impact of carbon nanotube reinforcement on mechanical properties is observed. However, currently achieved mechanical properties are far from levels based on theoretical calculations [24-27]. In this work attempts to modify structure and properties of austenitic stainless steel, with use of carbon nanotubes, by TIG remelting were performed. For comparison TIG remelting with carburizer as modifying agent was done. The conducted tests were not intended to determine the risk of increasing the susceptibility to intergranular corrosion of the tested steel.

2. Experimental

In this work, research on influence of multiwalled carbon nanotubes (MWCNTs), produced in Catalytic Chemical Carbon Vapor Deposition, NANOCYLTM NC7000CNTs (Fig. 1, Table 1) on a structure and properties of X10CrNi18-8 (EN 10088-1:2014) steel remelted by TIG arc (Fig. 2, Table 2).

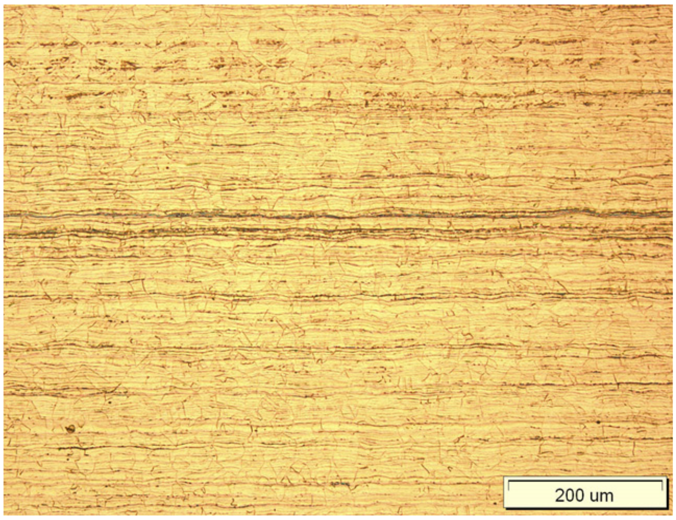

Fig. 1. X10CrNi18-8 steel microstructure

In the assessment of influence a type of carbon on properties and structure of austenitic steel, as a carbon filler was used also carburizer. In the specimens (X10CrNi18-8 plates) with dimensions 155×60×7 [mm] were drilled holes with 1.3 [mm]

TABLE 1

Chemical composition of X10CrNi18-8 (EN 10088-1:2014) steel

Chemical composition, %								
C	**Si**	**Mn**	**Cr**	**P**	**S**	**N**	**Mo**	**Ni**
0.05÷0.15	≤2.0	≤2,0	16.0÷19.0	≤0.045	≤0.015	≤0.011	≤0.08	6.0÷9.5

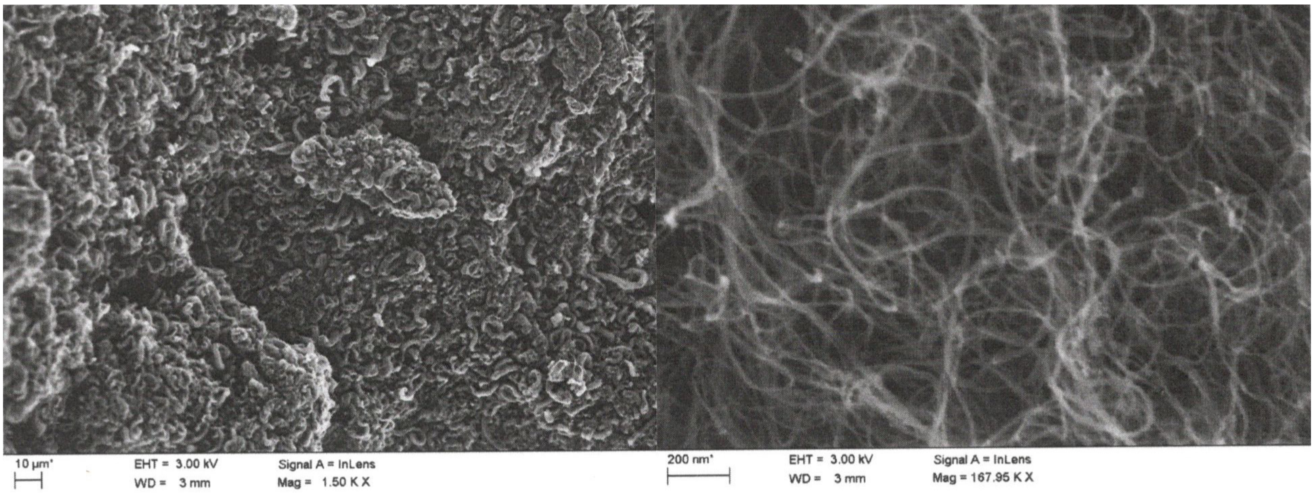

Fig. 2. SEM pictures of NANOCYLTM NC7000 carbon nanotubes

TABLE 2

Parameters of NANOCYLTM NC7000 CNT's

Properties	Value	Units	Measurement method
Average diameter	9.5	nm	TEM
Average length	1.5	µm	TEM
CNT's purity	90	%	TGA
Metals oxides inclusions	10	%	TGA
Surface area	250÷300	m^2/g	BET

diameter and placed 0.5 [mm] under specimen surface (Fig. 3). Next, to the drilled holes was implemented CNTs, carburizer and mixture of these both powders. Prepared specimens were remelted by TIG method on the CASTOTIG 2202 power source with 2.4 [mm] tungsten thoriated electrode with parameters sets for obtain 3.0 [mm] penetration depth (Table 3). Remelted specimens were cut into the half of the remelted beads distance and prepared for metallographic examinations. Cross sections of the specimens were tested on classical metallography microscopes, hardness tests, SEM analyses (on JEOL 5800 LV SEM EDX equipment) and phase identification by X-ray phase analysis on Philips APD X'Pert PW 3020 diffractometer.

3. Results and Discussions

The analysis of the microhardness of penetration areas revealed various hardness values in comparison with the base material of austenitic steel. Seven microhardness tests were performed in remelted areas. Highest and lowest values were discarded from remining five mean value was calculated (Fig. 4, Table 4). The modification of steel using a carbon additive (carburite) leads to slight bead hardness changes, whereas the modification performed using carbon in the form of CNTs (carbon nanotubes) increases hardness by approximately 25% in comparison with that of the base material.

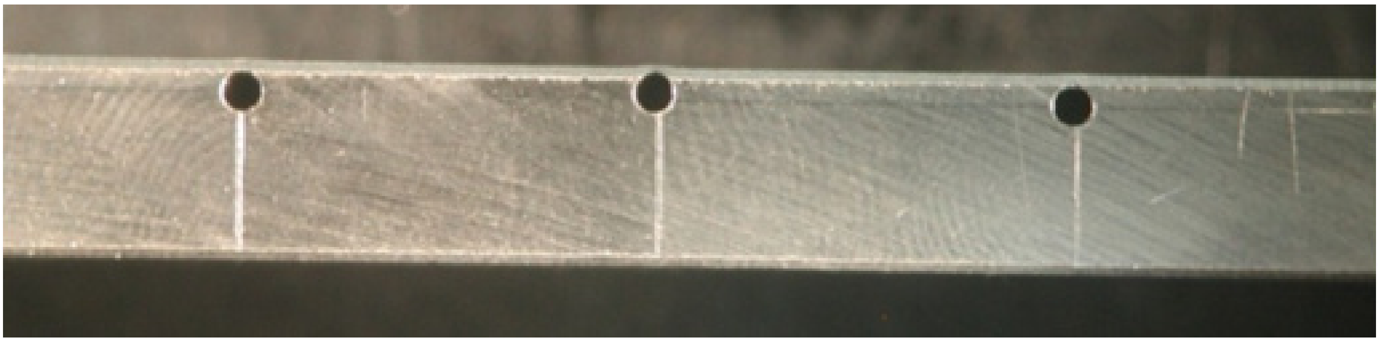

Fig. 3. X10CrNi18-8 steel specimen with holes prepared for feeds

TABLE 3

TIG remelting parameters on X10CrNi18-8 steel specimens with feed drilled holes

Designation of remelted bead	Feed type	Remelting speed [mm/s]	Welding current [A]	Arc voltage [V]
1	99.5% Fe + 0.5% CNTs	2,0	80	12
2	99.0% Fe + 1.0% CNTs			
3	100.0% CNTs			
4	99.5% Fe + 0.5% KR			
5	99.0% Fe + 1.0% KR			
6	100.0% KR			

Remarks: gas flow rate (argon) – 7.0 [l/min], KR – carburizer

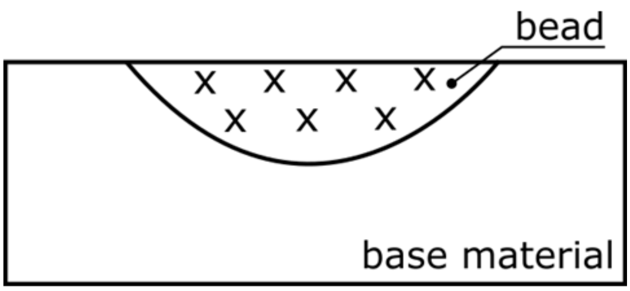

Fig. 4. Microhardness measurement points

TABLE 4

Average from five values of microhardness tests (HV0.1) taken in remelted zone

X10CrNi18-8 steel	Remelted X10CrNi18-8 steel with powder					
	Fe + 0.5% CNTs	Fe + 1% CNTs	100% CNTs	Fe + 0.5% KR	Fe + 1% KR	100% KR
200	258	250	258	200	208	200

Remarks: 7 hardness measurements were made, the highest and the lowest values were rejected, and the average value was calculated from the remaining ones

SEM analyses of remelted areas on X10CrNi18-8 specimens modificated with CNTs, indicates that dark areas, initially interpreted as one of the phase (based on optical microscope, Fig. 5) is finally densely packed bladders with dimensions from 50 [nm] up to a few [μm], Fig. 6. These bladders are not present in the specimens with carburizer filler. High resolution scanning microscopy allow to observe in this area protruding, longitudinal particles with 100-300 [nm] length, Fig. 7. For identification of this phase, X-ray analysis was done. A diffraction pattern obtained for steel X10CrNi18-8 corresponds to austenitic steel (Fe-Cr-Ni). One additional peak of very low intensity at 2θ = 39.0527° can be treated as a disturbance. In spite of a distinctly different microstructure, the diffraction pattern obtained for the penetration area of austenitic steel modified using 100% CNTs powder is identical with the diffraction pattern of the base material. Similar to the BM, an additional

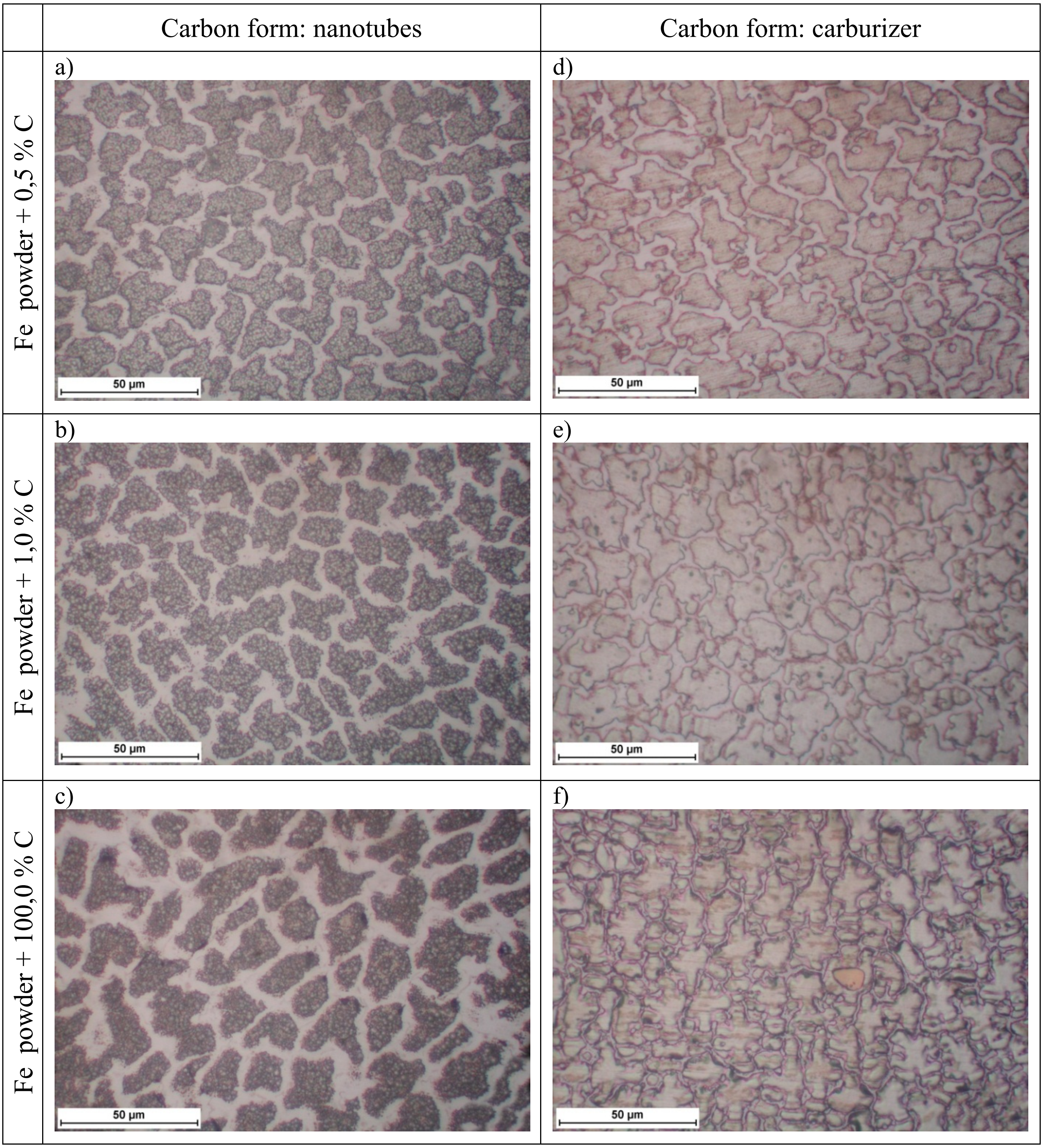

Fig. 5. Microstructures of X10CrNi18-8 remelted areas: modified with carbon as a nanotubes (a-c) and carburizer (d-f)

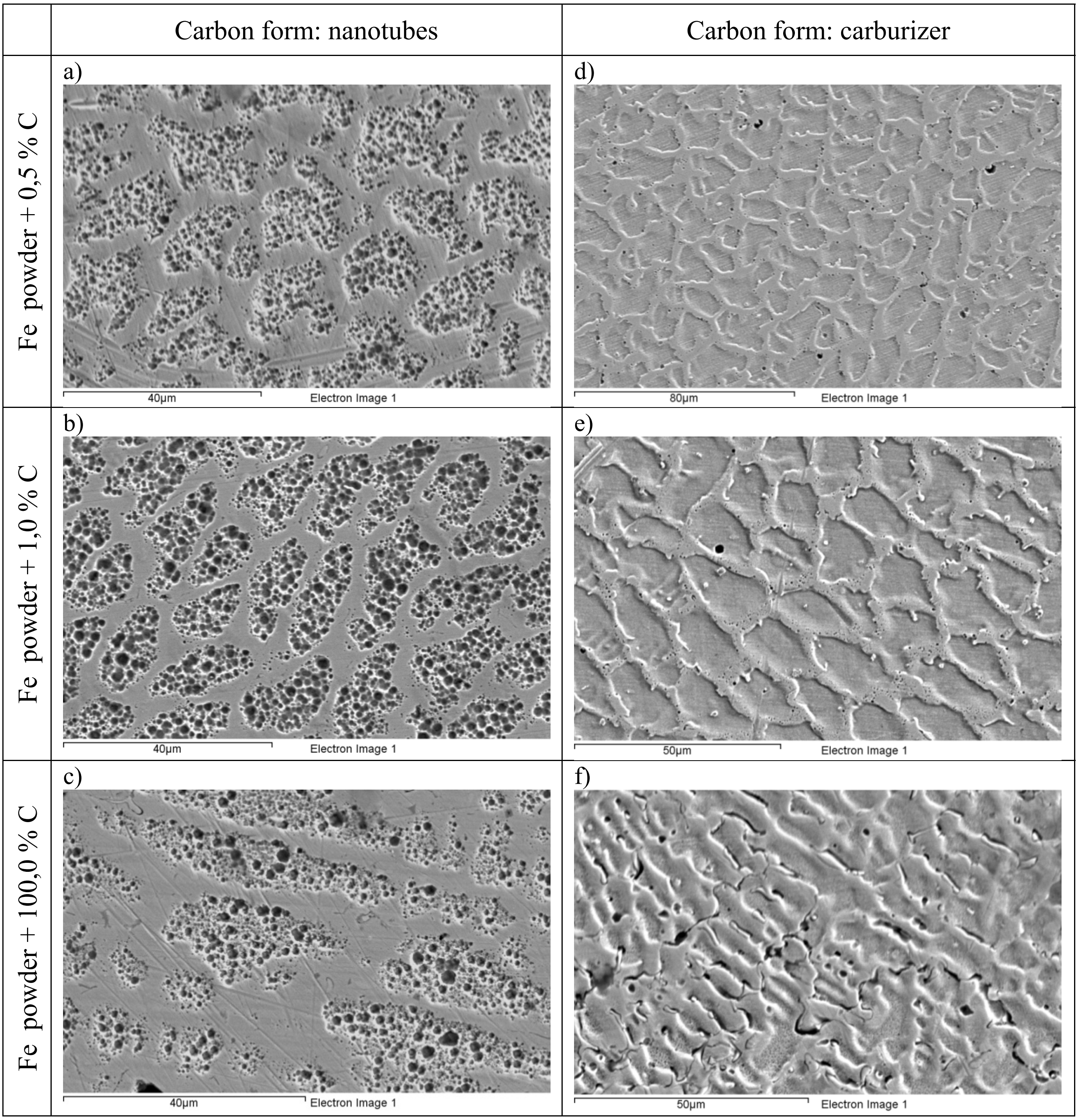

Fig. 6. Microstructures of X10CrNi18-8 remelted areas: modified with carbon as a nanotubes (a-c) and carburizer (d-f) – SEM pictures

peak of very low intensity at 2θ = 29.4355° can be treated as a disturbance. No peaks were observed at 2θ = 26°, 2θ = 42.4° and 2θ = 77.7°, which could indicate the presence of carbon nanotubes, Fig. 8, table 5,6. Almost identical microstructures of the penetration areas of austenitic steel X10CrNi18-8 modified using powders having various carbon nanotube contents, i.e. Fe + 0.5% CNTs, Fe + 1% CNTs and 100% CNTs, could imply that during the TIG arc melting of specimens with additives of the highest CNTs content, a significant part of carbon nanotubes burnt out and only their small amount took part in the modification of the steel structure. Very small dimensions of used CNTs (diameters about 9,5 [nm]), random orientation and small weight amount can make difficult or impossible to CNTs detection during XRD tests. It means that it is not possible to clearly determine nature of particles filling the cavities, it is only possible to suppose that they are CNTs beams or nanoparticles comes from their disintegration.

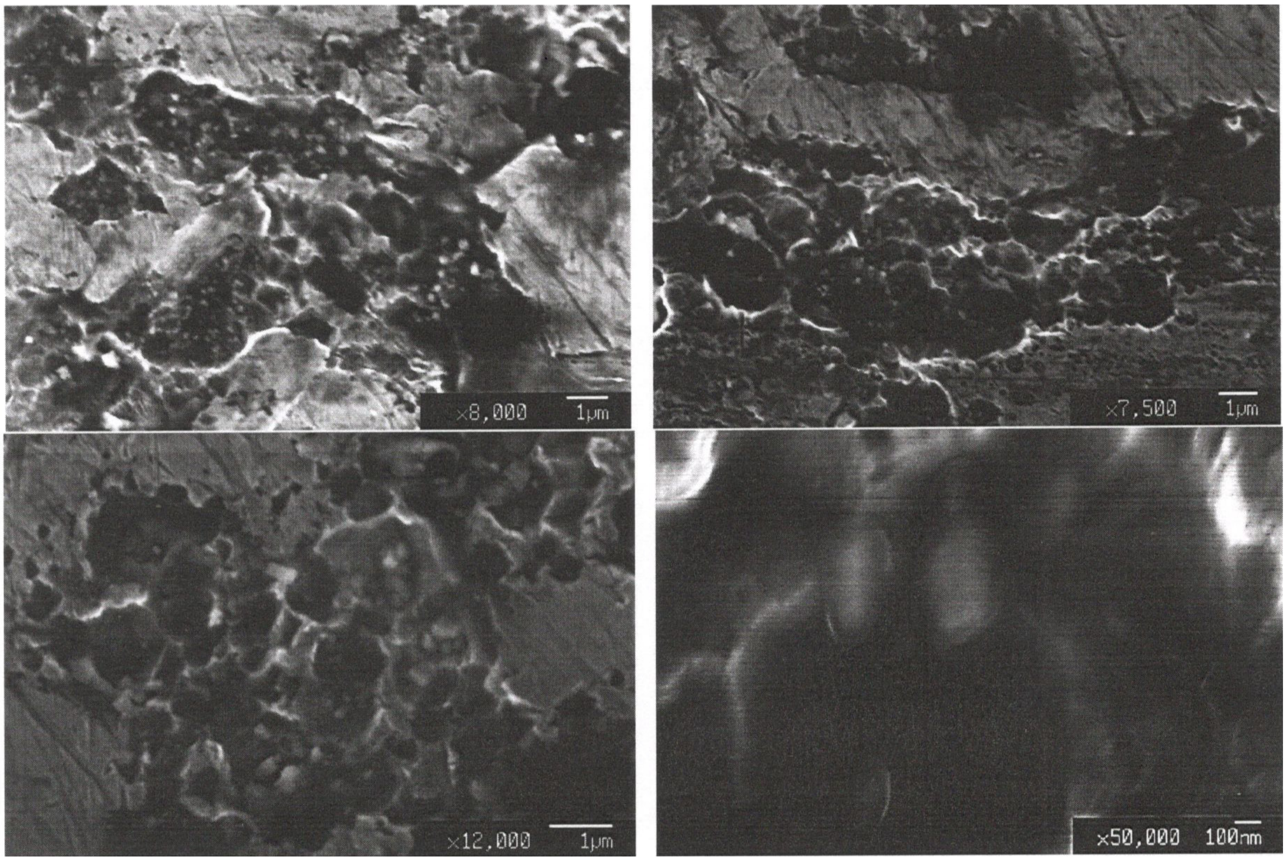

Fig. 7. Particles with size about 100-300 [nm] fill the microbladders in remelted area on X10CrNi18-8 steel modified with 100% CNTs powder

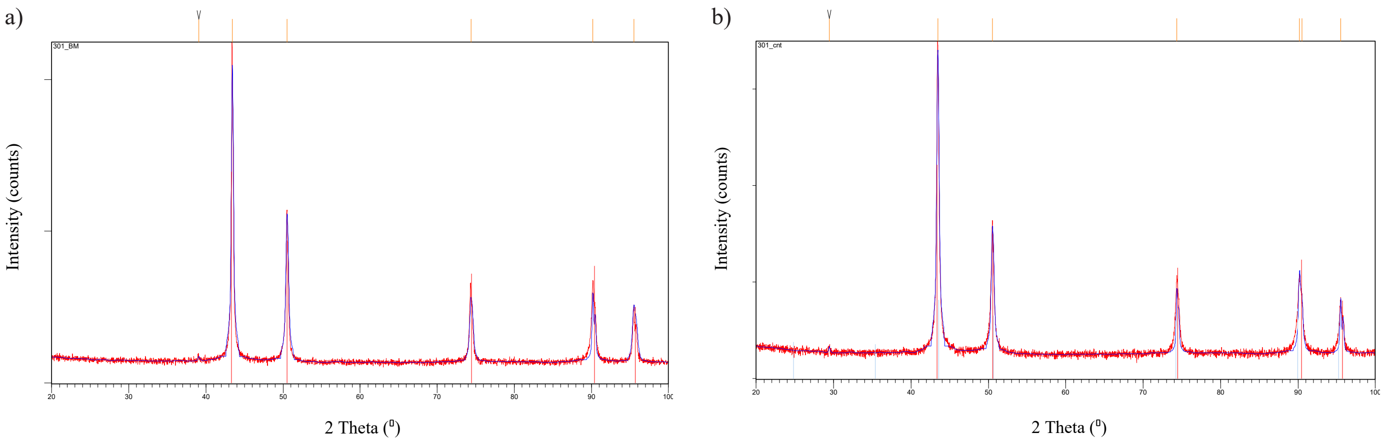

Fig. 8. Diffraction pattern obtained for: a) X10CrNi18-8 austenitic steel, b) X10CrNi18-8 austenitic steel 100% powder CNTs modified

TABLE 5

Positions and intensities of the diffractogram peaks obtained for X10CrNi18-8 austenitic steel, Fig. 8a

Position [°2θ]	Max. [cts]	FWHM [°2θ]	d-spacing [Å]	Rel. Int. [%]	Tip width [°2θ]	Phase*
39.0527	24.55	0.2362	2.30653	0.21	0.2834	—
43.4056	11834.53	0.1968	2.08479	100.00	0.2362	Fe Cr Ni
50.5055	3185.22	0.2755	1.80711	26.91	0.3306	
74.3729	853.97	0.3149	1.27552	7.22	0.3779	
90.1956	1077.74	0.1968	1.08841	9.11	0.2362	
95.5174	540.68	0.3840	1.04049	4.57	0.4608	

* Based on the database The International Centre for Diffraction Data® (ICDD®), 2010
Remarks: step: 0.02°, time for step: 30 s

TABLE 6

Positions and intensities of the diffractogram peaks obtained for X10CrNi18-8 austenitic steel modified with 100% CNTs powder, Fig. 8b

Position [°2θ]	Max. [cts]	FWHM [°2θ]	d-spacing [Å]	Rel. Int. [%]	Tip width [°2θ]	Phase*
29.4355	22.31	0.1574	3.03450	0.31	0.1889	—
43.4496	7135.87	0.2362	2.08278	100.00	0.2834	Fe Cr Ni
50.5160	1499.58	0.2755	1.80676	21.01	0.3306	
74.3599	608.28	0.1968	1.27571	8.52	0.2362	
90.2075	649.61	0.2880	1.08740	9.10	0.3456	
95.5237	360.80	0.1920	1.04044	5.06	0.2304	

* Based on the database The International Centre for Diffraction Data® (ICDD®), 2010
Remarks: step: 0.02°, time for step: 30 s

4. Conclusions

Results of the researches indicates, that fill in the weld pool with different form of carbon (CNTs and carburizer) it is possible to achieve remelted beads with different structure and hardness distribution. It confirms validity of the research continuation with CNTs as a modifier of steels and also other metals and theirs alloys. The tests conducted justify the statement that the melting of sheets with openings filled with powder of a strictly specified chemical composition is a good method for supplying carbon nanotubes to a liquid metal pool. The lack of disturbing factors, such as the presence of alloying additions in the cover of a filler metal wire and/or the effect of a melting atmosphere, is decisive for the efficiency of the method and facilitates the optimisation of process parameters. The method developed for supplying carbon nanotubes to a liquid metal pool can be used for testing the chemical and structural stability of carbon nanotubes in liquid alloys for various melting methods. The XRD analysis did not reveal the existence of peaks which could indicate the presence of carbon nanotubes in the beads subjected to the analysis. Due to high temperature accompanying the melting of the austenitic steel, carbon nanotubes probably decomposed. For this reason, when testing the use of CNTs as a composite hardening material, it is recommended that metals or alloys of lower melting points than that of the analysed austenitic steel should be used. Up until recently mostly tries low and high alloy metal modifications were made by introduction of alloying elements promoting formation of high melting point precipitations acting as heterogenous nucleation sites [28,29]. Successful grain refinement is possible also in welding of aluminum alloys, where Titanium and Zirconium form intermetallic compounds Al_3Ti and Al_3Zr, which promote growth of uniaxial grains [30,31]. In referred instances heterogeneous nucleation sites are in form of particle precipitations with dimensions in region of several μm. An interesting development direction is introduction of nanoscale precipitation in form of carbo nanotubes, with specific morphology and high surface area, into molten metal pool. It produces "spatial web" of heterogenous nucleation sites, which in effect causes drastic change in crystallization mode and parameters resulting in refinement of remelted, with addition of nanostructural carbon materials, zone parameter, e.g. welded joints.

REFERENCES

[1] S. Bakshi at al., Carbon nanotube reinforced metal matrix composites – a review, Int. Mater. Rev. **1** (55), 41-64 (2010).

[2] J. Coleman at al., Small but strong: A review of the mechanical properties of carbon nanotube-polymer composites, Carbon **9** (44), 1624-1652 (2006).

[3] E. Neubauer at al., Mechanical properties of bulk composites based on aluminum alloy reinforced with CNT with ex-situ TiC layer, Compos. Sci. Technol. **16** (70), 2228-2236 (2010).

[4] S. Boncel, J. Górka, S. Milo, P. Shaffer, K. Koziol, Shear-induced crystallisation of molten isotactic polypropylene within the intertube channels of aligned multi-wall carbon nanotube arrays towards structurally, Mater. Lett. (116), 53-56 (2014).

[5] P. Barai, G. Weng, A theory of plasticity for carbon nanotube reinforced composites, Int. J. Plasticity (27), 539-559 (2011).

[6] H. Tan at al., The effect of van der Waals-based interface cohesive law on carbon nanotube-reinforced composite materials, Compos. Sci. Technol. **14** (67), 2941-2946 (2007).

[7] T. Chmielewski, D. Golański, W. Włosiński, J. Zimmerman, Joining of alumina (Al_2O_3) with metals by the friction welding method, Bull. Pol. Acad. Sci.-Te. **1** (63), 201-207 (2015).

[8] X. Zeng at al., Selective laser melting of high strength Al-Cu-Mg alloys: Processing, microstructure and mechanical properties, Mater. Sci. Eng. **20** (527), 5335-5340 (2010).

[9] S. Bakshi, R. Batista, A. Agarwal, Quantification of carbon nanotube distribution and property correlation in nanocomposites, Composites **8** (40), 1311-1318 (2009).

[10] A. Lisiecki, Titanium matrix composite Ti/TiN produced by diode laser gas nitriding, Metals **5** (1), 54-69(2015). DOI: https://doi.org/10.3390/met5010054

[11] M. Burda, A. Lekawa-Raus, A. Gruszczyk, K. Koziol, Soldering of carbon materials using transition metal rich alloys, ACS Nano **9** (8), 8099-8107 (2015).

[12] J. Liao, M. Tan, Mixing of carbon nanotubes (CNTs) and aluminum powder for powder metallurgy use, Powder Technology **1** (208), 42-48 (2011).

[13] Y. Wu, G. Kim, Carbon nanotube reinforced aluminum composite fabricated by semi-solid powder processing, J. Mater. Process. Tech. **8** (211), 1341-1347 (2011).

[14] S. Boncel, J. Górka, S. Milo, P. Shaffer, K. Koziol, "Binary salt" of hexane-1,6-diaminium adipate and "carbon nanotubate" as a synthetic precursor of carbon nanotube/Nylon-6,6 hybrid materials, Polym. Composite **3** (35), 523-529 (2014).
[15] J. Liao at al., Carbon nanotube evolution in aluminum matrix during composite fabrication process, Mater. Sci. Forum (690), 294-297 (2011).
[16] S. Cho S at al., Multiwalled carbon nanotubes as a contributing reinforcement phase for the improvement of thermal conductivity in copper matrix composites, Scripta Mater. **4** (63), 375-378 (2010).
[17] A. Kurc-Lisiecka et al., Analysis of deformation texture in AISI 304 steel sheets, Sol. St. Phenomena (203-204), 105-110 (2013).
[18] T. Chmielewski, D. Golański, W. Włosiński, Metallization of ceramic materials based on the kinetic energy of detonation waves, Bull. Pol. Acad. Sci.-Te. **2** (63), 449-456 (2015).
[19] S. Uddin at al., Effect of size and shape of metal particles to improve hardness and electrical properties of carbon nanotube reinforced copper and copper alloy composites, Compos. Sci. Technol. **16** (70), 2253-2257 (2010).
[20] D. Janicki, Improvement of wear resistance of stainless steel AISI 304L by diode laser surface alloying with chromium carbide, Appl. Mech. Mater. (809-810), 363-368 (2015).
[21] K. Kondoh at al., Characteristics of powder metallurgy pure titanium matrix composite reinforced with multi-wall carbon nanotubes, Mater. Sci. Eng. **16-17** (527), 4103-4108 (2010).
[22] Q. Li, Ch. Rottmaira, R. Singera, CNT reinforced light metal composites produced by melt stirring and by high pressure die casting, Compos. Sci. Technol. **16** (70), 2242-2247 (2010).
[23] M. Musztyfaga-Staszuk, L.A. Dobrzański at al., Application of the finite element method for modelling of the spatial distribution of residual stresses in hybrid surface layers, Arch. Metall. Mater. **59** (1), 247-252 (2014).
[24] Y. Xu, G. Ray, B. Abdel-Magid, Thermal behavior of single-walled carbon nanotube polymer-matrix composites, Compos. Part A-Appl. S. **37** (1), 114-121 (2006).
[25] D. Chunfeng, Z. Xuexia, W. Dezuna, Chemical stability of carbon nanotubes in the 2024Al matrix, Mater. Lett. **61** (3), 904-907 (2007).
[26] Y. Morisada, Y. Miyamoto at al., Microstructures and mechanical properties of Al_2O_3-C refractories with addition of multi-walled carbon nanotubes, Int. J. Refract. Me. H. (25), 322-327 (2007).
[27] K. Lau, D. Hui, The revolutionary creation of new advanced materials-carbon nanotube composites, Compos. Part B **33** (4), 263-277 (2002).
[28] G. Heintze, R. McPherson R, Solidification control of submerged arc welds in steels by inoculation with Ti, Weld. J. **65**, 71-82 (1986).
[29] J. Yao at al., Microstructure and wear property of carbon nanotube carburizing carbon steel by laser surface remelting, Appl. Surf. Sci, **254**, 7092-7097 (2008).
[30] B. Pearce, H. Kerr, Grain refinement in magnetically stirred GTA welds of aluminum alloys, Metall. Trans. **12B**, 479-486 (1981).
[31] H. Yunjia et al., Grain refinement of aluminum weld metal, Weld. J. **68**, 280-289 (1989).