PITTING CORROSION BEHAVIOR OF TITANIUM ALLOY PT-7M IN HOT AQUEOUS SODIUM CHLORIDE SOLUTIONS

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ANNOTATION

Pitting corrosion (PC) resistance of the PT-7M α–titanium alloy in hot sodium chloride solutions over the range of potentials comparable in value with the alloy corrosion potentials has been studied by a potentiostatic polarization method. The possibility of PC initiation of the alloy under the above conditions is shown and areas of PC potentials, pitting potential (φ_{pit}), inhibition potential ($\varphi_{inh.}$) and critical temperature values are determined on the (φ_{pit}– T) coordinates. Functions $\varphi_{pit.}$=f(lg C_{NaCl}) have been determined for temperatures of 150, 200, and 250 °C. Their analysis has allowed to reveal a critical NaCl concentration (~6%) which determines the change in φ_{pit} value (its increase or decrease) when increasing the solution temperature. Corrosion potentials depending on the solution concentration, pH, temperature and aeration level are presented.

Key words: titanium, pitting corrosion, pitting potential, corrosion potential, inhibition potential

INTRODUCTION

The results of numerous investigations of titanium and its alloys, and data on the operation of equipment made of them show that these alloys have high resistance to PC in aqueous chloride solutions. However, if chloride concentration, temperature and pH values exceed the threshold ones, titanium may be subjected to PC attack[1–4]. At present threshold values for some alloys and φ_{pit} values in such environments are determined. Unfortunately, $\varphi_{pit.}$ values obtained in a number of studies do not characterize PC resistance completely. Even in hot concentrated chloride solutions a φ_{pit} value, as a rule, exceeds 1.2 V (SCE), pointing to the fact that PC is not possible though immersion corrosion tests under the same conditions may initiate PC in titanium and some titanium alloys. Discrepancy between the results of immersion corrosion tests and electrochemical measurements allowed to suppose that PC of titanium and its alloys is possible in two areas of potentials [5].

- at potentials higher than film breakdown potentials ($\varphi_{break.}$) and exceeding corrosion potentials of alloys to a considerable extent;
- in the area of potentials comparable in value with corrosion potentials of alloys.

In the area of high potentials $\varphi_{break.}$ is easy to reveal by electrochemical methods not only at elevated temperatures but at a room temperature over a wide range of NaCl concentrations while $\varphi_{pit.}$ revealing in the area of corrosion potentials by electrochemical methods is rather difficult even in concentrated hot chloride solutions. In particular, according to the data obtained by F.A. Posey and E.D. Bohlmann[3] $\varphi_{pit.}$ of commercial titanium in 1N NaCl makes up 0.0 V (SHE) at a temperature of 220 °C. However, the data also obtained for commercially pure titanium by T.Koizumi and Sh. Furuya[6] have shown that φ_{pit} exceeds 1.0 V (SHE) even at a temperature of 250 °C.

Data on the resistance of alloys to PC in the area of corrosion potentials are sure to be the most important for practical application. The aim of the present work is to determine the resistance to PC for a conventionally processed PT-7M α–titanium alloy in the area of corrosion potentials in hot chloride solutions by electrochemical methods. Special attention has been paid to the determination of the area of PC potentials of and corrosion potential ($\varphi_{cor.}$) values of the alloy.

EXPERIMENTAL PROCEDURE

A commercial PT-7M α-titanium alloy [2.2% Al, 2.5% Zr] has been used in the study. NaCl solutions have been made of high-purity reagents with distilled water. The desired pH values have been obtained by introducing hydrochloric acid (HCl) or caustic alkali (NaOH) to solutions. The deaeration of working chambers has been carried out by repeated filling the gas space of a cell with high-purity argon and its removal until obtaining a calculated oxygen concentration of ~ 0. 015 mg/l in the working solution. A high-temperature electrochemical cell has been designed taking into consideration a number of recommendations[7,8]. To measure the working electrode potential an external reference electrode (Ag/AgCl) with a 201 mV potential at 20 °C relative to the standard hydrogen electrode has been used under room temperature conditions. The stable operation of a high pressure electrolyte bridge of the working and electrode solution (satd. KCl) was provided for due to porous ZrO_2 plugs and a buffer chamber filled with ceramic powder.

To prevent the solution boiling at temperatures above 100 °C and to provide the stable operation of the high pressure electrolyte bridge an excessive initial argon pressure of about 5 kg/cm^2 has been set in the cell. It allowed to take reliable electrochemical measurements up to 260 °C with the working solution pH values of 1.0-13.5. All potential values are given relative to a saturated silver-chloride electrode without correcting for the change in potentials by diffusion and thermodiffusion. A smooth platinum electrode with a visible area of ~8 cm^2 or VT1-00 titanium wire of 100 cm^2have been used as an auxiliary electrode.

After heating the cell up to a predetermined temperature the working electrode was subjected to anodic polarization under potentiodynamic conditions at a rate of 2 mV/s up to a predetermined potential value and was held at the above value for 12- 20 hours if there was no pitting before it. Pitting potential was taken to be the minimum potentiostatic polarization potential at which sharp and stable increase in current after the incubation period has been observed and pitting corrosion has been revealed on a specimen after testing. A step of change in the imposed potential was 100 mV for all studied temperature and solution concentration values. A new specimen and a newly made solution were used for each test. When measuring corrosion potentials ($\varphi_{cor.}$) the specimen was heated at a rate of 3 °C /min up to a temperature of 250 °C. At this temperature the specimen took on a stationary value for 1 - 2 hours. At temperatures below 250 °C the corrosion potential was taken to be the corrosion potential of a specimen obtained during slow cooling of the solution at a rate of ~1-2 °C /min. Corrosion potential values obtained are averaged ones for 2-3 specimens.

RESULTS AND DISCUSSION

A series of experiments carried out in a 3% NaCl solution at temperatures ranging from 120 to 250 °C has allowed to reveal a new area of PC potentials of the alloy (Fig.1) limited by (0.25 - 0.45) V at 150 °C and 0.5 - ~(0.8–0.9) V at 250 °C . The critical pitting temperature for the above range is 145 °C. The characteristic features of the area of PC potentials are as follows:

- $\varphi_{pit.}$ increases when increasing temperatures above the critical one;
- PC inhibition potential exists;
- a narrow range of PC potentials (~150 mV at 145-200 °C) and its extension with increase in temperature;
- a long-duration (till some hours) induction period of PC .

Increase in $\varphi_{pit.}$ of titanium and its alloys when increasing temperature in chloride solutions has not been noted before. Such an «abnormal» change in $\varphi_{pit.}$ may be explained by the competitive absorption of activating ions (Cl^-) and water oxygen . The increase in the solution temperature from 140 to 250 °C seems to result in the reduction of the ratio of chlorion to oxygen activity (α_{Cl}/α_W) that inhibits the corrosion initiation. Besides, the possibility to inhibit PC is determined by the change in the ratio of the activities of activating and passivating ions in the solution. It is known that during the electrolysis of pure aqueous chloride solutions of alkaline metals oxygen-containing chlorine compounds may be formed (ClO^-, ClO_3^-), e.g., due to the simultaneous discharge of Cl^- and OH^- (or H_2O) by the following reaction:

$$Cl^- + 6OH^- - 6e^- = ClO_3^- + 3H_2O \quad (1)$$

whose standard electrode potential value makes up 0.43 B (NHE). The comparison of the reaction potential (1) with the PC inhibition potential allows to suppose that when $\varphi_{inh.}$ is achieved the oxidation of an activating ion (Cl^-) to a passivating ion (ClO_3^-) takes place on the electrode. Due to it the ratio of the activities of chlorion and water oxygen decreases and promotes PC inhibition. Moreover, chlorate-ions as a strong oxygen-containing oxidizer may react by a chemical mechanism with the metal and take a direct part in the formation of a passivating layer and, as a consequence, to intensify the passivating characteristics of water.

A narrow range of PC potentials (~0.15 V) at temperatures ranging from 145 to 200 °C explains to a great extent difficulties related to its determination by a potentiostatic method with a short-duration holding

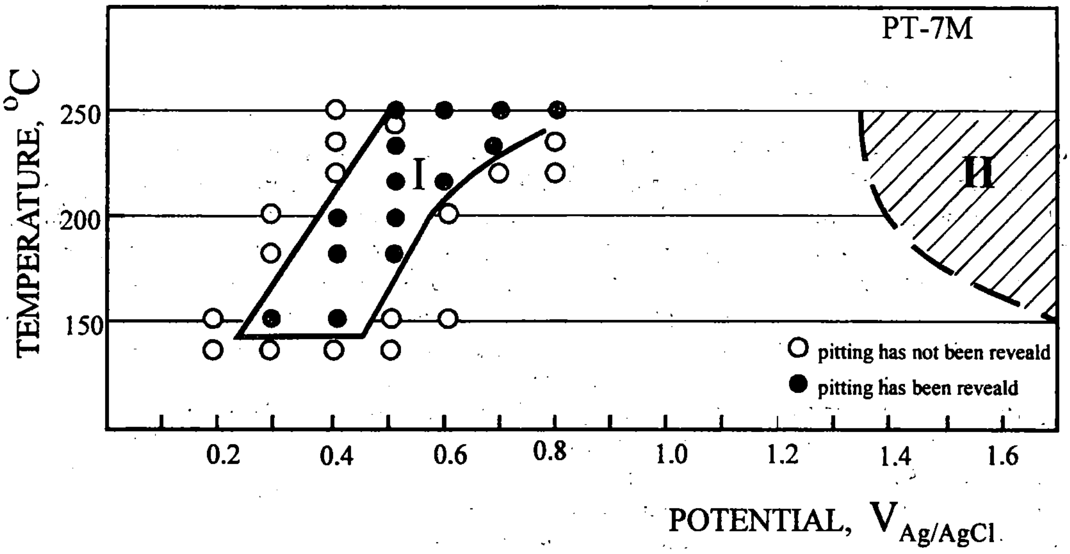

Fig. 1. Areas of PC potentials of the alloy in a 3% NaCl solution.
I - Areas of PC potentials revealed after long-term holding of a specimen at the applied potential.
II-Areas of film breakdown potentials.

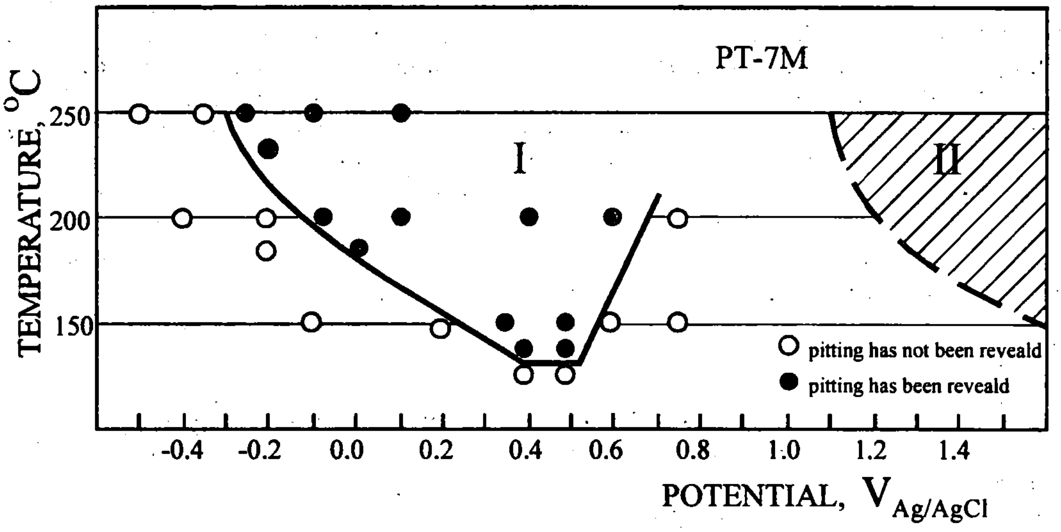

Fig. 2. Areas of PC potentials of the alloy in a 20% NaCl solution.
I - Areas of PC potentials revealed after long-term holding of a specimen at the applied potential.
II-Areas of film breakdown potentials.

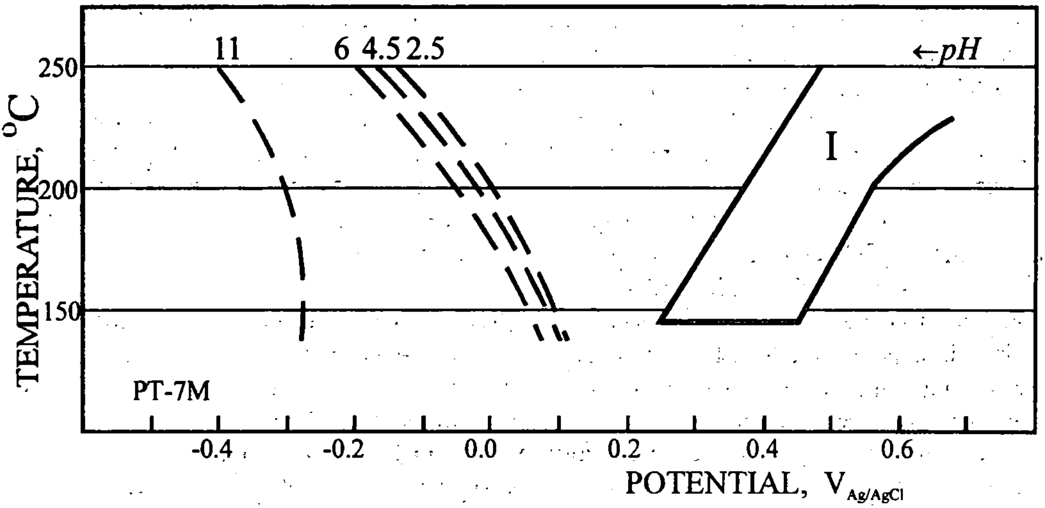

Fig. 3. Comparison of the area of PC potentials of the alloy (I) in a deaerated 3% NaCl solution with the alloy corrosion potentials obtained at different pH values. (Figures near the curves designate a pH value.)

and a step of the change in potential of 0.1-02 V. The increase in potential up to values exceeding $\varphi_{inh.}$ ruled out the PC initiation till reaching the breakdown potential ($\varphi_{break.}>1.2$ V). At a temperature exceeding 200 ^{0}C, where the possibility of revealing pitting is higher, long-term electrochemical studies have not be conducted before.

In the above experiments stable PC was initiated after 5-14 hours of testing though already after 2-3 hours instantaneous bumps inherent in delocalized pitting took place. No clear dependence of the period preceding the PC initiation on the temperature or potential in the above area of PC has been revealed. It points to the fact that a number of factors characterizing the solution and properties of the alloy surface, which are difficult to take into consideration, affect the time preceding the PC initiation. Both separate pits and their clusters have been revealed on the surface of specimens subjected to PC. At temperatures ranging from 235 up to 250 ^{0}C and potentials more positive than 0.7 V pits were formed together with nonuniform surface etching. At potentials more positive than 1.0 V over the above range of temperatures only nonuniform surface etching has been revealed. No visible surface changes have been revealed in the area of potentials inhibiting PC at temperatures of 140 - 220 ^{0}C.

A series of similar experiments on the alloy in a concentrated (20% NaCl) solution (Fig. 2) has also revealed the area of PC potentials which has the following features:

- decrease in $\varphi_{pit.}$ when increasing the temperature;
- PC inhibition potential existence;
- PC potential range increases when increasing the temperature (up to 0.6 V at a temperature of 200 ^{0}C);
- a long-duration induction period (till 0.5 - 8.0 hours).

As one should expect, the increase in the solution concentration resulted in considerable expansion of the area of PC potentials. In the case in question it is limited by potentials within 0.25 - 0.50 V at a temperature of 150 °C and from (–0.30) to (0.80)V at a temperature of 250 ^{0}C. The expansion of the area of PC potentials when increasing the chloride concentration is mostly due to the decrease in pitting potentials which is especially noticeable when increasing the temperature. At 150 ^{0}C pitting potential values are nearly the same for 3 and 20% NaCl solutions whereas at 170 ^{0}C their difference reaches 0.3V, and at 250 ^{0}C the difference in $\varphi_{pit.}$ values is 0.7V. At the same time, $\varphi_{pit.}$ values of 3 - 20% chloride solutions remained nearly the same. The increase in the chloride concentration resulted in the reduction in the critical temperature of pitting which makes up about 135 ^{0}C for a 20% NaCl solution.

To obtain functions (pitting potential–NaCl concentration) at a temperature of 250 ^{0}C in addition to the data available on pitting potential in 3 and 20% NaCl solutions, $\varphi_{pit.}$ values in 6 and 10% NaCl solutions were determined experimentally and are 0.0 and (-0,17) V respectively. The analysis of the results obtained has shown that the function $\varphi_{pit.}$ of NaCl concentration is well presented on the ($\varphi_{pit.}$–lg C_{NaCl}) coordinates as a linear function $\varphi_{pit.}^{250^0}$= 0.80–0.82 lg C_{NaCl}. Assuming that the function remains linear at other temperatures $\varphi_{pit.}^{200^0}$=0.60–0.55 lg C_{NaCl} and $\varphi_{pit.}^{150^0}$=0.35–0.1 lg C_{NaCl} may be taken for 200 and 150 ^{0}C.

The analysis of these functions shows that the effect of chloride concentration on the pitting potential depends to a great extent on the temperature of testing. Thus, the «b» coefficient increases from 0.10 at a temperature of 150 ^{0}C up to 0.82 at 250 ^{0}C. Functions $\varphi_{pit.}$=f(lg C_{NaCl}) for different temperatures have been analyzed graphically. As shown in Fig.4 the functions intersect at a point corresponding to about 6% NaCl concentration. When exceeding this concentration the increase in the solution temperature results in the decrease in $\varphi_{pit.}$ of the alloy. If the concentration is lower than the above, the increase in temperature has the reverse effect, i.e. $\varphi_{pit.}$ of the alloy increases. Thus, with a 6% NaCl concentration $\varphi_{pit.}$=f(T) undergoes qualitative changes. Taking into consideration the above, the changes are considered to be due to the nature of change in the relation of chlorion and water oxygen activities when increasing the solution temperature. With reference to the conditions in question the above 6.0% NaCl concentration is critical.

To predict the alloy resistance to PC the areas of PC potentials obtained have been compared with $\varphi_{cor.}$ of the alloy measured in deaerated and undeaerated solutions at temperatures ranging from 120 up to 250 ^{0}C and pH values from 1.5 - 2.0 up to 12. The data have shown (Fig.3), that in a deaerated 3% NaCl solution pitting may not be initiated at any pH values in question, $\Delta\varphi_{pit.}$ = φ_{pit} –$\varphi_{cor.}$ increasing when increasing the solution temperature and reaches no less than 0.6 V at 250^{0}C. The solution acidification from pH = 6 to pH = 2.8 results in slight increase in corrosion potential which does not exceed 0.1V. The effect of pH is more considerable in the undeaerated solutions (Fig.5). In the above case pH ranges in value from 6.5 to 2.0 and this change results in a 0.4V increase in the potential. So, conditions initiating PC in the alloy arise at a temperature of 250 ^{0}C and pH=2.0. If pH = 3–4, pitting may be initiated at lower temperatures.

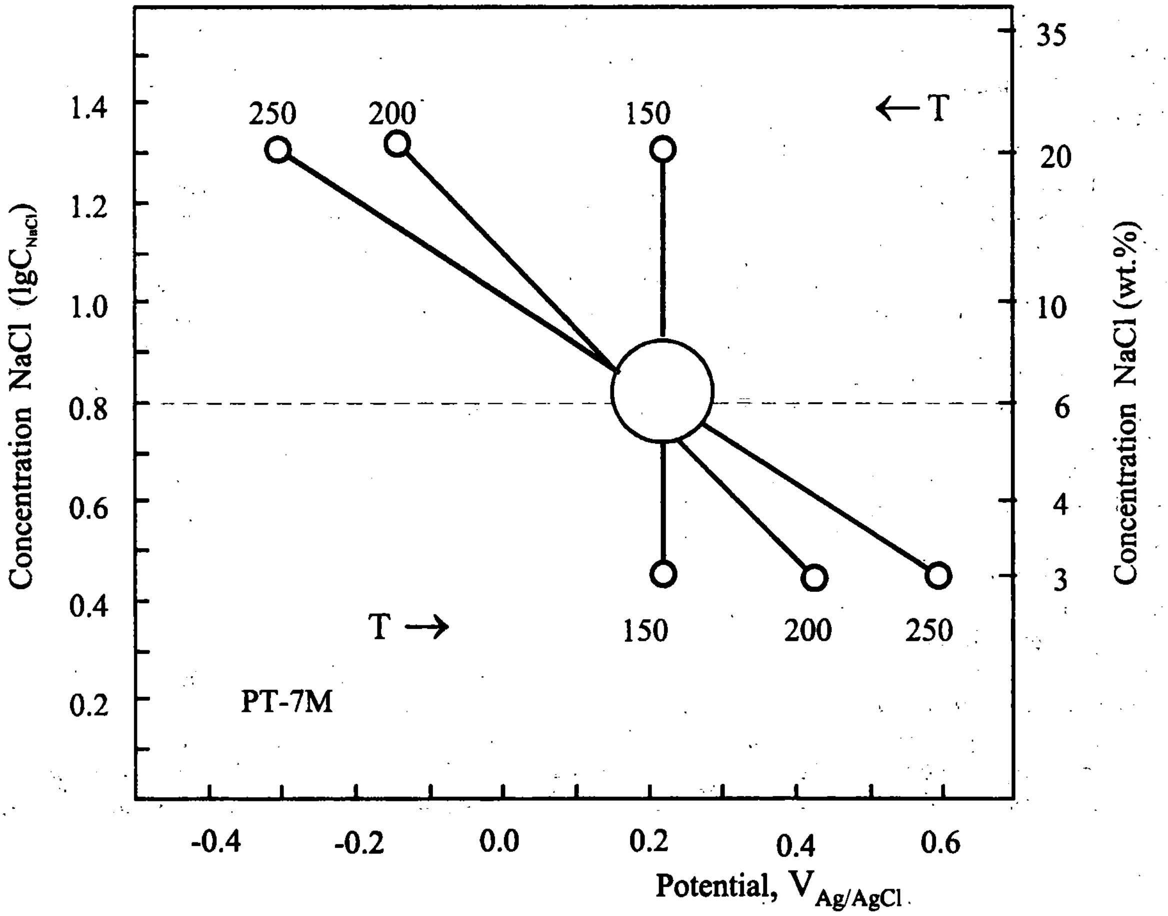

Fig. 4. Change in pitting potential φ_{pit} depending on the concentration and temperature of NaCl solution.

However, further acidification down to pH =1.5 prevents the alloy PC as in this case corrosion potential swings to negative values. It seems to be due to the anodic process activation that is confirmed by the results of immersion corrosion tests. The alkalization up to pH=11 increases the alloy resistance to PC over the whole range of temperatures under examination.

So, in a deaerated 3% NaCl solution at 250 ^{0}C pitting may not be initiated. PC becomes possible only when acidating the solution to pH = 2-3. The initiation of PC in the case in question is not due to the increase in pitting potential but to a considerable displacement of the alloy corrosion potential to positive values.

The nature of change in the alloy potential depending on the solution temperature and pH value for the two levels –of oxygen concentration in a 20% NaCl solution is shown in Fig.6-7. The comparison of the alloy potentials with a 0.01 mg/l oxygen concentration in the solution with the area of PC potentials shows that in this case PC is possible in the alloy only when pH values are close to 2.0-3.0 at temperatures ranging from 180 to 250 ^{0}C. To increase the alloy resistance to PC under the above conditions it is efficient to alkalify the solution. So, beginning from pH=5 the alloy $\varphi_{cor.}$ reduces to a considerable extent and $\Delta\varphi_{pit.}$ is more than 0.2 V that reliably prevents the initiation of PC.

In an undeaerated 20% NaCl solution PC is possible at a temperature of up to 250 ^{0}C over a much wider range of pH values, namely from 2 up to 12. To supress PC in this case pH is to be much higher than in a deaerated solution. To ensure the alloy resistance to PC at temperatures below 250 ^{0}C the solution pH should not be less than 12.5.

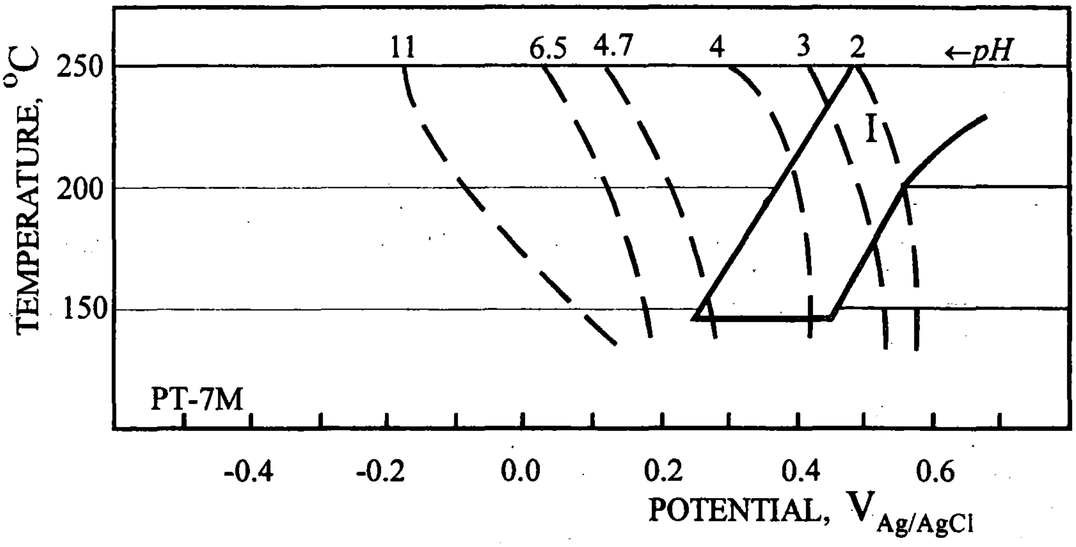

Fig. 5. Comparison of the area of PC potentials of the alloy (I) in an undeareated 3% NaCl solution with the alloy corrosion potentials obtained at different pH values.

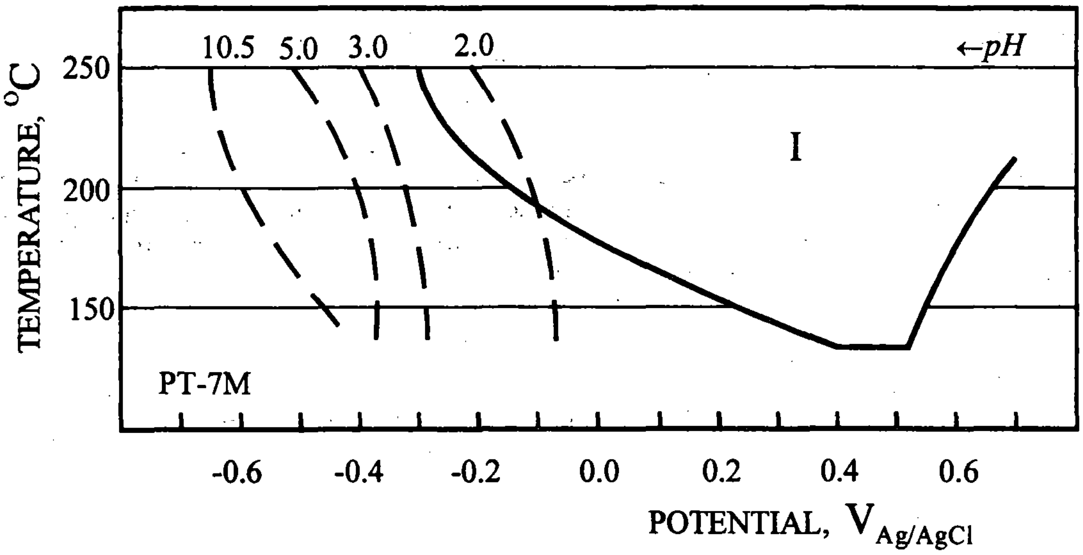

Fig. 6. Comparison of the area of PC potentials of the alloy (I) in a deaerated 20% NaCl solution with the alloy corrosion potentials obtained at different pH values.

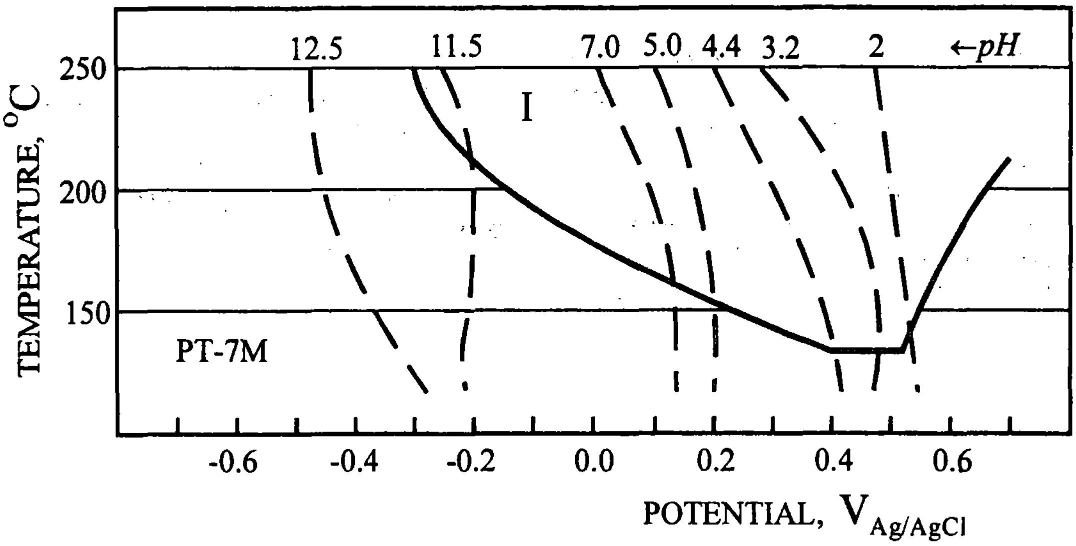

Fig. 7. Comparison of the area of PC potentials of the alloy (I) in an undeaerated 20% NaCl solution with the alloy corrosion potentials obtained at different pH values.

CONCLUSIONS

1. The PT-7M α–titanium alloy (2.2%Al, 2.5% Zr) may show susceptibility to PC at potentials comparable with corrosion potentials in NaCl solutions at temperatures exceeding 130 °C up to 250 °C. The method of potentiostatic polarization with a long-duration holding (up to 20 hours) is an efficient electrochemical method for the determination of PC potentials in the area of corrosion potentials.

2. The area of PC potentials of the alloy in a dilute 3 % NaCl solution has been determined at temperatures of up to 250 °C. The characteristic features of the area are as follows:
- $\varphi_{pit.}$ increases when increasing temperatures above the critical one;
- PC inhibition potential exists;
- a narrow range of PC potentials (~150 mV at 145-200 °C);
- a long-duration (till 5 -14 hours) induction period of PC ;
- a critical PC temperature is 145 °C in the above area of potentials.

3. The area of PC potentials of the alloy in a concentrated 20 % NaCl solution has been determined at temperatures of up to 250 °C. The characteristic features of the area are as follows:
- $\varphi_{pit.}$ decreases when increasing temperatures above the critical one;
- PC inhibition potential exists;
- increase in the range of PC potentials when increasing temperatures (up to 0.6 V at a temperature of 200 °C);
- a long-duration (till 0.5 -10 hours) induction period of PC ;
- a critical PC temperature is 135 °C in the above area of potentials.

4. Functions $\varphi_{pit.}$= a–b lg C_{NaCl} for temperatures of 150, 200, 250 °C have been obtained using which a critical concentration of chloride, about 6% by NaCl, has been determined. When exceeding the critical concentration $\varphi_{pit.}$ decreases with increasing the temperature. If the concentration is lower than the above one, the increase in temperature has the reverse effect. Such a change in the dependence of pitting potential on the solution temperature is explained by the change in the activities of activating ions (Cl^-) and passivating ones (OH^-) when increasing the temperature. The alloy inhibition seems to be related to the possibility to initiate ClO^-_3 ions showing protective properties at inhibition potentials.

5. The comparison of the areas of PC potentials obtained with corrosion potentials of the alloy has shown that in an undeaerated dilute 3 % NaCl solution PC is possible at temperatures exceeding the critical one only in case where pH=(2-4.5), but in a deaerated solution (oxygen concentration is about 0.010-0.015 mg/l) the alloy remains resistant to PC up to 250 °C over the whole range of pH values.

In a concentrated solution (20% NaCl) at temperatures of up to 250 °C PC is possible in the alloy at pH ranging in value from 2.0 to 12.0 if the solution is undeaerated, and at pH values of about 2.0-3.0 only if the solution is deaerated. The increase in pH of these solutions up to 12.5 and 5.0 respectively ensures pitting corrosion protection in the alloy at temperatures of up to 250 °C.

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