'DOI: https://doi.org/10.37434/tpwj2023.12.03

METAL-CORED WIRES BASED ON TITANIUM AS MATERIALS FOR ADDITIVE MANUFACTURING OF PARTS

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ABSTRACT

The paper shows the possibility of manufacturing metal-cored wires based on high-strength titanium alloys of different compositions (Ti–5Al–5Mo–5V–1Fe–1Cr and Ti–5Al–5Mo–5V–4Nb–1.5Cr–1Fe–2.5Zr systems), an alloy based on medical grade titanium (Ti–13Zr–13Nb system) and structural titanium VT6 alloy (Ti–6Al–4V system), reinforced with TiC particles. The technological moments of the experimental production of metal-cored wires by the method of drawing and subsequent pulling are shown. A study was conducted on using these materials as a filler metal in WAAM technology both in the methods of argon arc as well as electron beam surfacing.

KEYWORDS: high-strength titanium alloys, metal-cored wire, WAAM, TIG, xBeam 3D Metal Printing

INTRODUCTION

Additive manufacturing technologies became an alternative to conventional methods of part manufacturing with high added cost, including those, related to aerospace industry, and biomedical products, which require very complex and individual approaches at small volumes. Additive manufacturing allows producing these necessary component parts in a short time at a constant cost.

Among different materials titanium-based alloys are more and more often used in Wire Arc Additive Manufacturing (WAAM) method due to their application in the aerospace industry for fabrication of airframe structures. Strong, such as Ti-6Al-4V (VT6), and high-strength two-phase titanium alloys are in great demand in the aerospace industry, due to their high specific strength, corrosion resistance, damage resistance and compatibility with composite materials from graphite fiber [1]. Among the different accessible approaches, the WAAM process has a number of advantages over other 3D printing technologies, including the high coefficient of material utilization (99 % [2]) and energy efficiency (~ 70 % [3], lower capital equipment costs, and high productivity of the printing process [4].

At present, there are a number of titanium-based solid wires, produced by industry. Commercial wires from pure titanium are used as filler material for TIG welding of parts from titanium alloys with a low con-

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based on titanium with a higher content of alloying elements. Ultimate strength of metal of such wires is not higher than 870 MPa. Manufacture of sound solid wires from high-strength titanium alloys is very complicated, as higher strength of the metal does not allow producing wires without defects. Attempts at producing wires from Ti–5Al–5Mo–5V–1Fe–1Cr alloy (VT22), with higher than 1000 MPa strength, were made earlier [5]. Cracks and tears were found on this wire surface, which can be a source of deposited metal contamination, and, consequently, deterioration of its quality. That is why there is no commercial production of wires from high-strength titanium alloys.

tent of alloying elements. There are also solid wires

Despite a large number of studies on part manufacturing by WAAM method, the majority of them are focused only on producing parts with solid wire application. Investigations on flux-cored wire application to produce parts from high-strength titanium alloys by this method are practically absent. Flux-cored wire application to produce parts by WAAM method allows manufacturing parts from high-strength titanium alloys and greatly increasing the range of titanium alloys, which can be used to make parts by this method.

One of the important and complex technological properties in metal-cored wire manufacture is preparation of their core, namely the metal component, i.e. the powder proper. At present in Ukraine there are two methods to produce titanium-based powders.

By the first method crushing of alloyed titanium is performed using the method of thermochemical



Figure 1. Schematic of a drawing machine for producing titanium flux-cored wire: *1* — cassette; *2*, *3* — roller stands; *4* — dosing unit; *5* — U-shaped strap; *6* — drum; *7* — page

embrittlement with hydrogen application — Hydrogenation-Dehydrogenation (HDH) method [6]. In this process the metal blocks of titanium are subjected to hydrogenation to increase titanium brittleness. Brittle titanium block is crushed mechanically and sieved by fractions. The totality of technological solutions for production of such titanium powders allows producing a denser material with a lower content of impurities, which increases the powder quality and improves its morphology.

Another process to produce powders based on titanium alloys is the method of plasma atomization of the billet - Plasma Rotating Electrode Process (PREP) [7]. The method consists in the following: the electrode of the alloy which is sputtered, turns around a horizontal axis, and its free end is melted by the plasmatron. The molten metal drops fall off the rotating electrode, and crystallize in free flight before colliding with the sputtering chamber walls. The chamber, where the electrode rotates and atomization occurs, should have an atmosphere protecting from oxidation. It allows producing powders with a high surface purity. Powder particles are smooth and spherical, and the average particle size is 200 µm, the yield of particles of 50 to 500 µm size is equal to 75 %. One of the advantages of powders produced by this method is their high fluidity and purity (low oxygen content) [8].

THE OBJECTIVE OF THE WORK,

considering the complexity of making sound solid wires based on strong and high-strength titanium al-

loys, was production and application of metal-cored wires based on these alloys for additive manufacturing of parts, where powders prepared by HDH and PREP methods, are used as the core.

RESULTS AND THEIR DISCUSSION. PRODUCING METAL-CORED WIRE

Development and production of titanium alloy based metal-cored wires is performed by the methods of drawing and subsequent pulling through the dies in a unit designed for producing of titanium flux-cored wires (Figure 1). Used as the sheath is 0.2 mm titanium foil of VT1-00 grade. Depending on powder type, the respective charge dosing unit is used. When using powder, produced by PREP method, the granules inside the formed tube are not in a sufficiently good contact. That is why, when the arc hits such a wire, the granules are released, and a greater part of them does not fall into the weld pool, but sticks to the tungsten electrode, disturbing the process stability. For this reason, their shape is changed before that through deformation.

Charge dosed feeding into the formed tube is performed through the guide nozzle of the dosing hopper, equipped with a gate regulator (Figure 2, a). To ensure prior compacting of the charge, and the required value of overlapping of the strip edges, a rotating die is used, which is mounted after the last pair of forming rollers. The direction of the die rotation should coincide with the direction of strip overlapping for tube closing (Figure 2, b, c). Further pulling of the formed



Figure 2. Process of forming and further pulling of metal-cored wire: a — charge dosing; b — sheath closing scheme; c — rotating die

 Table 1. Chemical composition of VT22 titanium alloy, wt.% (GOST 19807–91)

Ti	Al	V	Мо	Fe	Cr	[O]	[H]	[N]
Base	4.4–5.7	4.0-5.5	4.0-5.5	0.5-1.5	0.5–2.0	0.18	0.015	0.05



Figure 3. Schematic of a unit for layer-by-layer TIG deposition using metal-cored filler wire

wire is conducted using a set of dies, with 0.1 mm step. The wire is fed into the die so that it is positioned with the seam facing outside on the drum, as tension of outer fibers leads to additional closure of the seam, and prevents distortion (corrugation).

APPLICATION OF METAL-CORED WIRE BASED ON VT22 TITANIUM ALLOY

A 2.9 mm metal-cored wire based on VT22 titanium alloy of PPT-22 grade with fill factor of 65 % was developed earlier [9]. This wire core includes powder of high-strength VT22 titanium alloy and flux of CaF_2 -SrF₂-BaF₂ system in the amount of 7 % relative to the filler. This wire is designed for TIG welding and surfacing of VT22 titanium alloy.

This wire was also applied as filler wire at multilayer deposition. Experimental three-layer deposition was performed, using the produced filler wire



Figure 4. Macrosection of the produced three-layer sample made with flux-cored filler wire based on titanium alloy VT22

with granules of high-strength VT22 titanium alloy. Deposition of high-strength titanium alloys is made difficult, primarily, by their high content of alloying elements, such as aluminium, vanadium and molybdenum (Table 1). More over, compared to regular alloys these titanium alloys are more sensitive to interstitial impurities, such as nitrogen and carbon, as the solubility of the latter in BCC lattice of titanium β -phase is much lower. They are more prone to development of chemical and physical heterogeneity in the cast metal and HAZ during deposition, which may result in formation of brittle interlayers. Correct selection of deposition modes in most cases allows producing sound welded joints of high-strength titanium alloys.

The deposition process was conducted in the unit for TIG welding/surfacing titanium alloys, which was adapted for the process of layer-by-layer deposition (Figure 3). The deposition process was conducted in the following mode: $I_w = 200 \text{ A}$, $U_a = 12 \text{ V}$, $V_w = 8 \text{ m/h}$, $V_f = 30 \text{ m/h}$; $L_a = 4 \text{ mm}$.

Experimental deposition using the produced wire demonstrated a stable running of the process (without spilling of unmelted granules), which pointed to sufficient density of the charge and its uniform distribution



Figure 5. Roentgenogram of the deposited sample



Figure 6. Microstructure of a three-layer sample made with application of flux-cored filler wire based on VT22 titanium alloy: a — base metal; b — weld metal; c — fusion zone

along the wire length. As a result, a sound three-layer sample (Figure 4) without any pores along its entire length (Figure 5) was produced.

VT22 alloy, on which TIG welding was performed with flux-cored wire application, consists of large polyhedral primary β -grains. Alongside equilibrium grains, non-equilibrium grains are present in the base metal structure, and the grain shape factor (grain length to width ratio) is in the range of 1–3, grain width being 1–2.5 µm (Figure 6, *a*).

In the deposited metal the degree of alloying by β-stabilizing elements is somewhat lower compared to VT22 alloy due to weld metal dilution by commercial titanium of the flux-cored wire sheath. It most probably leads to precipitation of dispersed particles of α' -phase from β -solid solution. Formation of a fold in β -grains is probably attributable to delamination of β-solid solution into volumes enriched and depleted in certain alloying elements. Formation of a substructure is observed in the weld metal (Figure 6, b). Substructure appearance is attributable to polygonization under the impact of internal stresses in the welded joint. Residual stresses are caused by temperature gradients, phase transformations in the heating zone at welding thermal cycle, as well as processes of liquid metal solidification in the weld area. At substructure formation, rotation of individual volumes of coarse β -grain to a small angle relative to another one, takes place. Presence of a subgranular structure promotes increase of strength and lowering of ductility. Intensity of β -phase decomposition in the HAZ is much lower than that in the weld, which is indicative of higher stability of β -solid solution in VT22 alloy than in the weld metal, due to a high content of β -stabilizing elements (Figure 6, c).

After mechanical testing the deposited sample ultimate strength, equal to 1025 MPa, was determined. Gas content in the deposited metal is not higher than their permissible values in the base metal; [O] = 0.098 wt.%, [H] = 0.0027 wt.%, [N] = 0.014 wt.%.

APPLICATION OF METAL-CORED WIRE BASED ON TITANIUM ALLOY T120

Multilayer samples were also produced using fluxcored filler wire based on high-strength titanium alloy T120 (Ti-5Al-5Mo-5V-4Nb-1.5Cr-1Fe-2.5Zr system), developed at PWI [11]. 2.2 mm metal-cored wire with 50 % fill factor was used as the filler. This wire core was from powder of T120 titanium alloy, produced by HDH method. Deposition was performed by nonconsumable electrode argon-arc process (Figure 2) in the following mode: $I_w = 160-180$ A, $U_a = 12$ V, $V_w = = 6$ m/h, $V_f = 40-45$ m/h, $L_a = 2$ mm. A five-layer sample was produced as a result of the conducted work (Figure 7).

Deposited metal ultimate strength is equal to 878.7 MPa, impact toughness is 15.1 J/cm², which is much lower than the values of base metal mechanical characteristics: $\sigma_t = 1145.8$ MPa, KCV = 30.6 J/cm². This is attributable to presence of pores in the deposited metal. In order to prevent pore initiation in the deposited metal, it is necessary to introduce the flux component into the core metal. The high-strength two-phase titanium alloys and the produced joints of these alloys are also subjected to mandatory heat treatment, which, in its turn, allows improving the level of mechanical characteristics [12].

APPLICATION OF METAL-CORED WIRE BASED ON Ti–13Zr–13Nb TITANIUM ALLOY

Titanium alloy application in endoprosthetics has been the most intensively developing over the last thirty



Figure 7. General view of a five-layer sample after the process of deposition with flux-cored filler wire based on T120 titanium alloy



Figure 8. General view of a nine-layer sample after the process of deposition with metal-cored filler wire based on Ti alloy of Ti–Zr–Nb system

years due to unique characteristics of their biocompatibility and the most optimal combination of mechanical and biomechanical properties [13]. The main requirements to manufacturers of titanium alloys for medical purposes include a complex of mechanical properties: low modulus of elasticity, high strength and fatigue fracture resistance. Such a characteristic as modulus of elasticity deserves special attention. Over the recent years, the need to produce alloys for endoprostheses with a low modulus of elasticity has become important, which is related to application of cementless fixation of prostheses and lowering the risks of development of diaphyseal dysplasia and bone fracture after long-term use of the prostheses. These are exactly β -alloys which often have the modulus of elasticity lower than the values for $(\alpha+\beta)$ -alloys for medical purposes, while being characterized by a high strength. Nontoxic alloying elements are β-stabilizers of titanium or alloy strengthening elements. Therefore, one can judge the wide possibilities for their application in different concentration ranges exactly for creation of biocompatible titanium alloys [14, 15]. Zirconium-containing titanium alloys and ternary Ti-Zr-Nb alloys have the most promising combination of strength and modulus of elasticity. Binary Ti-Zr alloys are characterized by strength in the range of 600-1450 MPa and modulus of elasticity of 72-110 GPa, while Ti-Zr-Nb compositions have the strength in the range of 600-1000 MPa and modulus of elasticity in the range of 58–80 GPa, which is much better than the combination of the same parameters in VT6 alloy [16].

Having analyzed the urgency of application of low-modulus titanium alloys for endoprosthetics and technologies of manufacturing finished products from them, which envisage availability of rods for fixation, or other loaded and massive elements, a conclusion was made about the rationality of WAAM method as an alternative to the currently-available additive manufacturing methods. To achieve the defined objective, a metal-cored wire was developed (3.0 mm diameter, 62 % fill factor), where the core is a powder of 50–70 μ m size from titanium alloy of Ti–13Zr–13Nb system. The powder was produced earlier by HDH process.

The produced metal-cored wire based on a titanium alloy for medical purposes was used to conduct multilayer TIG deposition in a predefined mode: $I_w = 210 \text{ A}, U_a = 12.7 \text{ V}, V_w = 8 \text{ m/h}, V_f = 34 \text{ m/h}, L_a = 3.5 \text{ mm}. \text{ As a result, a nine-layer sample was pro$ $duced (Figure 8).}$

The deposit height is 15.2 mm, and width is 11.8 mm. At present, analysis of the produced sample metallography, assessment of its mechanical properties (ultimate strength and modulus of elasticity) and determination of gas content in the deposited metal are performed.

APPLICATION OF METAL-CORED WIRE BASED ON Ti-6Al-4V-40 % TiC POWDER

Some of the few disadvantages of titanium alloys are their low hardness and insufficient wear resistance during operation of structures made from them. Such disadvantages can be overcome by development of titanium-based metal matrix composites, reinforced by hard high-modulus phases. One of such examples is reinforcement of the titanium alloy matrix by high-modulus and light particles of titanium carbide (TiC) [17]. To improve the dispersity and homogeneity of titanium carbide powders, they are made by powder metallurgy method [18].

Both in the case of high-strength titanium alloys, and of alloys reinforced by hard particles, there is the problem of producing solid section wires. So, the objective was to obtain metal-cored wire based on strong VT6 alloy (Ti–6Al–4V system), reinforced by



Figure 9. Configuration of xBeam[®] 3D Metal Printing process: xGun design schematic (*a*); configuration of a heated zone in the feeding point during deposition (*b*); photo of the actual deposition process (*c*) [21]



Figure 10. General view of the samples: A — single-layer; B — multilayer

TiC particles. As a result of experiments, test wire of 3.0 mm diameter (fill factor of 62 %) with a core from Ti-6Al-4V + 40 % TiC powder was produced.

Advanced additive manufacturing technology called xBeam 3D Metal Printing (Figure 9), developed by "Chervona Hvilya" Company [19] demonstrated the possibility of manufacturing titanium alloy products with a controlled microstructure, stochiometric chemical composition and also with desirable mechanical characteristics [20]. Deposition with experimental wire was conducted by this technology.

By the results of experiments on 3D printing using metal-cored wire, single- and multilayer samples were produced (Figure 10).

One of the essential advantages of xBeam process is the possibility of simultaneous melting of the filler wire and the substrate, due to the peculiarities of the electron beam. However, at application of metal-cored wire as the filler, part of the electron beam hitting the wire, instantly melted its thin sheath, resulting in the powder being released, scattered and not coming to the weld pool. For this reason, not all the powder, but just part of it got into the weld metal, leading to deviations from the predicted chemical composition of the deposited bead metal. More over, the spilled powder partially penetrated into the electron gun discharge chamber and onto the cathode, leading to failures, which considerably improved the deposition process stability, resulting in an even greater deterioration of the uniformity of TiC component distribution in the deposited metal.

In order to prevent the abovementioned problems, the configuration of relative placement of process elements (profiled electron beam, wire and substrate) was set up so that the electron beam did not directly fall on the wire. For this purpose the substrate was placed closer to the gun. In this configuration, all the electron beam energy hit the substrate, creating a wider and deeper melt pool, than it is usually done using solid section wire. Thus, the flux-cored wire was immersed into the molten pool and melted there, while preserving the sheath in the solid state above the pool during the entire melting process. Due to that, the sheath prevented powder release before it entered the liquid metal of the weld pool. This solution ensured a rather stable process of wire melting. Yet such a solution became possible under the condition of excess heat input into the substrate. However, the influence of such an overheating on the structure still needs to be studied.

CONCLUSIONS

Development of metal-cored wires based on titanium alloys for different purposes solves a relevant problem in the field of modern additive technologies, namely their application allows producing sound multilayer samples. The proposed metal-cored filler wires based on high-strength titanium alloys, as well as alloys for medical purposes, can be used as filler materials in additive manufacturing of parts from titanium alloys both at TIG, and at electron beam 3D printing processes.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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SUGGESTED CITATION

S.L. Schwab, R.V. Selin, S.V. Akhonin, M.M. Voron, D.V. Kovalchuk (2023) Metal-cored wires based on titanium as materials for additive manufacturing of parts. *The Paton Welding J.*, **12**, 24–30.

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Received: 20.10.2023 Accepted: 26.12.2023

