Phase transformations in nickel- and titanium-based alloys during chemical heat treatment

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\textbf{Abstract.} The structure of surface areas and cores of Ni-40Cr-4Al and Ti-6Al-5V alloys in the process of thermal and chemical heat treatment - nitriding, oxidation and carburizing was studied by X-ray diffractometry, optical microscopy and hardness measurement. Ni-40Cr-4Al alloy after quenching contains two supersaturated solid solutions based on fcc-Ni and bcc-Cr and a small amount of compound Ni\textsubscript{3}Al; subsequent aging leads to decrease in the degree of supersaturation of fcc-Ni and increase in the amount of bcc-Cr and Ni\textsubscript{3}Al. Nitriding leads to the formation of continuous CrN layer 3-4 \textmu{}m thick on the surface, decomposition of Ni\textsubscript{3}Al and formation of AlN in underlying layer 100-140 \textmu{}m thick. After nitriding high microhardness value of CrN (up to 1060 HV) and a slight decrease from 740 to 650 HV in the subsurface layers due to the transformation of Ni\textsubscript{3}Al to AlN were found. The surface layer of Ti-6Al-5V alloy is oxidized by erosion cutting in water, but the oxides formed during this process do not influence on subsequent diffusion saturation. During nitriding, oxidation, carburizing of Ti-6Al-5V alloy, diffusion layers are formed. They are characterized by the increased amount of \alpha{}-solid Ti solution and formation of the surface intermediate phases. The thickness of the hardened layers is 8-20 \textmu{}m. The hardness of these layers is 1000 HV for oxidation, 1000 HV for nitriding, 570 HV for carburizing.

1. Introduction

The most important task of modern technology is the creation of parts with improved characteristics and special properties of their surface. Parts from corrosion-resistant materials with adjustable thermal and chemical heat treatment with a set of parameters characterizing mechanical properties (strength and impact toughness) and special surface properties (hardness, wear resistance, contact endurance and corrosion resistance) are very promising. To improve the mechanical properties of the core of parts, heat treatment (HT) is now effectively used \cite{1-4}, and subsequent chemical heat treatment (CHT), for example, nitriding, oxidation, and carburizing \cite{5-10}, is used to change existing physical properties of the surface of parts. Such treatment makes it possible to improve the performance characteristics of the surface layers by diffusion saturation of the surface with elements that cause the formation of hardening phases or protective coatings of different phase composition in these layers. This approach allows transforming the chemical and phase composition, as well as the structure and properties of the surface layers of many materials \cite{7-13}.

The nickel-based (Ni-40Cr-4Al) and titanium-based (Ti-6Al-5V) alloys presented in this article are used in the aerospace industry and shipbuilding. Chemical heat treatment of such alloys allows...
increasing the operational properties of the surface without affecting the core, which expands the field of application of materials [6, 13].

During CHT, a complex system of phase regions is formed in the surface layer, which determines the special properties of the surface [10, 12]. The study of phase transformations during HT and CHT is the basis for understanding the essence of the processes taking place and, as a result, improving the properties of both the surface and the material itself.

The purpose of this work is to obtain the data on phase transformations in Ni-40Cr-4Al and Ti-6Al-5V alloys in the process of thermal and chemical heat treatment using X-ray diffraction (XRD) phase analysis, optical microscopy and measuring the mechanical characteristics of the alloy and its surface.

2. Research methods
The samples of alloys, the composition of which is given in Table 1 were objects of research.

Table 1. Chemical composition of alloys

| Alloy        | Base | Mass fraction of the element, % |
|--------------|------|---------------------------------|
|              | Cr   | Al    | V     | Zr   | Fe   | C    | O    | H    |
| Ni-40Cr-4Al  | Ni   | 39.0-41.0 | 3.3-3.8 | -    | -    | ≤0.6 | ≤0.03 | -   |
| Ti-6Al-5V    | Ti   | -     | 5.3-6.8 | 3.5-5.3 | ≤0.3 | ≤0.1 | ≤0.2 | ≤0.015 |

Heat treatment of the Ni-40Cr-4Al alloy consisted of heating the samples with dimensions of Ø20×10 mm in an oxidizing environment to a temperature of 1150 °C, holding for 40 minutes at this temperature and quenching in cold water. After quenching, aging was performed at 560 °C for 25 hours, followed by air cooling.

Ti-6Al-5V alloy samples were made from a hot-rolled bar without additional heat treatment. For metallographic and X-ray phase analysis of the initial state, samples with dimensions of Ø16×10 mm (without height restrictions), produced by abrasive cutting with intensive cooling, were used. For CHT, specimens with height restrictions (not more than 0.7 mm) were prepared by erosion cutting in water.

Before CHT the flat surfaces of the samples of both alloys were ground with emery cloth with a decrease in grain size, and then the samples of the Ni-40Cr-4Al alloy were subjected to electrolytic polishing in a solution of chromic anhydride in orthophosphoric acid. After CHT, the surface of the samples was not re-ground or etched.

Chemical heat treatment for the alloy Ni-40Cr-4Al consisted of nitriding in a glow discharge. The saturation temperature (540 °C) was chosen less than the aging temperature of the alloy. The duration of CHT was 24 h in an atmosphere of 95% N₂ + 5% H₂. Nitried samples both after quenching and after quenching, followed by aging were studied.

Such CHT types as nitriding, carburizing and oxidation were used for the Ti-6Al-5V alloy.

Nitriding and carburizing were carried out in a universal vacuum furnace at a temperature of 830 °C (below the temperature of polymorphic transformation of the alloy) in an atmosphere of molecular nitrogen and acetylene, respectively, oxidation was performed in a laboratory furnace with an oxidizing atmosphere under a carburizer at a temperature of 800 °C. The processing time was 6 hours.

X-ray studies were performed on a DRON-4 diffractometer in Co-Kα radiation. The Bragg-Brentano focusing scheme was used. A curved monochromator was placed between the sample and the detector. The number of detector pulses was measured in 4 seconds by points with a step of 0.1 degrees in the 0 / 2θ scan mode in the angle range 20-120 °. X-ray phase analysis was used according to the traditional scheme to determine the phase composition of samples using the database of interplanar spacing of the phases.

Metallographic studies were carried out on cross sections of samples prepared in the traditional way using an OLYMPUS GX-51 microscope with 500x magnification. To identify the structure of the
Ni-40Cr-4Al alloy. Marble reagent was used (4 g CuSO₄ + 20 ml HCl + 20 ml H₂O); a reagent (2 ml HNO₃ + 2 ml HF + 96 ml H₂O) was used for etching the Ti-6Al-5V alloy [14].

Durometric studies consisted of the measurement of microhardness by the Vickers method on a DuraScan-70 microhardness tester with a load of 1 N (100 g). The microhardness distribution was measured over the cross-section of the nitrided layer (on an etched metallographic section), and the microhardness of the sample surface was also measured.

3. Study formation of the phase state, structure and changes in the hardness of the alloy Ni-40Cr-4Al

The microstructure of the alloy in the quenching state (figure 1, a) is represented by small rounded and elongated light particles uniformly distributed in a dark grey matrix with well visible twins; the alloy hardness in this state does not exceed 300 HV. After aging (figure 1, b), the number of bright particles in a uniformly etched matrix increases significantly, and the hardness increases to 690-750 HV.

After quenching, according to XRD (X-ray diffraction) data (see figure 2), a formed state is characterized by two supersaturated solid solutions based on fcc-Ni (γ-solid solution) and bcc-Cr (α-solid solution) with a small amount of Ni₃Al phase. The hardness of such is small. A nickel-based supersaturated solid solution is characterized by the increased lattice parameter due to the dissolution of larger Cr and Al atoms in Ni. The lattice parameter of the α-Cr phase remains almost unchanged due to the dissolution of larger Al atoms and smaller Ni atoms in Cr.

![Figure 1](image_url)

**Figure 1.** The microstructure of the alloy Ni-40Cr-4Al after quenching (a) and after quenching, followed by aging (b), × 500; phase composition is set using X-ray phase analysis (figure 2)

In the process of the hardened structure aging, the degree of supersaturation of the γ-solid solution decreases, as evidenced by a decrease in the lattice parameter; at the same time, the amount of bcc-Cr and Ni₃Al phases increases, which leads to a regular increase in alloy hardness. It should be noted here that, due to the dispersion of the Ni₃Al intermetallic compound (γ'-phase), it is not detected by metallographic analysis (see figure 1).

During nitriding, a continuous layer of the CrN phase is formed with a thickness of 3-4 microns (figure 3) with microhardness up to 1060 HV on the surface of the alloy (figure 4); an area 100-140 microns thick is formed under the CrN phase and reduced by 90 HV compared to core microhardness. Such change in microhardness can be explained by the decomposition of the Ni₃Al intermetallic compound (γ'-phase) with the formation of aluminum nitride AlN, i.e. replacement of intermetallic hardening with nitride hardening; at the same time, the amount of bcc-Cr phase decreases in the surface layer. The results of X-ray phase analysis confirm such structural transformations (see figure 2).
The microstructure and hardness distribution in the surface area of the alloy after quenching and nitriding, as well as quenching, aging, and final nitriding, turned out to be almost identical (see figure 3, 4). Nitriding of a pre-hardened alloy compared to nitriding after quenching and aging leads to similar phase transformations (see figure 2). However, the hardness of the core during nitriding after quenching will be less due to the inconsistency of the optimal nitriding temperature and time of the alloy treatment (see figure 4).

**Figure 2.** XRD pattern of the alloy Ni-40Cr-4Al after quenching (1), after quenching and aging (2), after quenching and nitriding (3), after quenching, aging and nitriding (4)

**Figure 3.** Microstructure of the near-surface area of nickel alloy Ni-40Cr-4Al after quenching with aging and subsequent nitriding (a), after quenching and subsequent nitriding (b): 1 - nitride layer; 2 - diffusion layer; 3 - core; x 500
Figure 4. The distribution of microhardness in the surface layer of the nickel alloy Ni-40Cr-4Al, saturated with N for 24 hours at a temperature of 540 °C after quenching with aging (1) and after quenching (2).

4. Formation patterns of the phase state, structure and changes of the hardness of the alloy Ti-6Al-5V

The microstructure of alloy samples in the initial state after hot pressing (figure 5) has a two-phase (α+β) structure and is represented by light (α) and dark (β) crystals stretched in the direction of plastic deformation. The structures of alloy samples after different types of cutting are similar. However, the interphase boundaries in the microstructure after erosive cutting look thickened.

Figure 5. The microstructure of hot-rolled Ti-6Al-5V alloy samples after abrasive cutting with intensive cooling (a) and after erosive cutting (b); × 500

The XRD phase analysis method was used to detect lines of solid substitution solutions based on α- and β-Ti alloying with aluminum and vanadium (this is indicated by the shift of the maxima of x-ray lines towards smaller angles) and weak lines of TiO2 in the initial alloy after abrasive cutting and intensive cooling. A small amount of oxides in the initial sample indicates the formation of an oxide film on the surface due to the high chemical activity of titanium.

In contrast to the state after abrasive cutting with intensive cooling, the XRD pattern of the sample after erosion cutting shows, besides the α- and β-Ti lines, intensive lines of titanium oxides, both higher and lower, and their mixtures: for example, TiO, Ti2O, TiO2, Ti2O3, Ti4O9, Ti5O11, Ti8O15. The
presence of titanium oxide lines indicates intensive oxidation in the process of erosion cutting and the possible saturation of the surface layer with oxygen.

**Figure 6.** XRD pattern of alloy Ti-6Al-5V after abrasive cutting and intensive cooling (1) and after erosion cutting (2)

As the result of saturation with non-metals (N, O, C) during chemical heat treatment (nitriding, oxidation or carburizing) the quantity of α-phase crystals (light areas) increases (figure 7) and an almost continuous bright layer of the intermediate phase is formed on the surface. Its phase composition (nitrides, carbides, or oxides) depends on the type of treatment. The phase composition of the diffusion layers was identified by XRD phase analysis (figure 8).

**Figure 7.** The microstructure of the diffusion layer in the alloy Ti-6Al-5V after vacuum nitriding (a), vacuum carburizing (b) and oxidation (c); × 500

After nitriding besides α- and β-Ti lines and titanium oxide lines formed during erosion cutting (see figure 6), lines of nitride phases such as TiN, Ti$_2$N, Ti$_3$N$_2$, Ti$_5$N$_3$ and a solid solution of nitrogen introducing into α- titanium (which was indicated by the shift of lines towards low angles) were found.
After carburizing besides titanium and oxide lines X-ray peaks of titanium carbides TiC and vanadium VC were found. The shift of α-titanium lines is less than it was after nitriding because distortion of the α-titanium crystal lattice is less.

After oxidation lines of titanium oxides and their mixtures: TiO, Ti_2O, TiO_2, Ti_3O_3, Ti_6O_9, Ti_8O_15 were found.

![Figure 8. XRD pattern of alloy Ti-6Al-5V samples after erosion cutting and subsequent vacuum nitriding (1), vacuum carburizing (2), oxidation (3) and initial sample (4).](image)

The distribution of microhardness (figure 9) showed the presence of diffusion layers with increased hardness. Hardness is distributed across the thickness smoothly. The highest hardness of surface (1100HV) was obtained by oxidation. Nitriding also effectively increases hardness and gives hardness of surface 1000HV. The minimum hardening effect is observed after carburizing (570 HV). The thickness of the hardened layers was 8-20 microns.

![Figure 9. The distribution of microhardness in the surface layer of the titanium alloy samples VT6 after erosion cutting and subsequent nitriding (1), vacuum carburizing (2) and oxidation (3).](image)
Analysis results of the saturation show oxides formed after erosion cutting do not prevent penetration saturating elements in the diffusion layer during the subsequent chemical heat treatment. It can be assumed that during erosion cutting are formed fine isolated particles that do not cause blocking mass transfer.

The lines of the initial phases are preserved for both nickel- and aluminum-based alloys after chemical heat treatment, since the resulting diffusion layers have small thickness, not exceeding or comparable to the depth of penetration of X-ray.

5. Conclusion
1. Two supersaturated solid solutions of fcc-Ni (γ-phase) and bcc-Cr (α-phase) were detected after quenching of Ni-40Cr-4Al alloy. A small amount of intermetallic Ni$_3$Al phase was also found; the following aging causes reduction of supersaturation of γ-solution and increase amount of bcc-Cr and Ni$_3$Al. As a result, the hardness of alloy increased from 300 to 690-750 HV.
2. Subsequent nitriding causes the appearance of continuous CrN layer on the surface; the thickness of the layer is 3-4 μm with hardness about 1060 HV. Decomposition of Ni$_3$Al is noticed, and growth of AlN in the underlying layer with thickness 100-140 μm is detected. Because of replacing the intermetallic strengthening with the nitride one hardness in the undersurface layer is slightly decreased as compared with the core hardness (by 90 HV).
3. As a result of erosion cutting of Ti-6Al-5V alloy in the water a large amount of Ti oxides lines were detected with X-ray diffraction phase analysis. It indicates both oxidation processes during erosion cutting and possible oxygen saturation of the near-surface layer. However, oxidation of the near-surface layer doesn’t interfere on the subsequent diffusion. It is possible that dispersed particles formed during cutting don’t block the mass transfer.
4. Chemical heat treatment of Ti-6Al-5V alloy (nitriding, oxidation, carburizing) causes the formation of diffuse layers with an increased amount of α-Ti solid solutions and a thin layer of intermediate phases on its surface (nitrides, oxides, carbides respectively). Maximum hardness of the nitrided sample is 1000 HV, the maximum hardness of the oxidized sample is 1100 HV and 570 HV for the carburized sample. The thickness of the modified layers is 8-20 μm.

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