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AN ANALYSIS OF THE WETTING ANGLE OF LIQUID GLASS ON MULTICOMPONENT COATINGS OBTAINED BY MEANS PVD METHODS

Key words

PVD coating, wetting angle of liquid glass.

Abstract

The article presents an analysis of the possibilities of using modern surface engineering solutions to improve the durability of the tools used in the glass forming process. The process of forming glass is carried out at an elevated temperature above 300°C, with the impact of chemically active masses of glass and periodically changing mechanical stress. These difficult process conditions significantly reduce the performance and reliability of glass-forming tools.

A significant problem in maintaining the quality glass products is the phenomenon of the adhesion of the molten glass into the working surface. Due to the destruction of the forming tools, molten glass accumulates on the surface layer of materials that are increasingly used as solutions in the field of surface treatment.

The article presents the research results of the properties of different multilayer coatings based on Ti, Cr, Al, W, C, and Si, which are used to improve the durability of the tools used in the glass forming process. The studies presented in the article include an analysis of the surface morphology and microstructure of the produced coatings and an analysis of the contact angle of the molten glass. The analysis of the microstructure and surface morphology was carried out using scanning electron microscopy. The study on wettability was carried out using the droplet deposition technique.

1. Introduction

Analysis of the operating conditions of these tools made it possible to identify three main destructive factors in the technological process, i.e. cyclic thermal shocks, the corrosive effects of molten glass, and the friction caused by the presence of intensive sludge from molten glass remaining on the tool between the forming processes [1], [2]. One of the most important problems in the glass forming process is the adhesion of the molten glass onto the working surface of the tools [3]. This phenomenon can cause the intensification of tool wear, as well as cause the destruction of the glass product.

An effective way of preventing such phenomena is changing the wettability of the molten glass of the working surface of forming tools by the deposition thin coatings.

In recent years, TiN, CrN coatings were used to improve the performance of tools for glass forming due to their high hardness, abrasion resistance, and chemical resistance [4], [5]. However, the low oxidation resistance and wettability of the molten glass of these coating significantly reduces the ability to improve the durability of the glass-forming tools [6], [7].

The state of the art indicated that the addition of elements such as Si and Al [8], [9] to the chemical composition of the TiN and CrN coating significantly improve their resistance at elevated temperatures. Another solution is designing coatings based on refractory elements such as W or coatings based on Al_2O_3.

The article presents the research results of the properties of different multilayer coatings based on Ti, Cr, Al, W, C, and Si, which are used to improve the durability of the tools used in the glass forming process.

2. Experimental details

2.1. Preparation of PVD coatings

Samples for investigations were made of martensitic steel H17N2 according to PN-71/H-08620 (C-0.20, Cr-17.0, Ni-2.0). The investigated PVD coatings were created using two different methods, i.e. arc evaporation (ArcPVD) and electron beam evaporation (EBPVD), carried out using the technological devices presented in Fig. 1.

a) b)

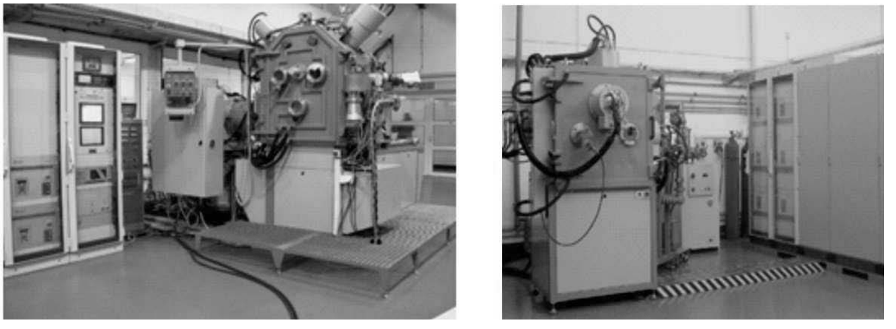


Fig. 1. Equipment for the production of PVD coatings: a) by EB-PVD method – Standard Special ITeE – PIB Radom, b) by ARC-PVD method – Standard 1 ITeE – PIB Radom

The W and Al_2O_3 coatings deposition process was executed by means of the electron beam evaporation method, with the use of Standard Special device (Fig.1a) according parameters presented in Table 1.

Table 1. Parameters of the Electron Beam Evaporation technology

Stage name	T [^oC]	I [mA]	U_{bias} [V]	t [min]	p [mbar]	Atmosphere
W						
W	470	680	0	40	< 10^{-4}	–
Al_2O_3						
Al_2O_3	390	750	0	7,5	< 10^{-4}	––

The Cr/CrN, Cr/CrN/AlCrTiN and CrN/AlCrN/AlCrTiSiN multilayer coatings deposition process was executed by means of the arc-evaporation method with the use of a Standart 1 device (Fig. 1b), according to the parameters presented in Table 2.

Table 2. Parameters of the Arc Evaporation technology

Stage name	T [°C]	I [A]	U_{bias} [V]	t [min]	p [mbar]	Atmosphere
Cr/CrN						
Cr	400	6 × 55	–50	5	5.0^{-3}	Ar
CrN	420	6 × 55	–150	90	3.5^{-2}	N_2
Cr/CrN/AlCrTiN						
Cr	390	6 × 55	–50	10	5.0^{-3}	Ar
CrN	390	2 × 60	–150	30	3.5^{-2}	N_2
AlCrTiN	400	4 × 60	–100	60	2.0^{-2}	N_2
CrN/AlCrN/AlTiCrSiN						
CrN	390	6 × 55	–50	10	5.0^{-3}	Ar
AlCrN	390	2 × 60	–150	30	3.5^{-2}	N_2
AlTiCrSiN	400	4 × 60	–100	60	2.0^{-2}	N_2

2.2. Characterization of PVD coating

In order to analyse the microstructure and surface morphology of the tested PVD coatings, the microscopic observation was carried out with scanning electron microscopy (Hitachi TM3000). The chemical composition of the tested PVD coating was determined by the EDS method. Hardness and Young's modulus of investigated PVD coatings were measured by means of the nanoindentation method with used the Nano-Hardness Tester of CSM Instruments. Measurements were carried out with the Berkovich indenter in a single cycle using the following parameters: $F = 10$ mN, $dF/dt = 20$ mN/min.

2.3. Characterization of the wetting angle of liquid glass

The molten glass wetting of the coating surface studies was carried out using the method of droplet deposition. This method consists in heating the sample to a temperature of about 900°C and then annealing for 30 min in this temperature with a glass ball (Ø = 10 mm) on its surface. These processes were performed in a furnace. The contact angle was measured using the camera's INFRATEC. Schematic contact angle measurements are shown in Figure 2. The first observations of the balls were carried out at 700°C. The next pictures were made increasing the temperature in steps by 50°C until the temperature reaches 900°C. Observations of the shape of balls were made after 30 minutes of annealing at a temperature of 900°C. Two thermocouples were used to control the temperature. One of them was placed in the sample material, and the other directly on the glass ball. As a result, it was possible to determine precisely the sample temperature, as well as the environment in which the ball was located. After the heating process, in order to determine their thermal resistance, microscopic observations were made of the surface layer of the coating using a scanning microscope (Hitachi TM3000). Measurements of the contact angles were carried out at temperatures in the range of 700 to 900°C.

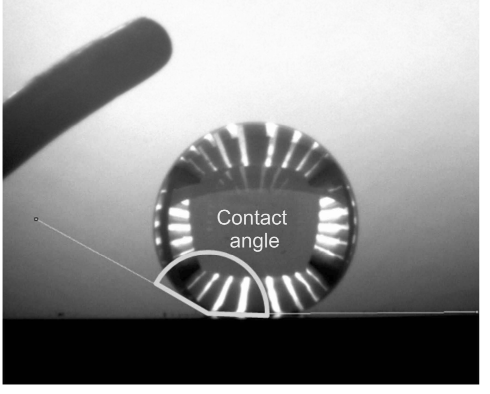
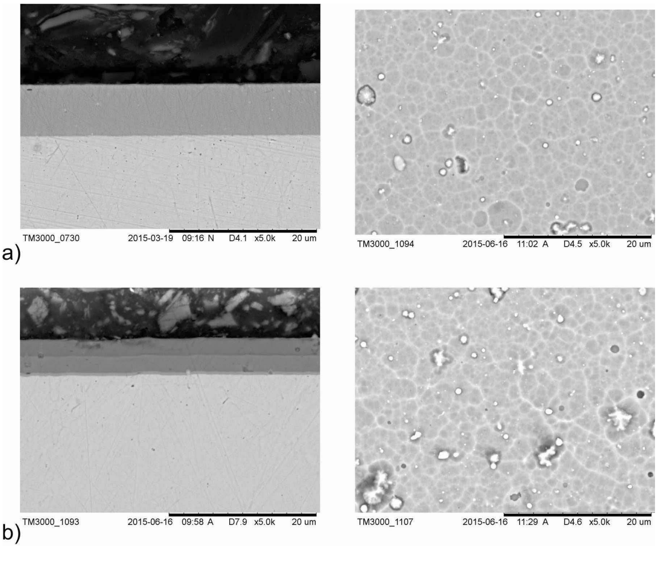


Fig. 2. Illustration of the measurement of the contact angle with liquid glass

3. Results

3.1. Characterization of hybrid layers

Photographic examinations of microstructure and surface morphology are shown in Figure 3.



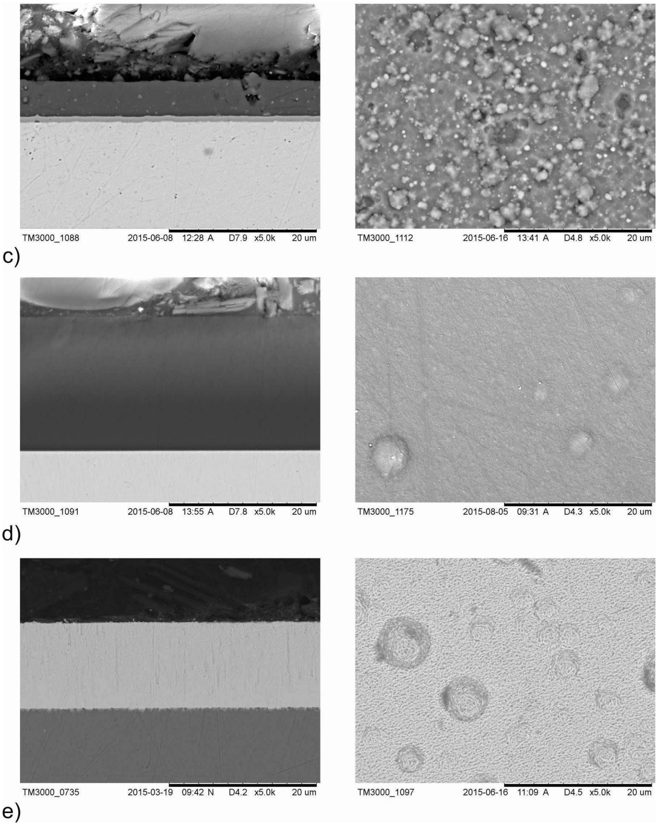


Fig. 3. The results of the observation of microstructure and surface morphology of coatings deposited on H17N2 steel: a) Cr/CrN, b) Cr/CrN/AlCrTiN, c) CrN/AlCrN/AlCrTiSiN, d) Al_2O_3, e) W

Selected PVD coatings characterized by different structural construction, surface morphology, and mechanical properties are presented in Table 3. The W and Al_2O_3 coatings produced by the EB-PVD method were characterized thickness (15 µm) three-times higher than other coatings obtained by the arc evaporation technique (µum). The presence of defects on the coating surface was observed for both deposition methods, EBPVD and Arc-PVD. However, many defects were found in coatings obtained using Arc-PVD. A larger number of defects formed by the share of the droplet phase in the deposition process cause the surfaces of these coatings to be rougher. Coatings produced by the arc evaporation method are characterized by a much larger share of the droplet phase with droplet diameters of approximately 0.1 to 2 µm. The structure of coatings obtained by electron beam evaporation are characterized by the presence of much larger defects in the form of microdrops (droplet diameter ≈ 3 to 7 µm), but their share is much smaller.

The basic mechanical properties of the deposited PVD coatings are presented in Table 3.

Table 3. Properties of the deposited PVD coatings

Coating	Thickness µm	Hardness GPa	Young modulus GPa
Cr/CrN	5.73	27 ±1.5	299 ±18
Cr/CrN/AlCrTiN	4.4	30 ±2.1	337 ±11
CrN/AlCrN/AlTiCrSiN	4.9	28 ±2.5	322 ±34
W	13.6	11 ±0.7	341 ±16
Al_2O_3	17.5	2.5 ±0.1	68 ±3

Of all the coatings deposited on the H17N2 steel substrate, the nitrides of transition metal (Ti, Cr) coatings deposited using Arc-PVD are characterized by higher values of hardness and Young's modulus ($H > 27$ GPa, $E = 300$ to 337 GPa) than are coatings produced by EB -PVD. The coating of pure metallic tungsten (W) and chromium nitride (CrN) and titanium-chromium-aluminium nitride (AlTiCrN) are characterized by acceptable adhesion to the substrate.

3.2. Characterization of the wetting angle of liquid glass

The test results of the contact angle with liquid glass for all the PVD coating are presented in Figure 4. Analysis of the results showed that all tested coatings are characterized by similar values of the contact angle of the molten glass with a temperature in the range of 700 to 800°C. With the increase in the temperature of molten glass, changes were observed in the wettability of coating surfaces. Analysis of the results of the wetting of the coating by the molten glass at a temperature range of 850–900°C and after a thirty minutes annealing at 900°C, allowed the distinguishing of the two groups of coatings that are characterized by different wettabilities. The first group include Al_2O_3 and AlTiCrN coatings, which are characterized a very low wettability by molten glass. The contact angle after the annealing process is in the range 127 to 135°. The second group include coatings characterized by very good wettability with molten glass. The contact angle with molten glass after a thirty-minute annealing process at 900°C is 42° for the Cr/CrN coating, 62° for the pure tungsten coating, and 67° for CrN/AlCrN/AlCrTiSiN coatings.

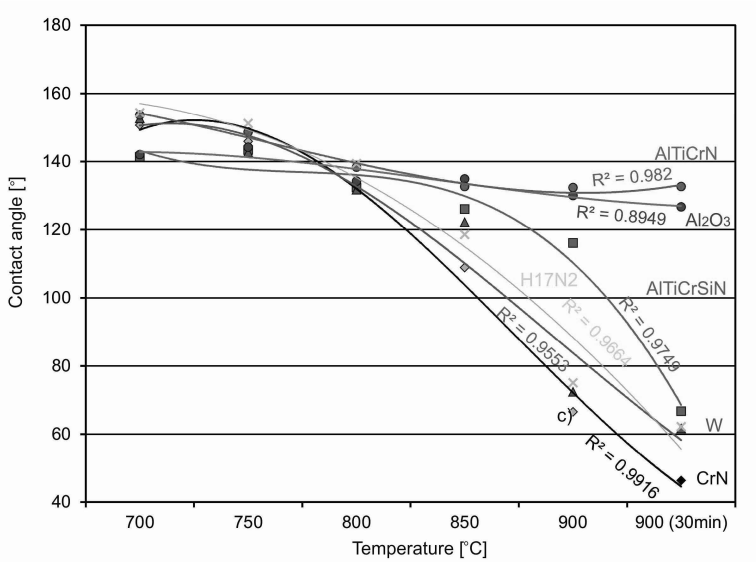
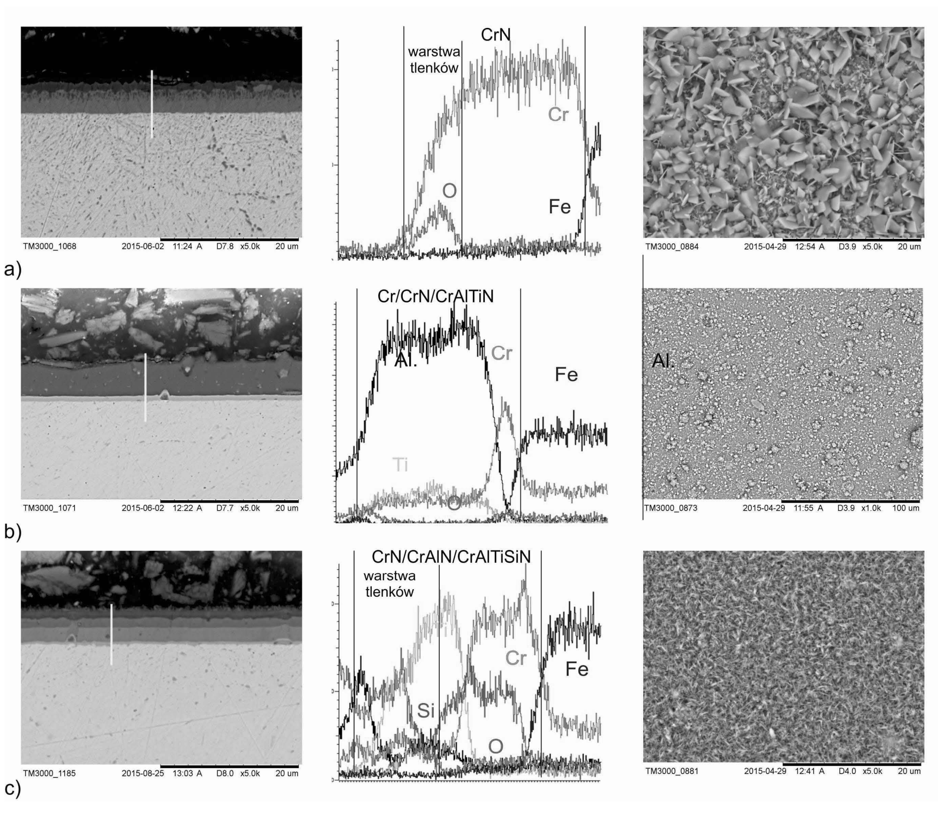


Fig. 4. The wetting angle with molten glass for all tested coatings



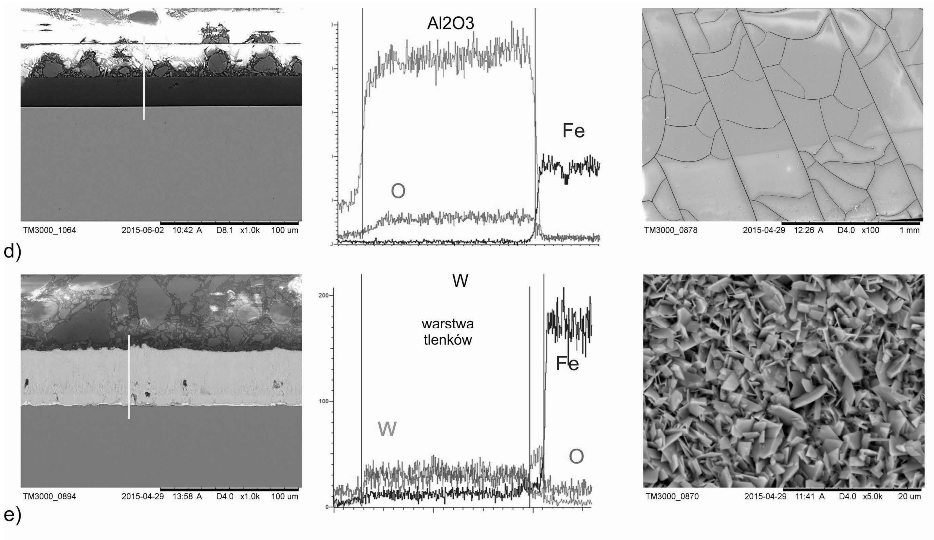


Fig. 5. Analysis of the chemical composition and surface morphology of the coating after the annealing process: a) Cr/CrN, b)Cr/CrN/AlCrTiN, c) CrN/AlCrN/AlCrTiSiN, d) Al_2O_3, and e) W

Analysis of the structure and surface of the coating after the annealing at 900°C confirmed the very low thermal resistance of the Al_2O_3 coating. The large difference in the coefficient of thermal expansion of these materials (Al_2O_3) relative to glass and steel substrates resulted in the appearance of cracks on the surface. On the surface on Cr/CrN/CrN and CrN/AlCrN/AlCrTiSiN coatings the formation of compact oxide films with a high roughness (Figures 5a and c) were observed, which significantly increases the wettability of the coating by molten glass. Similarly intense oxidation of the surface after the process of annealing at 900°C was observed for W (Fig. 5b). Only in the case of the coating of Cr/CrN/AlCrTiN were no changes observed in surface morphology and structure after the annealing process, which confirmed the very good resistance of this coating at elevated temperatures (Fig. 5a).

4. Conclusions

The studies of wettability with liquid glass at elevated temperatures were conducted on coatings with different properties that were deposited on a typical type of steel H17N2 used in the production of glass elements. Analysis of conducted research clearly shows that the AlTiCrN and Al_2O_3 coatings are materials with low wettability by molten glass in the examined temperatures. High wettabilities comparable to the base material (steel H17N2) were confirmed for CrN AlTiCrSiN and W coatings. In all three cases, there was no change in the contact angle in the temperature range of 700–800°C. This is due to the low deformation of the ball at this temperature. Above the melting point of soda-lime glass (~750°C), there is an increase in the plasticity molten glass and a change in contact angle.

The results confirmed the possibility of shaping the surface wettability by applying proper surface treatment.

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Analiza kąta zwilżania ciekłym szkłem powłok wieloskładnikowych wytwarzanych technikami PVD

Słowa kluczowe

Powłoki PVD, kąt zwilżania ciekłym szkłem.

Streszczenie

W artykule przedstawiono analizę właściwości powłok PVD dedykowanych do poprawy trwałości eksploatacyjnej narzędzi wykorzystywanych w procesie formowania elementów szklanych. Proces formowania wyrobów szklanych realizowany jest w podwyższonej temperaturze powyżej 300°C przy jednoczesnym oddziaływaniu chemicznie aktywnych mas szklanych oraz cyklicznie zmiennych obciążeń mechanicznych. Te trudne warunki procesowe znacznie zmniejszają wydajność, niezawodność narzędzi do formowania szkła. Istotnym problemem w zachowaniu jakości wyrobów szklanych jest zjawisko przyczepiania się stopionego szkła do powierzchni roboczych. Ze względu na fakt, że zniszczenia narzędzi formujących kumulują się w warstwie wierzchniej materiału, coraz częściej poszukuje się rozwiązań w zakresie obróbki powierzchniowej, których zadaniem jest przeciwdziałanie tym zjawiskom. W artykule przedstawiono wyniki badań właściwości różnych powłok wieloskładnikowych na bazie takich pierwiastków jak Ti, Cr, Al, W, C, Si dedykowanych do zwiększania trwałości matryc do formowania szkła. Metody badawcze zaprezentowane w artykule koncentrowały się na analizie morfologii powierzchni oraz mikrostruktury wytwarzanych powłok, jak również na analizie kąta zwilżania ciekłym szkłem. Analizę morfologii powierzchni oraz mikrostruktury przeprowadzono przy wykorzystaniu skaningowej mikroskopii elektronowej. Natomiast badania zwilżalności przeprowadzono metodą osadzania kropli.