Activation of $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy electrodes by hot alkaline solutions

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Abstract

Hot alkaline treatment of the multiphase alloy $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ results in significant surface corrosion, with at least some of the corrosion products being soluble in the treating solution. The corrosion process generates hydrogen that is largely absorbed by the alloy during treatment, resulting in heterogeneous particle cracking and significant electrochemical discharge capacity (C_0) even before the first deliberate charge. The discharge capacity (C_1) after the first deliberate charge is significantly increased by hot alkaline treatment. C_0 is a direct measure of alloy corrosion during the hot alkaline treatment and should be minimized in practice. C_1 is a measure of the electrochemical activation rate and should be maximized in practice. Another important parameter is the maximum capacity C_{max}. The effects of treatment time and temperature as well as solution (KOH vs. NaOH) on C_0, C_1 and C_{max} are presented, along with some long-time cyclic capacity data.

1. Introduction

The so-called "AB$_2$ family" of hydrogen storage alloys offers higher capacity alternatives to the AB$_5$ alloys for hydride battery applications. The "AB$_2$ family" consists not only of true, single-phase AB$_2$ intermetallic compounds (e.g. $ZrCr_{0.8}Ni_{1.2}$ [1]) but also complex multiphase alloys containing at least one AB$_2$ phase (e.g. $V_{22}Ti_{16}Zr_{16}Ni_{39}Cr_7$ [2] and $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ [3] among others).

One problem that exists with the AB$_2$ alloys is that they are harder to activate electrochemically and many charge–discharge cycles may be required to reach full battery capacity. This is usually associated with a deleterious, naturally occurring surface oxide that greatly reduces the charging efficiency. In the case of the Ovonic Battery family of V–Ti–Zr–Ni–Cr alloys an etching treatment is used to alter this surface oxide to increase the surface activity for charge acceptance [2]. The procedure consists of soaking the as-fabricated electrode in hot (70 °C) concentrated (31%) KOH solution [4]. This process results in substantial surface corrosion and partial solution of all alloy elements except Ni. Although the etching process is clearly beneficial, it is not completely clear to us why.

This paper re-examines the effect of hot alkaline treatment on the activation behaviour of the multiphase "AB$_2$" alloy $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ studied earlier by Sawa and Wakao [3]. Except for the absence of Cr, this alloy is similar to the commercially oriented base composition $V_{22}Ti_{16}Zr_{16}Ni_{39}Cr_7$ (also written as $Zr_{0.5}Ti_{0.5}V_{0.69}Ni_{1.22}Cr_{0.22}$) of the Ovonic Battery Company [2]. We examined the effect of solution (KOH vs. NaOH), temperature and time on the ease of electrochemical activation and related surface effects and bulk hydrogen effects.

2. Experimental procedures

$Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ samples were made from commercial purity elements using arc melting in an argon atmosphere on a cold Cu hearth.

Powder less than 26 μm in particle size was made by grinding in air. Alloy in the amount of 0.216 g was mixed with four times that weight of Ni (Inco type 255) powder and cold pressed at 4×10^8 Pa to form a pellet 13 mm in diameter to serve as an electrode. All rate and capacity data cited below are normalized to the original active alloy mass.

Electrodes were treated by immersion for various periods of time in either 6 N KOH or 10 N NaOH at controlled temperatures in the range 65–80 °C. The treated electrode was then removed, cooled and placed in the central compartment of a cell using a 6 N KOH electrolyte and an $Ni(OH)_2$–NiOOH positive electrode with greater capacity. Before the first deliberate charge the hydride electrode was discharged at 25 mA g^{-1} to determine C_0, the quantity of charge developed by the alkaline treatment itself. The sample was then cycled as follows: charged at 50 mA g^{-1} for 8 h, held for 10 min and finally discharged at 50 mA g^{-1} down to a cell voltage of 0.9 V. The capacity after the first deliberate charge, C_1, and the maximum capacity C_{max} were determined.

The cycle life experiment was started by activation at 50 mA g^{-1} for 2 or 32 cycles for an electrode treated for 3 or 1 h respectively, followed by charging at 200 mA g^{-1} for 2 h, holding for 10 min and finally discharging at 200 mA g^{-1} down to a cell voltage of 0.9 V at 20 °C.

Some unconsolidated powder (sometimes larger than 26 μm) was treated directly for metallographic studies (PMG3, Olympus) and surface observation by scanning electron microscopy (SEM), electron probe microanalysis (EPMA) and electron spectroscopy for chemical analysis (ESCA).

Surface analyses were carried out by means of X-ray photoemission spectroscopy (XPS) on an ESCA-850M (Shimazu, Japan). The alloy surface was treated with 6 N KOH solution for 20 h at 20 °C, then washed with purified water until pH=7 and dried. The base pressure in the spectrometer was 10^{-7} Pa and Mg Kα ($h\nu$=1253.6 eV) radiation was used at 10 kV and 30 mA. To measure depth profiles, Ar^+ ion bombardment (4×10^{-4} Pa) at 2 kV and 25 mA was used.

Selected treatment solutions were analysed for soluble species by spectroscopy (ICPS) using an IMSICP-1T (Jeol).

3. Results and discussion

The microstructure of $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ is a pseudo-binary Laves phase similar to that previously published for $V_{22}Ti_{16}Zr_{16}Ni_{39}Cr_7$ [2]; however, we noticed that a very non-uniform macroscopic distribution of the V-rich dendritic phase formed during solidification. Both the metallography and X-ray diffraction (XRD) results indicated the $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy to be a multiphase alloy. The alloy has a solidification instability that leads to an inhomogeneity in microstructure. There are some regions (about 80%) with a dendritic structure and some regions (about 20%) that are dendrite free (see Fig. 1(a)). The dendritic regions of the alloy contain three or four phases: (1) a dendrite phase very rich
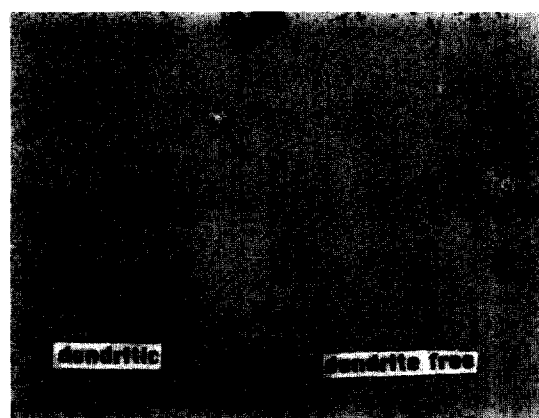
(a)
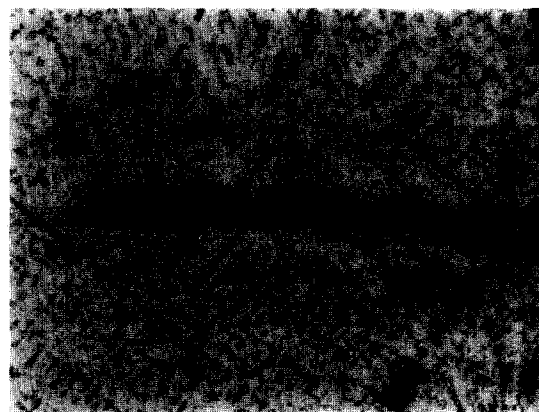
(b)
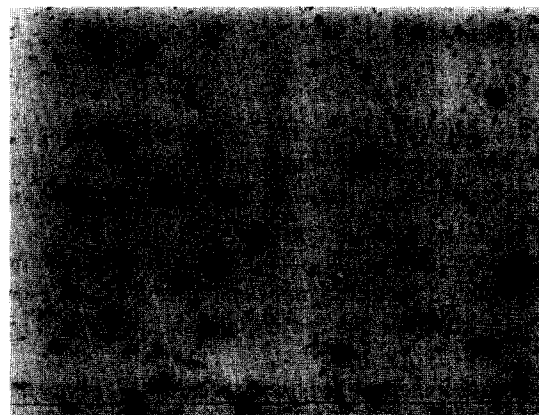
(c)

Fig. 1. Light photomicrographs of $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy (etched after polishing in $95H_2O$–$4.5HNO_3$–$0.5HF$): (a) dendrite and dendrite-free structure (magnification, $\times100$); (b) dendrite structure (magnification, $\times400$); (c) dendrite-free structure (magnification, $\times400$).

in V; (2) one or two AB_2 phases containing all elements but low V; (3) ZrO_2 particles (see Fig. 1(b)). The dendrite-free regions of the alloy contain the following phases: (1) one or two AB_2 phases containing all elements, with substantial V; (2) a little free Ti and Ti–Ni; (3) ZrO_2 particles (see Fig. 1(c)). The segregation occurs during solidification of the alloy and is also reflected in the XRD spectrum. In Fig. 2 the XRD
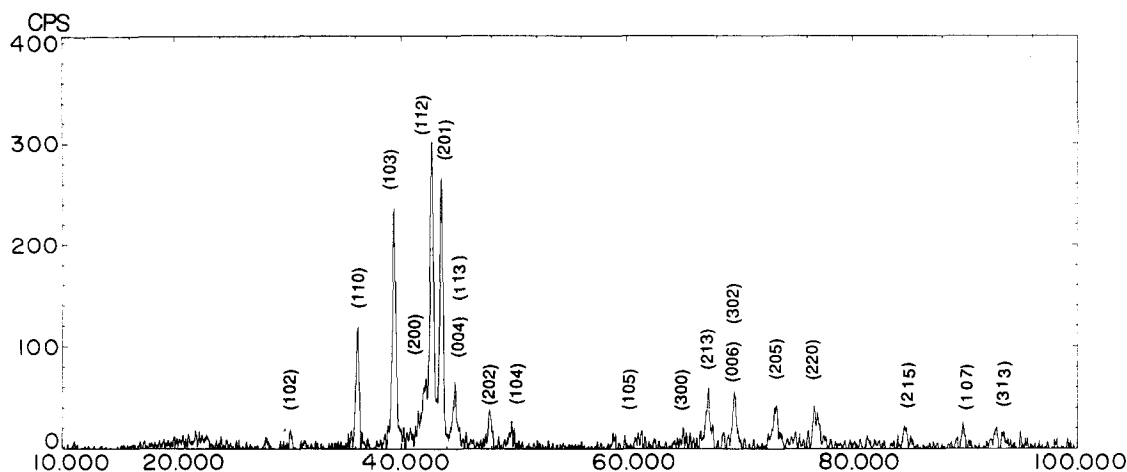
Fig. 2. X-ray diffraction pattern of $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ (Cu $K\alpha$ radiation).

peaks are rather broad and contain some "fine structure" or multiple subpeaks. The diffraction peaks were indexed as a hexagonal structure of the C14 Laves phase. Fig. 3 shows the pressure–composition (P–C) isotherm of the alloy at 40 °C. The P–C isotherm indicates that the grain boundary between hydrogenated and non-hydrogenated regions is very vague or does not exist. It is possible that hydrogen was absorbed in the alloy as a solid solution. The theoretical capacity C_{th} per unit weight of the alloy, 370 mA h g^{-1}, can be calculated

using H/M data according to

$$C_{th} = \frac{xF}{3.6M} \qquad (1)$$

where F and M are the Faraday constant and the molecular weight of the alloy respectively and x is the number of hydrogen atoms per alloy unit. The theoretical capacity is very close to the discharge capacity, 278 mA h g^{-1}, at 12.5 mA g^{-1} and 20 °C.

The effects of hot alkaline treatment on C_0, C_1 and C_{max} are shown in Table 1 as a function of treatment time and treatment temperature in 6 N KOH solution or 10 N NaOH solution. For reference, the first entry in Table 1 (25 °C) represents an electrode without pretreatment, i.e. simply placed in the room temperature test cell after fabrication. The following observations can be made.

(1) All treated samples show a finite C_0, i.e. hot alkaline treatment alone results in some H charging.

(2) Treatment results in greatly improved first-cycle activation, C_1 reaching 100% of C_{max} in some cases.

(3) The longer the time and the higher the treatment temperature, the higher are the values of C_0 and C_1/C_{max}.

(4) Higher treatment temperatures and/or longer times result in a reduced C_{max}.

(5) There is no significant difference between 6 N KOH and 10 N NaOH.

(6) The electrode composition influences the values of C_0 and C_1/C_{max} significantly. Under the same treatment conditions (70 °C for 20 h) the treated electrode without polytetrafluoroethylene (PTFE) shows a much larger C_0 and a much smaller C_1 than the treated electrode mixed with 5% PTFE.

Our hot alkaline experiments confirm the activation benefits described earlier [2,4].

After alkaline solution treatment the kinetic characteristics of the alloy electrode have been clearly improved. There are significant differences between the
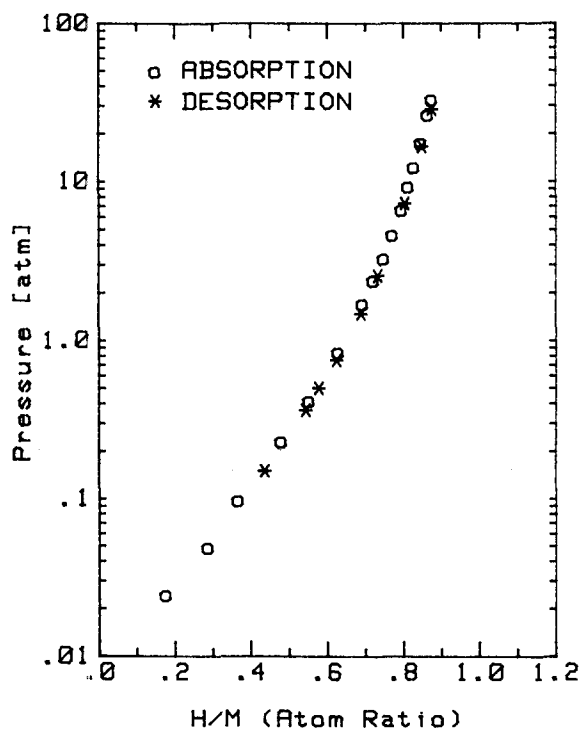
SAMPLE: K050-Zr0.5Ti0.5V0.75Ni1.25

TEMPERATURE: 40 deg.C

Fig. 3. P–C curve of $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy at 40 °C.

Table 1
Values of C_0, C_1, C_{max} and C_1/C_{max} after various hot alkaline treatments

Solution	Temperature (°C)	Time (h)	C_0 (mA h g^{-1})	C_1 (mA h g^{-1})	C_{max} (mA h g^{-1})	C_1/C_{max} (%)
6 N KOH	25	–	0	71.2	326.2	23
6 N KOH	65	1	2.5	257.5	323.5	80
6 N KOH	65	3	9.6	356.5	356.5	100
6 N KOH	65	5	19.6	331.8	338.0	98
6 N KOH	70	0.5	3.3	258.5	ND[b]	ND
6 N KOH	80	0.5	27.5	312.5	ND	ND
6 N KOH	80	5	96.5	281.7	ND	ND
6 N KOH	70	20	168.0	223.0	ND	ND
6 N KOH[a]	70	20	26.5	326.7	ND	ND
10 N NaOH	70	0.5	1.7	300	336	89
10 N NaOH	80	0.5	14.0	313	313	100
10 N NaOH	80	5	96.3	282	282	100

[a]Mixed with 5% PTFE.
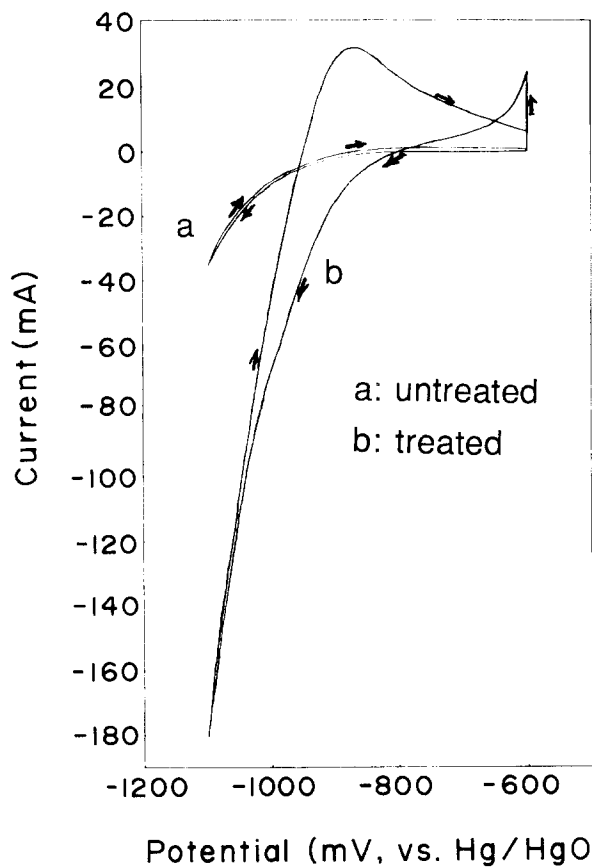[b]ND, not determined.

Fig. 4. Polarization curves of galvanostatic scan with triangular waveform for 10 N NaOH-treated and untreated Zr$_{0.5}$Ti$_{0.5}$V$_{0.75}$Ni$_{1.25}$ alloy at scanning speed of 0.05 mV s^{-1}.

two polarization curves (see Fig. 4). When charged at 20 mA (93 mA g^{-1}), the potentials vs. Hg/HgO are −0.91 V for the treated electrode and −1.10 V for the untreated one. There are clearly an initial discharge current and C_0 after starting scanning from −0.6 V vs. Hg/HgO. The charge retentions of Zr$_{0.5}$Ti$_{0.5}$V$_{0.75}$Ni$_{1.25}$

are 93.4%, 91.7%, 89.1% and 86.2% under KOH solution at 20 °C for 1, 2, 3 and 6 days respectively.

ICPS analysis of the treatment solutions together with light metallography and SEM also confirmed the proposal by Zitos et al. [4] that substantial corrosion and partial solution of alloy components occur during hot alkaline treatment. However, we were not able to completely confirm the extraordinarily high degree of Zr solution reported in Ref. [4], finding that V was dissolved more than Zr and relatively little Ti or Ni was dissolved (see Fig. 5). SEM showed substantial rounding of the sharp, as-crushed particles and a roughening of flat, cleaved surfaces by treatment.

Optical metallography of sectioned and polished particles, an example of which is shown in Fig. 6, also showed such solution effects. In addition, it can be seen that some (but not all) particles exhibited internal cracks typical of hydriding. The origin of hydrogen is perhaps a logical and expected consequence of corrosion, for example

$$M + 2H_2O \longrightarrow MO_2 + 4H \tag{2}$$
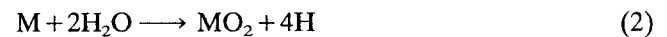
resulting in a soluble oxide or hydrated oxide and leaving atomic H available for hydriding of the un-
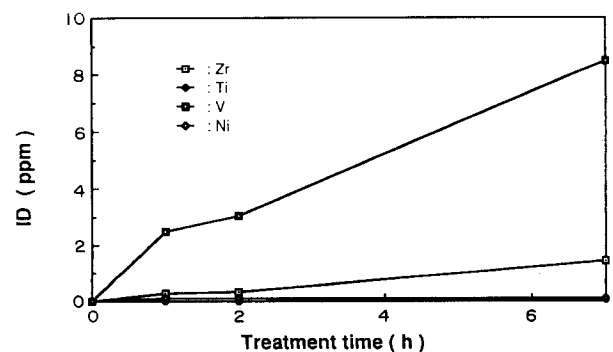

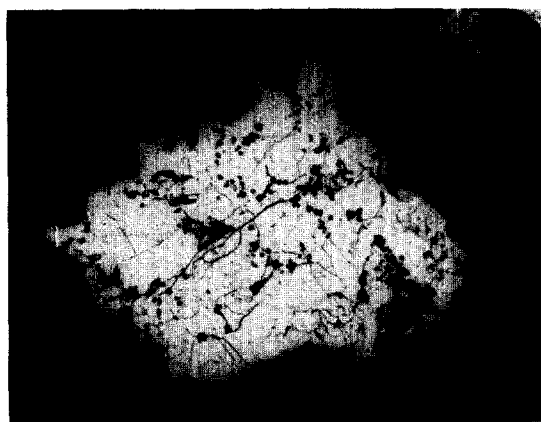Fig. 5. Ionic concentration in treatment solution by ICPS.

Fig. 6. Polished cross-section of alloy particles treated for 2 h in 10 N NaOH at 80 °C (etched after polishing in 95H$_2$O–4.5HNO$_3$–0.5HF) (magnification, ×300).
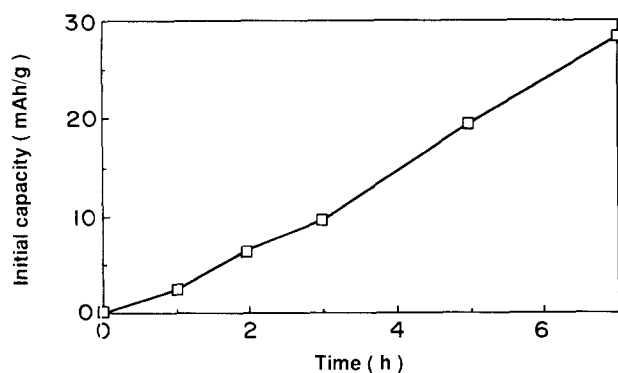

Fig. 8. Effect of treatment time at 65 °C in 6 N KOH on first-cycle capacity C_1 and maximum capacity C_{max} for Zr$_{0.5}$Ti$_{0.5}$V$_{0.75}$Ni$_{1.25}$ alloy (charged at 50 mA g^{-1} for 8 h, held for 10 min, discharged at 50 mA g^{-1} to 0.9 V).

Fig. 7. Effect of treatment time at 65 °C in 6 N KOH on initial capacity C_0 for Zr$_{0.5}$Ti$_{0.5}$V$_{0.75}$Ni$_{1.25}$ alloy (discharged at 25 mA g^{-1} to 0.9 V).

corroded remainder of the alloy. It is this hydrogen, of course, that directly results in some electrode capacity C_0 during the treatment itself. Thus C_0 is an indirect measure of corrosion.

The hot corrosion process aids activation but also destroys useful storage alloy, so there must be a careful balance developed in practice. More thorough 65 °C treatments were performed as a function of time in 6 N KOH. Fig. 7 shows C_0 as a function of treatment time. The corrosion-induced increase in C_0 is almost linear with treatment time. The corresponding effect of treatment on C_1 and C_{max} is shown in Fig. 8. A treatment time of 3 h results in 100% activation on the first deliberate charge cycle. Treatment times greater than 3 h provide no activation advantage and in fact decrease C_{max} by excess corrosion.

In addition to soluble corrosion products, sometimes a fine residue is seen in the cooled solution or on the as-treated electrode surface. It is presumably a Zr and/ or Ti oxide or perhaps a hydrated complex containing K or Na [5]. ESCA showed the existence of V, Zr and Ti oxides and metallic Ni on the treated alloy surface (see Fig. 9). The Zr 3d, Ti 2p, V 2p$_{3/2}$ and Ni2p$_{3/2}$
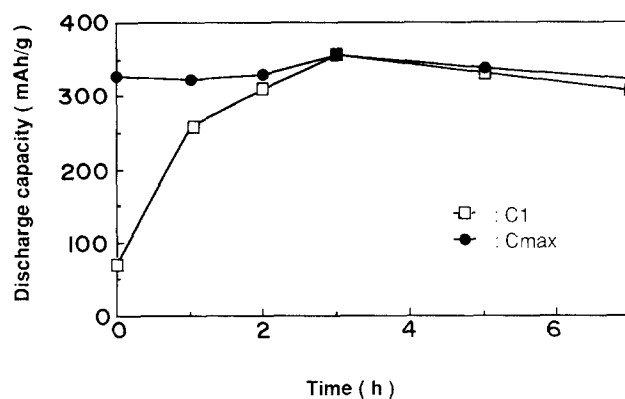
core level spectra were determined for the sample treated by 6 N KOH solution for 20 h at 20 °C, along with the spectra after various sputtering periods. The chemical states were examined by determining the binding energy (E_b). The top layer of the treated alloy surface exhibits a Ti enrichment in the form of TiO$_2$. The result is consistent with ICPS analysis. More V and Zr dissolve in the treatment solution, so their peaks are weaker before sputtering (at zero time). There is no Ni in the top layer. The sublayer consists of TiO$_2$ (E_b = 459.1 eV), ZrO$_2$ (E_b = 182.4 eV), V$_2$O$_3$ (E_b = 516.2 eV) and Ni^0 (E$_b$ = 852.7 eV). The analyses are consistent with Ovonic results [2], specifically showing that the surface structure consists of Ti, Zr and V in the oxidized state with underlying metallic Ni.

The 3 h optimum treatment time for activation purposes is not necessarily the optimum for long-time cyclic life. Fig. 10 compares the cyclic data of a 3 h, 65 °C treated electrode with a 1 h, 65 °C treated electrode, in both cases using the relatively rapid discharge rate of 200 mA g^{-1}. Although the 1 h treated electrode was somewhat slower to fully activate than the 3 h treated electrode, its cyclic life was clearly better. The hot alkaline solution treatment strongly influences not only the initial capacity for the first cycle but also the fast rate discharge capacity and durability. After alkaline solution treatment some pitting or corrosion holes appeared on the alloy surface. These pitting or corrosion holes can accelerate the corrosion during electrochemical charge–discharge (C–D) cycling and decrease the cycle life. A comprehensive evaluation of the optimum treatment conditions should include the three main factors above. From this viewpoint the 1 h treated electrode is more attractive. Its C_0 and C_1 are 2.5 mA h g^{-1} at 25 mA g^{-1} and 257.8 mA h g^{-1} at 50 mA g^{-1} respectively. C_{500}/C_{max} of the treated electrode is 98% (C_{max} is 258 mA h g^{-1} at 200 mA g^{-1}). ICPS analysis showed that after 1500 C–D cycles the ionic concentrations of V, Zr, Ti and Ni in the electrolyte
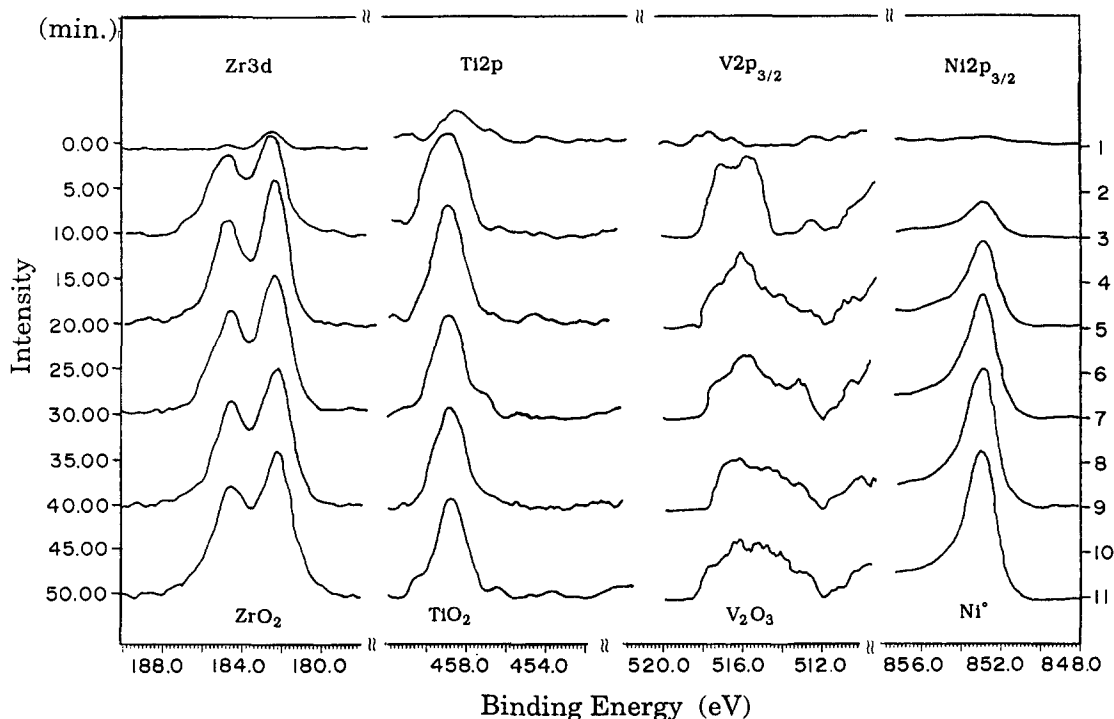
Fig. 9. Zr 3d, Ti 2p, V $2p_{3/2}$ and Ni $2p_{3/2}$ core level spectra of $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.25}$ alloy after 6 N KOH treatment at 20 °C for 20 h.
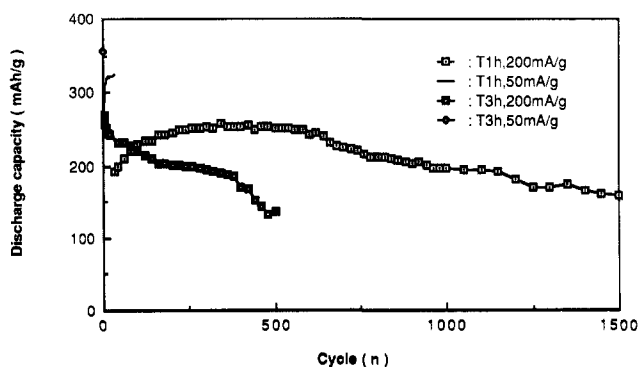

Fig. 10. Effect of treatment time at 65 °C in 6 N KOH on long-time cyclic capacity (1 h treated electrode activated at 50 mA g^{-1} for first 32 cycles; 3 h treated electrode activated at 50 mA g^{-1} for first 2 cycles; both electrodes charged at 200 mA g^{-1} for 2 h, held for 10 min, discharged at 200 mA g^{-1} to 0.9 V).

solution were 149, 149, 5.95 and 0.473 ppm respectively. The degradation of the alloy electrode was mainly caused by the dissolution of elemental V and Zr.

4. Conclusions

We agree with previous proposals [2,4] that hot alkaline treatment of multiphase "AB₂" alloys improves activation by modifying the natural oxide layer, partially dissolving it and resulting in catalytically active metallic

Ni near the surface. However, the treatment also results in corrosion-induced charging of the alloy with atomic H, which in turn results in partial cracking and fresh new surface before the first deliberate electrochemical charge is started. In addition to promoting activation, controlled hot alkaline treatment seems to offer potential benefit to cyclic life.

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