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Corrosion of V–Ti–Cr alloys in liquid lithium: influence of alloy composition and concentration of nitrogen in lithium

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Abstract

The effect of V–(0–70)Ti–(0–30)Cr (at.%) compositions on their compatibility with nitrogen-containing lithium (0.0015–0.67 at.% N) at 7000°C under steady-state test conditions and long-term contact with lithium (up to 2000 h) has been studied. The conditions for formation and stable coexistence of nitride layers on the surface of various compositions under variable nitrogen concentration in lithium have been defined. The V–(8–10)Ti–(4–5)Cr compositions showed the best characteristics from the standpoint of corrosion resistance, nitride layer stability under conditions of variable nitrogen concentration in lithium, and the possibility of 'in situ' protective nitride layer formation. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

When in contact with lithium, vanadium absorbs nitrogen and carbon from lithium and donates oxygen to it [1–3]. The titanium doping of vanadium enhances nitrogen and carbon pick-up and suppresses oxygen loss; chromium has the opposite effect. Such titanium and chromium effects allow optimization of the V–Ti–Cr composition for service in lithium with variable nitrogen concentration. In comparison with carbon and oxygen, the nitrogen has the highest solubility in lithium, it also dissolves in vanadium (up to 4 at.% at 7000°C) and can form nitride phases which are stable in lithium. The aim of this paper is to study the influence of nitrogen concentration in lithium on the corrosion behavior of V–Ti–Cr composition.

2. Experimental procedure

Samples manufactured from cold-deformed (30%) 1-mm thick rolled stock were annealed at 1000°C for 1 h in vacuum of 1×10^{-4} Pa. Lithium was charged in ampoules with samples in an argon–nitrogen atmosphere. Then the ampoules were sealed hermetically in the same atmosphere. Different purity lithium was used. The initial nitrogen concentration was determined by the charging temperatures and was 0.18 and 0.67 at.% in Li-1 and Li-2, correspondingly. The holding time of the samples in Li-1 and Li-2 at 700°C was 500 h.

In Li-3 the nitrogen content (0.0015 at.%) was maintained unchanged due to the effectiveness of the nitrogen 'source', which was powder baked from a mixture of the lowest nitrides of vanadium. The samples were held at 700°C up to 2000 h.

Exposure was followed by a gravimetric, microstructural, micro-X-ray spectral, fractographic and Auger-spectral examinations of the samples. Microhardness was measured on cross-microsections and the following values were determined:

- $I_{0.2}$ – the depth of impurity penetration into the alloy, characterized at the point at which the microhardness is 0.2 GPa higher than in the center of the sample;
- I_4 – the distance from the exterior surface to the point at which the microhardness is equal to 4.0 GPa. This value characterizes a zone of interior nitriding;
- H_{10} – the value of microhardness at a distance of 10 μm from the profile plane of a sample;
- H_c – the value of microhardness in the center of a sample.

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3. Results

3.1. Characteristics of corrosion interaction of V–Ti–Cr alloys with Li-1 and Li-2

The gravimetric examinations of V–Ti–Cr composition after holding in Li-2 revealed two results (Fig. 1(a)):

- the mass increase is typical of all V–Ti and V–Ti–Cr alloys with the dominant content of titanium (I);
- the compositions with typical loss of mass tend to be Cr-rich (II).

The mass loss increases with increasing content of chromium in the alloy and of nitrogen in the lithium.

Results of the X-ray diffraction, general chemical and Auger-spectral analyses show absorption of V–Ti alloys with nitrogen impurity. Lithium was also detected in the samples and its concentration (~0.8 wt%) did not depend on the alloy composition [6,7].

Generally, under the action of nitrogen-containing lithium in V–Ti alloys, a heterogeneous structure is formed:

- a thin surface nitride film of up to 10 μm thickness (I_N);
- an underlying V + TiN two-phase zone of interior nitriding (I_4 in Fig. 1(b));
- a V–Ti–N solid solution zone ($I_{0.2}$ in Fig. 1(c)).

The relation between theses zones depends on alloy composition and nitrogen content in the lithium, and it determines the mechanical properties and plasticity of the alloy after corrosion tests.

Vanadium and a V–5Ti alloy exhibit nitrogen penetration with nitride phase formation and loss of plasticity after 500 h in Li-1 and in Li-2. A continuous nitride film and an interior nitriding zone are formed on the surface of alloys containing more than 10 at.% titanium. The higher the content of titanium, the better are the protective properties of a nitride layer ($I_N + I_4$) and the smaller is the nitrogen penetration depth in the alloy ($I_{0.2}$). In V–30Ti and V–40Ti alloys, the zone of interior nitriding (I_4) is significantly wider than the one in V–10Ti and V–20Ti.

3.2. Corrosion processes kinetics of vanadium alloys in Li-3 with a constant concentration of nitrogen (0.0015 at.% N)

Holding samples in Li-3 was accompanied by weight gain in all materials (Figs. 2(a) and (b)). The weight gain kinetics of vanadium follows a linear relation, while the alloys approximately follow a parabolic law. In alloys with a continuous nitride film (~3 μm) there is a zone of interior nitriding with 6–8 GPa hardness which does not exceed 15 μm after 2000 h (Fig. 2(c)). In deeper layers the microhardness of these alloys does not change.

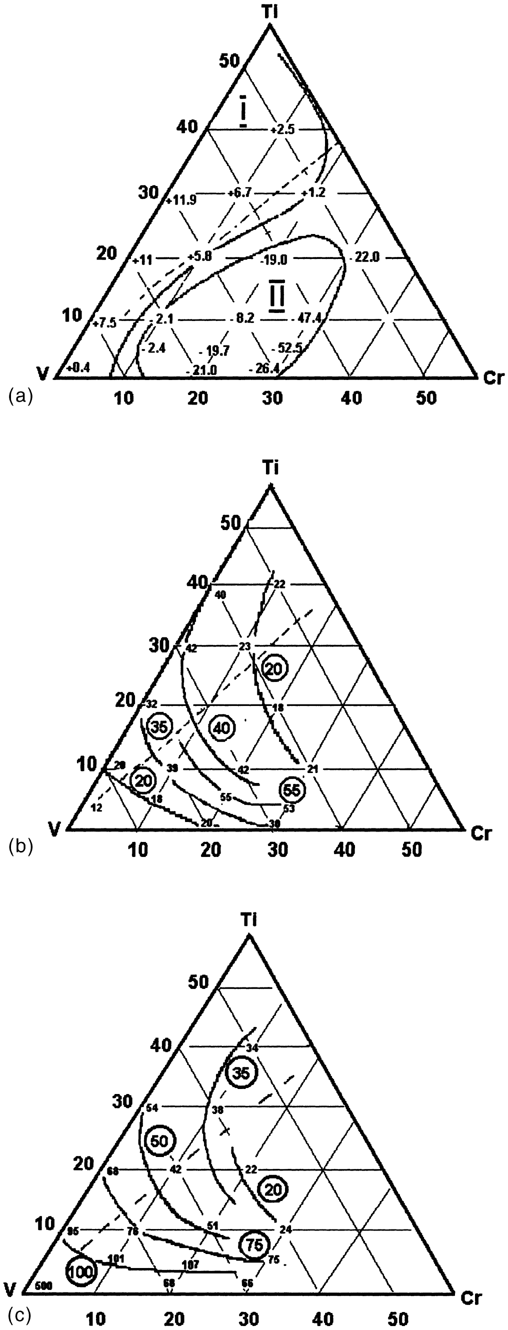

Fig. 1. (a) The compositions of V–Ti–Cr alloys with increase (area I) and decrease (area II) of mass Δm, (g/cm^2); (b) isolines of interior nitriding zone I_4 (μm); (c) isolines of the depth of impurities penetration in the alloy $I_{0.2}$ (μm) after holding of samples in Li-2 ($C_N = 0.67$ at.%) at 700°C, 500 h. The dotted curves show the relation of Ti:Cr = 2:1 [4,5].

The chemical analyses after different exposures show increasing nitrogen concentration. The saturation of vanadium by nitrogen is accompanied by a growing

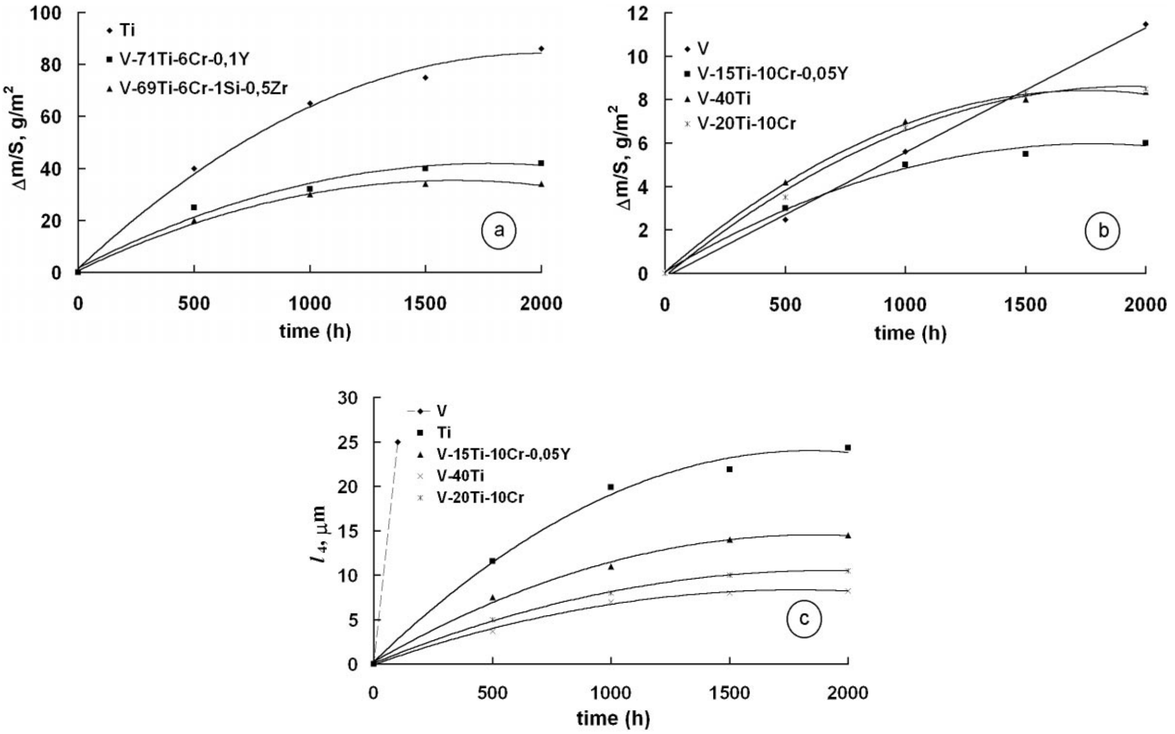

Fig. 2. (a, b) Kinetics of the weight gain; and (c) zones of interior nitriding in non-doped metals and alloys after contact with Li-3 ($C_N = 0.0015$ at.%) at $T = 700$°C.

strength and decreasing ductility. The mechanical properties of the alloys, however, change very little (Fig. 3).

Prolonged exposure to lithium promotes dissolution of second phase particles in the alloys. This process is especially intensive in the near-surface layers contacting the lithium, where there is grain boundary migration and growth. Lithium is present in the samples, and its content (~0.9 wt%) does not depend on the holding period or alloy composition, except for V–70.9Ti–6Cr–0.1Y alloy, in which lithium content was 0.49 wt%.

4. Discussion

4.1. V–Ti alloys

According to the phase diagram, the addition of titanium to vanadium sharply reduces the solubility of non-metallic admixture in it. The V–(3–20)Ti alloys are in a two-phase state even with a rather low content of non-metallic admixture in them (400–1000 wt ppm O, N, C). According to [8,9] all the titanium in the V–4Ti–4Cr alloy is connected with the impurities with their total content 1000 wt ppm (or ~0.32 at.%). Full dissolution of particles is possible only in alloys containing more than 20% of titanium [10]. This phase-state peculiarity of V–Ti–N (O, C) system explains the different behavior of V–Ti composition under conditions of decreasing nitrogen concentration (Li-1, Li-2). By interaction with nitrogen-containing lithium, the nitride layer forms quickly on the sample surfaces. With time, the nitrogen concentration in lithium decreases; this promotes dissolution of the exterior nitride layer and diffusion of free nitrogen into the samples. According to the equilibrium state of V–Ti–Cr system, the nitride layers formed for V–(5–20)Ti compositions are stable and do not dissociate compared to V–30Ti and V–40Ti alloys.

4.2. V–Ti–Cr alloys

As a result of titanium interaction with nitrogen, the chromium's relative concentration in solid solution increases. Hence, the thermodynamic activity of a matrix in relation to nitrogen is diminished. The analysis of weight gains after contact with Li-2 shows that Ti:Cr = 2:1 compositions (marked by a dotted line in Fig. 1) contain the optimum quantity of chromium. For the alloys with Ti:Cr = 1:1 composition, and even more for those with Ti:Cr = 1:2, appreciable corrosion losses occur along with a decrease in the chromium content in near-surface layers. Apparently, in lithium with high nitrogen activity on the surface of chromium-containing alloys, the non-coherent $Cr_xLi_yN_z$ compounds are

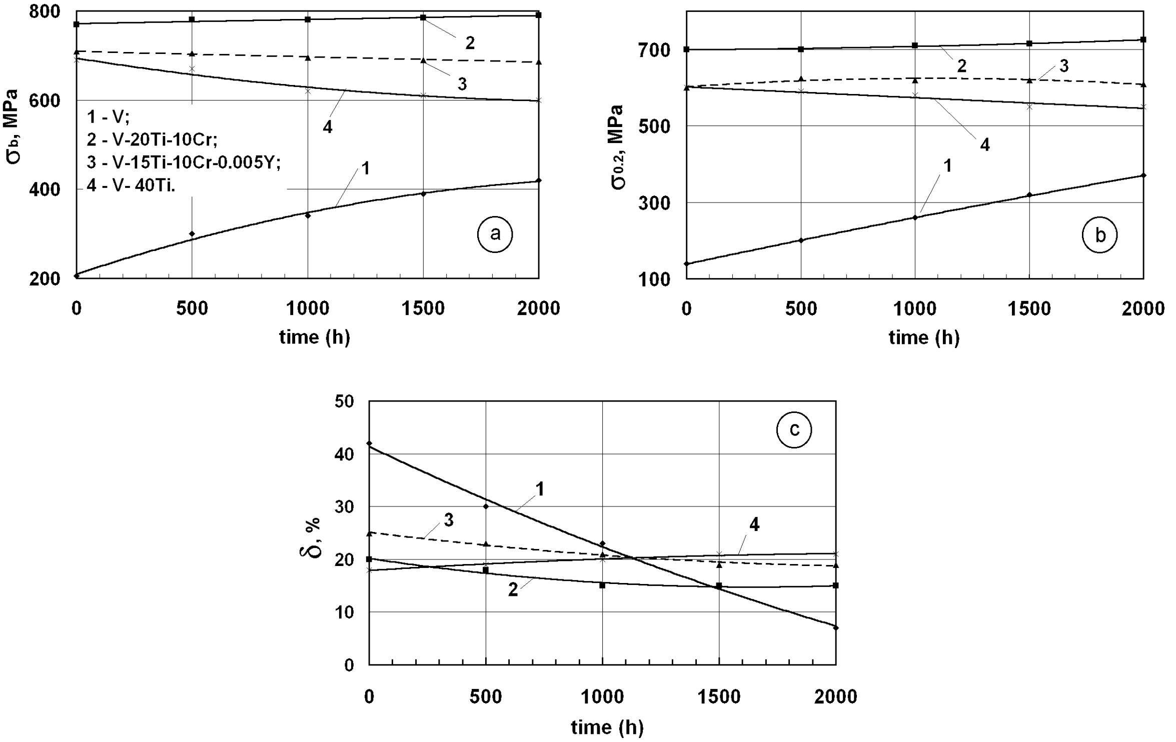

Fig. 3. (a) Ultimate strength (σ_b); (b) yield strength ($\sigma_{0.2}$); (c) relative elongation (δ) of vanadium alloys after holding in Li-3 ($C_N = 0.0015$ at.%) at $T = 700°C$.

formed [3]. In Ti:Cr = 2:1 compositions the formation of undesirable chromium compounds is suppressed by a more active titanium which generates nitride protecting films on the alloy surface. After holding in Li-2, the Ti:Cr = 2:1 alloys always have a golden surface, typical of titanium nitride, and the cores of the samples are invariably hard.

In Li-3 the probability of continuous TiN nitride layer formation is diminished. In this case, chromium plays an extremely important role, because it reduces the saturation of vanadium by nitrogen from lithium [1–3]. This is confirmed by a minor weight gain and golden sample surface of the V–15Ti–10Cr–0.05Y alloy after 2000 h in Li-3 (Fig. 2). Chromium cancels the negative influence of titanium intensifying the uptake of nitrogen. For the same reason, in the case of decreasing nitrogen in lithium, chromium will hinder titanium nitride film dissolution.

A comparison of nitrogen redistribution coefficients in the systems Li–V, Li–Ti, Li–Cr [1,3] shows that to compensate for the activity of titanium, which is in the solid solution and promotes nitrogen absorption, approximately the same quantity of chromium is needed. It is necessary to take into account that about 4% of titanium is in Ti(O,N,C) precipitate and only the remainder is in the solid solution after fabrication (Table 1).

Table 1
Titanium distribution between solid solution and precipitate in V–Ti compositions and estimated chromium content for operation in different purity lithium

	Composition (at.%)	V–4Ti	V–8Ti	V–10Ti	V–20Ti
1	Content of titanium in precipitates*	4	4	4	4
2	Content of titanium in a solid solution	0	4	6	16
3	Content of chromium for operation in lithium with low nitrogen concentration	0	4	6	16
4	Content of chromium for operation in lithium with high nitrogen concentration (Ti:Cr = 2:1)	2	4	5	10

* Total impurity level (O + N + C) = 0.32–3.2 at.%.

Thus, the necessity for alloys to operate in variable purity lithium imposes contradictory conditions on the V–Ti–Cr composition:

- for operation of an alloy in lithium with low nitrogen potential, equal amounts of titanium and chromium are desirable;
- for protection of an alloy against corrosion losses in lithium with a high nitrogen potential the amount of titanium should be twice that of chromium.

To pick an optimum composition from the standpoint of corrosion resistance, it is necessary to have a certain criterion. If the criterion is the optimum composition for operation in lithium with high and low nitrogen contents, then from Table 1 it appears that V–(8–10)Ti–(4–5)Cr composition may be optimum.

The final composition of the optimum V–Ti–Cr alloy (including the level of non-metallic impurities) can be determined only by considering the whole system: ‘alloy-coolant (including purification system)-coating’.

5. Conclusions

The conditions for the formation of protective nitride layers on the surface of V–(0–70)Ti–(0–30)Cr at.% composition were determined, and the conditions for its stability in the presence of nitrogen concentration change in Li (0.0015–0.67 at.% N) were considered. The V–(8–10)Ti–(4–5)Cr composition appears to have the best characteristics from the standpoint of the corrosion resistance in nitrogen-containing lithium, stability of the nitride layer under the conditions of variable concentration of nitrogen in lithium, and also for realization (in situ) of liquid-metal technologies for the self-healing nitride coatings formation. The final V–Ti–Cr composition (including non-metallic impurities) can be determined only by considering the whole system: ‘alloy-coolant (including purification system)-coating’.

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