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*Вивчено анодну поведінку твердих сплавів ВК20КС, ВН8, ВНЖ, ВНДС. Показана можливість селективного анодного розчинення металевого зв'язуючого без окиснення твердого компоненту (вольфраму/карбіду вольфраму). Проведено гальваностатичну селективну анодну обробку лома твердого сплаву ВК20КС. Визначено склад вольфрам-вмісних продуктів: 23 % WO$_3$ або H$_2$WO$_4$, 73 % WC*

*Ключові слова: тверді сплави, пасивація, селективна анодна обробка, вольфрам, карбід вольфраму*

*Изучено анодное поведение твёрдых сплавов ВК20КС, ВН8, ВНЖ, ВНДС. Показана возможность селективного анодного растворения металла-связки без окисления твёрдого компонента (вольфрама/карбида вольфрама). Проведено гальваностатическая селективная анодная обработка лома твёрдых сплавов ВК20КС. Определен состав вольфрам содержащих продуктов: 23 % WO$_3$ или H$_2$WO$_4$, 73 % WC*

*Ключевые слова: твердые сплавы, пассивация, селективная анодная обработка, вольфрам, карбид вольфрама*

# SELECTIVE ANODIC TREATMENT OF W(WC)-BASED SUPERALLOY SCRAP

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## 1. Introduction

Superalloys are pseudo-alloys that are composed of W, WC or other solid components and binder metal (Ni, Co, Fe), that are manufactured by means of powder metallurgy [1, 2]. Superalloys possess high durability and heat resistance, which allows for their application in various fields: materials for drilling bit, high-speed cutters for steel processing,

kinetic penetrators, rocket nozzles. Their brittleness and low plasticity [3] make them vulnerable to impact and deformation. However, high prices of raw materials and monopoly of some countries, make the idea of recycling super alloys, for instance, for cutting tools, more attractive [4]. The recycling can be achieved using various methods, for instance hydrometallurgy [5]. However, the high corrosion resistance of superalloys complicates hydrometallurgical reprocessing [6]. It is proposed to employ other methods, which allows for not only reprocessing of materials into superalloys [7], but also for use of extracted components in other fields. For instance, recycling of Ni or Co binder is proposed [8]. Production of ultrafine (10–50 μm) metal binder powders, and especially solid components (W/WC) is a complicated and expensive process. Thus, development of simple methods of extracting tungsten or tungsten carbide from superalloy scrap, as the most expensive components, is very relevant.

## 2. Literature review and problem statement

Recycling or reprocessing of any material is mainly governed by their structure. Superalloys are not solid solutions but composites. Usually, composite materials of organic [9], or inorganic [10] nature are composed of matrix material and filler. While superalloys have a different structure: a large number of solid material particles are bound by a metal binder (mainly Ni or Co). Due to high hardness of superalloys and manufacturing process, the mechanical reprocessing is almost impossible. For reprocessing of superalloy scrap, a complete dissolution or selective treatment can be utilized.

Complete dissolution can be realized chemically, by treating with hot sulfuric acid [7], hydrochloric acid [7, 11], hydrochloric acid with chlorine purging [7, 12] or thermal reduction with carbon [7]. Pyrometallurgy methods are also used [7]. For complete dissolution, electrochemical methods are used, particularly anodic dissolution in sodium chloride solution, [4], acidic solution [7]. An electrochemical method has been employed in the work [11], but not for direct anodic dissolution of superalloy scrap, but for production of chlorine gas which oxidized superalloy surface that is prone to passivation.

The main disadvantage of complete dissolution is that complete regeneration of solid component, mainly tungsten or tungsten carbide, requires preparation of finely divided tungsten oxide, followed by reduction with hydrogen, thus greatly increasing the cost of the secondary component.

The alternative is a selective dissolution of metal binder. Selective treatment in mixed metal melt [5], and also in molten zinc [12] has been proposed. During treatment, the metal binder is dissolved and the metal solvent is removed under vacuum. However, the disadvantage of such method is impurities of zinc or other more volatile metals in regenerated nickel or cobalt. As a result, during production of superalloy goods, these impurities evaporate, leaving cavities, which greatly reduces mechanical properties. Such method of recycling components for manufacturing superalloys has not been employed.

The selective dissolution of metal binder can be conducted electrochemically. It has been proposed to utilize electrochemical dissolution of superalloy scrap in acidic solutions [11], including under controlled potential [13]. However, the detailed analysis of papers shows, that anodic dissolution is proposed to be conducted at the current density of $3-5 \, \mathrm{A/dm^2}$, while anode potential (superalloy) reaches 1500–2000 mV. Under such conditions, tungsten and tungsten carbide would be oxidized and precipitate in oxidized from – tungsten oxide or tungstic acid. The method is selective, i. e. the binder metal is leached into solution while the oxidized form of the solid component precipitates. The solid component is oxidized, leading to anodic dissolution under these conditions having the same problems as a complete dissolution – difficulties with further reprocessing to obtain finely divided tungsten or tungsten carbide.

At the same time, the selective electrochemical treatment of superalloy scrap with dissolution of binder metal only is very promising because it is conducted at low temperature and is easily controlled by current density, allowing to obtain a solid component powder which can be directly used in manufacturing of superalloys. Thus, the development of selective anodic reprocessing of superalloy scrap is very relevant. However, conditions of such selective anodic dissolution (current density, electrolyte composition, dissolution potentials) have not been found in literature, and special research is required for their determination.

## 3. The aim and objective of the study

The aim was to develop a method for selective anodic treatment of superalloys. Additionally, it is required to dissolve the metal binder and to obtain tungsten or tungsten carbide powder with binder content less than 1 %. Such powder can be directly used for manufacturing superalloy goods.

To achieve the set aim, the following objectives must be accomplished:

– to determine the electrolyte composition for electrochemical treatment;

– to study the anodic behavior of some superalloys;

– to conduct anodic dissolution of super alloy samples, and to determine the composition of tungsten-containing products.

## 4. Methods used in the development of selective superalloy treatment

### 4. 1. Types of studied alloys

Table 1 lists the composition and the purpose of superalloys, which scrap have been used in studies.

Table 1

Superalloy samples used in the study

| Superalloy | Composition | Purpose |
|---|---|---|
| VK20S | 20 % Co, 80 WC | Drill cutting element |
| VN8 | 8 % Ni, 92 % WC | Penetrator for armor-piercing munitions |
| NVG | 5 % Ni, 5 % Fe, 90 % W | Penetrator for armor-piercing munitions |
| VNDS | W, Ni, Cu | Fragment of rocket nozzle |

It should be noted, that two groups of alloys with fundamentally different solid components were:

1) tungsten carbide based alloys – VN8, VK20KS;

2) metallic tungsten based alloys – VNG, VNDS.

## 4. 2. Choice of electrolyte

The choice of electrolyte composition must be based on chemical properties of the solid component (tungsten or tungsten carbide) and metal binder (nickel, cobalt, iron). Additionally, the possible passivation of these components also must be taken into account.

## 4. 3. Methods of studying the selective anodic dissolution of superalloys

In order to determine the possibility of selective dissolution of binder metal, the anodic behavior of superalloy samples has been studied in the chosen electrolyte. The anodic polarization characteristics have been recorded using custom-built cell (Fig. 1).
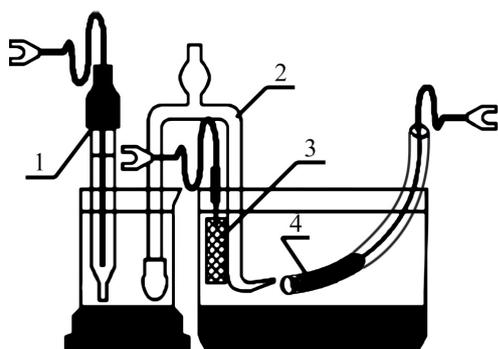
Fig. 1. Cell for recording polarization curves of the samples:
1 — Ag/AgCl reference electrode; 2 — salt bride;
3 — counter-electrode (Pt);
4 — working electrode — superalloy sample

In order to ensure electrical contact, a copper wire has been tied around samples and placed into a tube-like PVC container to separate from the electrolyte. Polarization curves have been recorded in a potentiodynamic mode using Ellins P-8 potentiostat (Russian Federation), in an anodic scan from stationary potential to +2000 mV at 5 mV/s.

The anodic dissolution of superalloy samples has been conducted galvanostatically in the chosen electrolyte under current densities corresponding to the higher rate of metal binder dissolution. A steel grate has been used as the cathode. Super alloy scrap samples have been placed into the perforated titanium basket.

## 5. Results of studying the electrochemical behavior of superalloy samples

### 5. 1. Choice of the electrolyte for selective anodic treatment of superalloys

Because superalloy is composed of metal binder and tungsten (tungsten carbide) the electrolyte has been chosen theoretically, based on standard potential values (Table 2).

Based on the data from Table 2, it should be noted that in the basic medium the tungsten would be first to oxidize and binder metal (nickel, cobalt, iron) would passivate, while in acidic media the binder metal (nickel, cobalt) is oxidized first. Thus, in order to obtain non-oxidized tungsten or tungsten carbide powder, an acidic electrolyte is required for anodic treatment of superalloys. An HCl has been chosen, because chloride-ion is an effective depassivator and would ease the anodic dissolution of metal binder. The hydrochloric acid concentration of 9 % has been chosen.

Table 2

Standard potential values of superalloy components in different media

| Compo-nent | pH<7 (acidic medium) | | pH>7 (basic medium) | |
|---|---|---|---|---|
| | Reaction | $E^0$, B | reaction | $E^0$, B |
| Co | $Co^{2+}+2e=Co^0$ | −0.29 | $Co(OH)_2+2e==Co^0+2OH^-$ | −0.71 |
| W | $WO_3+6H^++6e==W+3H_2O$ | −0.09 | $WO_4^{2-}+6e==W+8OH^-$ | −1.05 |
| Ni | $Ni^{2+}+2e=Ni^0$ | −0.228 | $Ni(OH)_2+2e==Ni^0+2OH^-$ | −0.72 |

### 5. 2. Results of studying the anodic behavior of superalloy samples

For tungsten carbide based superalloys (VK20KS – Fig. 2, VN8 – Fig. 3) the polarization characteristic has the following character. A peak corresponding to the highest rate of metal binder dissolution can be observed on potentiodynamic curves. At higher potential values passivation occurs (a passivation plateau is observed on the curve), with another oxidation process starting afterwards.
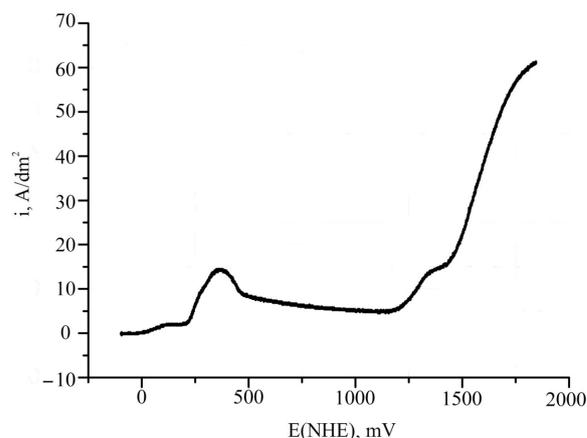
Fig. 2. Anodic polarization curve of VK20KS alloy
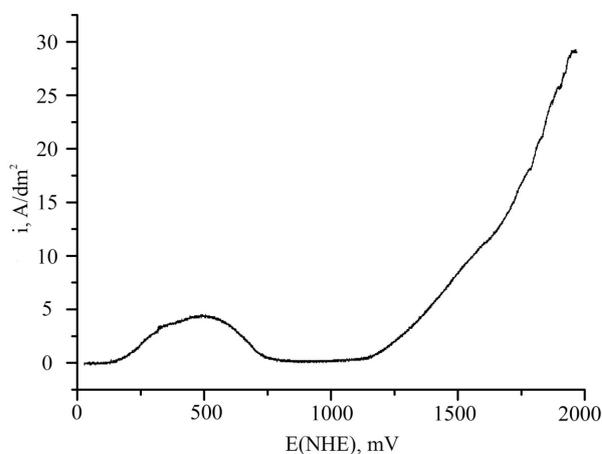
Fig. 3. Anodic polarization curve of VN8 alloy

Polarization curves of tungsten based VNG (Fig. 4) and VNDS (Fig. 5) superalloys demonstrate a different character.

It should also be noted that the dissolution peak current densities of VN8 and VK20KS superalloys are significantly higher than those of VNG and VNDS alloys.
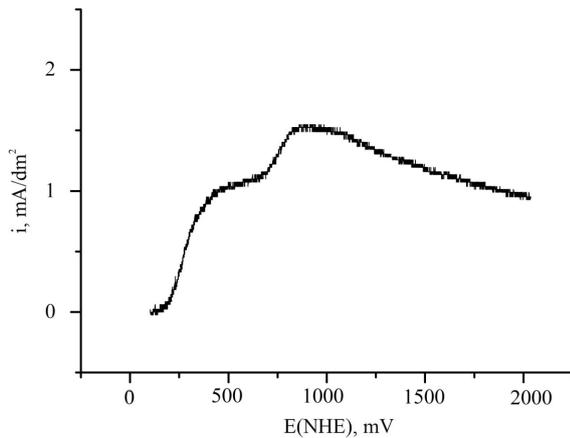
Fig. 4. Anodic polarization curve of NVG alloy
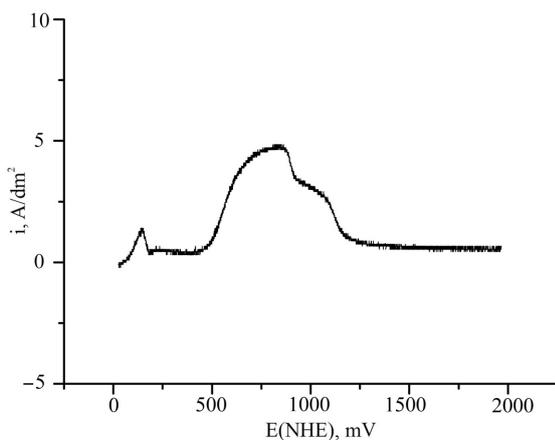


Fig. 5. Anodic polarization curve of VNDS alloy

### 5. 3. Experimental results of anodic dissolution of VK20KS alloy

The experimental anodic dissolution of VK20KS superalloy samples has been conducted in perforated titanium basket at the current density of 15 $A/dm^2$. The chosen current density corresponds to the dissolution peak current density, that has been established according to the anodic polarization curve (Fig. 2). The composition of the obtained powder has been determined gravimetrically and is presented in Fig. 6.
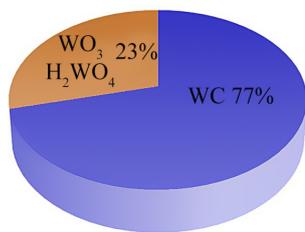


Fig. 6. Product's composition of galvanostatic anodic dissolution of VK20KS superalloy (i=15 $A/dm^2$)

Because the oxidized form of tungsten could be observed visually, it has been removed by dissolving it using 25 % aqueous ammonia. In order to separate tungsten carbide powder containing an excessive amount of cobalt as a metal binder, a permanent praseodymium-neodymium magnet has been used. Cobalt is the metal binder in VK20KS superalloy (Table 1). Cobalt is known to be ferromagnetic, and powder with the content of metallic cobalt above 1 % would be sep-

arated by the magnet. It has been determined that tungsten carbide has precipitated (cobalt contents is lower than 1 %, which is supported by magnetic properties) along with tungstic acid and tungsten anhydride (Fig. 6).

### 6. Discussing the results of selective anodic treatment of superalloy samples

It should be noted, that hydrochloric acid-based electrolyte was a correct choice for anodic reprocessing of superalloys with the aim of dissolving binder metal.

It is necessary to mention that two types of superalloys with different types of the solid component have been chosen for this study:

1) alloys with tungsten carbide (VN8, VK20KS);
2) alloys with tungsten (VNG, VNDS).

*Anodic behavior of superalloy samples.* It has been shown that anodic polarization curve of all superalloys, demonstrates behavior characteristic for passivating materials with one or more dissolution peaks and significant passivation plateau, which is in agreement with the literature [13, 14].

Superalloys with tungsten carbide are less prone to passivation than alloys with tungsten. For VK20KS (Co binder) and VN8 (Ni binder) alloys, one peak corresponding to metal binder dissolution at +370÷+400 mV (Co dissolution) with current density of 15 $A/dm^2$ (Fig. 2) and at +490÷ ÷+520 mV (Ni dissolution) with current density of 5 $A/dm^2$ (Fig. 3) can be observed on the anodic curve. After both dissolution peaks, a metal binder passivation plateau in the range of +1190÷+1220 mV is observed. It should be noted that passivation of VN8 is more pronounced (passivation current densities are 0.2 $A/dm^2$ and 5 $A/dm^2$ correspondingly). Upon potential shift above +1250 mV, an undesired process of tungsten oxidation along with oxygen evolution occurs. Thus, the anodic oxidation at high potentials leads to oxidation of tungsten-containing solid component, which has not been considered in the work [13]. As a result, all components of superalloy have been oxidized.

The passivation is more pronounced for metallic tungsten-based alloys (VNG and VNDS). A few dissolution peaks can be observed on anodic curves. The VNG alloy demonstrates two dissolution peaks, which likely correspond to the dissolution of Fe and Ni, contained in the binder. However, the dissolution current densities are rather low (1 $A/dm^2$ and 1.5 $A/dm^2$ correspondingly), which indicates low reactivity of the alloy. Upon repeated recording of the polarization curve without refreshing the sample surface, a sharp drop of dissolution rate was observed — current density dropped to 0.1÷0.25 $A/dm^2$, indicating rapid and strong passivation of the VNG alloy surface. There is no description for this phenomenon in literature. On the anodic curve of VNDS alloy (Fig. 5), three oxidation peaks are observed. The nature of the first peak is not clear yet, while the second and the third correspond to dissolution of Cu and Ni. At potentials above +1250 mV a passivation plateau till +2000 mV is observed, which is characterized by low current density of 0.4– 0.52 $A/dm^2$. Additionally, no oxidation of tungsten in this potential range is observed.

The fundamental difference between metallic tungsten and tungsten carbide based alloys can probably be explained by the following fact. During manufacturing of tungsten carbide based alloys, the WC doesn't dissolve in metal binder. As a result, the metal binder demonstrates a char-

acteristic anodic behavior, with nickel being more prone to passivation than cobalt. In case of superalloys based on metallic tungsten, the latter partially dissolves in metal binder, causing significant passivation of the metal binder.

*Experimental anodic dissolution of VK20KS superalloy.* The initial anodic dissolution of VK20KS alloy has been conducted in a stationary titanium basket. The dissolution started at the potential of +480 mV, however, after 0.5 h the voltage has risen to +1500 mV. This led to titanium basket being damaged and oxidation of tungsten carbide. This likely occurred because of the depletion of Co binder on the surface of superalloy, leading to a higher content of passive tungsten carbide. To prevent this, it was necessary to mechanically remove tungsten carbide particles from the surface. A rotating titanium basket (Fig. 7) has been proposed for this purpose.
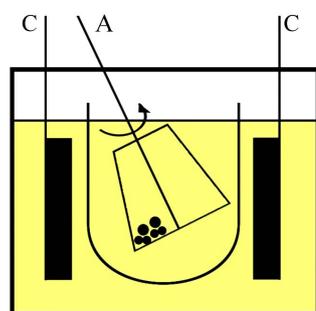


Fig. 7. A concept scheme of an electrolyzer with rotating anodic titanium basket aimed at selective anodic dissolution of VK20KS superalloy: A — rotating titanium basket with superalloy scrap; C — inert cathode

When rotating titanium basket is used, the piece of superalloy scrap would grind against each other, thus removing tungsten carbide powder from the surface.

## 7. Conclusions

1. It has been theoretically justified and proposed to use a 9 % solution of hydrochloric acid as an electrolyte for selective anodic dissolution of superalloys. The effectiveness of the electrolyte has been demonstrated experimentally.

2. The anodic behavior of VK20KS, VN8, VNG and VNDS superalloys has been studied. The possibility of selective anodic dissolution of binder metal without oxidation of solid component (tungsten/tungsten carbide) has been demonstrated. The parameters (potential and current density values) have been determined. It has been found that the potential of superalloy anodic oxidation should not exceed +500 mV. The higher degree of passivation of tungsten-based alloys in comparison to tungsten carbide-based alloys has been demonstrated.

3. The galvanostatic selective anodic oxidation of VK20KS superalloy scrap has been conducted. It has been found that surface passivation of VK20KS superalloy occurs because of the dissolution of metal binder and accumulation of tungsten carbide. In order to prevent passivation, the use of rotating perforated titanium basket has been proposed. It has been demonstrated that tungsten-containing products are composed of 77 % WC and 23 % of the oxidized form.

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