Investigation of microstructure and thermal stability of pulsed plasma processed chromium ferritic-martensitic steels

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Abstract. This paper presents results of the microstructural evolution and thermal stability of the promising Russian ferritic-martensitic steels (EP 823, EP 900, EK 181 and ChS 139) for the nuclear and fusion application after surface modification by high temperature pulsed plasma flows (HTPPF) treatment. Investigations of microstructure, topography and elemental content changes associated with irradiation by nitrogen plasma with energy density 19-28 J/ cm^2 and pulse duration 20 μs were carried out. Changes in microstructure and elemental content occurring in the modified surface layer were characterized by means of scanning electron microscopy (SEM) and X-ray microanalysis (EDS and WDS). It was shown that independently of initial microstructure and phase composition, HTPPF treatment of ferritic-martensitic steels leads to formation of ultrafine homogeneous structure in the near surface layers with typical grain size ~100 nm. Results of microstructure investigations after annealing during 1 hour demonstrates significant thermal stability of nanostructure formed by HTPPF treatment.

1. Introduction

12% chromium ferritic-martensitic steels are planned to be used as structural materials for novel fission (Generation IV) and fusion reactors. Development of these new facilities demands to increase the operation temperature range of the materials up to 650 °C. Operating 12% chromium steels at the elevated temperature leads to new requirements both to the bulk properties and to the surface which will ultimately determine the applicability of the materials under corrosion/erosion effects of the environment. Hence, the optimization of surface structure has become a feasible and effective method of improving the overall properties of structural materials. Relatively novel methods such as ultrasonic treatment [1], electron and ion beams [2,3], pulsed laser and plasma irradiation [4,5] have been admitted as a promising methods for surface modification over the last few years. Such treatment results in the evolution of dislocation structure of the material, grain refinement and increase of the grain misorientation angles, etc., and eventually allow to create nanocrystalline materials. Ultrafine grains and large density of grain boundaries of nanomaterials possess unique properties in particularly increased strength/hardness, enhanced diffusivity, improved toughness/ductility, corrosion and erosion resistance. Numerous papers have been focused on the investigation of the nanostructuring methods and unique properties of produced materials [1-5], though, their thermal stability for high temperature applications such as nuclear and fusion industry is far from being clarified.

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2. Materials and methods

The samples for this study are 12% Cr steels EP823, EP900, ChS139, EK-181 (Table 1) in the heat treated condition (quenched from 1100 C, followed by tempering at 720 C for 3 hours, provided by Bochvar institute, Moscow) and EK-181 nanostructured by severe plastic deformation by torsion under high pressure (further HPT, samples provided by Ufa State Aviation Technical University). HPT nanostructuring technique was performed in Bridgman anvil cell by torsion for 10 turns under pressure P ~ 6 GPa at a temperature of 400 ºC. Processing of samples by HTPPF conducted in experimental z-pinch type pulsed plasma device "Desna-M" [4]. "Desna-M" is designed to produce and study gas plasma flows with energy of flow up to ~ 50 kJ and energy of ions up to 2 keV. HTPPF action with power densities above the critical value for irradiated material leads to melting and subsequent high-speed (up to 10^6 K / s) cooling of the surface layer [4]. This process, in turn, leads to the formation of gradient microstructure of the material surface: a modified surface layer with enhanced physical-mechanical and physico-chemical properties without pronounced interface between modified layer and bulk material. The microstructural investigation and the elemental composition analysis of the samples were carried out by scanning (EVO 50 XVP SEM) and transmission electron microscopy (Technai G2 TEM) and X-ray microanalysis using energy-dispersive spectrometer (EDS) Inca x-act and wave-dispersive spectrometer (WDS) Inca Wave 500 (Oxford Instruments, UK).

Steel	Concentration of main alloying elements (% wt.)														
	C	Si	Mn	Cr	Ni	Mo	Nb	Ti	W	V	B	Ta	Ce	N	Zr
EP823	0.14-0.18	1.2	0.6-0.7	11.0-12.0	0.7	0.8	0.3	-	0.3-0.6	0.3-0.4	0.006	-	-	-	-
EP900	0.15	1.14	0.7	11.5	0.7	0.7	0.3	-	0.75	0.3	0.0045	-	0.03	0.15	-
ChS139	0.19-0.25	0.1-1.0	0.5-0.8	10.0-12.5	0.5-0.8	0.4-1.1	0.2-0.4*	0.03-0.3	0.5-2.0	0.2-0.4	0.002-0.006	0.2-0.4*	0.001-0.10	0.02-0.15	0.05-0.2
EK181	0.10-0.21	0.1-0.8	0.5-0.8	10.0-12.5	<0.1	<0.01	<0.01	0.03-0.3	0.8-2.5	0.2-1.0	0.003-0.008	0.05-0.2	0.001-0.10	0.02-0.15	0.05-0.2

3. Results and discussion

Figures 1 *a*, *d* show typical electron micrographs of the microstructure of 12% chromium steels in the heat treated state. Electron microscopic studies and the results of elemental analysis showed that in the initial state steel EP823 and EP900 have two-phase microstructures of the lath martensite, ferrite and finely dispersed precipitates of different types (Figures 1 *a*, *b*). In particular, in EP823 steel complex carbides based on niobium were observed. EP900 steel, which is additionally doped with nitrogen, as well as large carbides type (Fe, Nb, Cr) C were observed fine nitrides (Figure 1 *b*) on the basis of Fe and Cr. At the same time nitrogen has not been observed in the matrix of EP900 steel.

Steel CHS139 in heat treated state demonstrates structure of lath martensite with carbide precipitates of $M_{23}C_6$ type, mostly located along the grain boundaries of the martensitic plates and a size of about 150-200 nm. The transverse dimension of the martensite plates varies in the range from 0.1 to 1 μm. Also, there are relatively large (about 1 μm) niobium carbide precipitates in the CHS139 steel.

Steel EK181 has similar microstructure with ChS139 steel (Figure 1 *c*), except of the presence of minor amount of ferrite phase. Carbide precipitates in this steel has less volume fraction and sizes which might be due to reduced carbon content and absence of a strong carbide-stabilizing elements such as molybdenum and niobium in EK181 steel in comparison with ChS139 steel. Also in the structure of the EK181 steel large (up to 5 μm) precipitates of zirconium nitride were observed.

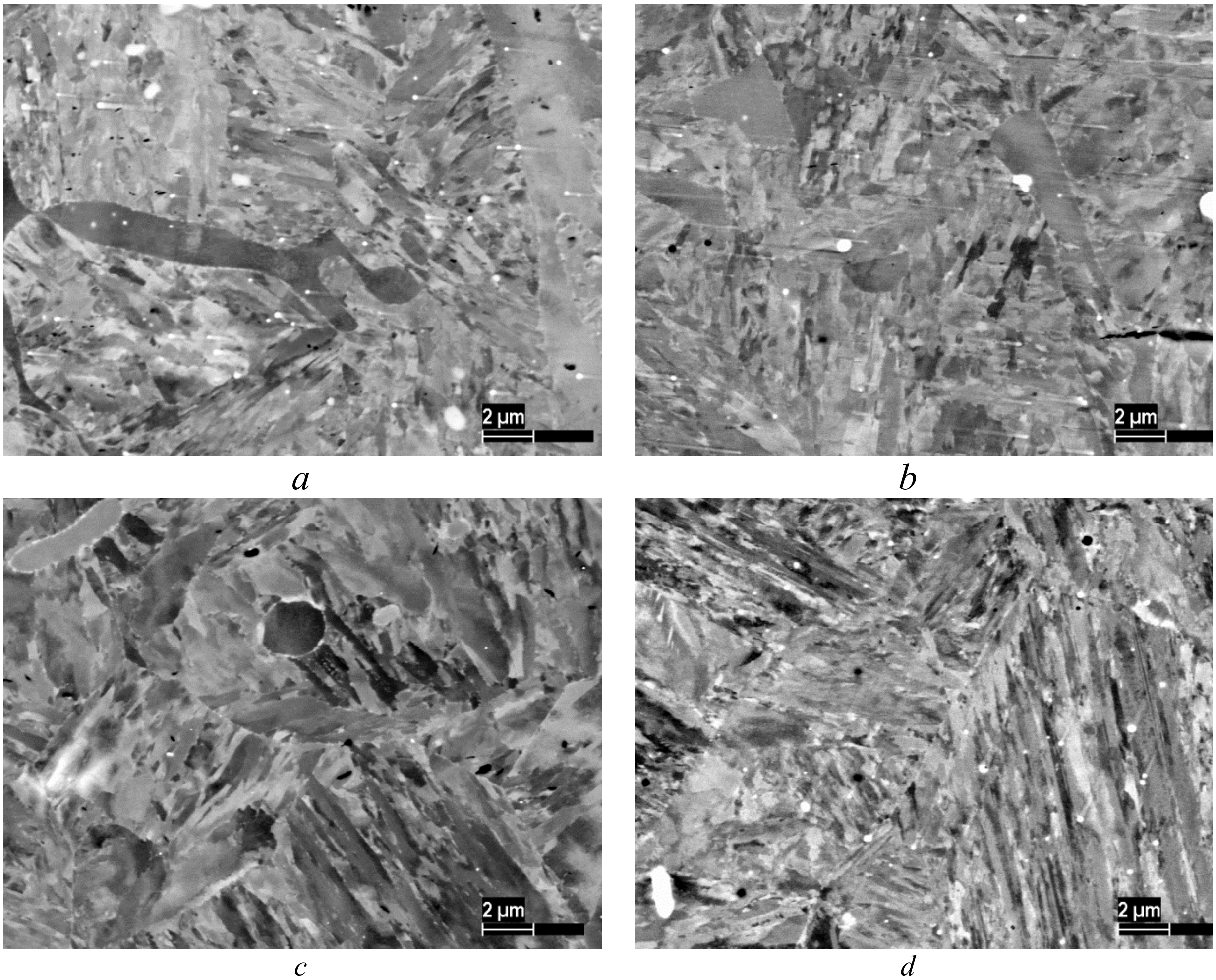

Figure 1. Microstructure of fuel cladding tubes made of EP823 (*a*), EP900 (*b*), EK-181 (*c*), ChS139 (*d*) in initial state.

Figure 2 shows electron micrographs of the sample surface after the processing by nitrogen HTPPF. It can be seen that wave-like structure of the solidified melt was formed on the surface of EK-181 steel after treatment by pulsed plasma flows (Figure 2, *a*). Under the high magnification (Figure 2, *b*), the surface cellular structure with an average size 80-150 nm of sub-grains is observed. Importantly, precipitates typical for untreated EK-181 steel are completely dissolved during HTPPF processing which indicates the transition of alloying elements to the solid solution and corresponding homogenization of the material elemental content. Dissolution of carbides occurs throughout the thickness of the modified layer. Analysis of cross section SEM micrographs shows that modified layer has columnar microstructure with transverse grain size about 2 μm (Figure 2, *c*). However precision TEM cross-section investigations reveal formation of columnar ultrafine subgrains in near surface layer (Figure2, *d*). Combined analysis of SEM and TEM cross-sectional data leads to conclusion that HTPPF treatment results in formation of two-dimensional nano-sized structure with transverse subgrain size ~80-150 nm and longitudinal size ~1-1,5 μm. Also it was found that processing by nitrogen plasma leads to additional doping of steel surface by nitrogen up to 4 % wt. (depending on the plasma processing regime).

It was shown that for the same plasma processing conditions there are no significant differences in microstructure formed of steel samples EP823, EP900, ChS139 and EK181: the phase composition and grain/subgrain size are independent of the initial state of the material, the distribution of alloying elements between matrix and carbide particles in the initial material which is due to close the elemental composition and the initial structure of the investigated steels, and therefore they are almost identical thermal properties.

This leads to the same values of characteristics of the processes occurring during high speed quenching surface layer, particularly the cooling rate. As for HTPPF treatment, formation of cellular microstructure is the result of the cellular solidification of a melt, and can be described by constitutional supercooling model [6]. Due to intense heat transfer inside the bulk material the cooling rate reaches very high level (more than 10^6 K / s), thus leading to realization of the extreme conditions of this phenomenon.

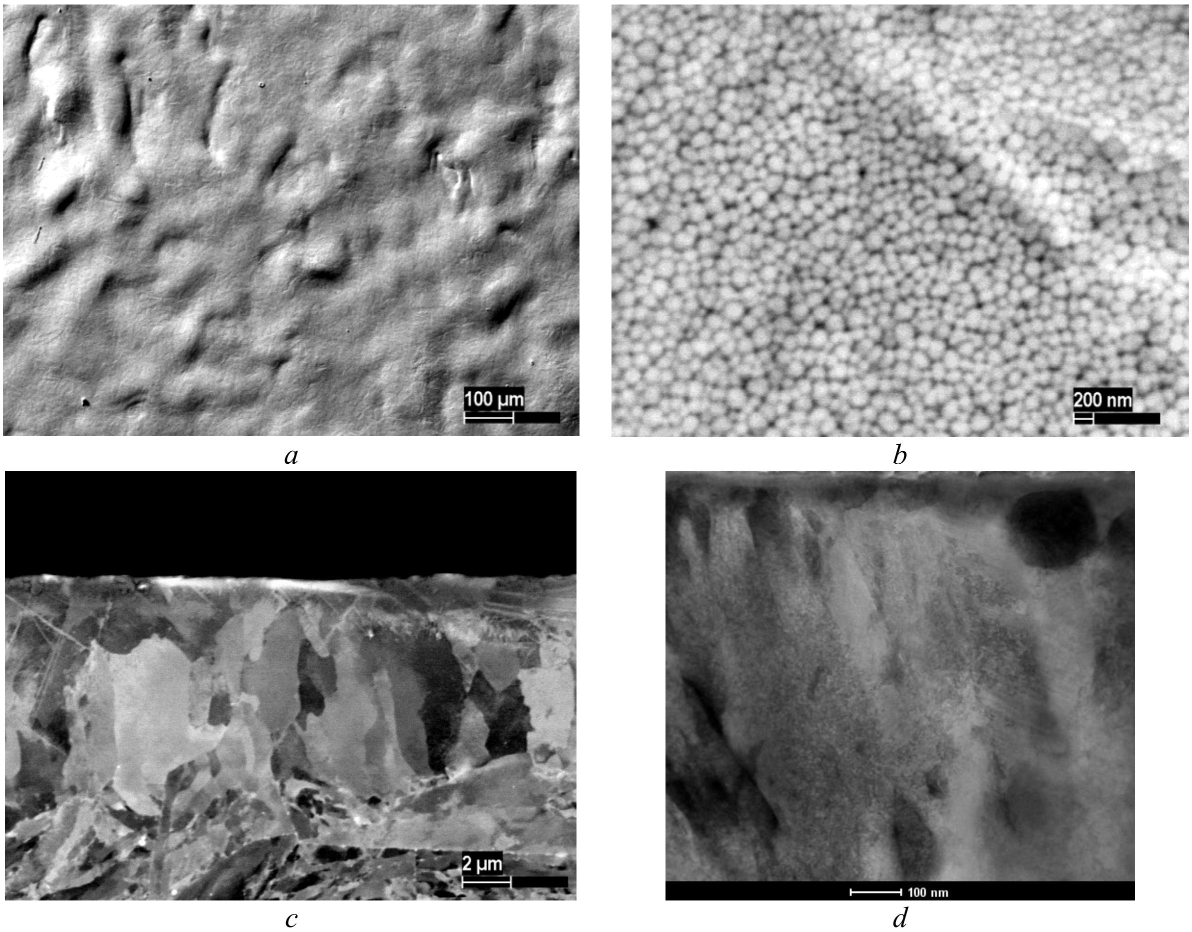

Figure 2. Surface (a, b) and cross-section (c, d) microstructure of EK-181 steel after nitrogen pulsed plasma treatment (Q = 28 J/cm^2, N = 3).

In order to identify the thermal stability of nanostructures obtained by HTPPF annealing was conducted at a temperature of 650 ºC for 1 h (the temperature corresponding to the limit operating temperature of structural material in fast breeder reactor). For comparison tests on the thermal stability were made simultaneously to HPT nanostructured EK-181. Figure 3 *a* shows SEM micrographs of the samples microstructure after the plasma treatment and subsequent annealing at 650 ºC. Comparison of the images showed that there are no changes in the microstructure of the modified layer, as the size of the subgrains in material does not change. On the other hand, HPT nanostructured (Figure 3 *b*) after annealing showed a significant increase in the grain size from 170 nm to the initial state to 1 micron after annealing due to past processes of recrystallization.

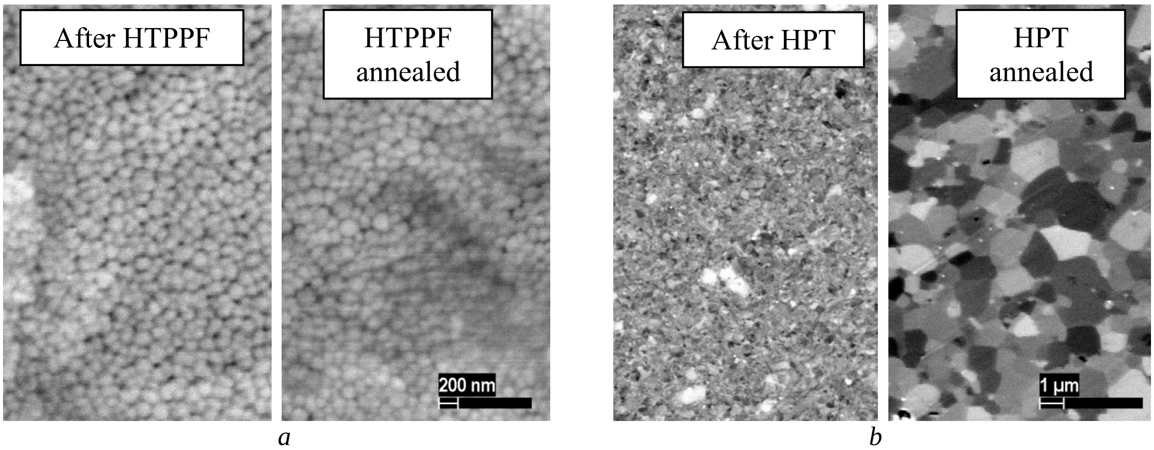

Figure 3. Change of microstructure of EK-181 in HTTPF (a) and HPT (b) as-processed state and annealed at 650°C for 1 h (right part of image).

4. Summary

It was shown that surface modification of 12 % chromium ferritic-martensitic steels EP823, EP900, and EK181 CHS139 by pulsed nitrogen plasma flows leads to formation of two-dimensional (2D) surface nanostructure with a main grain size 80-150 nm. It was revealed that the characteristics of formed nanostructure such as thickness of the modified layer and grain size are independent on the initial steel microstructure (phase composition and / or grain size). It was found that the modified layer manifests significant thermal stability and annealing of the samples at the temperature up to 650 °C, 1 hour, has almost no effect on its microsctructure.

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References

[1] Panin A V , Melnikova E A , Perevalova O B , Pochivalov Yu I , Leontyeva-Smirnova M V , Chernov V M and Ivanov Yu F 2009 *Phys. Mesomech.* **12** 150
[2] Fangjun Xu, Guangze Tang, Guangwei Guo, Xinxin Ma and Ozur G 2010 *Nucl. Instrum. Methods Phys. Res. B* **268** 2395
[3] Uglov V V, Remnev G E, Kuleshov A K, Astashinski V M and Saltymakov M S 2010 *Surf. Coat. Tech*. **204** 1952
[4] Kwok C T, Leong K I, Cheng F T and Man H C 2003 *Mat. Sci . Eng. A* **357** 94
[5] Kalin B A, Yakushin V L, Vasiliev V I and Tserevitinov S S 1997 *Surf. Coat. Tech*. **96** 110
[6] Glicksman M E 2011 *Principles of Solidification* (Springer-Verlag New York) pp 213–235