

THE INFLUENCE OF PHASE COMPOSITION OF Ti-Cr ALLOYS ON THEIR ANODIC ACTIVATION IN CHLORIDE AND BROMIDE SOLUTIONS

Bukhanko N.G.¹, Glukhov L.M.², Davydov A.D.³

¹*Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory, 1, b.3, Moscow, GSP-2, 119992 Russia*

²*Zelinsky Institute of Organic Chemistry RAS, Leninskiy pr. 47, Moscow, 119991 Russia*

³*Frumkin Institute of Physical Chemistry and Electrochemistry RAS, Leninskiy pr. 31, GSP-1, Moscow, 119991 Russia*

ABSTRACT

The influence of phase composition of Ti-Cr alloys (Ti-xCr, where $x = 20, 64$ at. %) with identical chemical composition on their anodic behavior in the non-activating solutions (boric buffer solution (BBS: 0.15 M H_3BO_3 + 0.075 M $\text{Na}_2\text{B}_4\text{O}_7$), 0.1 M Na_2SO_4 , 0.5 M H_2SO_4) and on the passivity breakdown (anodic activation) processes in the halogenide solutions (the saturated KCl solution, 3.5% (0.6 M) NaCl, and 0.6 M KBr solutions) were studied using the voltammetry method.

Key words: *Ti-Cr alloys, phase composition, anodic activation*

INTRODUCTION

Much research is devoted to the activation processes on the Ti-based alloys with different chemical composition; however, the influence of phase composition on the activation processes was not considered. The Ti-Cr system is a very interesting object for investigating the effect of phase composition of alloys (with identical chemical composition) on the activation process. The phase diagram of Ti-Cr system is presented on Fig. 1.

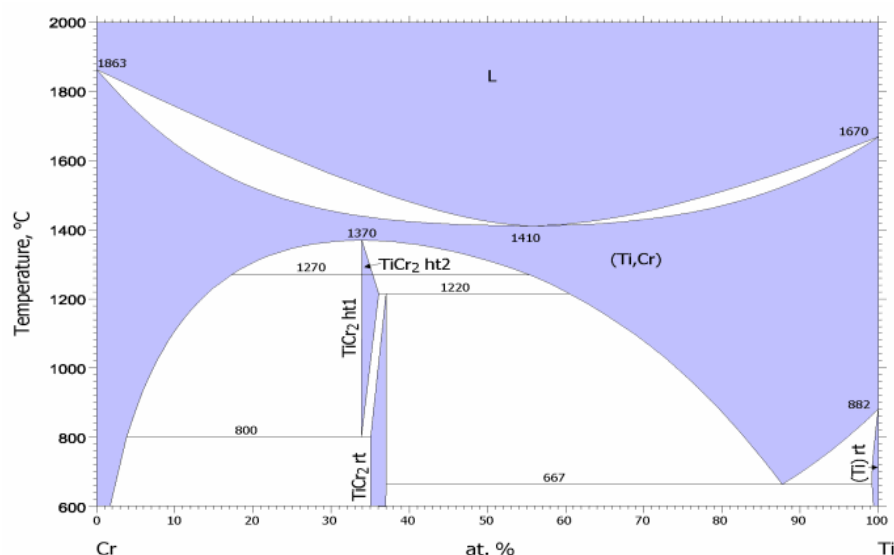


Fig.1. The phase diagram of Ti-Cr system [1].

In the literature it was repeatedly shown that the electrochemical properties of alloy components are determined by the properties of individual components and depend on the ratio between the components in the alloy.

The corrosion resistance of amorphous Ti-Cr alloys, which were fabricated by the sputter-deposition method on the plates of pure Cr and Ti, was studied in detail [2-4]. It is known [2] that this method leads to the formation of Ti-Cr alloys with a higher corrosion resistance than that of pure metals due to the formation of protective oxide film containing both titanium and chromium cations. The effect of heat treatment on the corrosion resistance of sputter-deposited Cr-Ti alloys containing 22, 48, 60, and 72 at. % titanium was studied in 6 M HCl solution [3]. The as-deposited homogeneous Cr-Ti alloys are spontaneously passive in 6 M HCl, except for Cr-72 at. % Ti alloy, although both chromium and titanium metals undergo active dissolution in this solution. The air-formed surface films on the alloys containing sufficient amounts of both chromium and titanium are highly protective, being responsible for spontaneous passivation. The heat treatment of the alloys leading to the formation of α -Ti (hcp) or (bcc)-Cr with a grain size of 20–25 nm as well as Cr_2Ti is detrimental for the high corrosion resistance of these alloys. However, when Cr_2Ti and bcc solid solution of titanium containing ~ 14 at. % chromium are formed, the high corrosion resistance of as-deposited alloys is sustained. The high corrosion resistance of the sputter-deposited Cr-Ti alloys is significantly reduced by the formation of less corrosion-resistant (hcp) -Ti or bcc-Cr phases; however, it remains high when only phases containing certain amounts of both elements are formed by heat treatment. The regularities of corrosion behavior of sputter-deposited amorphized Cr-Ti alloys, contained 30–65 at% Ti alloys were studied in [3]. It was found that the open - circuit potentials of sputter-deposited Cr-Ti alloys fall in the passive regions of both titanium and chromium in 6 M HCl solution open to air at 30°C, and all Cr-Ti alloys are spontaneously passivated.

The X-ray photoelectron spectroscopy (XPS) analysis reveals that the spontaneously formed passive film, as well as the air-formed film, is slightly enriched in titanium ions mainly because of preferential oxidation of titanium. According to the angle-resolved XPS measurement, the formation of homogeneous double oxyhydroxide film containing both Cr^{3+} and Ti^{4+} cations is responsible for extremely higher corrosion resistance of homogeneous single-phase Cr-Ti alloys in 6 M HCl open to air at 30°C in comparison with the corrosion resistance of chromium and titanium metals.

Here, we will reveal the effect of phase composition of Ti-20Cr alloys on their anodic behavior in the non-activating solutions and their anodic activation in the chloride and bromide solutions.

EXPERIMENTAL PROCEDURE

The specimens of Ti-20 at. % Cr and Ti-64 at. % Cr alloys and pure Cr metal, the boric buffer solution (BBS 0.15 M H₃BO₃ + 0.075 M Na₂B₄O₇), 0.1 M Na₂SO₄, 0.5 M H₂SO₄, 3.5% NaCl, 0.6 M KBr, and saturated KCl solutions were used for the investigations. The alloys were produced from titanium iodide and electrolytic nickel in an electric arc furnace in the argon atmosphere. The ingots were subjected to homogenizing annealing for 1 month at the different temperatures: Ti-20 at. % Cr at 630°C (No. 1), 800°C (No. 2) and 900°C (No. 3); Ti-64 at. % Cr at 900°C with quenching in the ice water. This regime of annealing was chosen according to the phase diagram of Ti-Cr system [1], Fig.1.

The phase composition of the alloys was determined by XRD method using DRON-4 diffractometer (CuK α - radiation). The data identification was carried out using STOE program. In all cases, the phase composition of the alloys corresponded to the equilibrium composition at the annealing temperature according to phase diagram: Ti-20 at. % Cr at 630°C – α -Ti + TiCr₂, Ti-20 at. % Cr at 800°C – solid solution Ti(Cr) + TiCr₂, Ti-20 at. % Cr at 900°C - solid solution Ti(Cr) + Cr, and Ti-64 at. % Cr - TiCr₂.

The microstructure of alloys was studied using a «NEOPHOT-32» microscope at 400x magnification. The results are shown on Fig.2. It is seen that, on the surface of alloy No. 1, a lot of small grains of intermetallic phase TiCr₂ on the matrix α -Ti are present. As for alloy No. 2, it is seen, that considerably smaller amount of intermetallic phase TiCr₂ is present, and in the alloy No. 3, the solid solution of Cr (β -Ti) is present, whereas the intermetallic phase TiCr₂ is absent. These results are in good agreement with XRD data.

For the electrochemical measurements, plates measuring ~8×8×3 mm were cut out of ingots, and a copper current feed was glued to one side of each plate with a conducting glue. This side of a plate and the end-faces were insulated with epoxy resin, and the working surface was polished to a mirror finish with emery paper and rinsed with ethanol and distilled water.

The voltammograms (a potential scan rate of 5 mV/s) were measured using a computer-controlled potentiostat PI-50-1, an “L-Card” DAC/ADC, programmer PR-8. A saturated calomel electrode (*s.c.e.*) was used as a reference electrode, and a Pt plate was used as the auxiliary electrode. To investigate the effect of potential scan rate on the activation potential E_A, a series of voltammograms were measured on the alloys No. 2 and No. 3 в 3.5% NaCl solution with different potential scan rates (2, 5, 10, 20, 50, and 100 mV/s).

The activation potentials (passivity breakdown potentials) were determined by recording the potential of abrupt increase of current density in the voltammograms measured

in 0.6 M KBr, 3.5% NaCl and the saturated (~ 4.5 M) KCl solutions. The anodic behavior of alloys in the non-activating solutions was studied in the boric buffer solution (BBS) (0.075 M $\text{Na}_2\text{B}_4\text{O}_7 + 0.15$ M H_3BO_3), 0.1 M Na_2SO_4 , and 0.5 M H_2SO_4 solutions with a potential scan rate of 5 mV/s from the steady-state potential to 8 V and reversely to -1.5 V. The solutions were prepared using the distilled water.

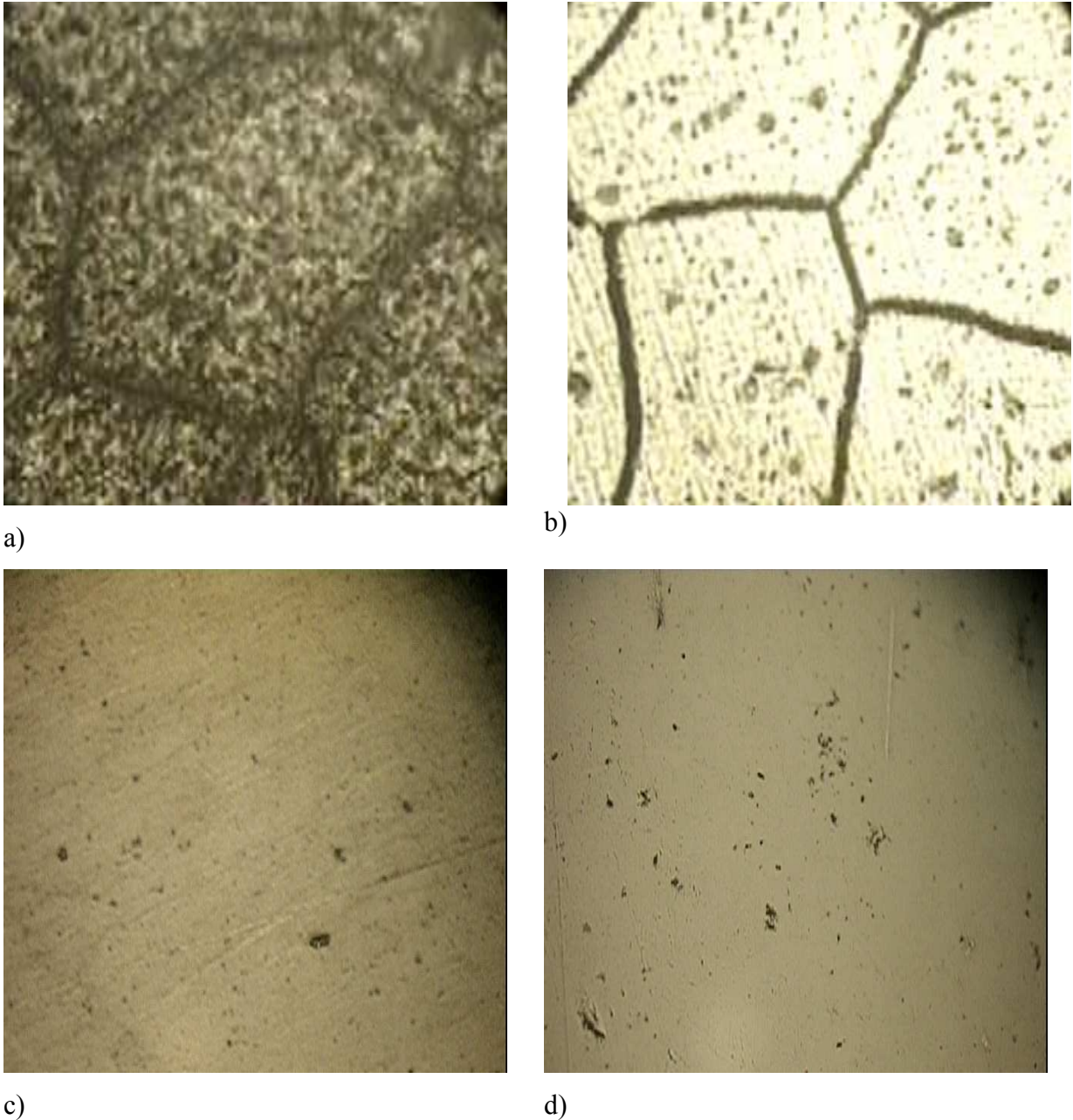


Fig.2 Microstructure of Ti-20Cr alloys annealed at the temperatures: 630°C (a), 800°C (b), 900°C (c) and alloy Ti-64Cr (d) (magnification 400-).

RESULTS AND DISCUSSION

Activating solutions

In the solutions of activating ions, upon reaching a certain anodic potential E_A , an abrupt increase in the current is observed, which is caused by the breakdown of the oxide film and the onset of alloy dissolution (the anodic-anion activation). If the potential is further increased to obtain a sufficiently large area of pits, and, then, the scan is reversed, a potential, at which the current decays to zero (the repassivation potential), appears to be considerably more negative than the activation potential.

Figure 3 gives the voltammograms measured on the alloys in 0.6 M KBr solution. It is seen that on all voltammograms, the current increases, which is associated with the oxygen evolution or/and the beginning of oxidation Cr to Cr(VII). This is also confirmed by visual observation: the solution becomes yellow at the potentials above 1 V. Further, for Ti-20Cr No. 1 (α -Ti + TiCr₂) alloy, the lowest activation potential ($E_A = 1.21$ B), which is close to that for Cr and for TiCr₂ intermetallic compound, is observed. However, on the voltammograms for alloys No. 2 (β -Ti + TiCr₂) and No. 3 (β -Ti + Cr), extended ranges of primary and secondary passivation are observed, and the anodic activation occurs later – at the potentials $E_A = 2.73$ V and $E_A = 2.50$ V, respectively. It is seen that all Ti-20Cr alloys have an activation potential higher than that of alloy Ti-64Cr, which consists of intermetallic compound TiCr₂ solely. This supports the fact that activation proceeded predominantly at small grains of phase TiCr₂, which is present in large amount in the Ti-20Cr No. 1 (α -Ti + TiCr₂) alloy.

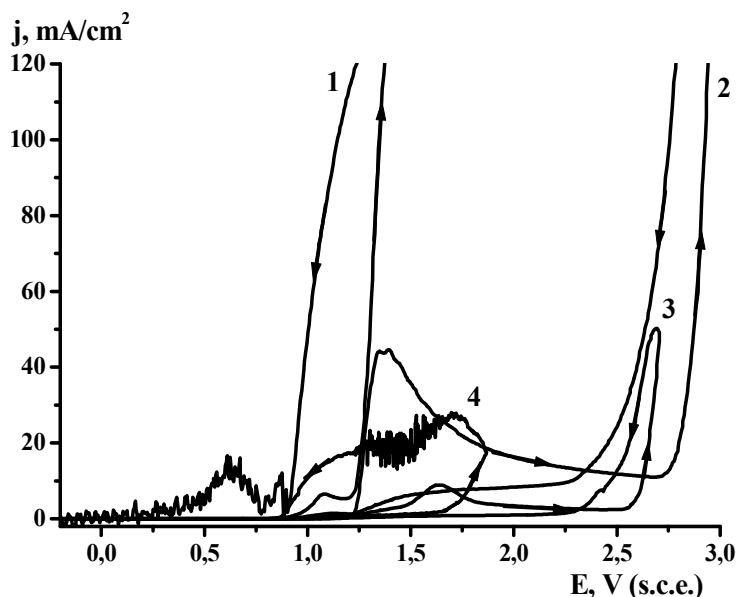


Fig.3 The voltammograms, which are measured in 0.6 M KBr solution for alloys: 1 – Ti-20 at. % Cr (T = 630°C), 2 – Ti-20 at. % Cr (T = 800°C), 3 – Ti-20 at. % Cr (T = 900°C), 4- Ti.

In the dilute chloride solution (3.5% NaCl), another situation is observed. (Fig.4). For instance, for Ti-20Cr alloys, in this solution a significant difference between the current in the primary passivation range, current of oxygen evolution, and current of beginning of metal dissolution is observed for alloys No. 1, 2, and 3. This may be associated with the changes of thickness, composition [2] and conductivity of oxide film formed on the alloys surface (it can be supposed, due to a change in the conductivity type of Cr_2O_3 [5]). For the alloy No. 1, the highest current at the potentials near 1 V can be explained by the beginning of selective dissolution of small grains of intermetallic phase TiCr_2 from the matrix $\alpha\text{-Ti}$ and the dissolution of the matrix itself. Then, up to 8 V, in the reverse branch of voltammogram, an abrupt increase in the current and the "loop" in the reverse branch of VA curve, which is typical for the beginning of anodic activation, are not observed. Instead of this, a consequent decrease of the current in potential range of 1.99 to 4.66 V, which is typical for secondary passivation process, is observed. This effect can be explained by the fact that on the surface of the alloy, the "weak points" (small grains of intermetallic phase), on which an activation process is started at first, are absent. Instead of this, the protective oxide-hydroxide films form on the Ti-rich alloy surface.

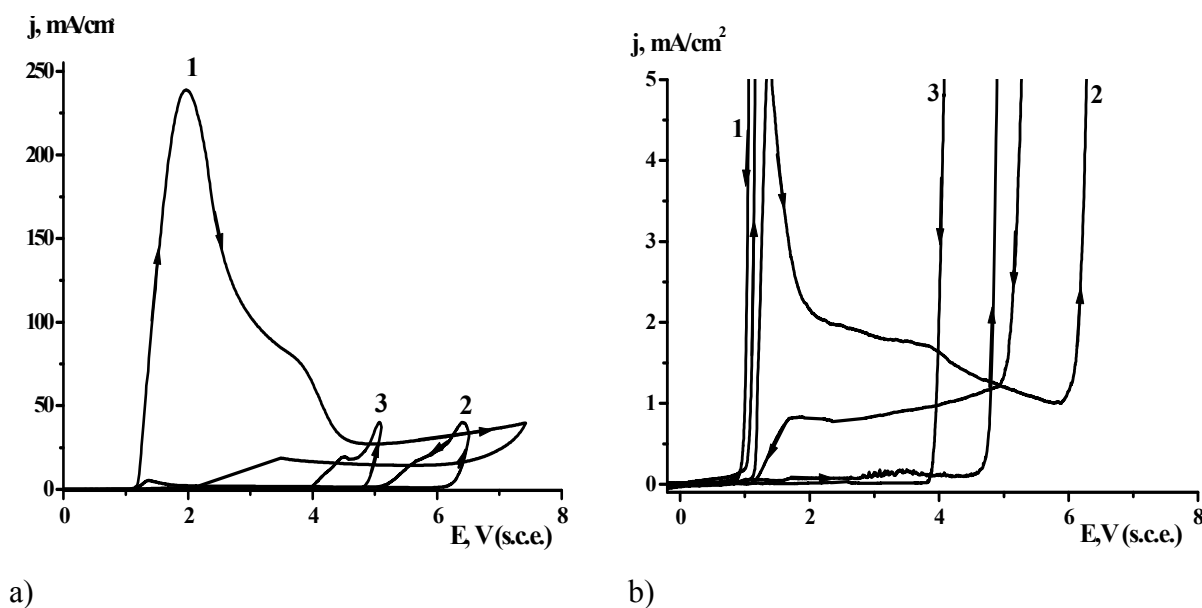


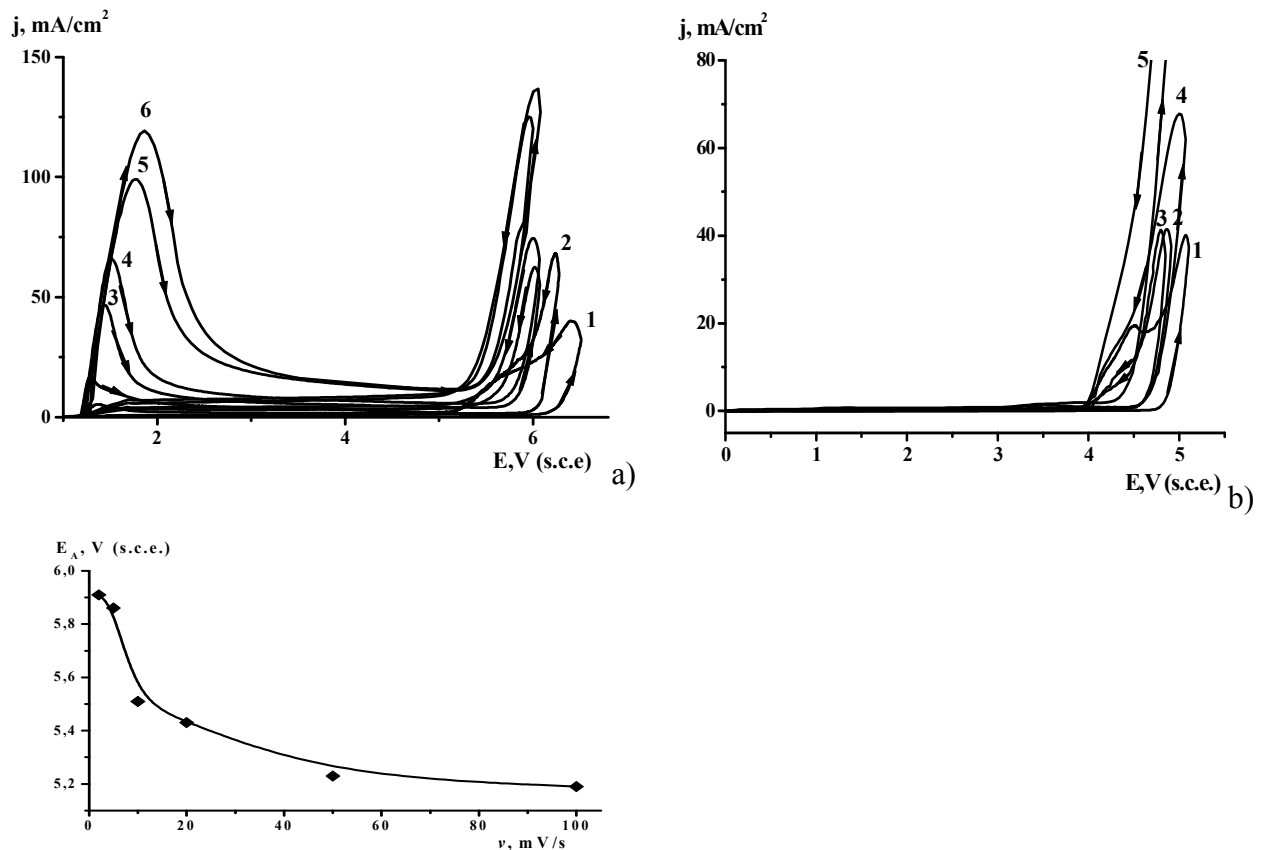
Fig.4. The voltammograms obtained in the 3.5% NaCl solution for alloys (potential scan rate 5 mV/s): 1- Ti-20 at. % Cr ($T = 630^\circ\text{C}$), 2 – Ti-20 at. % Cr ($T = 800^\circ\text{C}$), 3 – Ti-20 at. % Cr ($T = 900^\circ\text{C}$) (a) and 1- Ti-64 at. % Cr, 2 – Ti-20 at. % Cr ($T = 800^\circ\text{C}$), 3 – Ti-20 at. % Cr ($T = 900^\circ\text{C}$) (b).

On the Ti-20 at. % Cr No. 2 and No. 3 alloys, an activation process begins at much lower potentials: 5.42 and 4.53 V, respectively. The grains of intermetallic phase TiCr_2 on matrix of $\beta\text{-Ti}$ (alloy No. 2) are smaller and are present in small amount. This allows proposing that, in this case, the activation process proceeds exactly on these surface defects.

For the Ti-64Cr alloy, corresponding to TiCr_2 phase composition, the passivity breakdown process start even at 1 V; however, for pure Cr in the dilute chloride solution, an active dissolution is observed.

The data obtained is clear illustration of the effect of both the intermetallic phase grain size and the matrix nature, where the crystallization proceeds, on the process of passivity breakdown in the dilute chloride solution.

A change of potential scan rate during a voltammogram recording also affects the activation process. Figure 5 gives the voltammograms, which are measured with various potential scan rate (2, 5, 10, 20, 50, 100 mV/s) on the Ti-20Cr No. 2 alloy. It is seen that, with increasing potential scan rate, an increase in the current of Cr dissolution and/or oxygen evolution and the monotonic decrease in the activation potential from 5.9 to 5.19V are observed. This type of dependence shows that, of two competing processes proceeding on the alloy surface, in this case, the alloy surface passivation is slower and the passivity breakdown by Cl^- ions proceeds with a much higher rate. However, this effect is almost absent on Ti-20Cr No. 3.



c)

Fig.5. The voltammograms, which were measured in 3.5% NaCl solution for Ti-20 at. % Cr (a) No. 2 ($T = 800^\circ\text{C}$) alloy and (b) No. 3 ($T = 900^\circ\text{C}$) alloy with various potential scan rates

(mV/s): 1 – 2, 2 – 5, 3 – 10, 4 – 20, 5 – 50, 6 – 100 and (c) the dependence of activation potential on the potential scan rate for Ti-20 at. % Cr No. 2 ($T = 800^{\circ}\text{C}$) alloy.

In the case of saturated ($\sim 4.5\text{ M}$) KCl solution, all voltammograms, which are obtained for Ti-Cr alloys, are similar to those measured in the dilute 3.5% NaCl solution, and the values of E_A are also similar to E_A .

Using the voltammograms obtained, the dependences of E_A on the phase composition of Ti-20Cr alloy (annealing temperature) were constructed (Fig.6). It is seen that, in both chloride solutions, the dependences are linear. The E_A value for Ti-20Cr No. 1 alloy, probably, is higher than 8 V; however, for other alloys, E_A monotonically decreases from alloy No. 2 to No. 3. In the bromide solution, by contrast, the lowest E_A value is observed for Ti-20Cr No. 1 alloy, which is close to E_A of pure TiCr_2 intermetallic phase. This allows proposing that the activation process proceeds predominantly on the intermetallic phase grains. Thus, a strong effect of phase composition of Ti-Cr alloys on their passivity breakdown in the halogenide solutions with various concentrations is shown.

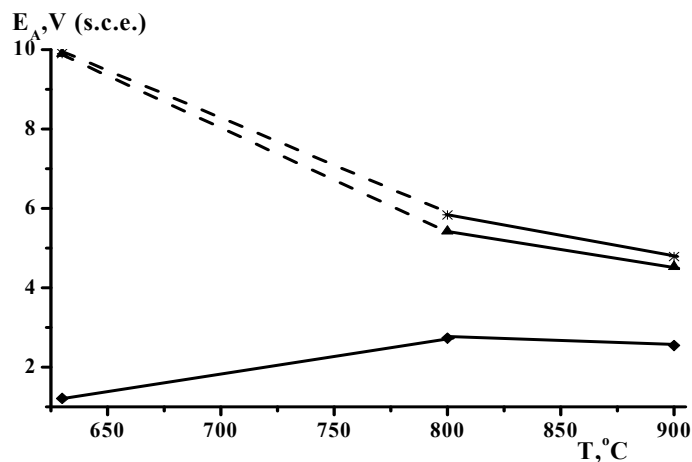


Fig.6. Dependences of activation potential of Ti-20Cr alloys in KCl (1), KBr (2) and NaCl (3) solutions on the annealing temperature.

It was shown [3] that Ti-Cr alloys consisting of β -Ti and TiCr_2 phases, are characterized by the higher resistance against the action of Cl^- ions than the alloys consisting of α -Ti + TiCr_2 phases. In our case of dissolved chloride solutions, an opposite effect is observed: the alloy consisting of α -Ti + TiCr_2 , where the activation process does not start up to 8 V, is most resistant against the anodic activation. On the alloy Ti-20Cr No. 2 consisting of β -Ti and TiCr_2 , the activation process starts earlier, at the at potentials of 5.42 to 5.43V.

Non-activating solutions

The voltammograms for the alloys studied in the BBS and 0.1 M Na₂SO₄ solutions are presented on Fig.7 (a), (b). It is seen that for Ti-20Cr No. 1 and No. 2 alloys, the primary passivity range is extended from a steady-state potential to the potential of the onset of oxygen evolution (~1.09-1.2 V in BBS, ~1.4 V in Na₂SO₄). Further, an abrupt increase of the current, which is associated with the oxygen evolution and the alloy dissolution, is observed and, then, a wide secondary passivity range is observed. In the voltammograms, which was measured in BBS, the current in the passive range gradually decreases according to decreasing TiCr₂ phase content in the alloy – from Ti-20Cr No. 1 to No. 3. The currents of onset of oxygen evolution and the start of alloy dissolution abruptly decrease from Ti-20Cr No. 1 to No. 3 alloy. It is typical that, in both solutions, the voltammograms for Ti-20Cr No. 3 alloy are similar to those for pure Ti [6].

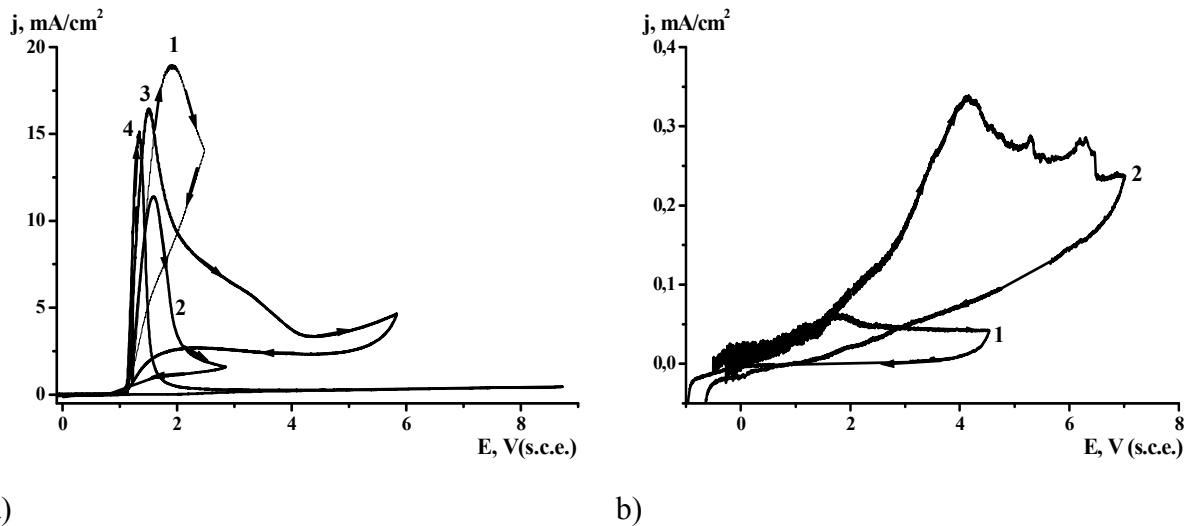


Fig.7. The voltammograms for alloys: 1- Ti-20 at. % Cr (T = 630°C) in BBS, 2 – Ti-20 at.% Cr (T = 800°C) in BBS, 3- Ti-20 at. % Cr (T = 630°C) in 0.1M Na₂SO₄, 4 – Ti-20 at. % Cr (T = 800°C) in 0.1M Na₂SO₄ (a) and Ti-20 at. % Cr (T = 900°C) in the solutions: 1- BBS, 2 - 0.1M Na₂SO₄ (b). The potential scan rate is 5mV/s.

The same regularities are observed also in 0.5M H₂SO₄ solution (Fig.8). It is evident that the currents of oxygen evolution and alloy dissolution processes are significantly distinct. This is due to the difference in the phase composition and morphology of these alloys. The voltammogram of Ti-20Cr No. 3 alloy in the 0.5M H₂SO₄ solution is similar to that for pure Ti (Fig.8(b)). It is seen that, with decreasing TiCr₂ content on the alloy surface, the metal dissolution current and/or oxygen evolution current decrease. Thus, for solid solution (Ti-20Cr No. 3 alloy) the voltammogram is similar to that for pure Ti in the same conditions [7].

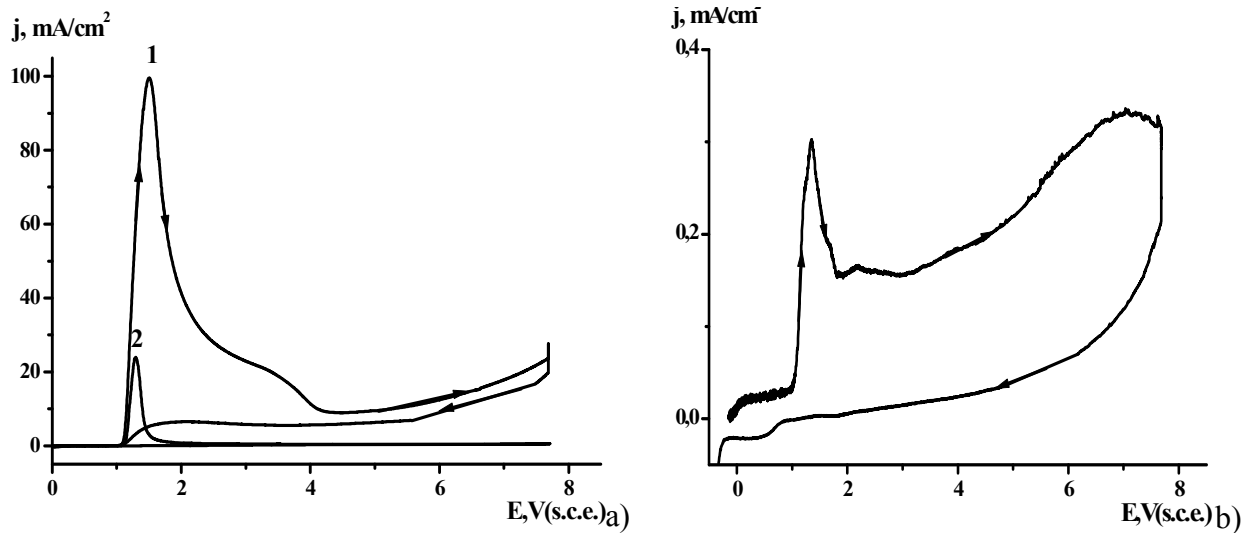


Fig.8 The voltammograms obtained in 0.5M H_2SO_4 solution for alloys: 1- Ti-20 at. % Cr ($T = 630^\circ C$), 2 – Ti-20 at. % Cr ($T = 800^\circ C$) (a) and Ti-20 at. % Cr ($T = 900^\circ C$) (b). The potential scan rate is 5 mV/s.

CONCLUSIONS

1. The influence of the phase composition of alloy at the same chemical composition on the activation potentials for Ti-20Cr alloys, which were annealed at different temperatures, in comparison with pure Ti, Cr and $TiCr_2$ is studied. For the alloy with phase composition α -Ti+ $TiCr_2$ (No. 1), it is supposed that, in the chloride solutions (3.5% NaCl, saturated KCl), a higher current at a potential of $\sim 1V$ is caused by the onset of dissolution of phase $TiCr_2$, which is crystallized as small grains on the alloy's surface. For alloy Ti-20Cr No. 2 ($Ti(Cr)+TiCr_2$), containing smaller amount of intermetallide $TiCr_2$ on its surface, and Ti-20Cr No. 3 ($Ti(Cr)+Cr$), the currents in this area are significantly lower. It is found that in the chloride solutions for Ti-20Cr alloys, an abrupt decrease of E_A from alloy Ti-20Cr No. 1 to No. 3 is observed.
2. It is shown that, in 0.6 M KBr solution, the lowest activation potential is observed for alloy Ti-20Cr No. 1, a highest one– for Ti-20Cr No. 3.
3. The dependence of activation potential E_A on the potential scan rate for alloy Ti-20Cr No. 2 ($Ti(Cr)+TiCr_2$) in 3.5% NaCl solution is obtained.
4. It is shown that, in the non-activating solutions (H_2SO_4 , Na_2SO_4 , BBS), similar differences in the alloy properties, which are caused by the intermetallic phase $TiCr_2$ dissolution, for the alloys Ti-20Cr No. 1 and No. 2 are observed. It should be noted that the anodic behavior of Ti-20Cr No. 3, consisting of solid solution, is similar to that of pure Ti.

REFERENCES

1. *Pauling File "Binaries Edition"* Inorganic materials database and design system.
2. *Kim J.H., Akiyama E., Habazaki H., Kawashima A., Asami K., Hashimoto K.* // *Corros. Sci.* 1993. V.34. P.957
3. *Mehmood M., Akiyama E., Habazaki H., Kawashima A., Asami K., Hashimoto K.* // *Corros. Sci.* 1999. V.41. P.1871
4. *Li X.-Y., Akiyama E., Habazaki H., Kawashima A., Asami K., Hashimoto K.* // *Corros. Sci.* 1997. V.39. P.935
5. *Oshe E.K., Rosenfeld I.L.* In book: *A Science and Technology Results. Corrosion and Corrosion Protection.* M.: VINITI. 1978. V.7. P.111.(in Russian)
6. *Kamkin A.N., Bukhanko N.G., Davydov A.D., Kazakova E.F.* // *Russian Journal of Electrochemistry (Elektrokhimiya).* 2001. V.37. P.606. (in Russian)
7. *Balyanov A., Kutnyakova J., Amirkhanova N.A., Stolyarov V.V., Valiev R.Z., Liao X.Z., Zhao Y.H., Jiang J.B., Xu H.F., Lowe T.C., Zhu Y.T.* // *Scripta Mater.* 2004. V.51. P.225