Application of Color Metallographic Techniques to Study the Microstructure of Titanium Alloys

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Abstract

The Foundry Research Institute conducts scientific research on melting, casting, heat treatment and physical metallurgy of titanium alloys. One of the important parameters of product quality is microstructure, which is tested on the entire product cross-section. The main method, which is very successful for revealing the microstructure of the Ti6Al4V alloy, is selective color etching by immersion. Also, the polarization phenomenon has been utilized to reveal the anisotropic hexagonal closed-packed alpha phase while the isotropic body-centered cubic beta phase remains dark. This paper presents the results of metallographic investigations using color etching, polarized light and interference differential contrast.

The procedure of selective color etching was very useful for differentiating between alpha and beta phases, including the microstructure at the surface, where the alpha phase may be enriched with nitrogen or oxygen. The measurement of microhardness, which was conducted from the surface to the middle of many specimens, confirmed the changes of microstructure revealed by color etching. Examination of the microstructure with polarized light was also useful for revealing the alpha-beta structure of Ti6Al4V alloy. Use of differential interference contrast method was helpful to obtain the better picture of Ti alloy microstructure after black & white etching.

Thanks to selective color etching the microstructure of castings which were made of Ti6Al4V alloy in different molds could be determined in a consistent way.

1. The casting of titanium alloys

The casting of titanium alloys in spite of scientific researches, which was conducted intensely since many years, is still very difficult and complicated process. These difficulties are due to:
- very high melting and pouring temperature;
- high chemical activity of liquid metal;
- low mass density at high viscosity in liquid stable;
- small choice of mold materials characterized by resistance to the activity of melted metal.

Due to reaction on the boundary: mold - melted metal roughness changings of casting surface and white layer microstructure as well as chemical composition, are observed.
In case of titanium castings the most common reactions on that boundary are:
- dissolving of casting mold;
- dissolving of casting mold combined with reaction at the phase boundary;
- penetration of mold with liquid metal.

The Foundry Research Institute conducts the scientific researches on the lost-wax process technology of Ti6Al4V alloy.

The Ti6Al4V casting alloy is made in vacuum arc furnace provided with gornisage crucible and action of centrifugal force takes place during pouring the lost-wax process molds. Temperature of liquid metal is 1760 +20C and temperature of molds is +20C.
The methods of casting moulds preparation are as below:

- ceramic moulds (made of ZrO_2);
- graphite molds;
- metallic molds (copper chill molds).

The common feature of titanium casting alloys is gas porosity resulting from turbulent movement which is created during pouring of mould cavity and a reaction at the phase boundary. Therefore HIP process (high isostatic pressing process) must be provided to improve the mechanical properties of castings.

2. Color metallographic techniques used for testing of titanium alloy microstructure

One of basic methods used for quality control of pure titanium and titanium alloy castings is testing of their microstructure. This investigation is carried out on the entire product cross section.

Color metallographic techniques used with successful in Foundry Research Institute are:
a) immersion selective etching;
b) polarized light;
c) differential interference contrast.

The above three methods are shortly described as follow:

<u>ad.a.</u> [1]

Satisfactory color, or tint, etchants are balanced chemically to produce a stable film on the specimen surface. This is contrary to ordinary chemical etchants, in which the corrosion products during etching are redissolved into the etchant. Color etchants have been classified as anodic, cathodic, or complex systems, depending on the nature of film precipitation.

Chemical etching is a controlled corrosion process based on electrolytic action between surface areas of different potentials. For pure metals and single-phase alloys, a potential difference exists between grain boundaries and grain interiors, grains with different orientations, between impurity phases and the matrix, or at concentration gradients in single-phase alloys. For multiphase alloys, a potential difference also exists between phases. These differences alter the rate of attack, revealing the microstructure when chemical etchants are used.

For a two-phase alloy, the potential of one phase is greater than that of the other. During etching, the more electropositive (anodic) phase is attacked; the more elctronegative (cathodic) phase is not attacked appreciably. The magnitude of the potential difference between two phases is greater than the potential differences existing in single-phase alloys. Therefore, alloys with two or more phases etch more rapidly than single-phase metals or alloys.

Color etchants are usually acidic solutions, using water or/and alcohol as the solvent. They have been developed to deposit a 0.04- to 0.5 μm-thick film of an oxide, sulfide, complex molybdate and so on, on the specimen surface and commonly work by immersion.

The thickness of the film controls the colors produced. As film thickness increases, interference creates colors - viewed using white light - usually in the sequence of yellow, red, violet, blue, and green. With anodic systems, the film forms only over the anodic phase, but its thickness can vary with the crystallographic orientation of the phase. For cathodic systems, because the film thickness over the cathodic phase is generally consistent, only one color is produced, which will vary as the film grows during etching. Therefore, to obtain the same color each time, the etching duration must be constant. This can be accomplished by timing the etch and observing the macroscopic color of the specimen during staining.

<u>ad.b.</u> [2]

Polarized light as used in metallography is based on the different colors produced by optical anisotropy and surface topography. Anisotropic metals have a noncubic crystal structure and react to polarized light. Anisotropic metals or phases have different optical characteristics in different crystallographic directions. Therefore, the intensity of light reflected from a certain grain will depend on grain orientation, and a contrast will be obtained.

Polarized light can be used to reveal grain structure, to detect preferred orientation in polycrystalline materials, to identify phases in multiphase structures. Polarized light often enhances the color contrast of surface layers produced by color etching, and is also used in conjunction with attack-polishing procedures.

<u>ad.c.</u> [3]

Differential interference contrast belongs, like polarized light, to methods for optically revealing

microstructures in color. With this method, topographical differences in the specimen result in differences in the light reflected from the microtopographical features on the surface, even as small as 1 nm or 10 Å. For producing interference contrast, a Wollastone prism splits the reflected rays into partial images, which are left to interfere in a polarizer. A polarized light beam is split into two beams that are superimposed after reflection from the specimen surface. Differences in height on the specimen surface result in path length between the two beams, which affects the degree of interference when superimposed. These differences are next transformed into differences in color. Thanks to this method finer details of microstructure are revealed and generally the total microstructure is visible much better.

3. Testing of Ti6Al4V alloy and pure titanium microstructure in Foundry Research Institute

The most useful method for revealing the microstructure of double-phase Ti6Al4V alloy is selective color etching by immersion while the polarized light and differential interference contrast could be rather supplemental ones.

The first mentioned methods tend towards differentiation of two basic phases: the anisotropic hexagonal closed-packed alpha phase and isotropic body-centered cubic beta phase [4]. These features make that during selective etching cathodic alpha phase is colored into different colors changing from light cream through yellow to brown, sometimes to dark-blue while the cathodic beta phase remains not tinted and only grain boundaries are attacked after etching in reagent, as follow [5]: 2g of ammonium acid fluoride, 100 ml of distilled water, 50 ml of alcohol. The deviation from that rule occurs when casting surface is saturated with nitrogen or oxygen. Then parameters of alpha phase crystallographic lattice are changed and the anodic character of that phase is transformed into cathodic one making it stainless in this region of casting called "alpha case"or "white layer". Therefore selective color etching is a very good method for revealing that defective layer while commonly used black & white etching method does not give that chance.

The microstructures of castings which were made under different methods of mould preparation are presented in Figures 1 - 6 and revealed by etching specimens in reagent as above.

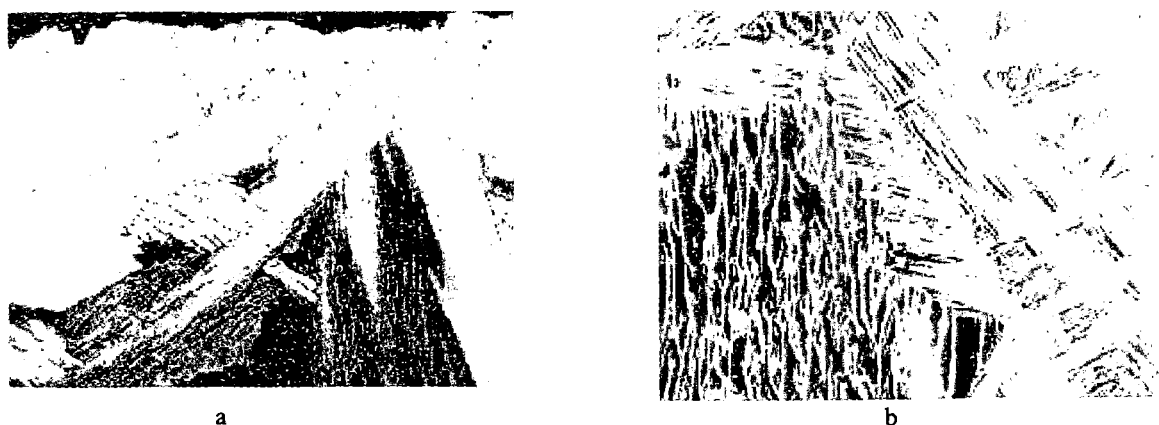a   b

Fig.1. Lamellar alpha-beta microstructure (Widmannstätten structure) of casting made in ceramic mold, sp.no.2C: a) the nitrogen-enriched zone near surface has not colored; b) microstructure of casting middle region enriched with beta phase, 320x.

The measurement of microhardness which was conducted from surface to the middle of casting confirmed the usability of selective color etching for revealing the depth of nitrogen or oxygen influence to its microstructure.

In Table 1 the results of microhardness testing are presented and in Figure 6 dimension change of indentations in microhardness testing has been shown.

In Figures 7 - 9 the advantages of employing the other two methods of testing the Ti6Al4V alloy are presented.

The comparison of traditional black & white and color etching results is shown in Figure 10 to emphasize the merits of color etching for revealing the microstructure of "white laye".

In Figure 11 the microstructure of cold-worked wire made of CP titanium (99,45%) is presented while in figure 12 we can see microstructure of the same CP titanium wire after remelting in graphite crusible and next poured into ceramic mold. This microstructure consists mainly of alpha phase but some of white, unetched phase was also revealed.

Table 1. Results of microhardness testing

| Distance from surface of casting [mm]	Microhardness HV0.5
0.020	479
0.055	479
0.090	456
0.125	420
0.160	413
0.190	407
0.225	377
0.265	371
Middle of casting	369

a

b

c

Fig.2. Lamellar alpha-beta microstructure (Widmannstätten structure) of casting made in ceramic mold with HIP process (version A), sp.no.31: a) the nitrogen-enriched zone near surface has not colored, 100x; b) microstructure of casting middle region enriched with beta phase, 100x; c) - like b), 500x.

a

b

c
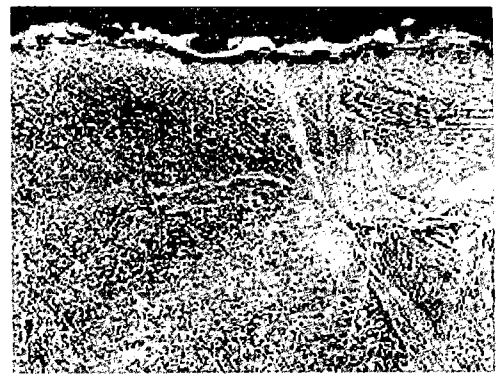
d
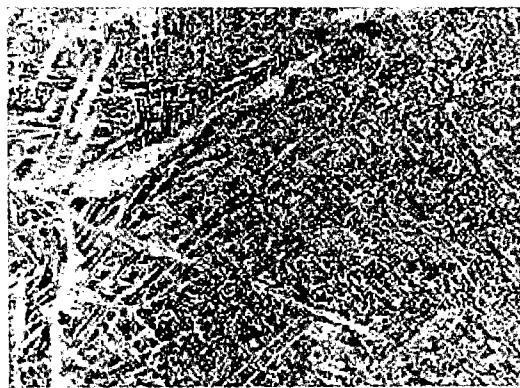
e

Fig.3. Lamellar alpha-beta microstructure (Widmannstätten structure) of casting made in ceramic mold with HIP process (version B), sp.no.E: a) general view of casting cross section with the nitrogen-enriched white layer near surface and differentiated microstructure into three main zones: A, B and C, 10x; b) microstructure near surface of zone A, 100x; c) middle region of zone A enriched with beta phase, 500x; d) microstructure near surface of zone C 100x; e) middle region of zone B with very fine acicular microstructure, resembling the martensitic one, 500x

Fig.4. Fine lamellar alpha-beta microstructure (Widmannstätten structure) of casting made in graphite mold, sp.no.21: a) the nitrogen-enriched zone near surface has not colored, 100x; b) - like a), 500x; c) microstructure of casting middle region enriched with beta phase, 100x; d) - like c), 500x.
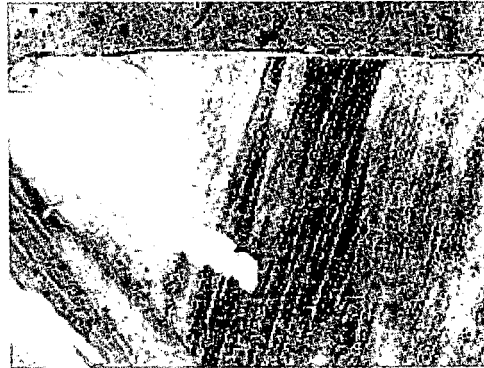
a

b

c

Fig.5. Lamellar alpha-beta microstructure (Widmannstätten structure) of casting made in metallic mold, sp.no.Ti: a) the very thin white layer near surface, 400x; b) microstructure of casting middle region enriched with beta phase, 100x; c) - like b), 500x.
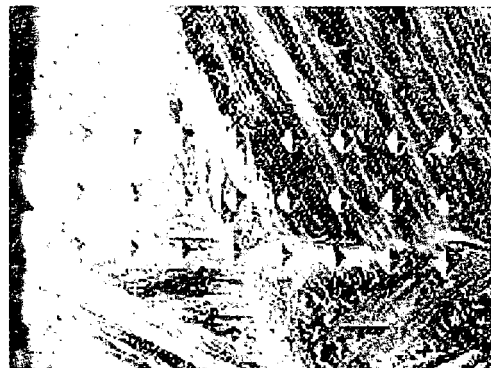
Fig.6. Indentations of microhardness testing, carried out near surface of casting, made in ceramic mold, Sp.no.4C, 250x
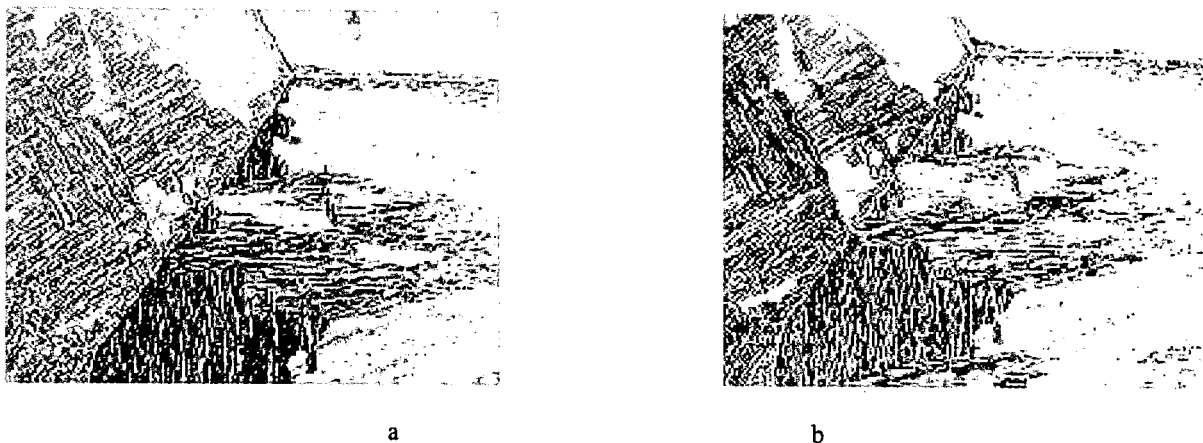
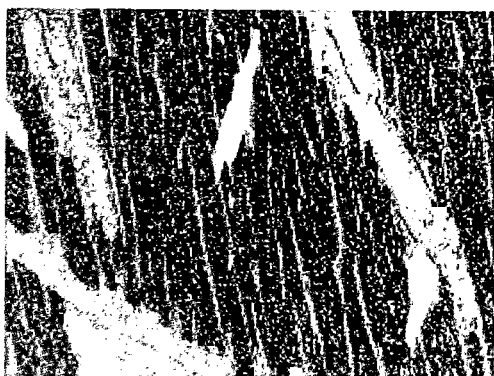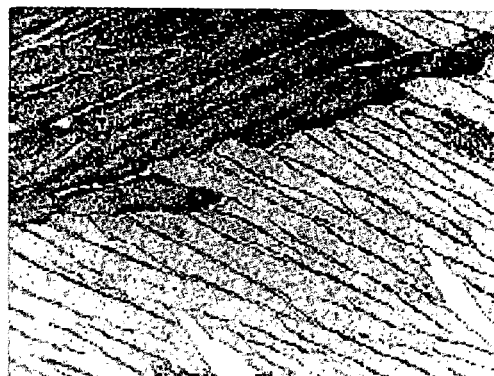a   b

Fig.7. Lamellar alpha-beta microstructure (Widmannstätten structure) of casting made in ceramic mold and revealed with black & white Keller's etchant, sp.no.1C: a) bright field illumination b) polarized light, 320x.

a

b   c

Fig.8. Lamellar alpha-beta microstructure (Widmannstätten structure) of casting made in ceramic mold, polarized light, sp.no.F: a) table of microskope is set in position "zero"; b-d) photographs were taken every 90° after table rotation in respect to positon "zero"; the isottropic beta phase remained white during table rotation while alpha phase has changed color from bright to dark, 800x
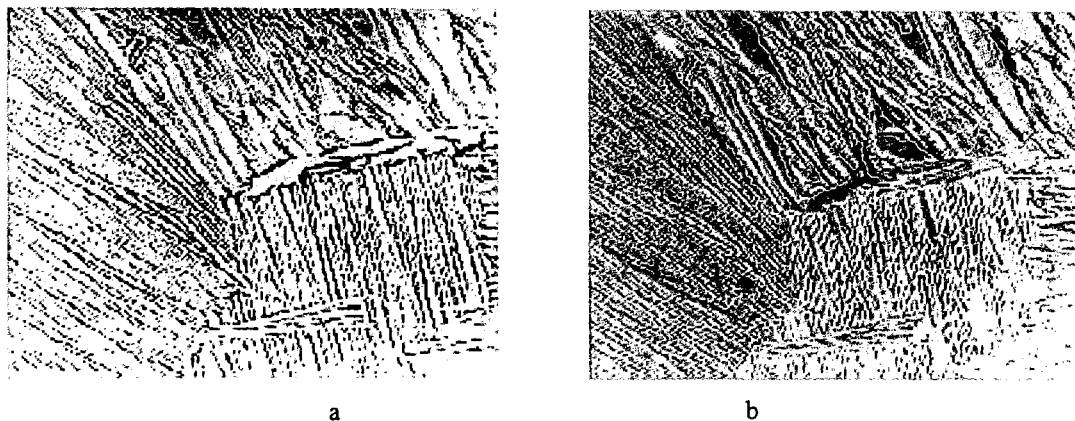
Fig.9. Lamellar alpha-beta microstructure (Widmannstätten structure) of casting made in ceramic mold: a) after black & white etching in Kroll's reagent, b) the same microstructure visible in differential interference contrast: beta phase is clearly visible in the spaces between coarser precipitates of alpha phase, 630x
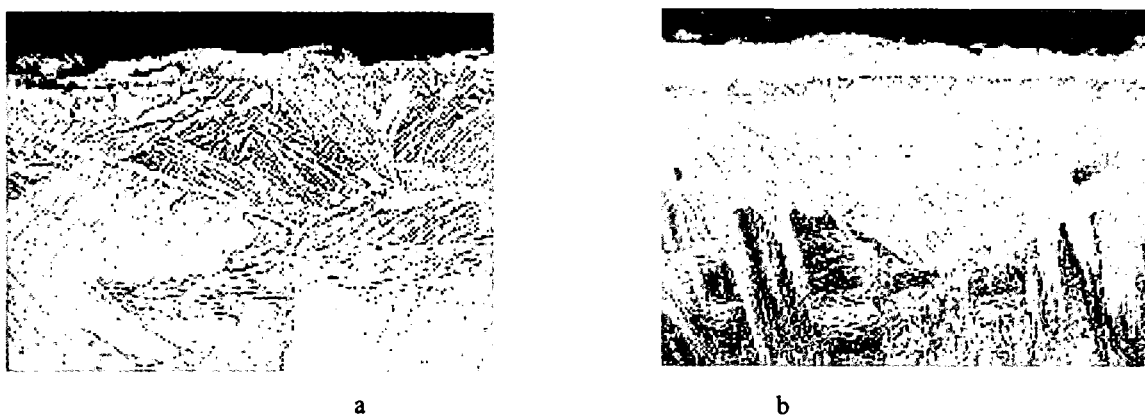

Fig.10. Lamellar alpha-beta microstructure (Widmannstätten structure) of casting made in ceramic mold: a) after black & white etching in Kroll's reagent, b) the same microstructure after etching in selective color etchant [5]: after selective color etching the nitrogen-enriched zone near surface is clearly visible, 250x
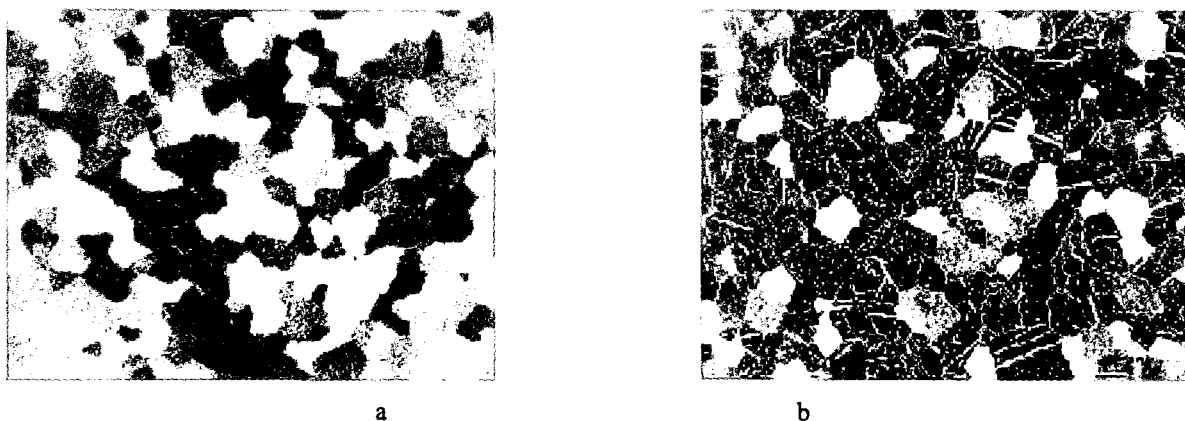

Fig.11. Microstructure of cold-worked wire made of CP titanium: a) not etched, polarized light: the different orientation of grains is visible; b) after etching: slip bands in crystalites as well as small amount of not colored hydrides are visible, 100x
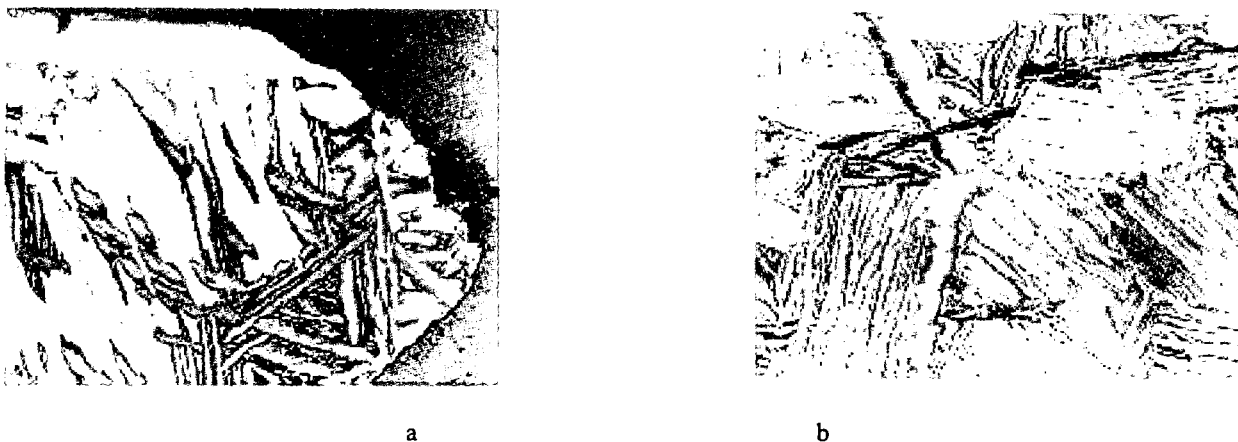
a   b

Fig.12. Lamellar alpha microstructure of PC titanium cold-worked wire after remelting: a) nitrogen-enriched zone near surface; b) microstructure in the middle of casting, 100x

4. Results

1. Selective color etching was the best method for revealing microstructure of castings made of Ti6Al4V alloy under different conditions of casting mold preparation.
2. Microstructure comparison of these castings enables us to state that:
   - in the surface zone of all castings the "white layer" was observed and it was almost of the same thickness. Only in the casting made in chill mold this layer was the most narrow one;
   - all castings had double-phase structure and the amount, distribution and shape of beta phase were quite different in all castings as well as on the cross section of each casting: the higher amount of this phase was observed near the middle of casting in comparison with the regions which were placed closer to the "white layer";
   - the casting which was made in graphite mold had a very fine Widmanstätten microstructure of alpha phase;
   - change in conditions of HIP process caused sharp differentiation of microstructure in casting no. E in comparison with castings nos. 2C and 31, namely:
     - microstructure of specimens 2C and 31 had a typical alpha-beta acicular shape on the whole casting cross - section;
     - microstructure of specimen E could be divided into three main zones: zones A and C had the typical, acicular alpha-beta structure while zone B had a very fine microstructure resembling the martensitic one.
3. It is difficult to identify the white phase in CP titanium after remelting, using described above metallographic color techniques. It rather could not be beta phase as none element stabilizing this phase was added so maybe some another tests should be done.
4. Use of polarized light was helpful in:
   - getting better contrast of casting microstructure which was revealed both with color and black & white etching methods;
   - revealing the variations of grains orientation in unetched microstructure of cold-rolled wire made of pure titanium.
5. The employment of differential interference contrast for testing of Ti6Al4V casting alloy microstructure after black & white etching considerably improved the quality of its picture.

Summing up the above results it can be firmly concluded that the selective, color immersion etching is the best method for examination of microstructure in double-phase titanium alloys, like Ti6Al4V, and as such it should find many advocates among those who by proffesson are expected to deal with the problems of metallography.

5. Literature

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