МЕТАЛЛУРГИЯ

A study was made of the aspects of forming highly resistant coatings in the surface zone of tool steels and solid carbide inserts by a two-stage method. At the first stage of the method, pure Ta or Nb coatings were electrodeposited on samples of tool steel and solid carbide insert in a molten salt bath containing Ta and Nb fluorides. At the second stage, the electrodeposited coating of Ta (Nb) was subjected to carburizing or boriding to form carbide (TaC, NbC) or boride (TaB, NbB) cladding layers.

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FORMATION OF HIGHLY RESISTANT CARBIDE AND BORIDE COATINGS BY A TWO-STAGE DEPOSITION METHOD

Introduction

Wear of parts and units in many modern machines is aggravated by their high loads and temperatures, at which simultaneous metal oxidation, diffusion, fatigue, abrasion, and etc. can occur. Wear of metal surfaces is a big problem for many types of machinery and a rather wide variety of solutions has been proposed for it. Specifically, application of coatings such as TiC or TiN coatings on cutting tools to extend their service life is a widely recognized and used practice. Two methods of depositing – PVD (physical vapour deposition) and CVD (chemical vapour deposition) are normally used to form these coatings. Higher temperatures involved with CVD, as compared with PVD, ensure a good bond of the coating to the substrate, though result in a higher decarburisation of the base-metal thus slightly affecting resistance properties of the transition layer between the coating and the base metal. A coating composed of a highly resistant phase, such as TiC, provided by PVD or CVD does not appear to be an obvious choice. Tantalum carbide (TaC) is known to have a higher wear resistance (a relative wear resistance of 1.50%) as compared with TiC (0.61%) though it has a lower microhardness number, 16000 MH/m^2 for TaC and 30000 MH/m^2 for TiC respectively [1]. Carbides of other elements, e. g. NbC, HfC, etc., appear to be rather promising from the point of view of a higher service life under heavy wear and high temperatures. However, higher melting points of Ta (2,996 °C) and Nb (2,477 °C) as against Ti (1,668 °C) do not allow for providing a proper TaC or NbC coating by PVD or CVD methods. That's why coatings composed of carbides and borides of the above elements must be formed by the electro-chemical method [2, 3].

The analysis disclosed in [2, 3] shows that metals composing highly resistant carbides can be electrically deposited on a base metal out of their fluorides in a molten eutectic mixture of specific salts. Basically, this method represents the high-temperature electrolysis. Electrodeposited ions of these metals form a very clean coating on a base metal. This «cladding» layer is strongly adhered to the base metal [3]. The method disclosed in [2, 3], firstly, makes possible a higher resistance of deposited layers through the use of certain strengthening elements, such as carbon, nitrogen, boron or silicon, that are generally retained either interstitially or in solid solution in the base metal. When the temperature of the base metal is sufficiently high, it ensures a thermal diffusion of these strengthening elements from the base metal to the layer of the deposited metal, where a cladding layer of carbides, borides or silicides is actually formed by a phase structural transformation. Some works, including [4], disclose a two-stage method of forming cladding layers of «clean» metals on a base metal by electrodeposition of certain metals in a molten salt bath and their subsequent carburizing or boriding. It produces highly resistant cladding layers on a base metal which are featuring a unique combination of higher wear resistance, heat resistance, hardness, and other properties.

Further to the disclosures provided in [4], the present work studies aspects of forming highly resistant cladding coatings of carbides and borides on tool steels and solid carbide inserts for cutting tools by two-stage method electrochemical (electrolytic) depositing the Nb and Ta layers on surface samples and subsequent carburizing or boriding the deposited metal layers. It should be noted that according to specific conditions under which this or that unit or part operates, the proposed method may be implemented to carry out electrolytic deposition of V, Cr, W, Mo, Ti, Zn, Hf and provide a highly resistant layer of carbides or borides of the above refractory metals on a base metal with subsequent proper carburizing or boriding. The application of the invented method looks promising for improving the service life of a wide range of parts utilized in the mining-metallurgical and machine-building equipment and that, in fact, determines the relevance of the undertaken research.

Research techniques and materials

Nb and Ta were deposited on test samples of M4 tool steel (SAE J438b) and solid carbide insert (WC-Co composite alloy) in a molten salt bath (eutectic mixture of Li, K, or Na fluorides) placed in a nickel container. Potassium heptafluoroniobate and potassium heptafluourotantalate added into the molten salt bath were used as «donor» agents providing Nb and Ta, respectively. Plates of Nb or Ta were used as the anode. Samples of tool steel and solid carbide insert were used as the cathode. The temperature of the molten salt bath was 700 °C to 900°C. The process of electrolysis was carried out at a current density of 5 mA/cm^2 to 100 mA/cm^2 for a time period ranging from 30 minutes to 3 hours, and under the protective atmosphere of argon at a pressure slightly above the atmospheric pressure.

To suppress formation of coarse dendrites of the deposited Nb and Ta and to obtain a uniform continuous layer of the electrodeposited metal, the initial stage of electrodeposition was carried out as a stepwise process with a current density and deposition time varying according to a set pattern per step. For instance, the pattern for electrodeposition of Ta was as follows: step 1–350 mA/cm^2 (1s); step 2–200 mA/cm^2 (5s); step 3–150 mA/cm^2 (2s). Then, the steps were repeated, with the time period per step increasing from 15 minutes to 2 hours, until the layer of Nb or Ta reached the required thickness.

Boriding of samples coated with Nb or Ta was carried out in the protective argon atmosphere in a molten salt bath of an anhydrous fused salt electrolyte comprising at least one halide from the group of alkali metal halides or alkaline earth metal halides and a boron or carbon bearing compound. Boriding conditions: current density from 200 to 300 mA/cm^2, at temperature of 800 °C for a time period from 1 hour to 5 hours.

When subjected to solid-phase carbonization (pack carburization), samples coated with pure Nb or Ta were immersed into containers with crystalline powder graphite. The containers with samples were placed into a vacuum oven (residual pressure of ~10–4 torr (1.5 kPsi). The carbonization of samples was carried out at 1,000 °C for 5 hours. Subsequently, the samples were subjected to cooling down to 700 °C for about 45 minutes. The pack carbonization in a protective atmosphere (0–4.0% H_2 + Ar) proved to be successful on several sets of samples.

Gas carburizing of samples coated with pure Nb or Ta, placed in a quartz tube, was carried out at 1,000 °C with a gas mixture of 0.5–2.0% CH_4 + H_2 in CO_2 atmosphere. The samples were held at the above temperature for 1 to 4 hours and then cooled down to 700 °C with a gas mixture of 0.5–2.0% CH_4 + H_2 in CO_2 atmosphere for not less than one hour.

The accelerated tests were performed to evaluate service durability of the obtained coatings and for these purposes the electrodeposited coating of TaC on cutting tool inserts was tested in the machining operations of certain classes automotive engine parts. Tests were taken as follows:

- Two involved machining operations on gray cast irons (mode 1, 2). The first was a rough bore turn on a Ford stator support made from G3500 (BHN = 207–255) (mode 1), while the second was a finish turn on an oil pump support made from G2500 (BHN = 170–229) (mode 2).
- The third machining operation used a rough turn on an axle shaft made from G 51500 forged steel with BHN = 208–302 (SAE J404) (mode 3).

In each case the results of the machining tests with the TaC coated inserts were compared to the results obtained with standard coated tool bits (Ti(C, N) + aluminum oxide + TiN outer layer) used by this machine parts in their normal machining operations.

Optical microscopy and scanning electron microscopy (SEM) methods were used to study structures of the electrodeposited «pure» metal (Nb and Ta) coatings, carbides and borides coatings, as well as structures in the surface area of the base metal. The phase composition of coatings was studied using the X-ray structural analysis. The elements distribution in the surface area of samples was observed by a SEM with an X-ray spectrometer (Oxford Instruments, UK).

Results and discussions

The disclosed herein experimental electrodeposition of Nb or Ta in a molten fluoride salt bath was performed at high temperatures, that's why when depositing atoms were diffusing, according to [4], deep into the base metal from its surface not forming any defects between the continuous layer of the deposited metal (Nb or Ta) and the base metal. Optical microscopy and SEM observation of the electrodeposited Nb –

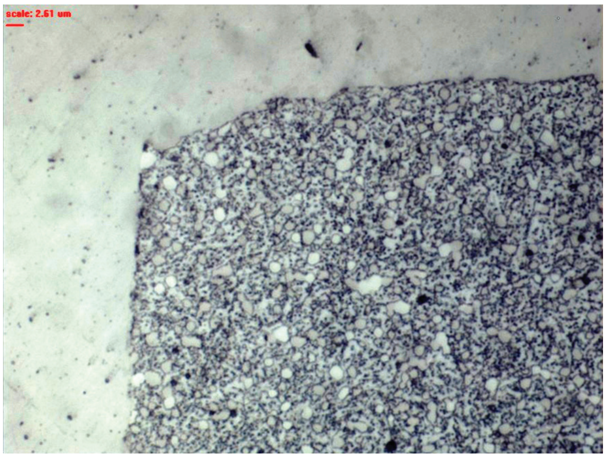


Fig. 1. Microstructure of the initial Nb – coating on a tool steel sample. x1000

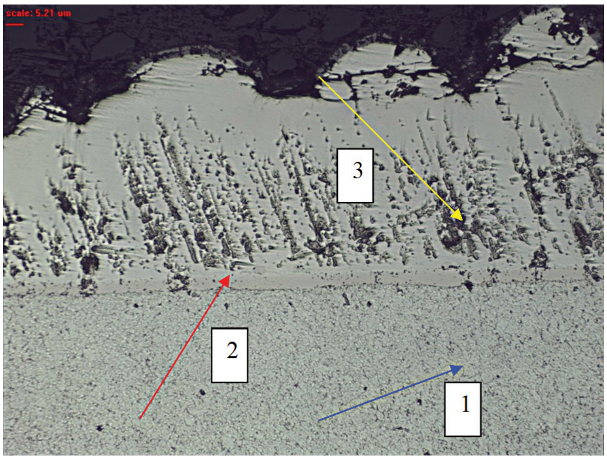
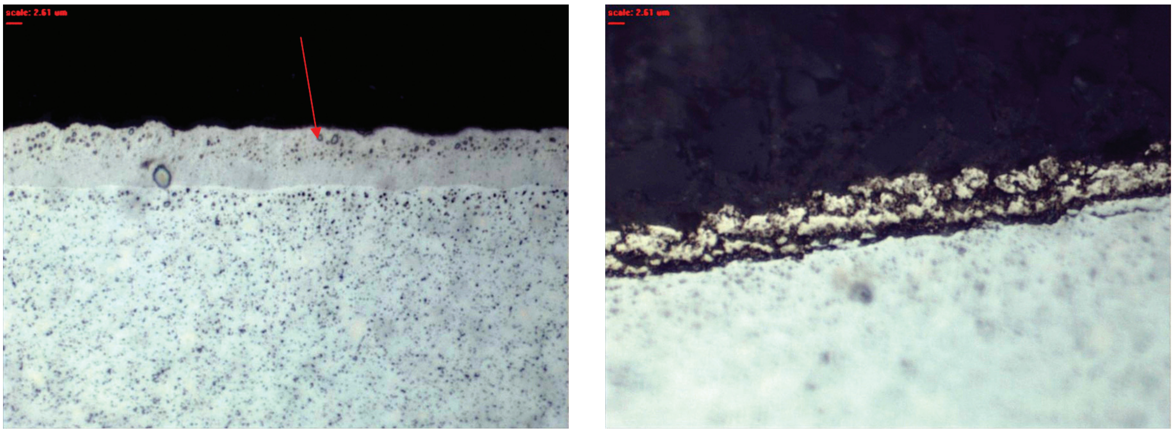


Fig. 2. Microstructure of a NbC-Nb-coating on a tool steel (blue arrow *1*), a transition zone (red arrow *2*) between the NbC-Nb-coating and the base metal (tool steel), a typical appearance of NbC formed by gas carburizing (yellow arrow *3*). x500

layer on tool steel indicate, as an example, that the Nb metal layer is bonded to the base metal free of any interface defects (Fig. 1). The transition zone formed between the uniform Nb – layer and the tool steel in the process of high temperature electrolytic deposition, containing (according to the results of X-ray spectral analysis) up to 84% by weight Nb and 10% Fe, reveals no defects (Fig. 1) and provides the high-strength bond between the Nb – cladding layer and the base metal. Grains in the Nb – coating were observed to transform into coarse formations at high temperatures in the result of secondary recrystallization. To suppress formation of a coarse-grain structure in the Nb cladding layer there was applied a purposely designed stepped method depositing that covered the initial and subsequent stages of the electrolytic process (until the metal layer achieved the required thickness).

Gas carburizing of the Nb metal coating on a tool steel produces a transition zone up to 8 µm thick (Fig. 2) bonding the NbC cladding layer and the base metal. The X-ray analysis indicates that the applied method of gas carburizing ensures transformation of about 80% of the Nb coating into niobium carbide, i. e. a big portion of it remains untransformed.

In the case of the stepped method of Ta electrodeposition, a Ta – coating with a relatively smooth surface is formed in the surface zone of the solid carbide insert (Fig. 3, *a*). Then this Ta – coating is transformed into TaC – coating by carburizing (Fig. 3, *b*). This is clearly identified by the gold-like color of the resulted coating and by the X-ray analysis. Carbides of other composition, for example, Ta_2C with a lower carbon content, cannot be formed by the applied method of carburizing. The TaC – cladding layers formed by this method had a higher density, however the strength joint between this cladding and the base metal was rather low. This suggests that TaC – coating is not high-strength bonded to the base metal in this case. Nevertheless, the two-stage method has certain advantages over other methods. One of the advantages lies in the freedom from decarburization in the surface zone of the base metal covered with a Ta layer depos-



a *b*

Fig. 3. Microstructure of Ta – coating (*a* – indicated arrow) electrodeposited on the surface of solid carbide insert and TaC – coating (*b*) formed by gas carburizing. x1000

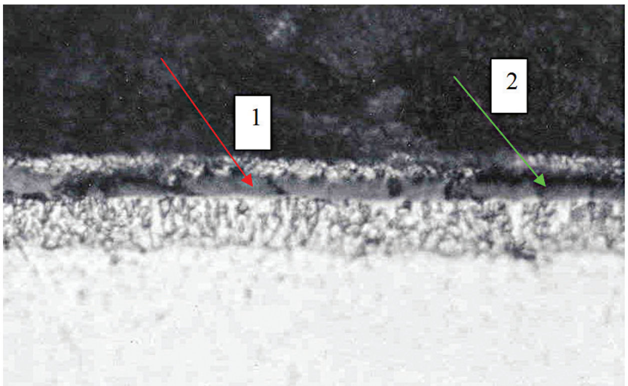


Fig. 4. Microstructure of a TiC – coating formed by the CVD method, featuring a brittle δ-phase (red arrow *1*) in the form of isolated inclusions and bands appeared in the surface zone in the result of local decarburization. Green arrow *2* points to a crack in the sub-surface band of a δ-phase formed in the result of a high brittleness this phase. x1000

ited by the above method and in the suppression of formation of a brittle δ-phase through an intensive outsourcing of carbon atoms both in the case of a solid phase carbonization and in the case of a gas carburizing. It should be pointed out that decarburization of the surface zone of the base metal during high temperature processes, such as CVD of WC-Co composite tool inserts, reducing resistance of the surface zone, results from a poor «donor» inflow of carbon atoms into this zone.

Fig. 4 shows a typical structure of a TiC – coating formed by gas deposition (CVD), with readily apparent crystals of a brittle δ-phase distributed across the bulk of the coating and adjacent to its surface in the form of bands which are disrupted in places.

When subjected to accelerated testing, tools with solid carbide inserts with a TaC coating formed by gas carburizing exhibited a lower durability in test rough turn on a stator support (mode 1) and an axle shaft (mode 3) it was 25% and 50%, respectively, of the durability of standard tool inserts. For the finish turn on an oil pump support (mode 2) the gas carburized samples gave about 50% of the tool life of the standard tool bits, while the pack carburized samples gave about 128% of the tool life compared to the standard. Consequently, the application of tools with solid carbide insert with TaC coating is promising for finishing turn on automotive engine parts owing to lower cutting forces.

A series of experiments performed in the frame of the present study has demonstrated that the invented method is also good for providing high quality boride coatings (NbB and TaB) on tool steels and solid carbide insert. Discussion of results obtained for NbB and TaB coatings on tool steels and solid carbide insert is limited by the size of the present article and will be detailed in separate publications.

A comparison between the invented method and other well known and widely used methods, such as CVD and PVD and a so called thermal diffusion method (TD) [5], has shown the following. The CVD and PVD methods, as it has been mentioned above, have been practiced for many years and have been demonstrating a sufficiently high productivity. They produce coatings of a controlled thickness, featuring a very smooth surface. High temperatures involved with the CVD method ensure a good bond between the coating and the base metal though may lead to surface decarburization of the base metal [4]. The PVD method involves rather low temperatures (<500 °C) thus avoiding any decarburization of the surface of the base metal. However this method cannot provide the high-strength bond between the coating and the base metal via a transition zone. This is because in the case of the PVD method the cladding layer of carbides forms directly on the surface of the base metal that has carbon and alloying elements already bound in carbides and other phases, that's why diffusion of elements in the contact zone between the coating and the base metal cannot take place. At the same time, the TD process involves diffusion between the coating and the base metal [5]. For thermal diffusion, the samples are immersed into a molten salt bath and kept there at temperatures from 870 to 1040 °C for 1 to 8 hours. The metal constituents of a carbide phase available in the molten salt as ions combine with carbon contained in the tool steel. Carbide layers are formed by diffusion taking place in the surface zone of the base metal and over a certain distance of it. The experimental results show that the TD carbide coatings have a better adhesion to the base metal compared with the CVD and PVD coatings. From the other hand, in the TD process, the unidirectional diffusion of carbon from the base metal leads to a partial decarburization of its surface thus affecting the bond strength between the coating and the base metal. In the case of hard-alloy inserts, decarburization leads to formation of a η-phase in the surface zone, which has the ratio of $(Co_6W_6)C$ and $(Co_3W_3)C$ type and a lower hardness number as compared with WC [1]. The invented two-stage method provides not only a better bond strength but also avoids decarburization of the surface the base metal and formation a η-phase owing to continuous outsourcing of carbon atoms, as distinct from the TD method. Carbide coatings formed by the invented method are dense and porosity free, because the intensive diffusion of the outsourced carbon into the metal coating and the transition zone during the process of carburizing ensures formation of the carbide phase across the bulk of the coating and extends its area towards the base metal. Besides, the invented method avoids probability of pores forming in the base metal adjacent to the transition zone due to a massive outflow of carbon atoms from the base metal into the coating, an inherent probability of the TD method.

One of major disadvantages of the TD method, as compared with the PVD and CVD methods, is the problem of controlling the thickness and the surface quality of the deposited carbide coatings. That's why in addition to the close control over the electrolytic deposition process variables the TD method involves subsequent manual cleaning of the deposited carbide coating in order to remove any salt buildup from the surface and to polish the surface. Whereas the invented two-stage method guarantees the required thickness and smoothness of the surface of the deposited carbide coating as well as other quality characteristics through the implementation of the above described stepped pattern of electrochemical deposition at the first stage of the process and by feeding a special additive into the molten salt bath at the stage of electrolytic process. Thickness of the coating is regulated through a strict control over the time of electrodeposition of carbide-forming elements. Besides, for emergency cases caused by violation of the process technology (depletion of the bath, uncontrolled variation of the deposition conditions, etc.), when the coating deposited by the invented two-stage method reveals a poor quality (rough) surface, the invented method offers the electrolytic polishing of the electrodeposited carbide metal coating. Compared to the manual polishing to be given to the deposited carbide coating within the TD method, the electrolytic polishing of carbide metal coatings on samples offered by the invented method has obvious advantages allowing to save material costs and time.

As shown above, the utilization of solid carbide inserts with a TaC – cladding layer deposited by the invented method is promising for cutting tools that are used for finishing automotive engine parts of certain groups. A lower durability of a tool coated with TaC by the invented method that was demonstrated during a rough machining, i. e. under a higher specific load, results from a higher brittleness of the deposited coating. Modern coating technologies offer combined coatings with two and more sub-layers of carbides and other phases aimed at ensuring a better performance of the coatings, and particularly at preventing their brittle fracturing. Thus, a combination of TaC, TiC with aluminum oxide (and, possibly, with other compounds and alloys) can give very hard and chemically stable coatings which are resistant to cracking even under substantial loads. For example, a combination of TiN – coating, sufficiently bonded to the base metal, with «strengthening» TaC – coating and a protective outer layer of aluminum oxide (protecting from high temperature oxidation) appears to be appropriate. Given the above, one of major directions for a future research in the frame of the invented two-stage method can be formation of combined coatings featuring high performance characteristics and a high quality smooth surface.

The study has shown that the invented method can be used as a method allowing to improve performance characteristics of not only tool steels and cutting tools, but it also has considerable promise for replaceable parts equipment in the mining and metallurgical industry and in the machine-building branch, for example, equipment of motor vehicles – internal combustion engines (ICE).

Ball mills for iron ore grinding have recently started to use combined rubber-steel linings [6]. The application of the invented method to provide a hardened layer on metal inserts (abrasion resistant steel and iron) of combined rubber-steel linings can substantially improve their resistance to abrasion-impact-corrosive wear and, thus, extend the life of these linings and of other rubber-steel replaceable parts in the mining and metallurgical equipment.

Wear of rolls and guides in rolling mills [7, 8] is still a pressing problem. Thereby, utilization of the invented method, for instance, for hardening working surfaces of rolls in cogging and section mills which are operating under high temperatures and specific loads, in combination with the traditionally used methods of hard-facing can contribute to solving this problem.

Traditionally, for a variety of ICE parts (crankshafts and camshafts, bushes, pins, valves, cylinder sleeves, rocker arms, push rods, etc.), different methods are utilized to improve wear resistance of working surfaces of these parts, these include gas and solid-phase carbonization, nitrogenization, cyanidation combined with thermal treatment, in some cases it can be laser thermal treatment, for example [9]. Taking into account the need for a precise thickness of the hardened layer on working surfaces of combustion engine parts and the need that the base metal of these parts maintains its high ductility and resistance to crack formation, the application of the invented method in this area appears to be very promising too.

Conclusions

From the studies disclosed herein covering formation of highly resistant coatings in the surface zone of tool steels and solid carbide insert for cutting tools, which are deposited under different conditions by the invented two-stage method, and from the analysis of application potential of this method the following conclusions can be drawn:

1. It has been found that formation of cladding layers consisting of highly resistant carbide (boride) phases in the surface zone of the samples under study is determined by carbon (boron) atoms outsourcing rather than by their massive diffusion from the base metal.

2. It has been determined that the carbide (boride) coatings deposited by the disclosed method have a higher specific density (free of pores, subsurface cracks and other defects) and a better bond to the base metal.

3. It has been shown that the intensive outsourcing of carbon (boron) atoms prevents decarburization of the surface zone in the material under study – tool steel and solid carbide insert for cutting tools.

4. It has been found that the required thickness and high surface quality of the coating provided by the invented method are insured by the controlled conditions of the electrochemical deposition, including conditions at the initial stage of the process.

5. It has been determined that the application of the invented method looks promising for producing strengthened working surfaces on replaceable parts in the mining mining-metallurgical equipment, on rolls and guides of cogging and section mills, and on parts of internal combustion engines (ICE).

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