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The Effect of Aging on the Microstructure of Alloys $(TiCr_{1.8})_{100-x}V_x$ after Electrolytic Hydrogen Charging

The microstructure transformation of ternary Ti-Cr-V alloys after introduction of hydrogen has been analyzed for a long time. Assessment of the impact of vanadium concentration and ratio of Ti and V concentrations on composition stability has been carried out. Investigated alloys system corresponds to relation $(TiCr_{1.8})_{100-x}V_x$. The atomic ratio Ti/Cr is constant. Vanadium content changes with the step 20 at.%. The hydrogen charging has been carried out in a thermostatic three-electrode electrochemical cell using 1M KOH electrolyte (i_c = 10–30 mA/cm^2) at 293 K for three hours. It was established that the hydrogen introduction leads to surface migration of alloy components. Their distribution oscillates as time passed. This is due to the fact that hydrogen interacts differently with titanium and vanadium. The electrolytic hydrogen introduction initiates deformation of the crystal lattice and self-diffusion of alloy atoms. The statistically nonuniform distribution of electrolytic hydrogen increases the intensity of the process. The relaxation of internal stresses leads to further redistribution of components. The observed changes depend on the vanadium content in the alloys and have a different character inside the grain and near grain boundaries. A significant change has been established for $(TiCr_{1.8})_{60}V_{40}$.

Keywords: $(TiCr_{1.8})_{100-x}V_x$, alloys, electrochemical hydrogen saturation, stability, elements, concentration, self-diffusion.

Introduction

Body-centered cubic (bcc) alloys have been studied as hydrogen storage materials for a long time. As an example, the system of TiVCr alloys can absorb and store hydrogen better, than most metal compounds. In fact, basic elements of TiVCr alloys have broad mutual solubility in solid state and can form solid solution with bcc crystal structure. However, optimal conditions of TiVCr hydrogenation are determined by different external factors: method of alloy obtaining, heat treatment, etc. Reversible hydrogen absorption fully depends on (Ti+V)/Cr ratio at normal conditions. Optimized alloy compositions demonstrate maximum of hydrogen absorption, which achieves 3.7 wt. % [1, 2]. Furthermore, for high and stable reversible properties (sorption/desorption of hydrogen) it is particularly important to have a stable and the same structure before each hydrogenation cycle.

To propose a formula for the basic bcc alloys, that provide optimal properties for hydrogenation / dehydrogenation, it is necessary to understand well the progressive effect of the influence of the composition on the H-sorption parameters associated with the saturation conditions. The correlation between the relative amount of Ti, V elements in alloy and the stability of $Ti_\alpha V_\beta Cr_\gamma$-H hydrides formed in the gas-solid reaction was shown in [3]. Increasing of concentration of hydride forming elements (Ti, V) leads to decreasing of hydrides stability and the temperature of hydrogen desorption [3–5]. Moreover, the investigations of hydrogen diffusion characteristics to Ti-V binary system [6, 7] demonstrated dependence of hydrides stability on Ti/V ratio. This could mean that nature of chemical bonding into metal-hydrogen interaction also not the same for each element of the metal in ternary alloy.

In this work, the effect of change in composition of $(TiCr_{1.8})_{100-x}V_x$ system was researched. For this purposes vanadium concentration in alloys was changed in the range from 0 to 60 at.%. Usually hydrogen sorption characteristics of alloys was studied by plotting diagrams "pressure–composition–temperature" as a result of hydrogen gaseous saturation of alloys under certain pressure at different temperatures [8–11]. As part of this work, the electrolytic saturation method was used, which allows the process to be carried out at room temperature [7, 12, 13] and there is the correspondence between cathode current density (electrochemical method) and hydrogen partial pressure on the sample surface (gaseous saturation). In addition, the surface of sample is a barrier to hydrogen penetration into the material regardless of hydrogen saturation method, so it is possible to define surface condition and its influence on sorption characteristics of alloys by electrochemical method [13, 14].

Experimental

The $(TiCr_{1.8})_{100-x}V_x$ alloys were obtained in two steps. At the first step $TiCr_{1.8}$ alloy (Laves phase, C14) was prepared in high-frequency melting furnace in a water-cooled crucible under argon atmosphere (components purity ~99.97 %). The $TiCr_{1.8}$ alloy was re-melted three times for homogeneity of structure. At the second step $Ti_\alpha V_\beta Cr_\gamma$ alloy was obtained by co-melting of the $TiCr_{1.8}$ ingot and vanadium (99.99 % purity). The ratio of $TiCr_{1.8}$ and V corresponds with the content of elements in ternary system $(TiCr_{1.8})_{100-x}V_x$ ($x = 20, 40, 60$). The samples were made in the CRETA laboratory (Center for National Research, Grenoble, France).

The samples for electrochemical hydrogen saturation were cut from ingots by mechanical method. The surface of samples was treated by grinds “Sic-Paper” class 220÷1000 (grain diameter 100÷50 μm). After the samples were polished with discs “MC-Dac” (Struers) (grain size 9÷10 μm) and diamond paste “DiaDuo” (Diamond Suspension and Lubricant in One) by polishing machine “STRUERS LaboPol-2”, electrodes for electrochemical saturation were obtained from prepared samples. After hydrogen saturation the electrodes were stored in a desiccator.

The electrochemical measurements were carried out in three-electrode electrochemical cell with cathodic and anodic compartments separated by a porous glass diaphragm. The temperature of electrolyte was 21±1 °C. The electrolyte was the 1M KOH solution prepared from high-purity reagent and de-ionized water. Hydrogen saturation condition (current of cathodic polarization) was chosen based on polarization studies conducted earlier [15]. Registration of cathodic polarization curves (rate of potential sweep 2 mV/sec) was carried out for determination of linear section (Tafel section). This section of potentials was used for electrochemical hydrogen saturation. Hydrogen saturation of samples was implemented at cathodic current density ($i_c = 10–30$ mA/cm^2) for three hours. As a result of electrochemical investigation the amount of reversible storage of hydrogen for all alloys was calculated [12, 16].

The microstructure study of samples surface before and after hydrogen saturation was carried out by scanning electron microscope “Hitachi” S-3400 with energy dispersing device, which allowed determining amount of alloys elements on the required point.

Results and Discussion

The following samples of $(TiCr_{1.8})_{80}V_{20}$, $(TiCr_{1.8})_{60}V_{40}$, $(TiCr_{1.8})_{40}V_{60}$ alloys were chosen for analysis of stability of microstructure after hydrogen saturation. These alloys were selected due to possibility of practical use because alloys with high vanadium content (80 at.% and higher) are much more expensive systems. For the other hand, Laves phase appears in alloy with low vanadium concentration (lower 20 at.%) [17]. Before hydrogen saturation all samples of alloys were tested by scanning electron microscope for determination of homogeneity of the material. Table 1 demonstrates the results (errors are obtained for each sample by averaging 5 measurements). Figure 1 illustrates an example of the distribution of elements in the samples.

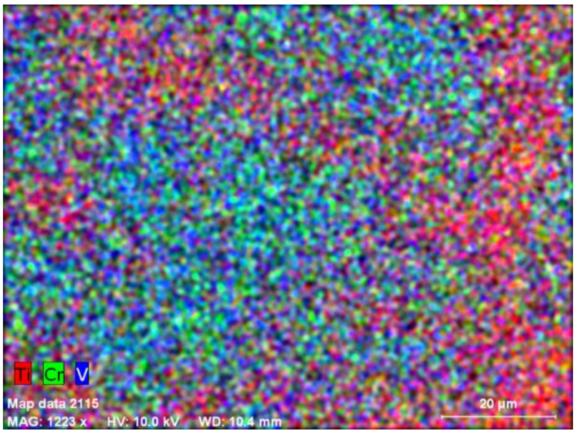


Figure 1. Image of elements distribution in $(TiCr_{1.8})_{80}V_{20}$ (×1200)

Table 1

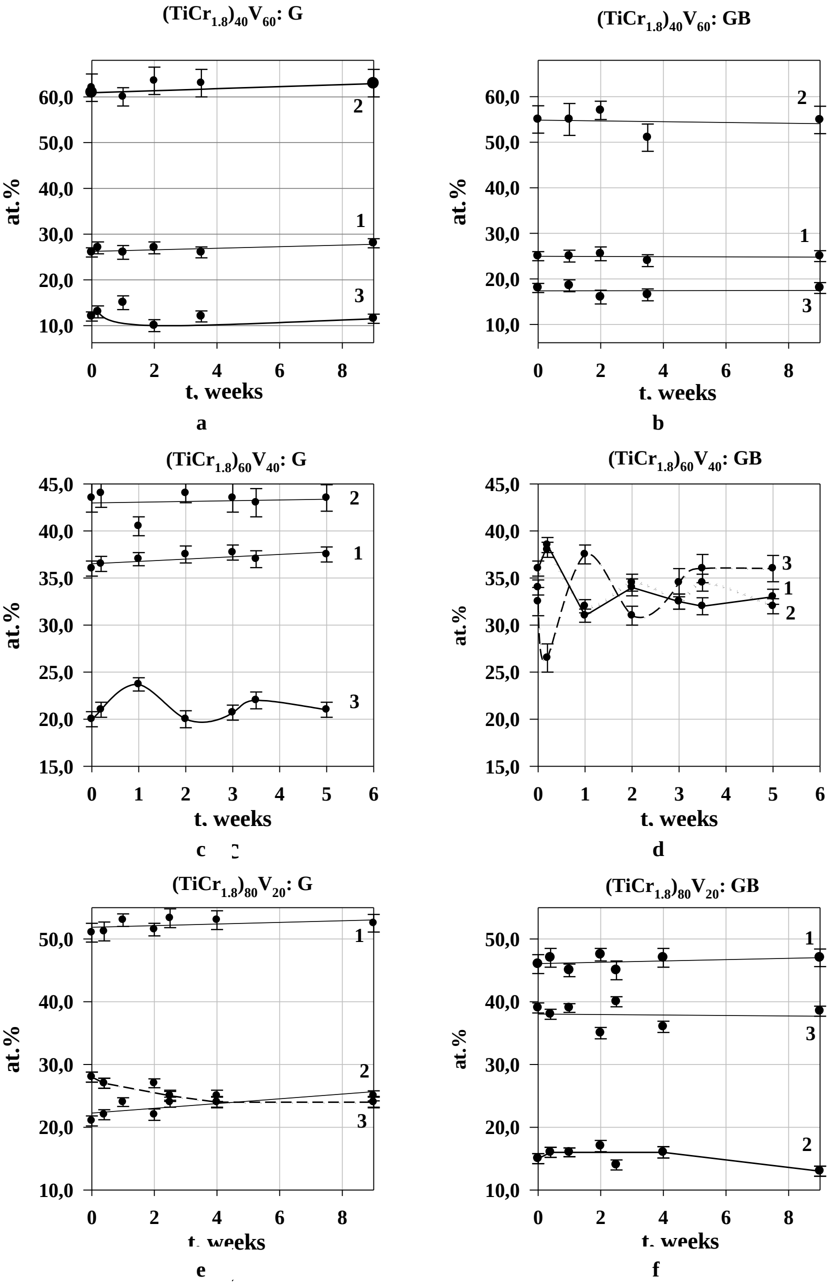
Composition of $(TiCr_{1.8})_{100-x}V_x$ alloys and concentration of Ti, Cr and V in grain and on grain boundary before hydrogen saturation

x, at.% V	Composition, at.%				
	Elements of alloy	Grade composition	Initial	Distribution of elements	
				Grain	Grain boundary
20	Ti	28.56	27.10±2.15	27.96±2.23	39.19 ±2.63
	Cr	51.44	52.47±4.13	51.05±3.40	46.01± 5.06
	V	20	20.43±3.78	20.99±6.23	14.80±5.80
40	Ti	21.42	20.60±2.43	20.01±2.06	31.89±2.48
	Cr	38.58	37.45±4.16	36.59±3.40	33.92±2.94
	V	40	41.95±6.00	43.36±6.10	34.17±5.91
60	Ti	14.28	13.77±0.93	11.32±1.13	18.44±1.87
	Cr	25.72	25.05±1.74	25.93±3.02	25.93±3.27
	V	60	61.18±3.93	62.76±4.80	55.62±6.15

From these results, it can be concluded that all samples correspond to the specified composition within the scatter of results. It is important to emphasize that all of the alloys have a single-phase ***bcc*** structure; however, the heterogeneity in the distribution of the components between the grain (***G***) and near grain boundary (***GB***) exists. Furthermore, increasing of vanadium concentration leads to decreasing of the difference in distribution of elements between grain and grain boundary. This result was previously confirmed by SEM investigations in secondary electrons [15]. The results (Table 1) demonstrate that initial state of the $(TiCr_{1.8})_{40}V_{60}$ alloy (before hydrogenation) has more homogeneity structure than others. Figure 2 represents the results of investigation of the degree of homogeneity of elements distribution of the alloy in the process of aging after hydrogen saturation. After saturation, all samples were washed with de-ionized water and dried. Samples were stored in a desiccator between studies. The point on the vertical scale corresponding to "0" on the time scale indicates the amount of elements in initial state of the alloys.

Experimental data demonstrate insignificant influence of the aging after charging with hydrogen on elements distribution in alloys. However, there is an exception — it is $(TiCr_{1.8})_{60}V_{40}$ alloy (Fig. 2). This alloy has significant fluctuations all of elements near grain boundary and as well titanium inside of grain. The fact of oscillating change of crystal structure occurring in alloy after electrochemical hydrogen saturation was presented in studies [18, 19]. It should be pointed out that this effect can be caused by instability of structural states of microgroups of atoms due to the hydrogen charging method. Moreover, radii of titanium, vanadium and chromium atoms have close sizes (1.45, 1.31 and 1.25 Å, respectively) and ratio of these elements at grain boundary of $(TiCr1.8)_{60}V_{40}$ alloy is approximately equal, therefore is more likely formation of unstable complexes of hydrogen with a metal and/or with couple of metal-defect. In this case, defect can be any irregularity of the regular structure of the crystal lattice, for example, vacancy and dislocation. The existence of these defects is especially likely near the grain boundaries. There is a relaxation of internal stresses in the hydrogen-saturated alloy over time, and the system passes into the equilibrium state.

On the other hand, there are no significant changes in the concentration of chromium in all the investigated alloys. It can be assumed, that relaxation process exists not only because of decreases of "mechanical" stresses during hydrogen charging, but also because of influence of type of chemical bond between hydrogen and metal atoms of alloys. Hydrogen dissolves in vanadium and forms hydrides according to the principle of a solid solution [20]. The chemical bonding between the metal atom and hydrogen is observed for titanium hydride [20]. It is noticeable that metals in $(TiCr_{1.8})_{100-x}V_x$ alloys are distributed statistically uniformly. However, it cannot be excluded that hydrogen distribution is not statistically even especially because of lack of saturate hydrogen saturation. In this case, unstable metal-hydrogen complexes will migrate and create another character of local ordering because of the relaxation processes and self-diffusion of metal atoms. Apparently, this phenomenon is observed in the experiment.



1 — Cr; *2* — V; *3* — Ti

Figure 2. Influence of retention time of alloys samples after hydrogen saturation on character of element distribution in grain (*a, c, e*) and on grain boundary (*b, d, f*)

Conclusions

In this work, we investigated the effect of electrochemical hydrogen saturation on surface migration of components of $(TiCr_{1,8})_{100-x}V_x$ alloys. Assessment of the impact of vanadium concentration and ratio Ti/V concentrations on composition stability was carried out. It was established that element distribution after hydrogen injection oscillates as time passed. Also, the electrolytic hydrogen introduction initiates deformation of the crystal lattice and self-diffusion of alloy atoms. The statistically nonuniform distribution of electrolytic hydrogen increases the intensity of the process. The relaxation of internal stresses leads to a further redistribution of alloy components. The observed changes depend on the V concentration in the alloys and have a different character inside the grain and near grain boundaries. A significant change was established for $(TiCr_{1.8})_{60}V_{40}$.

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Сутегімен электролиттік қаныққаннан кейінгі $(TiCr_{1,8})_{100-x}V_x$ қорытпалар микроқұрылымының эволюциясы

Ti-Cr-V үштік қорытпаларының сутегімен қаныгуынан кейінгі микроқұрылымының өзгеруі бірнеше сағат бойы талданды. Қорытпадағы ванадий құрамының және Ti мен V-дің өзара қатынасының қорытпаның тұрақтылығына әсері бағаланды (қорытпа құрамдары %-бен берілген). Барлық зерттелген үлгілер үшін Ti және Cr мөлшерінің өзара қатынасы тұрақты болды. Мақалада $(TiCr_{1.8})_{100-x}V_x$ құрамды қорытпалар зерттелді. Ванадий мөлшері 20 % қадаммен өзгерді. Қорытпа үлгілерін сутегімен қанықтыру 1 М KOH термостатталған үш электродты электрохимиялық ұяшықта катодтық токтың тығыздығы ic = 10–30 мА/см^2 кезінде үш сағат бойы 293 К температурада жүргізілді. Сутекті енгізу нәтижесінде қорытпа компоненттерінің беттік миграциясы жүретіні анықталды. Олардың беткі қабатта таралуы уақыт бойынша тербеледі. Бұл сутегі қорытпаның құрамына кіретін титан және ванадиймен әртүрлі әрекеттесетініне байланысты. Қорытпаның сутегімен электролиттік қаныгуы кристалдық тордың деформациясына және қорытпа атомдарының өздігінен диффузиясына әкеледі. Сутектің статистикалық біркелкі емес таралуы оны енгізудің бұл әдісімен процестің қарқындылығын арттырады. Ішкі кернеулердің босаңсуы компоненттердің қорытпаның бетінде одан әрі қайта бөлінуіне әкеледі. Байқалатын өзгерістер қорытпалардағы ванадийдің мөлшеріне байланысты және ішкі жағында сондай-ақ, шекара маңайында әртүрлі сипатта болады. $(TiCr_{1,8})_{60}V_{40}$. құрамының едәуір өзгергені анықталған.

Кілт сөздер: $(TiCr_{1.8})_{100-x}V_x$, қорытпалар, электрохимиялық гидрлеу, тұрақтылық, элементтер концентрациясы, өздігінен диффузия.

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Эволюция микроструктуры сплавов $(TiCr_{1,8})_{100-x}V_x$ после электролитического насыщения водородом

Трансформация микроструктуры тройных сплавов Ti–Cr–V после их насыщения водородом анализировалась в течение нескольких часов. Была проведена оценка влияния содержания ванадия в сплаве и соотношения компонентов Ti и V на стабильность сплава (составы сплавов приведены в ат.%). Соотношение количеств Ti и Cr было постоянным для всех исследованных образцов. В статье исследованы сплавы состава $(TiCr_{1,8})_{100-x}V_x$. Содержание ванадия изменялось с шагом в 20 ат.%. Насыщение образцов сплавов водородом проводилось в термостатированной трехэлектродной электрохимической ячейке из 1 М KOH при плотности катодного тока i_c = 10–30 мА/см^2 в течение трех часов при 293К. Установлено, что введение водорода приводит к поверхностной миграции компонентов сплава. Их распределение по поверхности осциллирует во времени. Это связано с тем, что водород по-разному взаимодействует с титаном и ванадием, входящими в состав сплава. Электролитическое насыщение сплава водородом приводит к деформации кристаллической решетки и самодиффузии атомов сплава. Статистически неравномерное распределение водорода при таком способе его введения усиливает интенсивность протекания процесса. Релаксация внутренних напряжений приводит к дальнейшему перераспределению компонентов по поверхности сплава. Наблюдаемые изменения зависят от содержания ванадия в сплавах, имеют различный характер внутри зерна и вблизи межзёренных границ. Установлено значительное изменение состава $(TiCr_{1,8})_{60}V_{40}$.

Ключевые слова: $(TiCr_{1.8})_{100-x}V_x$, сплавы, электрохимическое наводороживание, стабильность, концентрация элементов, самодиффузия.

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