SPECIFICS OF THE PRODUCTION TECHNOLOGY OF INGOTS AND SEMI-FINISHED PRODUCTS OF CORROSION RESISTANT 4201 TITANIUM ALLOYS

by

N. F. Anoshkin and Ye. I. Oginskaya

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ENGLISH TITLE: Specifics of the Production Technology of Ingots and Semi-finished Products of Corrosion Resistant 4201 Titanium Alloys

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AUTHOR: N. F. Anoshkin and Ye. I. Oginskaya


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SPECIFICS OF THE PRODUCTION TECHNOLOGY OF INGOTS
AND SEMI-FINISHED PRODUCTS OF CORROSION RESISTANT 4201 TITANIUM ALLOYS

On the basis of a study of the corrosion behavior of alloys in the system titanium-molybdenum, domestic and foreign investigators have established the possibility of sharply increasing the corrosion resistance of titanium by alloying with molybdenum [4,2]. As a result of laboratory investigations, compositions of certain alloys have been suggested on the basis of this system. Subsequently, work has been performed on the industrial testing of the production of semi-finished goods, evaluation of technological specifics of these alloys, studies of the structure and properties of the semi-finished products.

As a result of these investigations, the specifics of the technological properties of the alloys have been determined, pilot scale technology has been developed for the production of the ingots and semi-finished goods, the regularities of changes of the structure and properties of the alloys as a function of deformation modes and heat treatment have been studied, and the corrosion behavior of commercial semi-finished goods has been studied in certain corrosive media.

The investigations performed have allowed the following principal specifics of alloys such as 4201 and 4203 to be determined.

1. High content of the refractory alloying component - molybdenum - and absence in the composition of alloys of other additives, which might be used for the composition of a more easily melted master alloy.

2. Increased oxidizability of the alloys when heated or treated in ordinary atmosphere.

3. High resistance to deformation during hot working by pressure.

4. Sensitivity of the alloys to the cooling rate from high temperatures and embrittlement of the metal when held in the 300-600° temperature interval.
In the present article, on the basis of analysis of the specifics of the technological properties of 4201 alloy (containing 32% molybdenum) and 4203 alloy (additionally alloyed with 1.5% niobium), we discuss problems of optimal design of the technology of production of ingots and semi-finished products of these alloys.

Production of Ingots

The significant excess of the melting point of molybdenum (2625°) over the melting point of titanium and the possible temperature of liquid metal in the depression, as well as the great specific gravity of molybdenum create highly unfavorable conditions for its introduction under conditions of vacuum arc melting. During the production of ingots of ordinary series titanium alloys by this method, the molybdenum is introduced in the form of comparatively easily melted master alloys with aluminum, and sometimes with other elements included in the composition of the alloys. This allows its even distribution throughout the volume of the ingots and eliminates inclusions.

Testing of the introduction of molybdenum in the form of chunks of sintered molybdenum (moldings) and of a master alloy of molybdenum and titanium containing 70% molybdenum did not yield positive results, due to the formation of inclusions.

The usage of a powder leads to great losses of the powder during pressing of electrodes if it is attempted to displace it with the jaw, or even to the formation of inclusions due to sintering if it is introduced wrapped in aluminum or other foil in order to avoid these losses.

The melting of electrodes made up of bars of technical titanium and molybdenum moldings also leads to the formation of inclusions. In this case, due to the predominate melting of the bars of titanium, the arc may burn at the ends of the molybdenum moldings and drops of pure molybdenum may fall into the bath. These drops, not dissolving, solidify and form inclusions. It should be noted that the formation of inclusions by this method of melting is observed also in alloys of titanium with niobium. This type of inclusion can be avoided only by forming an alloy composition at the end of the electrode which is near the designed alloy composition, which is possible only if the refractory components do not protrude far beyond the melted end of the electrode.

The best results are produced by introducing molybdenum particles which are large enough to avoid sintering in the electrode during melting or losses during pressing, and small enough to provide complete solution.

1The possibilities of using other methods of melting for the preparation of these alloys will not be discussed in this article.
In order to determine the optimal size of particles, experimental and analytical investigations of the process of solution were performed, as well as the melting of a series of commercial ingots differing in the modes of melting, particle size and number of remelting cycles.

Analytical investigations were performed, designed to study the regularities of dropping of melted particles into the liquid bath (rate of movement, path of complete solution) as a function of particle size and physical properties of the particle and the melt.

An investigation was performed by solving the differential equation of movement of a particle of variable mass considering the effects of the force of gravity and the force of resistance of the medium:

$$\frac{dv}{dr} = \frac{\Delta \gamma \rho}{\rho g} - \frac{\nu}{\gamma K^2},$$

where $v$, $r$, $\gamma$ are the velocity, radius and density of the particle respectively; $g$ is the acceleration of gravity; $\Delta \gamma$ is the difference in density of the particle and melt; $\nu$ is the dynamic viscosity of the melt; $K$ is the linear velocity of solution of the particle per unit time.

This equation was produced on the basis of the Meshcherskiy equation for the movement of a point of variable mass, known in mechanics.

The solution of the equation leads to the following expression for the change in dropping rate of a particle as it dissolves:

$$r = \frac{\Delta \gamma \rho}{\nu K} (r^2 - r_{in}^2),$$

where

$$\nu = \frac{\Delta \gamma \rho}{g K^2}.$$ 

$r$ is the radius of a particle at the moment it enters the liquid bath.

This expression can be used under the condition that

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1The analytic investigation was performed by the authors and A.M. Davydova.
Analysis of the analytic expressions produced and experimental results have allowed the following regularities to be noted:

In contrast to a particle of constant mass, the velocity of a dissolving particle falling through a liquid bath first increases, then decreases, approaching zero as the solution process is completed. As the initial radius of the particles decreases and the linear rate of solution increases, the maximum velocity and path length required for complete solution of the particle are significantly decreased. Increasing the viscosity of the melt and decreasing the difference in density between particle and melt act in the same direction. An increase in the current in the arc facilitates an improvement in solution of particles both due to increased depth of the bath and consequently, length of possible solution path, and due to increased temperature of the liquid metal.

Intensification of the movement of the liquid metal in the hole by increasing the magnetic field intensity of the solenoid facilitates an improvement in solution of the particles. This occurs due to increased rate of movement of the particle relative to the melt and also due to a certain increase in the path length travelled by the particle as it falls. Also, the improvement of the conditions of solution on the electrode resulting from increasing rate of movement of the cathode spot is of no little significance in this process.

In constructing the technological process of ingot manufacture, we should consider yet another important factor: incomplete solution of particles during initial remelting may lead to significant heterogeneities in the composition of the final ingot.

During the process of melting of an electrode with evenly distributed particles, if they do not dissolve completely, the particles are shifted along the axis of the ingot. The bottom portion of the ingot, over a distance equal to the sector with unstable melting conditions (2/3 the diameter of the ingot) includes not only the undissolved particles from the volume of metal which went into the formation of this portion, but also the particles which precipitated from the volume of a sector of the ingot whose height is equal to the depth of a stable liquid bath. Thus, if the depth of the bath is only 2/3D, the quantity of undissolved particles in the bottom portion will be double that in the sector of stable melting. The sprue portion of the ingot will contain no undissolved particles and, therefore, will be poorer in the alloying component. The maximum difference of the mean concentrations of the component over the cross section in the sprue and bottom portions of the ingot of first remelting will be
\[ \Delta C_{\text{max}} = C_0 \left( \frac{\beta h_0}{2D} + 1 \right) (1 - m), \]

where \( C_0 \) is the calculated concentration of the component in the alloy; 
\( h_0 \) is the depth of the stable bath; 
\( D \) is the diameter of the ingot; 
\( m \) is the ratio of the calculated concentration of the component to the concentration of the component in the melt.

This quantity of heterogeneity is retained to a significant extent in ingots upon subsequent remelting.

Thus, it is clear that during the first remelting, the most complete possible solution of the alloy in components should be assured.

On the whole, the technological process of melting of ingots should be adjusted in correspondence to the recommendations presented in [3].

The technological process suggested on this basis was used for the production of ingots 380mm in diameter of 4201 and 4203 alloys without inclusions, pores, cracks, with sufficiently even distribution of alloying components, homogeneous fine grained macrostructure and good surface quality. A study of the nature of the change of mechanical properties over the cross section of the ingots showed an even decrease of strength from periphery to center and low values of relative elongation and impact toughness over the entire volume of the ingot, particularly in the center portion of the cross sections. As follows from the results produced in the investigation of one ingot, 380mm in diameter, of 4201 alloy, the dispersion of values over the cross section was: strength 80.6-43.9 kg/mm\(^2\), relative elongation, 2-0.4%, impact toughness, 2.54-0.49 kgm/cm\(^2\). The reason for the low level of the properties was the great sensitivity of the alloys to the cooling rate. Heat treatment significantly improves the mechanical properties of the cast metal. Quenching in water from 1100-1200\(^\circ\) leads to evening of the properties and an increase in strength to 90 kg/mm\(^2\), relative elongation to 12%, impact toughness to 8 kgm/cm\(^2\). This makes it possible to use Type 4201 alloys in the cast state after heat treatment.

Hot deformation of ingots of alloys 4201 and 4203 causes no difficulties related to the presence of metallurgical defects in them.

Production of Deformed, Semi-finished Goods

The technological specifics of 4201 type alloys noted above complicate the technological process of manufacture of deformed semi-finished goods.

Investigations of the oxidizability of 4201 and 4203 alloys performed by continuous weighing showed that at temperatures up to 800\(^\circ\), the increase in weight of the specimens is practically nil. The most intensive oxidation
occurs at temperatures over 1000°. One characteristic feature of these alloys is that as a result of selective diffusion, oxidation on grain boundaries occurs at significantly higher rates than oxidation through the volume of the grains (Fig. 1). This fact must be considered in selecting a technology for heating and deformation, since under unfavorable conditions oxidation may cause surface cracking of the metal. The heating of ingots and billets before hot deformation should be performed in a protective medium or with the surface protected from oxidation by cladding or protective coating. The duration of heating should be as short as possible. The high plasticity of the alloys when the surface is reliably protected from oxidation allows the production of good surface quality of hot forged and hot rolled semi-finished goods. Even when there is a gas saturated layer of considerable thickness, only surface disruption occurs, the base metal withstanding the stress concentration created by the surface cracks quite well.

However, during cold working (rolling, bending, reeling), the gas saturated layer on the surface causes brittle rupture of the metal; therefore, in those cases when protection from oxidation cannot be assured, the technological plan of production of semi-finished goods should call for removal of the gas saturated layer before performance of cold working and from the surface of the semi-finished goods.

The performance of tensile testing and impact toughness testing at temperatures from 20-1200° shows that throughout the entire temperature interval, the alloy has high plasticity; however, at 400-600°, a retardation of the rate of increase occurs, and even a slight decrease in the values of relative elongation and reduction in area is noted.

Comparison of the strength at various temperatures for 4201 alloy and the commonest beta titanium alloy, VT15 shows (Fig. 2) that the former has lower strength up to 400-500°. With further increase in the temperature, the strength of 4201 alloy becomes considerably higher than that of VT15 alloy. The increase in impact toughness of 4201 alloy with increasing temperature is more rapid than that of VT15 alloy. Thus, for VT15 alloy the maximum impact toughness, 12-14 kgm/cm², is observed at 1000-1100°, after which it drops sharply. For 4201 titanium alloy, even at 800° a value of impact toughness of 35-40 kgm/cm² is reached, and as the temperature increases further, the specimens bend without breaking. The increased values of the strength indicators at high temperatures noted for 4201 and 4203 alloys result in significantly greater resistance to deformation during hot rolling, forging, pressing and other types of hot working. As investigations have shown, a change in the deformation (forging) temperature of cast specimens from 900 right up to 1300° had no noticeable influence on the mechanical properties. For example, in forging throughout this entire temperature interval the mechanical properties of specimens were within the following limits: strength 97.5 - 98.2 kg/mm²; relative elongation 10-12%; relative reduction in area 48-52%; impact toughness 5-5.5 kgm/cm². In connection with the low sensitivity of the structure and properties of 4201 and 4203 alloys to the temperature
of hot deformation right up to 1300°, it is possible to decrease the resistance to deformation by performing it at even higher temperatures. However, the sharp increase in the intensity of oxidation of the metal and the related worsening of the quality of the surface of the semi-finished goods forces us to give preference of selection of more powerful equipment, making it possible to perform deformation at an initial temperature of not over 1100°.

![Fig. 1. Microstructure of surface layer of specimen of 4201 alloy 300x. Heated to 1200° - 2 hours.](image)

![Fig. 2. Mechanical properties of 4201 (1) and VT15(2) alloys as a function of test temperature. 1 - annealing, 2 - quenching](image)

The sensitivity of the alloys to the rate of cooling and to holding at 300-600° noted above results in significant dependence of the properties of the deformed semi-finished goods on the cooling conditions, cross-sectional size of the product, temperature from which the metal is cooled after hot working and heat treatment regimes.

4201 and 4203 alloys, in correspondence with the equilibrium state diagrams of the titanium-molybdenum and titanium-niobium systems must be considered two phase alloys. The performance of microstructure investigations has shown the
separation of the second phase in cast and large grain deformed specimens.

Fig. 3. Influence of annealing and quenching temperatures on mechanical properties of 4203 alloy.
1 - annealing  2 - quenching
a. $\sigma_b$, kg/mm$^2$

Attempts to determine the nature of the separation by x-ray diffraction methods have been unsuccessful: in all cases, only the beta phase has been found. However, a stable relationship between the presence of these separations in the microstructure and the level of mechanical properties of the metal has been discovered. As the hardening temperature is increased for cast specimens, (with initial almost zero values of plasticity) to 1100° and above, these separations disappear, and the relative elongation and reduction area increase sharply (to 10-12% and 45-50% respectively). Similar data have been produced for the deformed metal as well. In order to establish the nature of the separations, additional more careful investigation must be performed. The rate of cooling has the strongest influence on the mechanical properties of the alloys only when cooling is performed from rather high temperatures. Fig. 3 shows the results of mechanical tests of forged specimen of 4203 alloy after annealing and quenching from various temperatures. We present below data on the influence of the rate of cooling of forged specimens of 4203 alloy from 1100° on their mechanical properties.
Cooling Method

<table>
<thead>
<tr>
<th>Method</th>
<th>( \sigma_b ) kg/mm(^2)</th>
<th>( \delta ) %</th>
<th>( \psi ) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>In water</td>
<td>90.5</td>
<td>14.0</td>
<td>55.0</td>
</tr>
<tr>
<td>In air</td>
<td>92.0</td>
<td>10.5</td>
<td>29.0</td>
</tr>
<tr>
<td>In air in asbestos</td>
<td>90.0</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>in the closed furnace</td>
<td>88.0</td>
<td>3.5</td>
<td>3.0</td>
</tr>
</tbody>
</table>

The rate of cooling has no influence on the strength indicators throughout the entire range of temperatures investigated. The values of relative elongation of annealed and quenched specimens are rather similar right up to 1050\(^\circ\), and only with further increases to 1150\(^\circ\) is the relative elongation of annealed specimens significantly lower. The relative reduction in area differs significantly in quenched and annealed specimens only at temperatures of 1150\(^\circ\).

This regularity is of great significance for the formation of properties of massive semi-finished goods, deformed at high temperatures, (forgings, stampings, large rolled and pressed bars, thick plates). The low cooling rate after working as a result of the low heat conductivity of these alloys leads to lower plastic properties, particularly in the internal volumes. Improvement of the properties in this case can be achieved by quenching from high temperatures. We present below the results of tests of bars 230mm in diameter of 4201 alloy in the initial hot pressed state and after quenching from various temperatures.

<table>
<thead>
<tr>
<th>State of Specimens</th>
<th>( \sigma_b ) kg/mm(^2)</th>
<th>( \delta ) %</th>
<th>( \psi ) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot pressed</td>
<td>96.1</td>
<td>0.6</td>
<td>2.1</td>
</tr>
<tr>
<td>Quenched from 800(^\circ)</td>
<td>109.9</td>
<td>9.1</td>
<td>32.1</td>
</tr>
<tr>
<td>&quot; from 1000(^\circ)</td>
<td>109.0</td>
<td>13.3</td>
<td>54.8</td>
</tr>
</tbody>
</table>

A good combination of strength and plastic properties can be achieved also by intensification of cooling of the metal after hot deformation (cooling in water).

When held in the 350-600\(^\circ\) temperature interval, alloys 4201 and 4203 show stable tendencies to losses of plasticity. With certain values of temperature and holding time, the relative elongation and reduction in area are decreased almost to zero and the impact toughness drops from its initial value of 4-5 kgm/cm\(^2\) for 4201 alloy after 24 hours holding at 350-500\(^\circ\) to 0.8-1.0 kgm/cm\(^2\).

In this connection, it would be interesting to analyze the problem of the influence of etching in an alkali-salt melt, which is conducted at 450\(^\circ\) for one hour before acid etching, and vacuum annealing, on the mechanical properties of sheets.

Table 3 shows the results of mechanical tests of sheets 4mm thick made of 4201 alloy in various states.
We can see from the data below that etching improves the plasticity of the initial specimens after hot rolling by removing the surface gas-saturated layer.

<table>
<thead>
<tr>
<th>State of Specimens</th>
<th>$\sigma$, kg/mm$^2$</th>
<th>$\delta$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>After hot rolling</td>
<td>96.0</td>
<td>5.7</td>
</tr>
<tr>
<td>After hot rolling and etching</td>
<td>93.8</td>
<td>7.0</td>
</tr>
<tr>
<td>After hot rolling and annealing at 850(^\circ) for 1 hour</td>
<td>87.7</td>
<td>6.6</td>
</tr>
<tr>
<td>After hot rolling and annealing at 850(^\circ) and etching</td>
<td>86.5</td>
<td>10.5</td>
</tr>
<tr>
<td>After hot rolling and quenching from 850(^\circ) and etching</td>
<td>87.8</td>
<td>4.7</td>
</tr>
<tr>
<td>After hot rolling, quenching from 850(^\circ) and etching</td>
<td>87.2</td>
<td>5.7</td>
</tr>
<tr>
<td>After hot rolling, etching and vacuum annealing at 850(^\circ)</td>
<td>86.0</td>
<td>17.1</td>
</tr>
</tbody>
</table>

Note. Etching in all cases performed as follows: etching in melt of caustic soda with potassium nitrate added at 450\(^\circ\) for 1 hour and subsequent etching in acid solution at 40-60\(^\circ\).

The positive influence of etching is also felt by the properties of quenched and annealed specimens. However, the best level of properties was achieved by the combination of etching of hot rolled sheets with subsequent vacuum annealing. A comparison of the properties of specimens in the state after hot rolling, annealing at 850\(^\circ\) and etching and after hot rolling, etching and vacuum annealing from 850\(^\circ\) shows that when it is the last operation, etching leads to decrease in plastic properties of the sheets. On the other hand, the effect of the relatively low rates of cooling in the 300-600\(^\circ\) temperature interval occurring during annealing in the vacuum furnace have no noticeable negative effect.

Thus, etching (using an alkali-salt melt) and vacuum annealing, when used as the final operations, provide high indicators of plasticity of sheets.

Conclusions:

1. When vacuum arc melting is used for the manufacture of type 4201 titanium alloy ingots, molybdenum should be introduced as particles whose dimensions do not allow them to sinter in the electrode and provide the greatest possible melting during first remelting. The remelting regimes should be designed so that solution of the molybdenum is provided first, followed by formation of a healthy ingot with good surface.

2. Cooling of prepared semi-finished goods from the temperature of hot working at rather high rates of cooling or the performance of quenching from high temperatures (1000-1100\(^\circ\)) made it possible to produce high plastic
properties. The best results as to quality of sheets of 4201 alloy can be achieved by using powerful equipment for hot rolling, the most reliable possible protection of the metal from oxidation or removal of the gas-saturated layers if formed.

BIBLIOGRAPHY


As a result of these investigations, the specifics of the technological properties of the alloys have been determined, pilot scale technology has been developed for the production of the ingots and semi-finished products, the regularities of changes of the structure and properties of the alloys as a function of deformation modes and heat treatment have been studied, and the corrosion behavior of commercial semi-finished products has been studied in certain corrosive media.
### Key Words

<table>
<thead>
<tr>
<th>Role</th>
<th>Line A</th>
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- Corrosion behavior
- Alloys
- Investigations
- Technological properties
- Ingots
- Semi-finished products