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DIFFUSION EFFECT OF PLASMA-SPRAYED Ti-N COATINGS IN COPPER ALLOY DIE CASTING MOLDS

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The effectiveness of thin plasma coatings with titanium nitride (TiN) applied by the method of condensation in ion baths (IB) on the working surface of molds under the pressure of copper alloys (steel 4Kh5MFS and 5KhNM) was investigated. It has been shown that coating with a thickness of up to 5 μm significantly increases the durability of molds: before the first regrinding by 1.5–2.5 times (3–5 thousand cycles versus 2 thousand without coating), and the core life before failure by 5–6 times (not less than 12 thousand cycles). It has been established that after removing the coating (when regrinding to a depth of ≥20 μm), the drying function is preserved due to the diffusion of titanium in the near-surface steel balls during thermal cycling. Titanium, which diffuses, creates dispersed inclusions of a foldable structure (Ti-N and Ti-V-N) with a size of 2…10 μm, which plays the role of the essential phase, moving between the dislocation and the moving support of the thermal fatigue. The microhardness of the surface ball after operation and regrinding increases up to 750…800 MPa (versus 450…480 MPa for uncoated steel). The phenomenon of the mechanism of "self-adhesive" value for the structure of cerated diffusion of titanium and the creation of non-metallic inclusions of optimal size has not been described before in the literature with ion-plasma coatings and is still new approach to increasing the resource of molds for casting under the pressure of aggressive copper alloys.

INTRODUCTION

In addition to the general requirements [1–7], plasma coatings used to protect copper alloy die-casting molds must meet specific requirements: low thermal conductivity, the ability to withstand thermal changes in an aggressive environment, and high corrosion and scale resistance. Coatings made of refractory compounds, primarily titanium nitride, best meet these requirements [1, 2].

Titanium nitride was chosen as a protective coating for a number of reasons:

– high resistance to destruction under significant fluctuations in temperature and stress;

– maintaining high strength characteristics (modulus of elasticity, microhardness) at elevated temperatures;

– low thermal conductivity;

– inertness to adhesion with copper alloys in the range of 20…1000 °C;

– high resistance to high-temperature corrosion and oxidation;

– availability and low shortage of consumables (titanium, nitrogen).

The available literature has studied in detail the properties of Ti-N coatings themselves and their impact on wear resistance and service life before the first regrinding. However, there is virtually no data on the behavior of the near-surface layers of tool steel after complete removal of the coating during operation and multiple regrindings, nor on the possible diffusion of titanium into the bulk of the metal and its role in the continued performance of molds.

The aim of the work is to establish the reasons for a five- to six-fold increase in the overall service life of press molds with thin plasma TiN coatings after the protective effect of the coating itself has been exhausted.

MATERIALS AND METHODS OF THE STUDY

The objects of the study were the forming parts of die casting molds for copper alloys made from 4Kh5MFS and 5KhNM steels, as well as specimens cut from them. The specimens were cut from the forming parts of the molds, which, after heat treatment according to the conditions listed in Table 1 and grinding, were coated using a Bulat-3T installation at a nitrogen partial pressure of 1 Pa and a substrate temperature of 500 °C with a titanium nitride coating no more than 5 μm thick. The specimens were examined before and after coating application, as well as after use.

Coatings were applied to laboratory test samples and injection mold components using ion bombardment condensation. Coatings produced by this method are characterized by high stability of properties, low porosity, and good adhesion to the substrate.

The coating appears as a light, non-etching coating A strip coated with nital has a smooth interface with the steel. The coating is followed by a transition zone, which appears as a highly etched layer 5…6 μm thick. X-ray microanalysis, conducted after coating application to determine the titanium distribution, revealed that most of the titanium is contained within the coating itself. Some Ti is present in the transition zone. No titanium is detected in the matrix (Fig. 1).

After the first regrinding, after 3,000 presses, a large number of small, randomly distributed inclusions (Figs. 2, 3) measuring 2…4 μm are observed in the working surface. These inclusions have a pinkish and lilac tint and sharply blackened edges, as illustrated well in Fig. 4.

After 12 thousand pressings, a small number of inclusions measuring 8…10 µm, located along the grain boundaries, are observed in the working surface.

The influence of partial pressure of nitrogen on the thermal endurance of the coating

Steel grade	Pressure, Pa				
	uncovered	$3\cdot10^{-3}$	$3\cdot10^{-2}$	$4\cdot10^{-1}$	1
	thermal endurance				
4Kh5MFS	2000	3000	5000	9500	12000
5KhNM	2000	3500	5000	9000	11500

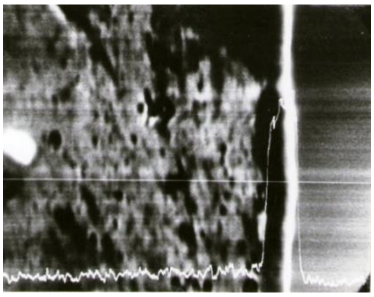


Fig. 1. Microdistribution of titanium in the coating, transition zone and surface layer before operation

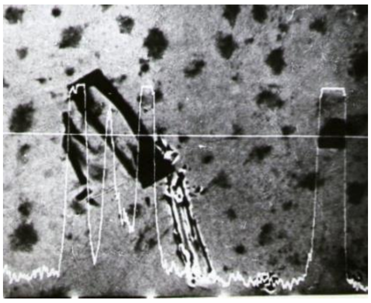
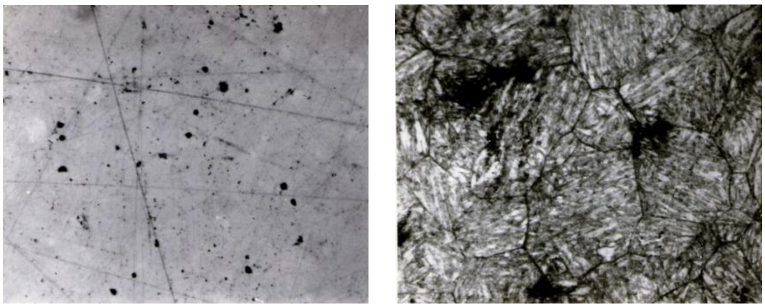
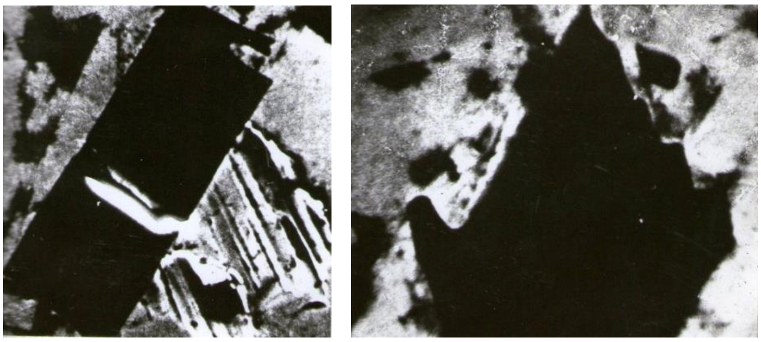


Fig. 2. Microdistribution of titanium in inclusions formed during operation (after removal of a surface layer 20 µm thick), ×2000



a *b*

Fig. 3. Microstructure of the working surface after operation for 3 thousand press-ins (20 µm layer removed): a – not etched, ×500; b – etched with nital, ×500



×5000 *×6000*

Fig. 4. Inclusions in the surface layers of mold parts formed during operation

RESULTS AND DISCUSSION

When comparing the microstructure of the working surface after operation for 3 and 12 thousand pressings (see Figs. 3, 5), it should be noted that there is a significant increase in the grain size and the size of inclusions, accompanied by a reduction in their number.

Microspectral analysis carried out on the Cambscan installation of one of the typical inclusions on the working surface of a sample cut from a part made of 4Kh5MFS steel after operation, in reflected electrons (Fig. 6,b) and in the characteristic rays Ti_{ka}, Cr_{ka}, Fe_{ka}, Si_{ka}, Mo_{ka}, V_{ka}, N_{ka} showed the presence of titanium, nitrogen, and vanadium in the composition (see Fig. 6).

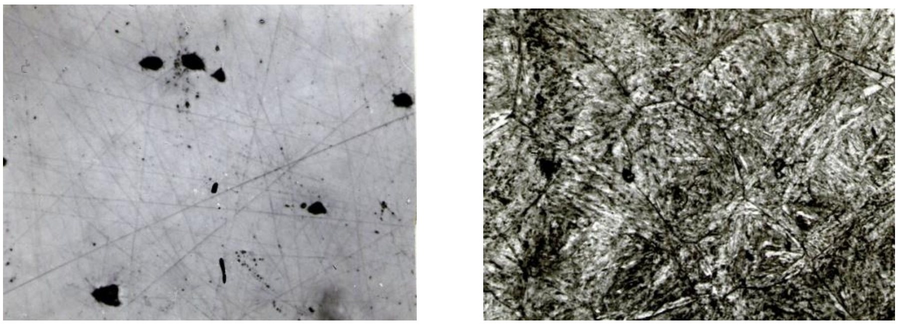


Fig. 5. Microstructure of the working surface after operation for 12 thousand press-ins (~ 80 μm layer removed): a – not etched, ×500; b – etched with nital, ×500

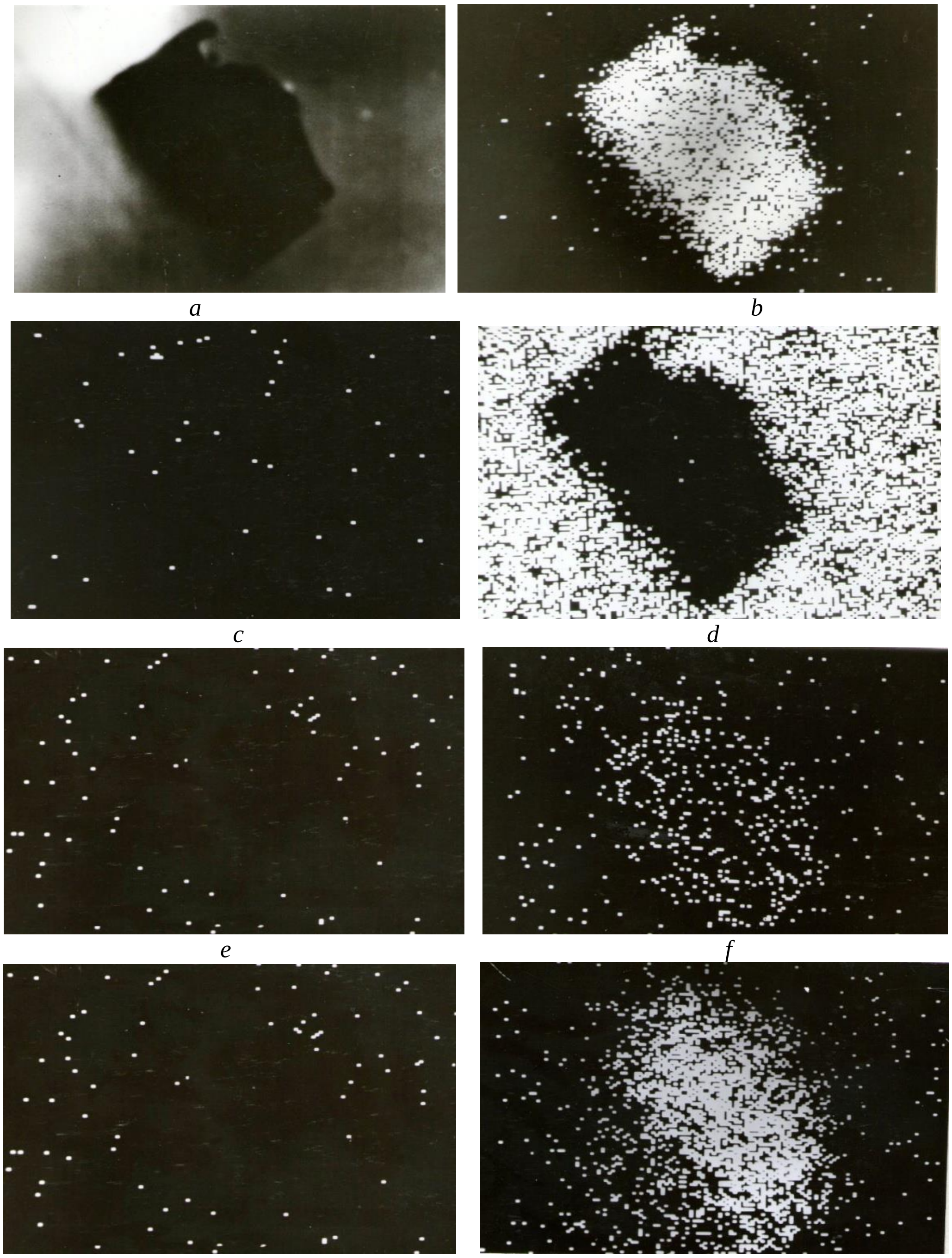


Fig. 6. Inclusion at the working surface of the sample: a – in reflected electrons; in characteristic rays: b – Ti_{ka}; c – Cr_{ka}; d – Fe_{ka}; e – Si_{ka}; f – Mo_{ka}; g – V_{ka}; h – N_{ka}

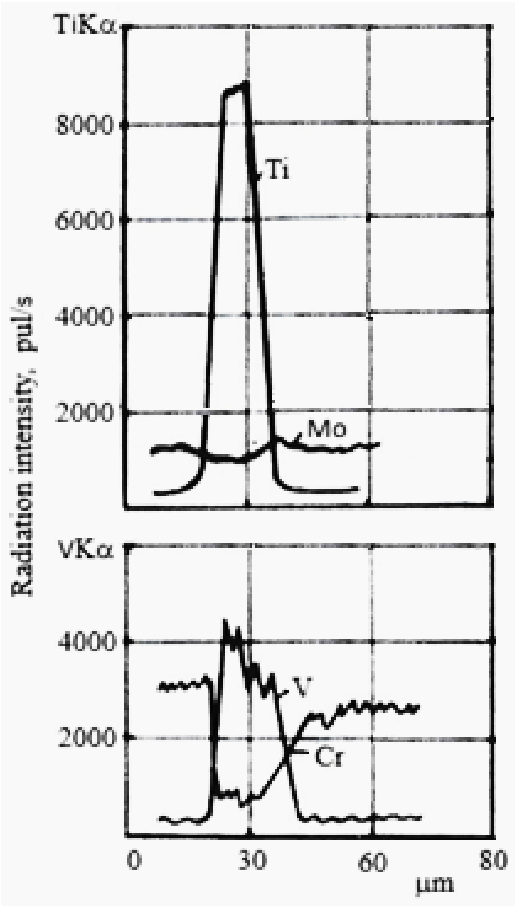


Fig. 7. Distribution of elements along a line intersecting a typical inclusion. Steel 4Kh5MFS

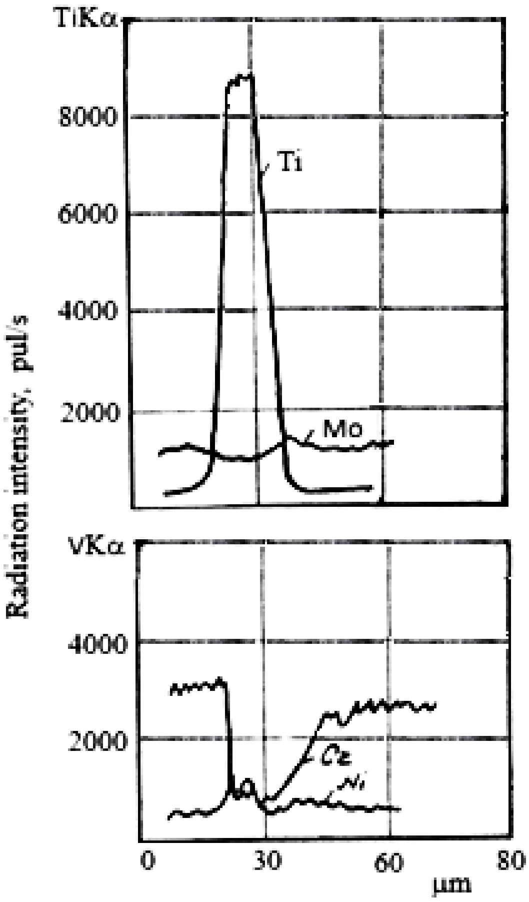


Fig. 8. Distribution of elements along a line intersecting a typical inclusion. Steel 5KhNM

Studies of inclusions formed during operation in the working surfaces of 5KhNM steel revealed the presence of titanium and nitrogen. No other elements were detected. Fig. 8 shows the distribution of elements contained in a 10 μm inclusion (5KhNM steel).

The formation of inclusions of complex composition in the working surfaces of press mold parts during operation is of interest, since such inclusions have not been described in works devoted to ion-plasma coatings.

It can be assumed that titanium deposited on working surfaces under the coating during ion bombardment diffuses from the surface into the depth of the metal during thermal cycles during operation.

In order to verify the validity of this assumption, we will estimate the distance from the surface to which titanium can diffuse during the operation of the press mold, before its first regrinding (it is 4000 cycles) using the formula [1]:

$$X = \sqrt{Do\tau}, \quad (1)$$

where X is the distance traveled; Do – diffusion coefficient; τ – time.

When calculating the diffusion time, we take into account only the warm-up time (0.5 cycle), i.e. if one cycle has a duration of 30 s, then the diffusion time is:

1) before the first regrinding

$$\tau = 400 \cdot 30\frac{1}{2} = 6 \cdot 10^4 \text{ s;}$$

$$\tau = 12000 \cdot 30\frac{1}{2} = 18 \cdot 10^4 \text{ s.}$$

2) the operating time of the press molds for 12 thousand pressings

$$D_{\alpha-Ti} = 6.4 \cdot 10^{-8} \text{ cm}^2\text{/s;}$$

$$x = \sqrt{6.4 \cdot 6 \cdot 10^{-8} \cdot 10^4} = 6.2 \cdot 10^{-2} \text{ cm} = 620 \ \mu m,$$

before the first regrinding

$$x = \sqrt{6.4 \cdot 18 \cdot 10^{-8} \cdot 10^4} = 10.7 \cdot 10^{-2} \text{ cm} = 1070 \ \mu\text{m}$$

for 12 thousand cycles.

Considering that thermal cycling accelerates the diffusion process [8, 9], the true penetration depth will be greater.

Based on diffusing titanium, compounds of regular shape are formed, evenly distributed in planes parallel to the coating.

Let's examine how the hardness and microhardness of parts change after heat treatment and grinding, after coating application, and after 5,000 cycles in a mold. The samples after use had a 20-μm-thick surface layer removed as a result of mechanical processing. Measurements were taken directly from the edge of the sample at intervals of 10 μm (Fig. 9).

Microhardness value (1000 MPa) is observed for the surface layer of the sample; with a titanium nitride coating, the microhardness at a distance of 10 μm from the edge of the sample is 800 MPa (see Fig. 9). This region corresponds to the transition zone, which, according to the results of the electron microprobe analysis (see Fig. 8), contains titanium, which explains its increased microhardness (II). At a distance of 20 μm from the edge of the sample, the microhardness is 450…480 MPa and does not differ from the microhardness of the uncoated sample (curve I). This serves as further confirmation of the absence of titanium or titanium-based compounds in the matrix of the samples, both with and without a titanium nitride coating before operation. The sample after operation for 5,000 cycles, from which a 20 μm surface layer was removed during regrinding, has a microhardness of the working surface of 750 MPa (curve III). At a distance of 100…120 μm, the microhardness of the samples after operation is 720…750 MPa. The increase in hardness in this region can be explained by the presence of inclusions of a complex Ti-V-N composition at this distance from the working surface.

Thus, at the beginning of service, the coating itself assumes the protective function. It resists destruction under significant temperature and stress fluctuations due to its high compressive stress and low thermal conductivity. It also exhibits low adhesion to molten brass, good adhesion to the steels used to make the mold components, and resistance to high-temperature corrosion and oxidation.

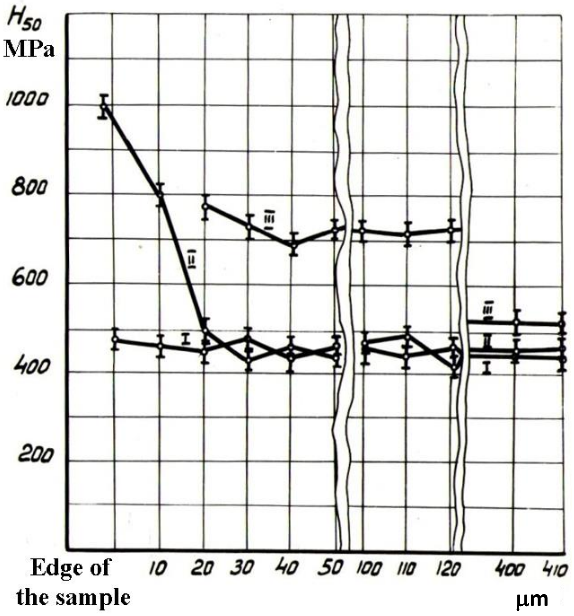


Fig. 9. Change in microhardness:
I – sample of 4Kh5MFS steel without coating;
II – sample of 4Kh5MFS steel with coating;
III – sample of 4Kh5MFS steel with coating after 5 thousand operating cycles – 20 μm layer removed

Thanks to these properties of the plasma coating, mold parts can be used for 3,000…5,000 cycles after application before the first regrinding (as noted previously, without the coating, they fail after 2,000 cycles). After regrinding, inclusions of complex composition were found in the surface layers of the mold parts. The formation of these inclusions can be explained as follows. Titanium, deposited on the working surfaces under the coating, diffuses into the metal during operation. Inclusions form from the diffusing titanium. The presence of vanadium in the inclusions can be explained by:

1) increased diffusion activity of vanadium [10];
2) increased activity when reacting with nitrogen, which is part of the steel [11];
3) the affinity of its electron structure with nitrogen [12].

The formation of titanium-based inclusions in the working surfaces of mold components is one of the primary strengthening mechanisms. Thus, to increase resistance to plastic deformation, which leads to the formation of microcracks, it is necessary to reduce the mobility of dislocations capable of displacement [13–15].

During operation, grain size increases, accompanied by coagulation of inclusions located along their boundaries (see Fig. 5). Inclusion sizes increase to 8…10 μm, after which cracks appear on the working surfaces of mold parts, leading to mold failure. During this time, plasma-coated parts can withstand at least 12,000 press-fits, which is six times longer than parts made from the same steels without coating.

The obtained results correspond to the data of works [16–20], where it is shown that non-metallic inclusions in steel play a strengthening role until, they reach sizes of about 8…10 μm, since they reduce the mobility of dislocations capable of moving, increasing the thermal endurance of steel.

When reaching critical sizes, non-metallic inclusions cause the accumulation of dislocations, the development of dislocation networks and boundaries, which leads to weakening and the emergence of microcracks [21, 22].

CONCLUSIONS

1. Thin (≤ 5 μm) plasma-sprayed TiN coating applied by the CIB method provides initial protection of molds due to low thermal conductivity, high thermal resistance and low adhesion to molten copper, increasing the durability before the first regrinding by 1.5–2.5 times.

2. After complete removal of the coating during regrinding, the service life of the molds increases by 5–6 times compared to parts without a coating due to diffusion hardening of the surface layers.

3. During thermal cycling operation, titanium diffuses from the transition zone into the steel to a depth of 100...120 μm, forming dispersed inclusions of Ti-N and Ti-V-N measuring 2…10 μm.

4. The resulting inclusions perform a strengthening function, increasing microhardness to 750…800 MPa and significantly slowing down the development of thermal fatigue.

5. When inclusions reach critical sizes of 8…10 μm and coagulate along grain boundaries, softening and the initiation of fire cracks occur.

6. The identified effect of controlled diffusion alloying with titanium with the formation of optimally sized strengthening inclusions is a new, previously undescribed mechanism for extending the service life of press molds after the protective effect of the coating itself has been exhausted.

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ДИФУЗІЙНИЙ ЕФЕКТ ПЛАЗМОВИХ ПОКРИТТІВ Ti-N У ПРЕС-ФОРМАХ ЛИТТЯ ПІД ТИСКОМ МІДНИХ СПЛАВІВ

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Досліджено ефективність тонких плазмових покриттів із нітриду титану (TiN), нанесених методом КІБ на робочі поверхні прес-форм лиття під тиском мідних сплавів (сталі 4Х5МФС та 5ХНМ). Показано, що покриття товщиною до 5 мкм значно підвищує стійкість прес-форм: до першої перешліфовки в 1,5–2,5 рази (3–5 тис. циклів проти 2 тис. без покриття), а загальний ресурс до виходу з ладу – в 5–6 разів (не менше 12 тис. циклів). Встановлено, що після зняття покриття (при перешліфовках на глибину ≥20 мкм) захисна функція зберігається завдяки дифузії титану в приповерхневі шари сталі в процесі термоциклування. Титан, що дифундує, утворює дисперсні включення складного складу (Ti-N та Ti-V-N) розміром 2…10 мкм, які виконують роль зміцнювальної фази, перешкоджаючи руху дислокацій та підвищуючи опір термічній втомі. Мікротвердість приповерхневого шару після експлуатації та перешліфовки зростає до 750…800 МПа (проти 450…480 МПа у сталі без покриття). Виявлений механізм «самовідновлюваного» зміцнення внаслідок керованої дифузії титану та утворення неметалевих включень оптимального розміру раніше в літературі з іонно-плазмових покриттів не описувався і є новим підходом до підвищення ресурсу прес-форм для лиття під тиском агресивних мідних сплавів.