06

The Physical features on the structure formation of cold spray coating Ti−TiN

© A.E. Chesnokov, A.V. Smirnov

Khristianovich Institute of Theoretical and Applied Mechanics of the Siberian Branch of the RAS, Novosibirsk, Russia
E-mail: chae@itam.nsc.ru

Received February 3, 2026
Revised March 24, 2026
Accepted April 7, 2026

The article presents the results of an experimental study of the structural features of a Ti−TiN cold spray coating, depending on the method of mixture preparation and subsequent heat treatment. The structure and elemental composition of the resulting coatings were investigated, and the quantitative phase composition of the coatings was estimated. It was shown that the titanium nitride content in a cold spray coating obtained by spraying a powder mixture using ultrafine TiN particles was 1.5 times higher than that of a coating obtained using decamicrons of titanium nitride particles. The mechanism for changes in the structure of cold spray coatings during heat treatment is presented.

Keywords: cold spray, composite material, titanium, titanium nitride, X-ray analysis.

DOI: 10.61011/TPL.2026.07.63833.20644

One of the most promising materials for fabrication of protective surface layers capable of withstanding mechanical and chemical impacts is titanium nitride, which is a refractory compound of a transition metal, which limits the methods of its application. Titanium nitride is known to be formed from a chemical reaction of titanium with nitrogen at a temperature above 500 °C [1,2]. One of the methods for producing titanium nitride-based coatings is high-speed flame spraying of metallic titanium powder. It should be emphasized that titanium is more susceptible to oxidation (compared to the nitrogen saturation process), therefore, the disadvantages of this method of coatings fabrication include the presence of phases such as $TiN_{0.3}$, Ti_2O_3 and TiO_2 in the material, which are the cause of defects in the structure because of lower hardness and strength compared to titanium nitride [3,4]. Specifics of the cold gas spraying (CS) process is the possibility of applying surface layers of particles of unlimited thickness without their significant heating [5]. Therefore, spraying particles characterized by low plasticity of the material (carbides, borides, oxides, etc.) will be similar to the process of abrasive surface treatment, and higher time of the particle flow interaction with the surface of the substrate leads to its erosion, while the number of fixed particles does not increase [6]. To create more favorable conditions for the formation of CS coatings from non-deformable materials, it is necessary to use mixtures of metal powders with non-metallic powders or composite particles. The study is focused on investigating the structure of composite CS coatings of Ti−TiN depending on physical characteristics of the applied material and thermal effect on the coating.

The paper studies titanium composite coatings obtained by CS method. To apply the coatings, a mixture of titanium powder (grade PTS 1) with the addition of 25 and 50 wt.% titanium nitride was used. To prepare the powder mixture, a *V*-shaped mixer and „Activator-2Sl“planetary mill were used. The granulometric composition of the powders was determined using a laser diffraction particle analyzer LS 13 320. A specific area of the powder surface was measured by Brunauer−Emmett−Teller method (BET) using „SORBI M“ instrument. The coatings were applied using a CS setup (ITAM SB RAS) using an axisymmetric Laval nozzle with a length of 140 mm and critical and exit section diameters of 2.8 and 6.5 mm, respectively. Air was used as the working gas, the pressure in the chamber was maintained at 4.0 MPa, the temperature in the chamber was 400 °C. The distance from the nozzle exit to the substrate was 30 mm, the nozzle moved relative to the substrate at a rate of 25 mm/s. Steel plates of grade ST20 with dimensions 40 × 40 mm and a thickness of 3 mm were used as a substrate. Three series of samples with coatings of different thicknesses (from 0.15 to 3 mm) were obtained for each powder mixture. High-temperature treatment of the coatings was carried out for 2 h at a temperature of 550 °C in a nitrogen atmosphere in PM-1700AV [7,8] muffle furnace. Sample preparation for studying the structure of the material was carried out using Presi systems. Microstructure images were made using EVO MA15 scanning electron microscope equipped with X-Max 350 energy-dispersive X-ray spectrometer. Quantitative assessment of structural defects and determination of the elements content were carried out using ten micrographs of the prepared section in the ImageJ software package. X-ray phase analysis was performed using D8 ADVANCE diffractometer.

Ultrafine particles of titanium nitride powder were obtained by plasma-chemical reduction from a mixture of titanium tetrachloride, ammonia and hydrogen [9]. Micron- and decimeter-sized titanium nitride particles were obtained

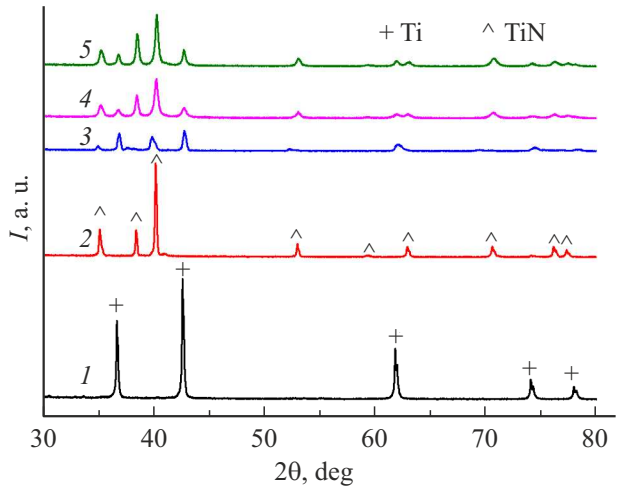


Figure 1. X-ray diffraction patterns of initial (*1*, *2*), spheroidized (*3*) and machined (*4*, *5*) particles of titanium (*1*), titanium nitride (*2*, *3*), mixture of Ti + 25 wt.% TiN (*4*), mixture of Ti + 50 wt.% TiN (*5*).

by processing titanium powder in a nitrogen plasma jet [10]. X-ray diffraction patterns of spheroidized particle samples showed peaks corresponding to titanium and titanium nitride compound (Fig. 1). The characteristics of particles are given in Table 1.

It should be taken into account that during coatings deposition, the powder utilization factor is affected by the presence of particles in the sprayed material smaller than 5 μm (Table 1), which are characterized by low kinetic energy [11] or high microhardness of the particles. Thus, the formation of coatings by CS method using only spheroidized particles, in the phase composition of which the main element is a titanium nitride compound, is difficult. Therefore, for CS coatings deposition, powder mixtures of titanium and titanium nitride were prepared using a *V*-shaped mixer and a planetary mill.

Steel balls with a diameter of 5 mm and a total mass of 160 g were used as grinding media for mechanical treatment of a mixture of titanium and titanium nitride powders, and their acceleration was 117g. The material was processing in the air. Mechanical treatment of Ti+25 wt.% TiN powder mixture (average particle size of titanium nitride 1.26 μm) was carried out for 3 min (mixture 1) [12]. Ti+50 wt.% TiN powder mixture (average particle size 49 μm) was prepared in an *V*-shaped mixer for 4 h (mixture 2) and by grinding in a planetary mill under the same mechanical treatment parameters as for mixture 1 for 60 s (mixture 3). X-ray diffraction analysis of the prepared powder mixtures showed the presence of titanium and titanium nitride phases (Fig. 1). Table 2 shows the characteristics of powder mixtures prepared for spraying.

To study the structure of the coatings, thin sections were prepared, micro-photos of which are presented in Fig. 2.

In Fig. 2 it is evident that the coatings are formed by particles deformed during impact with the surface layer with clearly defined boundaries. One of the important characteristics of the coatings is the absence of cracks, discontinuities and pores. The formation of discontinuities is usually associated with changes in characteristics of key physical parameters of particles during sputtering (Fig. 2). It should be noted that such defects are stress concentrators and, with prolonged use of the material, develop into cracks, which contributes to a reduction in its service life. Table 3 gives an overall volume of discontinuities, cracks and pores.

Thus, from Fig. 2 and Table 3 it follows that the number of defects in the coating depends on the size of the titanium nitride particles used in the spraying powder mixture and the method of its preparation under constant application parameters. Preparing powders for spraying in a high-energy mill with an average particle size of titanium nitride of 1.26 μm allows obtaining the densest coating with the lowest defect content.

Fig. 3 shows a micrograph of the coating structure after high-temperature treatment. Using X-ray diffraction analysis of the coating surface after heat treatment, the presence of peaks corresponding to the titanium phase, titanium nitride, and a small amount of titanium dioxide was registered (Fig. 4). The formation of the titanium dioxide compound phase is associated with the interaction of residual oxygen in the furnace working chamber with the heated titanium surface.

High-temperature treatment of coatings leads to a redistribution of defects (Fig. 2, *d* and Table 3), and an increase in the volume of discontinuities is observed. A distinctive feature of CS process is the ability to produce coatings without significant overheating of the particles during their

Table 1. Characteristics of particles

Powder	Average size d_{pm}, μm	Standard deviation, μm	Specific surface S_{sp}; standard deviation, g/m^2
Titanium (PTS 1)	101.00	27.00	0.28; 0.09
TiN	1.26	0.59	11.73; 3.54
TiN (spheroidized)	49.00	25.00	0.15; 0.06

Table 2. Characteristics of powder mixtures

Powder	Size of particles d_{10}, μm	Average size d_{pm}, μm	Size of particles d_{90}, μm	Standard deviation, μm
Mixture 1	7.28	37.49	78.92	32.48
Mixture 2	10.98	48.98	103.70	36.90
Mixture 3	66.19	145.90	242.20	70.39

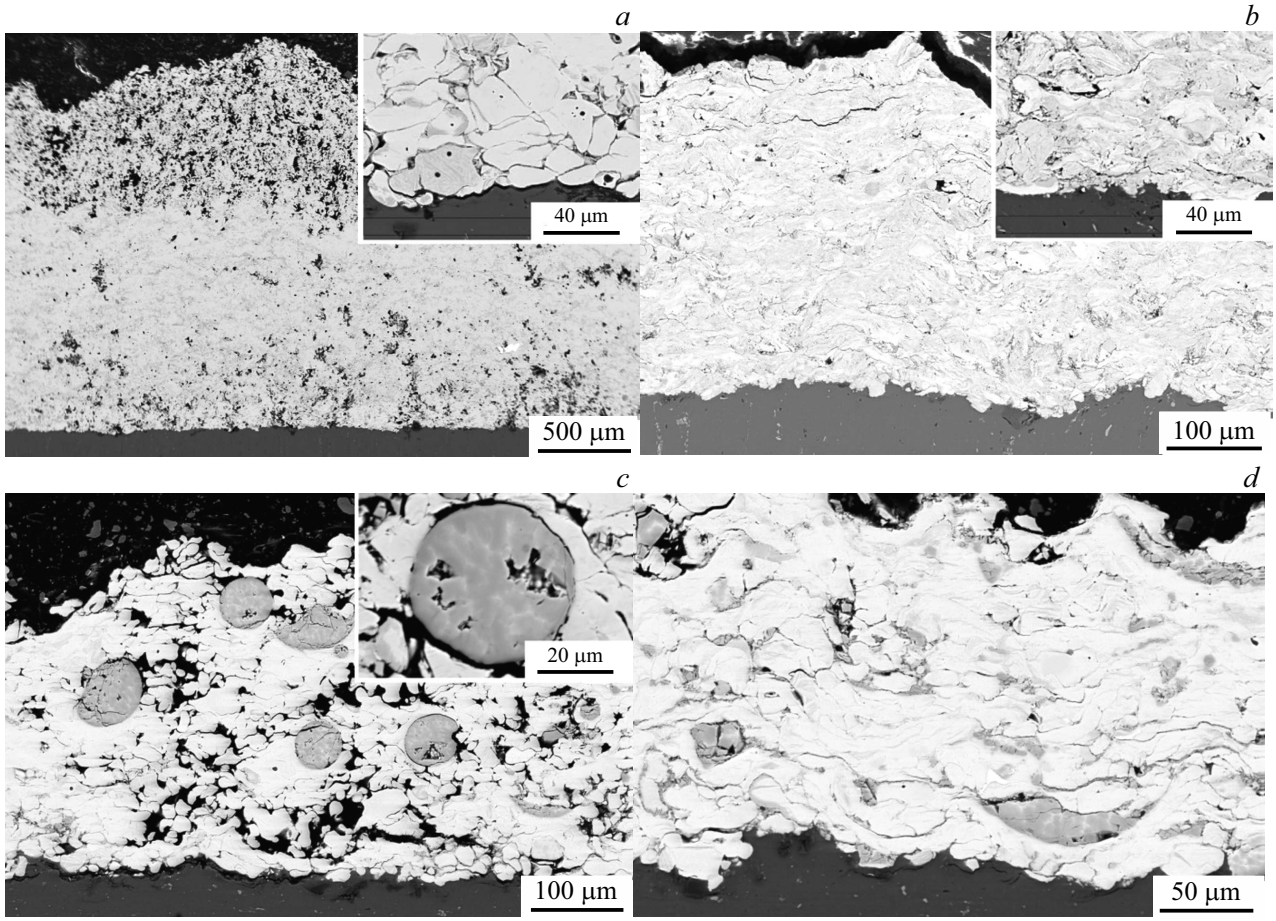


Figure 2. Micrographs of the cross-section of CS-coatings of various composition. *a* — titanium, *b* — Ti + 25 wt.% TiN (mixture 1), *c* — Ti + 50 wt.% TiN (mixture 2), *d* — Ti + 50 wt.% TiN (mixture 3).

deposition. Therefore, the mechanism for the formation of coatings consists of cold plastic deformation of particles upon impact with an obstacle, which is similar to the process of cold hardening. This results in loose packing of particles (interparticle voids are formed), as well as to the occurrence of numerous stresses in the coating material. The diffraction patterns (Fig. 4) on the surface of the initial powder and on the deposited coating show lower intensity and broadening of the reflections of the main peak, which is associated with a decline in the value of coherent scattering region because of particles deformation at the moment of high-speed impact during their deposition. It is known from the literature that minor heating (up to 200–300 °C) reduces the deformation resistance for some titanium alloys by 40–50 %, increases plasticity, sharply reduces the springback of the metal, and a further increase in temperature to 550–700 °C improves its deformability [13,14]. Titanium is a chemically active element, therefore on the surface of individual particles there is a thin layer of titanium dioxide, which is characterized by reduced plasticity (coefficient of linear expansion of titanium $9.2 \cdot 10^{-6}\,\mathrm{K}^{-1}$, titanium dioxide $1.4 \cdot 10^{-5}\,\mathrm{K}^{-1}$), high microhardness and, accordingly, is particularly brittle in relation to the base material (titanium). We also note the resulting magnitude of the force that occurs during the increase in gas pressure located in the pores and micropores of the coating when the material is heated. This force is directed deep into material, resulting in separation of

Table 3. Total volume of CS-coating defects

Composition coating	Initial coatings			Heat-treated coatings		
	Total volume defects; standard deviation, %	Volume discontinuities; standard deviation, %	Volume of pores; standard deviation, %	Total volume defects; standard deviation, %	Volume discontinuities; standard deviation, %	Volume of pores; standard deviation, %
Titanium	16.84; 6.84	4.520; 1.210	12.32; 5.21	17.27; 7.03	15.50; 5.37	1.77; 0.52
Ti + 25 wt.% TiN (mixture 1)	1.73; 0.35	0.013; 0.004	1.71; 0.48	3.24; 1.58	1.16; 0.58	2.08; 0.74
Ti + 50 wt.% TiN (mixture 2)	13.66; 5.45	1.060; 0.240	12.59; 5.02	12.42; 4.81	11.20; 4.83	1.22; 0.63
Ti + 50 wt.% TiN (mixture 3)	3.50; 1.14	0.040; 0.012	3.46; 1.74	5.78; 2.24	4.11; 1.45	1.67; 0.84

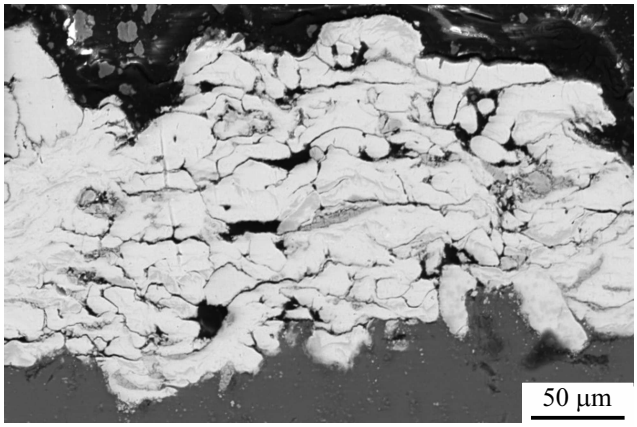


Figure 3. Micrograph of a cross-section of CS coatings after high-temperature treatment of Ti + 50 wt.% TiN composition (mixture 3).

the material along the surface boundaries of individual deformed particles, which leads to the formation of cracks. This explanation does not contradict the mechanism of crack formation in the structure of a titanium alloy during interaction of titanium with gases [15–17].

The titanium nitride content in the coating before and after heat treatment found using ImageJ software is given in Table 4.

From Table 4 it can be seen that the content of titanium nitride in the coating depends on the size of its particles and method of preparing the powder mixture for sputtering. The highest content of titanium nitride (25.36 %) in the coating was achieved when sputtering the mixture 1. Thermal treatment of coatings in a nitrogen atmosphere allows for a slight increase in the nitrogen content in the coating, which is proved by results of the analysis of the material elemental composition (Table 5).

The paper sheds light on the microstructure of CS coatings obtained using various composite powder materials based on titanium nitride. It was demonstrated that the number of defects in CS coating is influenced by the size of the titanium nitride particles used in the powder mixture and the method of its preparation under constant sputtering parameters. Preparing powders for sputtering in a high-energy mill with an average particle size of titanium nitride of 1.26 μm allows obtaining the densest coating (porosity less than 2 %), in which the titanium nitride content is 1.5 times greater than in the coating obtained from a mixture prepared in a *V*-shaped mixer using larger titanium nitride particles. The changes that occur in the coatings structure after heat treatment are explained.

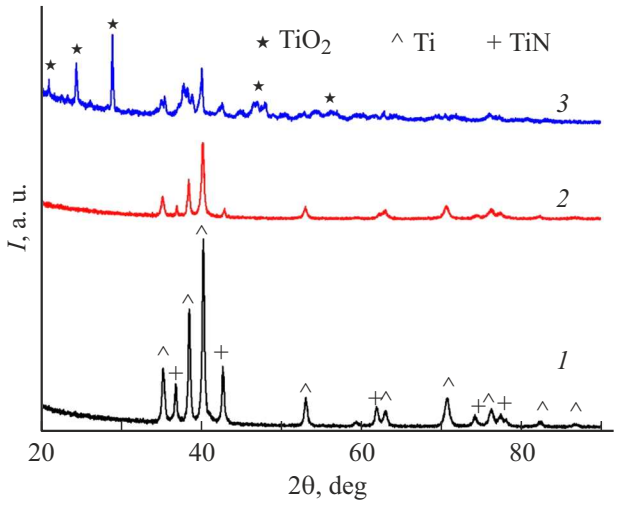


Figure 4. Diffraction patterns of Ti + 50 wt.% TiN (mixture 2). *1* — sputtering powder, *2* — CS-coating before heat treatment, *3* — after heat treatment.

Table 4. Titanium nitride content in CS coatings before and after heat treatment

Coating	Titanium nitride content; standard deviation, %		
	Ti + 25 wt.% TiN (mixture 1)	Ti + 50 wt.% TiN (mixture 2)	Ti + 50 wt.% TiN (mixture 3)
Initial	25.36; 9.25	15.60; 7.54	18.02; 9.84
Heat-treated	26.51; 10.04	17.25; 8.43	20.25; 10.32

Table 5. Content of elements in CS coatings before and after heat treatment (in wt.%)

Element	Ti + 25 wt.% TiN (mixture 1)		Ti + 50 wt.% TiN (mixture 2)		Ti + 50 wt.% TiN (mixture 3)	
	Initial coating	Heat treated coating	Initial coating	Heat treated coating	Initial coating	Heat treated coating
N	9.44	13.76	3.68	7.13	4.77	13.83
Ti	90.56	86.24	96.32	92.87	95.23	86.17

Acknowledgments

The authors wish to thank V.S. Shikalov for preparation of experimental samples.

Funding

The work was carried out as part of the state assignment of ITAM SB RAS (project code 124021500014-4) and using the equipment of the Core Shared Research Facility „Mechanics".

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] G.V. Samsonov, I.M. Vinitsky. *Tugoplavkie soedineniya* (Metallurgiya, M., 1976) (in Russian).
[2] G.G. Gnesin, I.I. Osipova, G.D. Rontal, V.S. Samoilov, V.P. Yaroshenko, *Keramicheskiye intsrumental'niye materialy* (Tekhnika, Kiev, 1991). (in Russian)
[3] Z. Mao, J. Ma, J. Wang, B. Sun, J. Coat. Technol. Res., **6**, 243 (2009). DOI: 10.1007/s11998-008-9105-9
[4] M.A. Jing, D. Yan, J. Hu, X. Zhang, Y Li, Trans. Nonferrous Met. Soc. China, **23** (4), 1011 (2013). DOI: 10.1016/S1003-6326(13)62560-1
[5] A.P. Alkhimov, S.V. Klinkov, V.F. Kosarev, V.M. Fomin, *Kholodnoye gasodinamicheskoye napyleniye: teoriya i praktika* (Fizmatlit, M., 2010) (in Russian).
[6] V.F. Kosarev, S.V. Klinkov, A.E. Chesnokov, A.V. Smirnov, V.S. Shikalov, J. Phys.: Conf. Ser., **1945** (1), 012072 (2021). DOI: 10.1088/1742-6596/1945/1/012072
[7] S.S. Kiparisov, Yu.V. Levinsky, *Azotirovaniye tugoplavkykh metallov* (Metallurgiya, M., 1972) (in Russian).
[8] Yu.M. Lakhtin, B.N. Arzamasov, *Khimiko-teoreticheskaya obrabotka metallov* (Metallurgiya, M., 1985) (in Russian)
[9] M.R. Predtechensky, A.N. Cherepanov, O.M. Tukhto, I.Yu. Koval, A.V. Alekseev, Liteischik Rossii, № 3, 28 (2010) (in Russian).
[10] A.E. Chesnokov, A.V. Smirnov, *A method for producing spherical hollow particles of deca-micron size based on titanium nitride by plasma-chemical synthesis*, patent RU № 2858536 C1 (2025).
[11] V.V. Kudinov, *Plasmenniye pokrytiya* (Nauka, M., 1977) (in Russian).
[12] V.O. Drozdov, A.E. Chesnokov, A.N. Cherepanov, A.V. Smirnov, J. Phys.: Conf. Ser., **1945** (1), 012005 (2021). DOI: 10.1088/1742-6596/1945/1/012005
[13] O.P. Solonina, S.G. Glazunov, *Titanoviye splavy. Zharoprochniye titanoviye splavy* (Metallurgiya, M., 1976) (in Russian).
[14] E.M. Lazarev, Z.I. Kornilova, N.M. Fedorchuk, *Okisleniye titanovykh splavov* (Nauka, M., 1985) (in Russian).
[15] B.A. Matyushkin, A.I. Gorshkov, Svarochnoye proizvodstvo, № 4, 11 (1976) (in Russian).
[16] N.M. Pul'tsin, *Vzaimodeistviye titana s gazami* (Metallurgiya, M., 1969) (in Russian).
[17] B.B. Chechulin, S.S. Ushkov, I.N. Razuvaeva, V.N. Goldfain, *Titanoviye splavy v mashinostroyenii* (Mashinostroyeniye, M., 1977) (in Russian).

Translated by T. Zorina