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Deposition of Thin (Ti,Si)N Reflecive Layers on Textiles Substrates

Streszczenie. *W artykule opisano budowę urządzenia oraz sposób nakładania na tkaniny cienkich warstw (Ti,Si)N stosowanych jako reflektory promieniowania podczerwonego. Jako metodę osadzania zastosowano magnetronowe rozpylanie jonowe o średniej częstotliwości MF (80 kHz). Tkaniny pokryte cienkimi warstwami wykorzystywane są do produkcji odzieży oraz elementów środków ochrony indywidualnej dedykowanych pracownikom (służby ratunkowe, siły zbrojne, hutnictwo, górnictwo i inne) wykonującym zadania w gorącym mikroklimacie.*

Abstract. *This paper describes the structure of the device and the method of applying thin (Ti,Si)N layers used as infrared radiation reflectors on fabrics. Ion magnetron sputtering at an average frequency MF (80 kHz) was used as the deposition method. Fabrics covered with thin layers are used for the production of clothes and elements of personal protective equipment dedicated to employees (emergency services, armed forces, metallurgy, mining and others) performing tasks in a hot microclimate environment. (**Depozycja cienkich warstw refleksyjnych (Ti,Si)N na podłoża tekstylne**).*

Słowa kluczowe: środki ochrony indywidualnej, ubrania specjalne, magnetron, cienkie warstwy.
Keywords: personal protective equipment, special clothing, magnetron, thin layers.

Introduction

This paper describes the structure of the device and the method of applying thin (Ti,Si)N layers used as infrared radiation reflectors on fabrics. Ion magnetron sputtering [1÷4] at an average frequency MF (80 kHz) was used as the deposition method. Fabrics covered with thin layers are used for the production of clothes and elements of personal protective equipment dedicated to employees (emergency services, armed forces, metallurgy, mining and others) performing tasks in a hot microclimate environment.

The magnetron sputtering system presented in Figure 1 was designed and run with two linear magnetrons and vacuum winder (see Fig. 2) for long textile substrate deposition of protective (Ti,Si)N films [2,5÷7]. Sputtering conditions for long term process were curried out for different textile type used in special application.

Fig.1. Vacuum equipment for protective film deposition

The device of the selected technology has been constructed and put into operation because this technique enables the coating of very long substrates (especially fabrics). The (Ti,Si)N layers were deposited while sputtering targets made of titanium-silicon sinters.

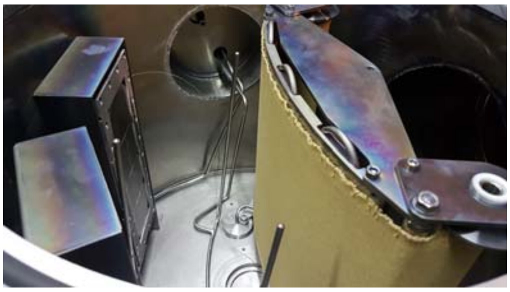

Fig.2. Vacuum winder for deposition on long fabrics

The sinters contained 10 % at. of silicon. The process required the maintenance of a certain temperature in the chemical reaction zone of film formation on the fabric surface. An example of protective clothing with applied heat-reflecting layers is shown in Figure 3.

Fig. 3. An example of solutions of a firefighter's personal protection system with the use of thin layers

Materials and Methods

The layers were deposited with the magnetron technique using two magnetrons with rectangular cathode surfaces. Targets are made of titanium-silicon sinters with 10 % at. Si.

The magnetrons were powered by DORA MF power supplies with a power of 10 kW and a frequency of 80 kHz. The station was equipped with a gas dosing system (N_2 and Ar) with flow controllers by MKS. The pumping system ensured the achievement of a vacuum required by the process technology, with a pressure not exceeding $5x10^{-3}$ Pa. The application technology was, to a large extent, patent-based [8]. The stand was equipped with a special vacuum fabric rewinder through the magnetron reactive zone. The time of stay in the zone determined the thickness of the applied layer. Detailed application conditions are presented in monograph [9]. The developed technology allowed for the application of a (Ti,Si)N or Ti,Si layer.

The work presents studies of heat transfer through fabrics covered with layers of different chemical composition in the magnetron sputtering technology. The research was carried out on single and multi-layer fabrics. Figure 4 shows a specially designed and made test stand [10] with the use of a radiator and a thermal imaging camera for continuous registration of temperature changes on the inside of the sample of the tested thermal shield.

Fig. 4. Diagram of the test stand for testing the effect of thermal radiation on material samples. 1 - support frame, 2 - test material, 3 – radiator, 4 – shutter, 5 - thermal imaging camera

The temperature on the inside of the material exposed to thermal radiation was measured with the FLIR T430sc thermal imaging camera [11]. Measuring range : -20 °C to + 650 °C. The camera recorded thermograms with the frequency of 30 Hz and saved them on the computer's hard drive (Fig. 5).

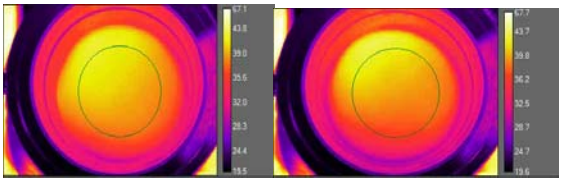

Figure 5. Thermograms of a material sample exposed to thermal radiation

The results were processed using the Flir ResearchIR Software program to determine the average temperature of the area of the marked sample fragment in Figure 6.

The obtained results were exported to Microsoft Excel, where the measurement data was processed with a proprietary program written in VBA in order to analyze temperature changes over time.

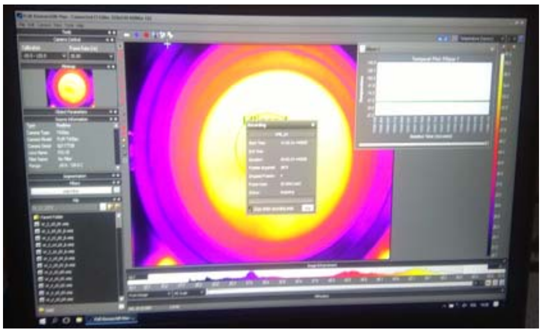

Figure 6. The Flir ResearchIR Software program - thermogram during analysis

The criterion adopted in the research was the course of temperature changes and the time needed to achieve the so-called the pain threshold (corresponding to a temperature of 60 °C the inner layer of the tested material) [4], The graph in Figure 7 shows the dependence of the temperature on the inner surface of the material (Natan without any coating on the outer layer) on the exposure time for the next set values of the heat flux. The graphs in Figures 8 and Figure 9 show the temperature dependence on the inner surface of the material (Natan with surface coating; composition I - Ti, Si 38 nm + (Ti, Si) N 110 nm + Ti, Si 38 nm; composition II - Ti, Si 36 nm + (Ti, Si) N 106 nm + Ti, Si 36 nm) from the exposure time for successive set values of the heat flux.

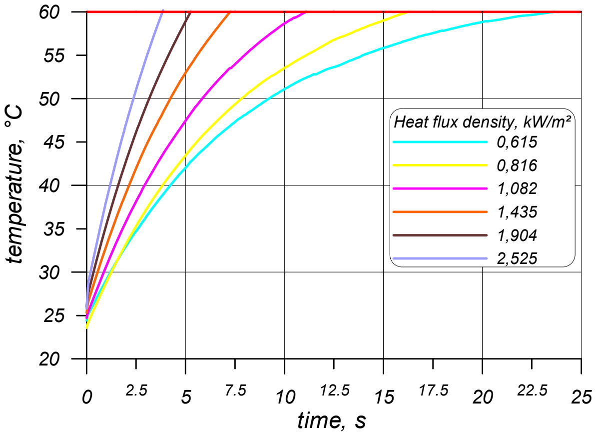

Fig. 7. Temperature on the inner surface of the material - Natan without surface coating

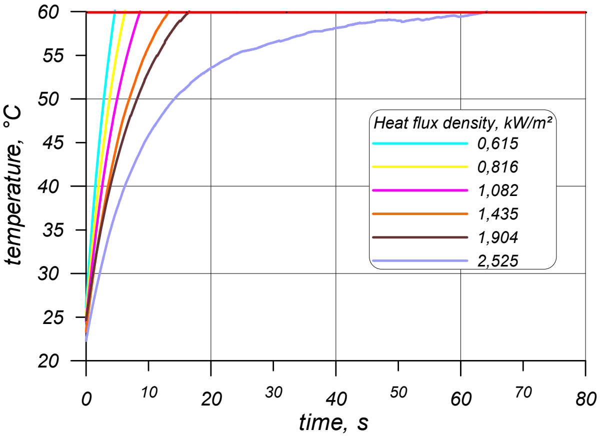

Fig. 8. Temperature on the inner surface of the material - Natan with surface coating – composition I

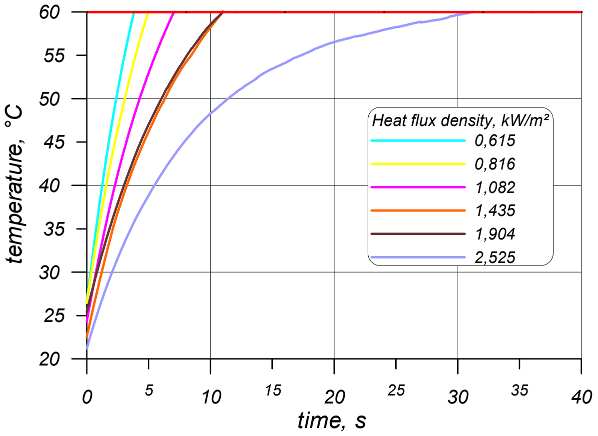

Fig. 9. Temperature on the inner surface of the material - Natan with surface coating - composition II

The results of the research indicate the influence of the layers of the applied reflective nanocomposite on increasing the resistance of the fabric subjected to the influence of the heat flux. The samples for the uncoated and nano-reflective materials for the two compositions were subjected to heat flux with densities of 0.615, 0.816, 1.082, 1.904 and 2.525 kW/m^2 [12].

The time course of temperature changes on the inner layer of materials with composite layers as compared to materials without coatings shows significant delays in the passage of energy streams through the shield.

Results and Discussions

The microscopic observations (SEM) [11,13,14] showed that the layer, approx. 300 nm thick, tightly covered the surface of individual fibers without forming a dense formation, so the fabric did not lose its elasticity. Figure 10 shows a photo of a PROTON fabric fragment with a (Ti,Si)N layer applied. Small losses of the layer are visible locally, which suggests that it was too thick in these places.

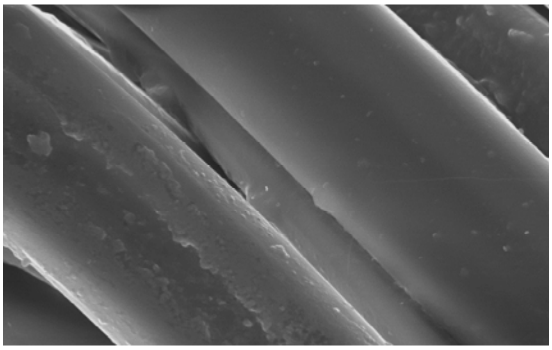

Fig. 10. SEM image of a PROTON fabric fragment covered with a (Ti,Si)N layer

The microstructure of the obtained (Ti,Si)N layers was visualized during observations carried out on a transmission electron microscope (HRTEM). Figure 11 shows the cross-section image of a layer removed from a single fabric fiber.

The photo (Fig. 11) shows a disordered microstructure of the layer. Numerous lighter and darker, small-sized structures can be seen, indicating both composite and amorphous structure of the layer. In layers applied at higher temperatures, a significant growth of crystallites is obtained, up to approx. 10 nm, and thus a significant reduction in the flexibility of the layer, which negatively affects its usability.

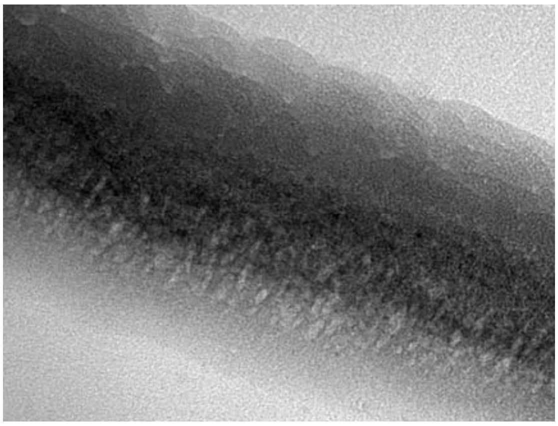

Fig. 11. Image of the cross-section of the (Ti, Si) N layer obtained on the HR TEM microscope

The phase composition of the applied (Ti,Si)N layers was investigated using the X-ray diffraction (XRD) method. A Panalytical X'PERT PRO high-resolution X-ray diffractometer with an adapter for thin-film system measurements was used for the tests. It was confirmed that the layers applied at the temperature not exceeding 70°C are largely amorphous - there are no peaks in the diffraction pattern that would allow phase identification. Only the diffractogram obtained for the layer applied at the temperature of approx. 200°C is characterized by several peaks enabling the phase identification to be made and proving the presence of titanium nitride crystallites. The change of the deposition conditions is visible in the diffraction pattern, which in addition to the high content of the amorphous phase also shows the peaks originating from the crystalline titanium nitride, according to the following data from the PDF-2 diffraction database. Silicon nitride was not found. It is likely that silicon nitride only exists in amorphous form. It cannot be ruled out that silicon is located in nodal positions in the titanium nitride network.

The paper also presents the results of research on heat transfer through fabrics covered with thin layers reflecting thermal radiation. The research was carried out on single and multi-layer fabrics. Moreover, the construction of an innovative system of devices for heat transfer tests was described.

Conclusions

Research on the effectiveness of thermal protection of materials used in personal shields according to the concept of modification with selected vacuum-plasma methods confirms their potential application [3,15,16].

The results achieved so far allow for a good forecast of the use of the results for their implementation in the production of personal protective equipment for various rescue service formations.

The magnetron sputtering equipment was design and constructed.

The protective films deposition on textile was carry out.

The measuring of heat transfert equipment was built and heat transfer throght textile was measured.

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