ALLOY THEORY
AND PHASE
TRANSFORMATIONS
Titanium is properly different from other light metals, aluminium and magnesium, by its polymorphism like iron has. This property gives the broad opportunities for titanium alloys structure and properties influence because it allows to use not only metastable solid solutions decomposition at quenching and ageing, but the allotropic $\alpha \rightarrow \beta$ transformation with some intermediate phases and chemical compounds that gives the broad spectrum of structures and properties. In the starting period of the titanium alloys theory development the main attention was pointed at the data base gathering about alloying elements influence on the titanium strength and the corresponding phase diagrams establishing.

To the finish of 60th the titanium alloys almost with all elements of periodic system were studied more or less carefully. As a result of these investigations the titanium alloys theory bases were established as described below.

1. The most prospect alloying elements group was defined, their influence on allotrophic titanium transformation temperature, solid solution regions with the both titanium allotropic modifications and the influence on properties complex were determined (Fig. 1). The basis titanium alloys classification by the structure type and alloying elements classification by their influence on titanium allotropic transformation temperature were established. The opportunity of additive estimation the joint $\beta$ -stabilizers influence by $\beta$ -stabilizing coefficient entering for each component being investigated (Fig. 2). This theoretical postulate simplifies the structure and properties prediction at the multicomponent titanium alloys developing.

The important part of titanium alloys and phase transformations theory is the undesirable eutectoid decomposition breaking possibility in chromium and iron containing alloys by $\beta$ -stabilizers (molybdenum, for example) doping. This allow to get the necessary thermal stability level. The example of this relationship is broadly usable in Russia VT3-1 alloy.
2. The main titanium particularities which differs it from other construction materials were pointed. The high chemical activity in melted conditions and under high temperatures in solid state gives the ability to form the alloys with gases of atmosphere and hydrogen. The high chemical resistance of titanium oxide is the main obstacle for manufacturing method development of pure titanium gathering by the direct oxide.
ores reduction. These physical and chemical properties of titanium are the powerful stimulus for new metallurgy branches developing, for example, haloid metallurgy, magnesium thermal metallurgy - by Croll, natrium thermal metallurgy by Hanter, iodide metallurgy - by Van Arcel and de Boer, and vacuum melting in copper water cooled crucible.

3. The practical use of oxygen, nitrogen and hydrogen alloying of titanium, that earlier were considered as determinant impurities, which concentration must be minimal, was pointed.

The large importance for titanium problem considering as reliable construction metal its interaction with hydrogen studying has. It was pointed that hydrogen, which is $\beta$-stabilizer with reversible solubility in titanium, is the powerful facility for phase and structure transformations in titanium alloys managing. The titanium alloy thermohydrogenous treatment was developed, which is principally new technological process combining the thermal treatment with reversible hydrogen alloying. This process includes three stages: metal hydrogenization till necessary concentration, thermal treatment, and vacuum annealing for hydrogen concentration decreasing till safe concentration. It was pointed that thermohydrogenous treatment allows to manage the deposited phases morphology during quenching material ageing: to transform the platelike structure in fine-graining equiaxial one with the mechanical properties increasing; to increase the two-phase $\alpha + \beta$ alloys hardenability; to harden the pseudo-$\alpha$-alloys by thermal treatment.

The thermohydrogenous treatment of titanium alloys is in its initial stage, but its potential possibilities are very high. For example, the opportunity of technological plasticity increasing of hard structure alloys is opening by their temporary transition into more plastic two-phase alloys type. For high strength two-phase alloys the opportunity of improving hardenability arises by temporary transition these alloys in pseudo-$\alpha$ or $\beta$-alloys (Fig. 3).

It is known that castings has the lower mechanical properties level than forgings of the same alloys. The reason of this fact is the remaining porosity and coarse-grained structure of cast metal. The first disadvantage is removed by hot isothermal treatment in gasostates. The structure refining and its transition from platelike to equiaxial one with simultaneous grain refining is get by hydrogen-thermal treatment. The phase hardening being arised as a result of specific volume variations under such a treatment substitutes the deformation, which was considered as the only one method of cast material mechanical properties radical increasing some time ago. This effect may be reinforced by another new process using-thermo-cycling. This allows to approach the cast metal properties level to the deformed metal one (Fig. 4).

4. As the experimental materials about titanium alloys were gathered the titanium-aluminium system role become more clear as the basis of practically all commercial titanium alloys. It is explained by the fact that the most of alloying ele-
ments are $\beta$-hardeners, but aluminium is one effective $\alpha$-phase hardener. The titanium alloys theory pointed that the titanium alloys mechanical properties optimal complex is achieved at equal strength of both $\alpha$ and $\beta$ phases. Tin and zirconium harden the $\alpha$-phase too, but not so effective as aluminium does. Aluminium decreases the titanium alloys density, and tin and zirconium increases it. Under the large volumes of titanium alloys manufacturing the economical factor has its importance as aluminium cost is lower than zirconium and tin one, and titanium too. Aluminium more effective increases the high-temperature strength than other elements, and in large quantities decreases the titanium oxidizability and inflammability.

Figure 3 - Transformation of Ti-$\beta$-stabilizers diagram after additional alloying by hydrogen: usual constitutional diagram; - - - the same after addition of hydrogen.
Microstructure of casting VT5L alloy
a - as cast;
b - 0,9ΔHV+vacuumannealing;
c - 0,5ΔHV+termocycling (5 cycles)+vacuumannealing.

<table>
<thead>
<tr>
<th>Condition of Ti-6Al-4V alloy</th>
<th>Endurance limit (10^7 cycles, bending)</th>
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<tbody>
<tr>
<td>cast+annealing</td>
<td>430-455</td>
</tr>
<tr>
<td>cast+quenching+aging</td>
<td>525-595</td>
</tr>
<tr>
<td>cast, termohydrogen treatment</td>
<td>700-735</td>
</tr>
<tr>
<td>deformed, annealing</td>
<td>455-665</td>
</tr>
<tr>
<td>deformed, quenching+aging</td>
<td>630-700</td>
</tr>
</tbody>
</table>

Figure 4 - Improving microstructure and endurance limit after thermo-hydrogenous treatment.

The next investigations opened another important property of aluminium - the opportunity of light high-temperature strength alloys of new type forming on the base of titanium and aluminium chemical compounds, that allowed to increase the titanium effective usage temperature till 900 °C to concure with nickel superalloys.

Except titanium-aluminium chemical compositions mononickelide NiTi has theoretical and practical interest, it has the homogeneity region of 54-58 mass. % and is the base of new alloys with special properties development.

The possible using branches may be as: for heat energy direct transformation to mechanical work; as sensitive thermomechanical transducer; for self-unrolling aerials, masts etc.; chemical equipment (corrosion resistance); for up-water and under-water ships (ultrasound absorption, wear resistance, corrosion resistance); as a material with high wear resistance and damping capacity standing up to an impact damphering equipment in motor transport; as a material able to do mechanical work till many cycles (many thousands) when any reversing equipment is; in medicine (internal prothesis etc.); for producing rivets with shape memory; for self-working conjuctive couplings for pipe-line; for new constructions of apparatus and equipment, working on the base of shape memory effect. The shape memory effect is of a great interest.
It appears in these alloys because of reversible martensite transformation which causes the reversing of shape having been took place before plastic deformation. This effect may be varied by additive alloying in temperature interval defined by working conditions. The good example is conjuctive coupling of pipe-lines of "cryofit" type and self-unrolling aerials of space ships (Fig. 5).

Figure 5 - The advantages of TiAl-based alloys.

The other high-doped titanium alloy is titanium-niobium system alloy based one, having high superconducting effect, and thus, having practical using in speed railway transport with magnetic suspension.

In the paper / is pointed the using of composite material "Tor-Supra" superconductors. This material is superconductive wire consisting of $10^4$ fibres of 22 mkm dia of titanium - 36.8 at. % niobium alloy in copper and copper-nickel matrix.

5. The using of last achievement of titanium alloys, structure and phase transformations theory in alloying and new technology using allows to increase strength in broad temperature region (-253 - +600 °C) in 6-8 times.

Fig. 6 shows that by rational alloying and thermal treatment at room temperature the titapiaum alloy strength may be increased from 25 to 150 kg/mm² under cryogenic temperature -
from 80 to 160 kg/mm², at 600 °C the temporary strength increases from several kg to 60-80 kg/mm².

Figure 6 - Strength of titanium and its alloys at different temperatures.

6. The high structural sensitivity of titanium alloys allows by structure varying to effects comparable with alloying. This confirms indirectly by some decelerating of new composite titanium alloys appearance last time. New methods of influence on titanium alloys structure and properties lead to new branch of titanium alloys theory appearing, which may be named "structural engineering".

The structural engineering includes metal alloys reliability new criteria appearing, as fracture toughness, fatigue crack propagation speed, and as for structure - the optimal structure defining for branches of using. Many achievements were done in melt cooling rate influence at titanium alloys properties and structure investigation, even for amorphous material of type with unique properties complex producing. The results of rapidly quenched layer on the titanium alloys surface producing by laser beam heating experiments may serve as examples. It is shown in Table 1 that structural modification allows to increase the fatigue characteristic of initial coarse grained structure in 1.5-1.7 times and at 10 % of fine grained structure. The structure of modified layer is shown in Fig. 7.

Macro- and microcomposite materials are new materials. They are semiproducts of high strength and intermetallic alloys, strengthened by silicium carbide fibres or other high-strength fibres.

The developing of structural engineering is mechanical alloying bases on solid phase components interaction. Other than
composite materials the components physical-chemical influence is not only allowed but is the base of new type material production process. The characteristic properties of this process are briefly given below:
- supersaturated unstable solid solutions producing ability;
- dispersed unsoluble solid solutions of oxides, nitrides, carbides strengthened alloys producing with the aid of high temperature strength, high temperature resistance and thermal stability increasing. The special meaning has the strengtheners and matrix interaction investigation under working temperatures;
- composition of two low- or unsoluble in themselves components producing;
- materials without liquation, coarse cast structure and easily melting eutectics producing ability.

Figure 7 - Influence of laser-treatment on mechanical properties of VT3-1 alloy.

The processes connected with melted metals superrapid cooling and alloys production by metal gas condensation on cooled base are investigated now. Metals and alloys producing with nanostructure is to be considered as the limit case, and it may be named the most impressioned structure engineering achievement. Surely for titanium alloys mechanical properties increasing even for pure titanium and low-alloyed Ti-alloys.
Table 1 - Laser Treatment Influence on VT3-1 Alloy Mechanical Properties

<table>
<thead>
<tr>
<th>Initial Structure</th>
<th>$G_{-1}$, MPa</th>
<th>$\text{Nb} \approx 2 \cdot 10^7$ cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>without laser treatment</td>
<td>with laser treatment</td>
</tr>
<tr>
<td>Coarse grained platelike</td>
<td>300-330</td>
<td>450-480</td>
</tr>
<tr>
<td>Fine grained globular</td>
<td>520-550</td>
<td>570-600</td>
</tr>
</tbody>
</table>

During last 15-20 years many investigation of superrapid cooling (SRC) influence on metal alloys structure and properties were undertaken. This fact can be explained by some advantages of superrapid cooling technology using in high strength, high temperature strength and special alloys producing.

SRC allows to produce the homogeneous alloys of basic metal with any alloying elements except the cause of dismixing (enlayering) in liquid state. SRC method broadens the different usage alloys producing abilities including new type alloys with increased mechanical and special properties.

SRC allows to broaden the solid solutions regions in basic binary systems, which manufacture alloys are based on and to increase the strengthening heat treatment effect. The possibility of thermally stable disperse strengthening is appearing and increased the high temperature strength and creep resistance alloys producing. SRC combined with today powder metalurgy methods allows to produce superfine microstructure and chemical composition for any size and mass products in the limits of technological equipment size.

It is known that under cooling rate increasing the degradation of equilibrium phase diagram takes place as it is shown in Fig. 8. We can seen that with cooling rate increasing the solid solutions region are enlarged, the specific points of diagram, as eutectic, peritectic points, chemical compounds are disappeared. The diagram simplifying and its transformation in continuous solid solutions system takes place. Then the solid-liquid state regions disappear, the liquidus and solidus become one line and liquid state exists above it, solid state - below it.

The solid material being produced in this case is amorphous or glasslike and has some specific properties. It has no crystal lattice and grain boundaries. Amorphous alloy is homogeneous by its chemical composition when compared with traditional technology of production alloy by casting.
Figure 1 - Phase diagram degradation with increasing of cooling rate /7/.

Phase Transformation in Titanium Alloy

All phase transformation taking place in titanium alloys under heat and pressure treatment are based on allotropic $\beta \rightarrow \alpha'$, $\beta \rightarrow \omega$ and $\alpha \rightarrow \omega$ transformations in titanium according to theories in polymorphic metals based alloys one modification to another transition must occur by shift. This gives us idea different from existed before, that under all temperature-rate conditions of thermal and thermomechanical treatment the main nucleous new phase forming is shifting. The final structure forming depending on kinetic conditions may occur by diffusionless (martensitic) or middle (diffusionless nucleation with diffusion growth) mechanisms. Some examples illustrating this idea are given below.

1. The transformation $\beta \rightarrow \alpha'$, $\beta \rightarrow \omega$ and $\alpha \rightarrow \omega$ are martensitic ones (MT) of the first kind, which occur under temperature or pressure with positive or negative hysteresis changing. MT $\beta \rightarrow \alpha''$ is reversible not only crystallographically but thermally too, that allows to provide shape memory effect (SME) (Fig. 9) and high demphirity /2-4/ plus to twin strain mechanism with invariant lattice.

2. Other than existing new points of view say, $\beta \rightarrow \omega$ and $\alpha \rightarrow \omega$ transformations we can investigate as shift hysteresisless transformations developing by slip mechanism /5-6/. They are transformations near second kind of transformations, which provides the continuous thermodynamic potential differing under these transitions and coherent spinodal exiting (Fig. 10). For example, $\beta_m$ to $\omega_M$ transition occurs by some $\beta$ ($\omega$) condition, which is characterized by "incommensurable" structure.
Figure 9 - Changing in crystallographically reversable ($E_{av}$) accumulated under stressing ($E_{ac}$) and recovered ($E_{r}$) by SME deformation in Ti-5Al-V alloys during $\alpha''$-$\beta$ MT ($\gamma'$ - heating arte).

Figure 10 - The diagram illustrating phase thermodynamic potential change in titanium-$\beta$-isomorphic stabilizer system (Ti-$X_B$) without concentration fluctuation calculating ($x_1$-$x_3$ and $x_{cr}$-$x^{\omega}_{cr}$ - spinodal).

Fig. 11 shows the temperature-concentration regions where the for-precipitating stage provides the different nucleation ways. The new phase nucleation under $\beta_m$-phase and $\alpha''$ mertensite decomposition in temperature region contact to $M_S$ and $A_S$. 
correspondingly, may occur by homogeneous nucleation way by concentration fluctuations, and in regions far from $M_a (A)$, $\beta_m$-phase and $\alpha'$ phase decomposition occurs by heterogeneous nucleation on grains and subgrains boundaries and on plane dislocations accumulations. Decomposition of $\alpha'$- and $\alpha''$-martensite in alloys of concentration near $x$ ($\alpha'$-$\alpha''$-transition) and decomposition in incommensurable $\beta$ ($\omega$)-structure alloys occurs by spinodal decomposition mechanism. This allows us to say that $\omega_{eq}$ and $\omega_{\beta}$-phase forming mechanisms are adequate and explain the $\omega_{\alpha'}$-phase precipitation process insensibility to dislocation construction and its high rate.

![Diagram](image)

Figure 11 - The diagram illustrating temperature-concentration regions of different nucleation realization during metastable phases decomposition in Ti-$x_\beta$ system HN-homogeneous nucleation, HGN-heterogeneous nucleation, SD-spinodal decomposition; HGN I - nucleation mainly on boundaries of $\beta$-grain; HGN II - nucleation at grain boundaries and body; HGN III - nucleation only in $\beta$-grain body.

4. Martensitic and $\beta_m$-phase isothermal decomposition occurs by middle mechanism, and its kinetic may be described by two types of $\alpha$-kind diagrams (Fig. 12). The special feature of these diagrams of early investigated /5, 7/ is the absence of special C-curves for $\beta$ ($\omega$), $\omega_{\alpha'}$ and $\omega''$ transformations of second kind. The onest C-curve describes the transformation beginning of future $\alpha'$-phase nucleous, which under high temperatures ($T > M_8$ and $T > 550 ^\circ C$) are $\alpha'$ and at low temperatures ($T > 550 ^\circ C$) - $\alpha''$-phase. The final $\omega_{eq} + \omega_{eq}$ structure formation occurs by diffusion poorment of $\alpha'$ and $\alpha''$ phases formed by martensite mechanism. In accordance to large volume in-correspondence of $\omega_{eq}$ and $\omega_{eq}$-phases /8/ it always leads to plate structure forming. The isothermal $\omega_{\alpha'}$-phase does not
take place in $\alpha$-phase forming but stimulates its nucleous forming in nearer to $\beta/\omega$ boundary microvolumes of $\beta_m$-phase.

Figure 12 - The diagrams illustrating the main stages of isothermal metastable phases decomposition and structure forming under thermal treatment of before-critic (a) and post-critic (b) composition alloys. (The lines shows the beginning: 1 - of nucleous $\alpha$-phase in $\beta$-phase forming; 2 - $\alpha$-phase forming of $\alpha''$-phase; 3 - martensite decomposition; 4 - nucleous of $\alpha''$-phase forming in $\beta$-phase; 5 - $\beta(\omega)$-phase forming; 6 - transition from nucleating to nucleous of new phase growth; 7 - ($d_{eq} + \beta_{eq}$)-structure forming finishing with equilibrium phase composition; 8 - three-phase region $\beta_m + \phi + \omega$).

5. Decomposition of $\beta_m$-phase under continuous cooling occur by the same mechanisms as under isothermal exposure. Different from traditionally used TTT-diagram /1, 9/ the phase composition and structure forming as a result of $\beta_m$-phase decomposition under continuous cooling we must describe by new type of diagrams: phase composition - chemical composition of $\beta$-phase - cooling rate ($PC-x-V'$) (Fig. 13). With the cooling rate decreasing beginning with the first critical ($V_{cr1}$) the diffusion growth part begins to overcome the diffusionless nucleation one, that firstly leads to indeterminate structures forming with contain coherent and inhomogeneous by chemical composition $d_{inh}, \alpha''_{inh}, \beta_{inh}$ and $\beta(\omega)_{inh}$ phase, and under rates less then second critical one ($V_{cr2}$) - to equilibrium $d_{eq} + \beta_{eq}$-structure. The rate $V_{\frac{5}{2}}$ is the par-
ticular one, when $\alpha'' = \alpha'$ transition realizes, cooling with this rate is undesirable as it leads to chemical phases inhomogeneity and maximum stress level, that causes the large alloys embrittlement.

Figure 13 - The diagram phase composition - vanadium concentration ($x_v$) - cooling rate ($V^0$), cooling from $\beta$-region Ti-5Al-V system.

References


