

Electrochemical behavior of Ti–V–Cr alloys in alkaline solution

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Polarization curves and electrochemical extraction have been used to analyze the electrocatalytic activity of (Ti,V)_{3-z}Cr_z alloys. The correlation between the composition and the optimal temperature of hydrogen desorption, overpressure of hydrogen evolution and amount of reversing hydrogen has been investigated. The obtained results help understand and optimize the process of electrochemical hydrogen saturation in alloys.

BCC alloys / Ti-V-Cr alloys / Electrocatalytic activity / Electrochemical extraction

Introduction

BCC alloys with body-centered cubic lattice (BCC lattice), for example in the Ti–V–Cr system, occupy a special place among the most promising materials for hydrogen storage [1-3]. They can absorb up to 3.8 wt.% of hydrogen in the favorable temperature range of hydrogen output, which is a key factor for their application in practice [4-6]. Recently, Ti–V–Cr alloys were also used as catalysts for magnesium alloys [5,7]. However, up till now these materials have mainly been saturated from the gas phase [8-10]. Still the electrochemical process of hydrogen saturation makes the process run at room temperature and atmospheric pressure. Besides, this method of hydrogen saturation makes model experiments to analyse the kinetics of the hydrogen penetration into the material possible. Here we see the relevance of our work.

Optimal conditions for electrochemical hydrogen saturation and for the influence of the alloy composition on the cathode behavior have been set in the work.

Experimental

Three-component alloys of the following compositions were the objects of the research: (Ti_{2.52-x}V_x)Cr_{0.48} (with $x = 0.54$ and $x = 1.98$), Ti_{1.0}V_{0.8}Cr_{1.2}, Ti_{0.33}V_{1.27}Cr_{1.4}, and wire specimens of titanium, vanadium and chromium.

X-ray diffraction (diffractometer SIEMENS D5000) with monochromized copper radiation was

applied to reveal the structure of the alloys. The program Powder Cell 2.4 was used to calculate the parameters of microstructure. A scanning electronic microscope Oxford Hitachi S-3400N with an energy-dispersive analyzer Bruker enabled us to study the component distribution in the alloys. We implemented the method of differential scanning calorimetry (DSC) with an instrument STA449C Jupiter (NETZCH) in an atmosphere of argon (heating rate 10°C/min) to analyze the phase transformation in the hybrids of the Ti_xV_yCr_z systems.

Electrochemical research was done using a standard electrochemical cell. The electrolyte was a KOH (approximate concentration 1 mol·l⁻¹) solution prepared with reagent grade KOH and deionized water from a Millipore system. The solutions of KOH were purified by precursory electrolysis on a platinum mesh electrode for two hours. A standard three-electrode electrochemical cell was used with a silver chloride electrode (Ag/AgCl) and a platinum electrode as reference and counter electrode, respectively. Samples prepared from the (Ti,V)_{3-z}Cr_z alloys were used as working electrodes (0.4-0.6 mm diameter and 0.2-0.3 mm thickness). The potentiodynamic polarization curves were obtained using a P-30I potentiostat with a potential sweep rate of 2·10⁻⁴ V·s⁻¹.

All the working electrodes for electrochemical measurements were armoured with polymerized ethoxyline resin to control the surface of the electrode material. The working surface was smoothed manually, polished by STRUERS LaboPol-2 reducing the grain diameter from 100 to 50 μm, and cleaned by ethanol.

The method of electrochemical extraction [11-13], which presupposes preparatory hydrogen saturation of the sample and further anode ionization of the saturated hydrogen, was applied to analyze the sorption capacity of the alloys. Preparatory hydrogen saturation of the surface of the working electrodes was done by electrode polarization with a cathodic current ($i = 10 \text{ mA} \cdot \text{cm}^{-2}$) for 15 min in an $1 \text{ mol} \cdot \text{l}^{-1}$ solution of KOH. The area of potentials – “two-layer area” – with hydrogen ionization, but without electrode dissolution, was identified to use the method of electrochemical extraction of hydrogen in the area of anode polarization of materials. The potential for the electrochemical extraction was chosen from this area.

The main kinetic parameters of hydrogen saturation and extraction from the materials under investigation were derived from the experimental time dependence of the current to hydrogen ionization according to the methodology proposed in [14,15].

The amount of extracted hydrogen was calculated by integration of the I, t -curve minus the amount of current obtained by multiplying the follow-on current and the time of extraction (t_{ex}):

$$Q_H^* = \int_0^{t_{ex}} Idt - I_b \cdot t_{ex},$$

where Q_H^* = amount of electricity for the oxidation of the extracted hydrogen, I_b = background current.

The amount of electricity (Q_H) corresponding to the hydrogen absorbed by one unit of alloy surface, was calculated in the following way:

$$Q_H = \frac{Q_H^*}{S},$$

Where S = working surface of the electrode during extraction.

Then, using Faraday's law, the total amount of extracted hydrogen was determined. The amount of hydrogen absorbed by the alloy (V_H) was expressed in $\text{cm}^3 \cdot \text{cm}^{-2}$, which corresponds to the amount of hydrogen absorbed by one unit square of sample surface.

All the potentials listed in the current work are given relative to the standard hydrogen electrode (SHE).

Results and discussion

It is known [11,16] that the amount of hydrogen in a metal/alloy depends on, under otherwise equal conditions, the surface concentration of adsorbed hydrogen (H_{ads}), thus on the rate and the mechanism of the hydrogen evolution reaction (HER) taking place on the surface of the analyzed material.

A very important characteristic of these alloys is that the distribution of the alloy components (titanium, vanadium and chromium) should be homogeneous throughout the material, and the local compositions agree with the nominal one. This was proven by the maps of element distribution in the alloys and the integrated range of elements (Fig. 1). An even surface will have a positive influence on the electrochemical behavior of the alloys.

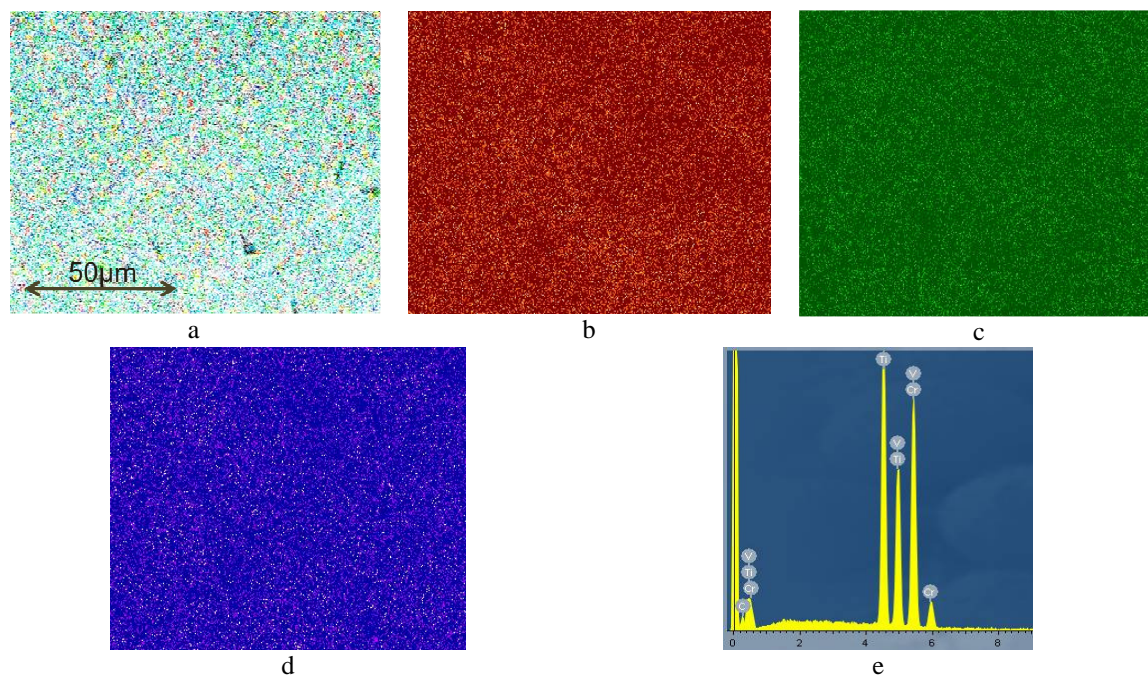


Fig. 1 Summarized map of distribution of the components in the alloy $\text{Ti}_{1.0}\text{V}_{0.8}\text{Cr}_{1.2}$ (a), distribution of titanium (b), vanadium (c), chromium (d) and integrated range of quantitative analysis of the composition (e).

To determine the mechanism of the HER and to compare the catalytic properties of the alloys, cathodic polarization curves were obtained and kinetic parameters (Tafel coefficients a_c and b_c) [17] were calculated. The measured cathodic polarization curves contain regions that were described by the Tafel equation (Fig. 2).

The analysis of the results given in Table 1 led us to deduce the following principles. An increase of the chromium content decreases the hydrogen overpotential (η) (Fig. 3, diagram 1), in other words, this means that ternary alloys with a large amount of chromium are preferable for cathodic processes.

We have used compositions with equal amounts of chromium, but different titanium to vanadium ratios in the alloy.

Under our experimental conditions the alloys ($\text{Ti}_{2.52-x}\text{V}_x\text{Cr}_{0.48}$, with $x = 0.54$ or 1.98 meet the imposed requirements. The obtained results (Table 1, Fig. 3, diagram 1) illustrate that the correlation between the components does not significantly influence the HER overpotential. This conclusion is quite unexpected, however, it may be used to develop BCC alloys for electrolytic hydrogen saturation.

The analysis of the experimental data (Table 1) reveals that the values of b_c for all the compositions under study are practically the same, which

demonstrates a similar mechanism of hydrogen evolution [17,18], however, the rate of the cathodic process (i_c) depends on the alloy composition. For two alloy compositions with equal amount of chromium the cathodic process was found to be much faster for the alloy with higher amount of titanium. This conclusion is contrary to the one made for two-component alloys [18,19]. Consequently, inclusion of chromium into the alloy provides conditions for dominating interactions between the alloy components that are likely to be seen in the hydrogen evolution reaction.

A decrease of the chromium content in the alloys leads to a decrease of the hydrogen desorption temperature (Fig. 3, diagram 2). At the same time it results in an increase of the HER overpressure.

The amount of hydrogen absorbed by the alloy (V_H) was calculated on the basis of the extraction curves ($I = f(t)$). The results of the electrochemical extraction (Fig. 3, diagram 3) qualitatively agree with the data on overpressure of hydrogen evolution from the surface of the analyzed alloys (Fig. 3, diagram 1). It should be noted here that, under the applied conditions for extraction (see Experimental), most of the hydrogen electrolytically absorbed by the alloys is used in the formation of hydrides (about 72-80%) [20], the rest being reversing hydrogen.

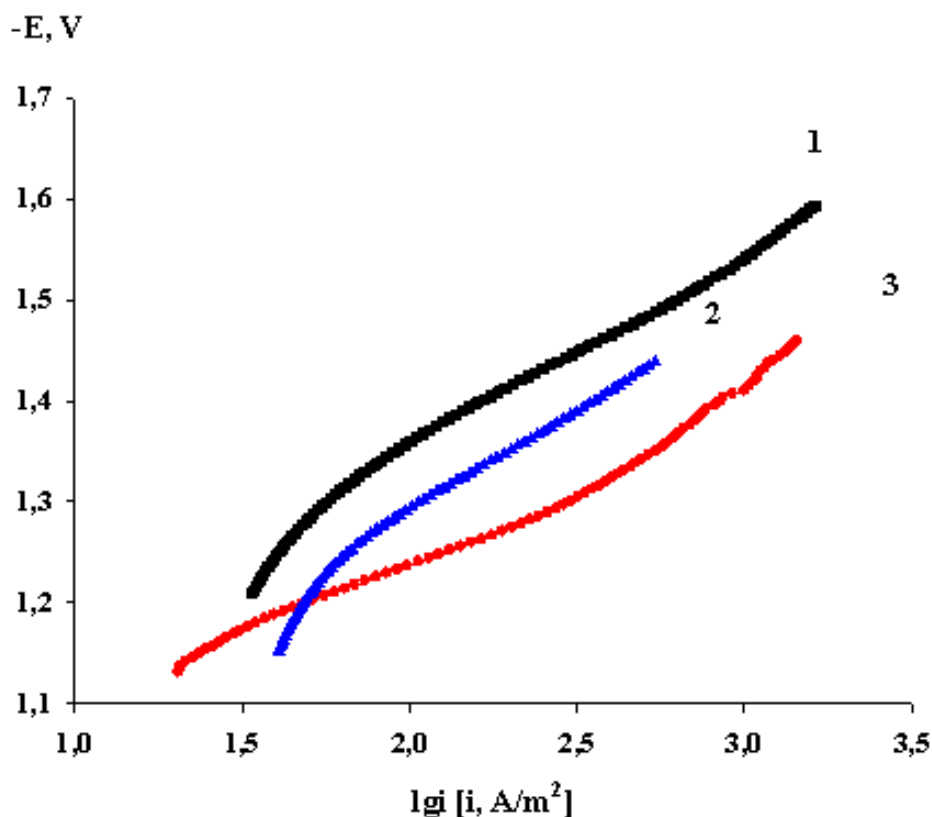


Fig. 2 Cathodic polarization curves for $\text{Ti}_{0.54}\text{V}_{1.98}\text{Cr}_{0.48}$ (1), $\text{Ti}_{1.98}\text{V}_{0.54}\text{Cr}_{0.48}$ (2) and $\text{Ti}_{0.33}\text{V}_{1.27}\text{Cr}_{1.4}$ (3) in $1 \text{ mol}\cdot\text{l}^{-1}$ solution KOH.

Table 1 Parameters of cathodic process in alloys of the system $(\text{Ti},\text{V})_{3-z}\text{Cr}_z$ in $1 \text{ mol}\cdot\text{l}^{-1}$ solution KOH.

(V+Ti)	Cr	b_c, V	η, V ($\eta = a_c$ at $i_c = 1 \text{ A}\cdot\text{cm}^{-2}$)	$I_c, \text{A}\cdot\text{m}^{-2}$ (at $E = -1.33 \text{ V}$)
$(0.54+1.98)=2.52$	0.48	0.19	0.85	72.4
$(1.98+0.54)=2.52$	0.48	0.17	0.87	161.9
$(0.8+1.0)=1.80$	1.20	0.13	0.69	-
$(1.27+0.33)=1.60$	1.40	0.12	0.65	413.3

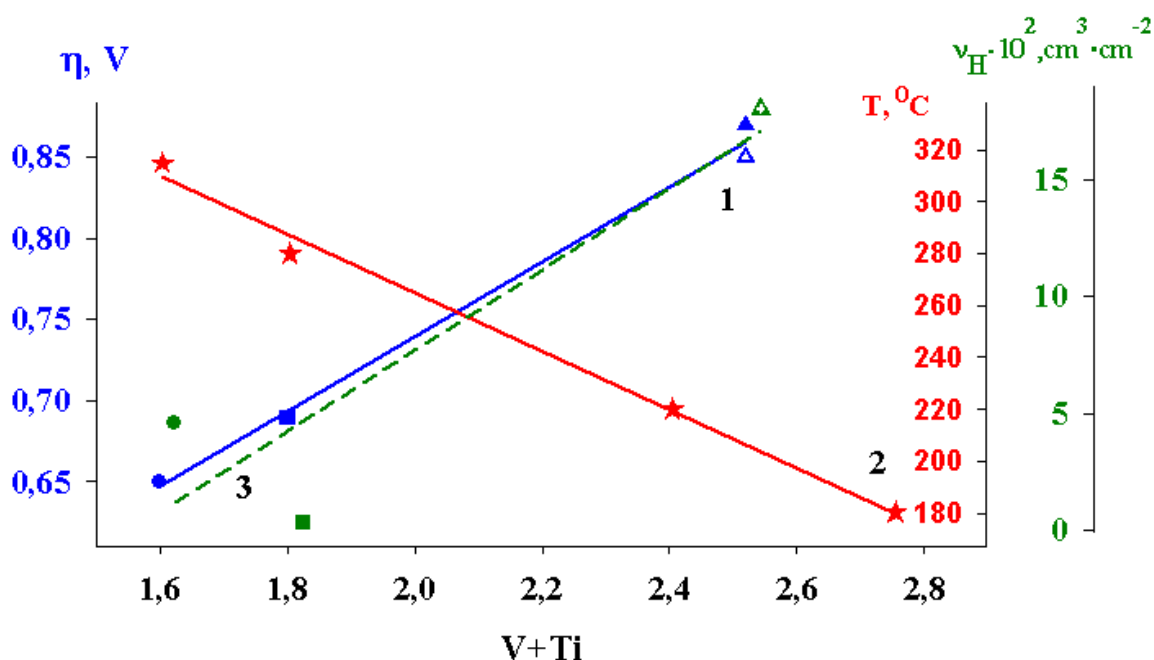


Fig. 3 Dependence of characteristics of $(\text{V},\text{Ti})_{3-z}\text{Cr}_z$ alloys and their hydrides on the sum of the coefficients of the hydride-forming components (V+Ti): HER overpotential (η) for alloys with compositions $(\text{Ti}_{1-x}\text{V}_x)_{2.52}\text{Cr}_{0.48}$, with $x = 0.54$ (Δ) and $x = 1.98$ (\blacktriangle), $\text{Ti}_{1.0}\text{V}_{0.8}\text{Cr}_{1.2}$ (\blacksquare), $\text{Ti}_{0.33}\text{V}_{1.27}\text{Cr}_{1.4}$ (\bullet) (1); temperature of the first phase transition in the hydrides (hydrogen desorption) (2); amount of hydrogen absorbed by the alloys $\text{Ti}_{0.54}\text{V}_{1.98}\text{Cr}_{0.48}$ (Δ), $\text{Ti}_{1.0}\text{V}_{0.8}\text{Cr}_{1.2}$ (\blacksquare), $\text{Ti}_{0.33}\text{V}_{1.27}\text{Cr}_{1.4}$ (\bullet) (3).

Conclusions

The research has led us to conclude that, in order to make a three-component Ti–V–Cr alloy work well under the conditions of repetitive cycling of hydrogen sorption/desorption, it is necessary to choose a composition that will satisfy two criteria: optimal (lowest possible for the conditions of the experiment) temperature of hydrogen desorption, and low overpotential to make the electrochemical hydrogen saturation of the alloy easier.

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References

- [1] E. Akiba, H. Iba, *Intermetallics* 6 (1998) 461-470.
- [2] S.-W. Cho, C. Han, C. Park, E. Akiba, *J. Alloys Compd.* 288 (1999) 294-298.
- [3] T. Tamura, T. Kazumi, A. Kamegawa, H. Takamura, M. Okada, *J. Alloys Compd.* 356-357 (2003) 505-509.
- [4] N. Skryabina, D. Fruchart, S. Miraglia, P. de Rango, M. Shelyapina, *Diff. Defect Data, Solid State Phenom.* 170 (2011) 302-306.
- [5] J. Huot, *Metals* 2 (2012) 22-40.
- [6] S.F. Santos, A.L.M. Costa, J.F.R. de Castro, D.S. dos Santos, W.J. Botta, T.T. Ishikawa, *J. Metastable Nanocryst. Mater.* 20-21 (2004) 291-296.

- [7] X.B. Yu, Z. Wu, B.J. Xia, N.X. Xu, *J. Alloys Compd.* 386 (2004) 258-260.
- [8] E. Akiba, M. Okada, *MRS Bull.* 27 (2002) 699-703.
- [9] K. Shirasaki, T. Tamura, T. Kuriwa, T. Goto, A. Kamegawa, H. Takamura, M. Okada, *Mater. Trans.* 43 (2002) 1115-1119.
- [10] M. Okada, T. Kuriwa, T. Tamura, H. Takamura, A. Kamegawa, *J. Alloys Compd.* 330-332 (2002) 511-516.
- [11] B.B. Kuznetsov, G.V. Khaldeev, V.I. Kichigin, *Hydrogenation of Metals in Electrolytes*, Mashinostroenie, Moscow, 1993 (in Russian).
- [12] A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, New York, 2001.
- [13] V. Breger, E. Gileadi, *Electrochim. Acta* 16 (1971) 177.
- [14] N.G. Krapivnyi, *Elektrokhimiya* 18 (1982) 1174-1178.
- [15] N.G. Krapivnyi, *Elektrokhimiya* 17 (1981) 672-677.
- [16] A.V. Vvedenskii, I.A. Gutorov, N.B. Morozova, *Elektrochim. Energ.* 8 (2008) 227-236.
- [17] B.E. Conway, B.V. Tilak, *Electrochim. Acta* 47 (2002) 3571-3594.
- [18] N. Medvedeva, N. Skryabina, P. Golovin, S. Dolukhanyan, A. Aleksanyan, *Int. Symp. Metal-Hydrogen Systems – Fundamentals and Applications (MH 2012)*. Kyoto, Japan, 2012.
- [19] P.V. Golovin, N.A. Medvedeva, N.E. Skryabina, *Vestn. Kazan. Tekhnol. Univ.* 17 (2012) 58-61.
- [20] P.V. Golovin, N.A. Medvedeva, N.E. Skryabina, *Kondens. Sredy Mezhfaznye Granitsy* 15 (2013) 99-105.