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COMPATIBILITY BETWEEN VANADIUM-BASE ALLOYS AND FLOWING LITHIUM: PARTITIONING OF HYDROGEN AT ELEVATED TEMPERATURES*

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COMPATIBILITY BETWEEN VANADIUM-BASE ALLOYS AND FLOWING LITHIUM: PARTITIONING OF HYDROGEN AT ELEVATED TEMPERATURES

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ABSTRACT

A major concern in fusion reactor design is possible hydrogen-isotope-induced embrittlement of structural alloys in the neutron environment expected in these reactors. Hydrogen fractionation occurs between lithium and various refractory metals according to a temperature-dependent distribution coefficient, K_H , that is defined as the ratio of the hydrogen concentration in the metallic specimen to that in the liquid lithium. In the present work, K_H was determined for pure vanadium and several binary (V-10Cr, V-15Cr, V-5Ti, V-15Ti, V-20Ti, V-30Ti) and ternary alloys (V-10Cr-5Ti, V-15Cr-1Ti, V-15Cr-5Ti, V-3Ti-0.5Si), and the commercial Vanstar 7 (V-10Cr-3Fe-1Zr). Hydrogen distribution studies were performed in an austenitic steel forced-circulation lithium loop. Equilibrium concentrations of hydrogen in vanadium-base alloys exposed to flowing lithium at temperatures of 350 to 550°C were measured by inert gas fusion techniques and residual gas analysis. Thermodynamic calculations are consistent with the effect of chromium and titanium in the alloys on the resultant hydrogen fractionation. Experimental and calculated results indicate that K_H values are very low; i.e., the hydrogen concentrations in the lithium-equilibrated vanadium-base alloy specimens are about two orders of magnitude lower than those in the lithium. Because of this low distribution

coefficient, embrittlement of vanadium alloys by hydrogen in lithium would not be expected.

INTRODUCTION

Vanadium alloys such as V-5Cr-5Ti, V-5Ti, V-5Ti-1Si, and V-20Ti are attractive candidates for use as structural materials in fusion reactor blankets because of their excellent resistance to neutron radiation damage, low induced radioactivity, high strength at elevated temperatures, and favorable thermophysical properties [1]. On the basis of extensive testing, they appear to exhibit the best combination of strength, ductile-brittle transition temperature (DBTT), swelling rate, and lithium dissolution rate for a structural material in a fusion reactor. Resistance to hydrogen embrittlement is another key issue; one potential contributor to hydrogen pickup is the transfer of hydrogen from the reactor coolant and breeder to the structural material.

Molten lithium has been proposed as both a coolant and breeder material because of its excellent heat transfer and tritium breeding characteristics. Local corrosion phenomena and mass- and interstitial-element transfer rates depend on the difference between the chemical activity of the alloy constituents in the structural material and that of lithium [2].

Understanding the parameters that affect the solubility and diffusivity of tritium in liquid lithium is important for evaluating the permeation and inventory of tritium in the blanket and for optimizing the tritium extraction process. Additionally, the issue of hydrogen-isotope-induced embrittlement is a major question for all structural alloys exposed to both the

neutron environment expected in a fusion reactor and a lithium reactor coolant. In this paper, experimental data on the partitioning of hydrogen between lithium and candidate vanadium alloys are summarized and the significance of the experimental results for the fusion reactor environment is discussed.

MA. TERIALS AND PROCEDURE

Vanadium-base Alloys

The compositions of the vanadium-base alloys in Table 1 were selected primarily because of their low neutron activation. Most of these alloys have been investigated with respect to compatibility with a lithium reactor coolant [2,3], yield strength before and after irradiation [1,4], swelling resistance [5], ductile-brittle transition temperature [6,7], and resistance to hydrogen, helium, and irradiation embrittlement [1,8,9].

In the current study, hydrogen fractionation was investigated utilizing a diversity of specimen types and test conditions. Specimens examined included corrosion coupons [2], tensile specimens [1], and specimens designed specifically for this study with approximate dimensions of 19 x 10 x 0.9 mm. The specimens were either mechanically polished or left in "as received" condition [4] before exposure to lithium.

Lithium Test Facility

The hydrogen distribution tests were conducted in a forced-circulation lithium loop, using three test vessels and a secondary cold-trap purification system, constructed of Type 304 stainless steel. A description of the lithium test facility has been presented previously [10]. The quantity of

lithium in the loop was ~20 L, and the lithium was recirculated at ~1 L/min from the high-temperature to the low-temperature test vessel. As shown in Table 2, the cold trap was maintained at 220-202°C (23°C above the freezing temperature of lithium).

During Tests 6 and 8 (Table 3), the hydrogen partial pressure in lithium (P_{H_2}) was monitored by a hydrogen activity sensor consisting of an alpha-iron membrane immersed in liquid lithium in the supply vessel [8]. The ion pump was valved out and the hydrogen was allowed to diffuse into the manifold until equilibrium was attained. Equilibrium pressure was measured with a dual-range ionization gauge [8]. The hydrogen concentration was determined both from the hydrogen activity meter and by yttrium equilibration procedures. Lithium samples, withdrawn from the equilibration vessel and filtered through 5- μ m metal frits, were analyzed for nitrogen, carbon, and trace metals (Table 3). The carbon concentration was determined by the acetylene evolution method [11], and nitrogen concentration was determined by micro-Kjehldal nitrogen combustion [12]. Trace metals were determined by inductively coupled plasma atomic emission spectroscopy. The procedure for lithium sampling and analysis has been described in more detail elsewhere [13].

Measurement of Hydrogen Pickup by Vanadium Alloys

Following exposure, the lithium was removed from the specimens by immersion in liquid NH_3 or in an alcohol mixture containing 50% ethyl alcohol and 50% methyl alcohol chilled to 5-10°C. This chemical dissolution procedure was strictly observed to avoid the introduction of hydrogen into the specimens [9]. The hydrogen content in the specimens following

lithium exposure was determined by one of three analytical methods (Table 4). Residual gas analysis (RGA) was the analytical technique preferred for hydrogen determination [8,9] because of its nondestructive nature. Total hydrogen in the specimens after exposure to the lithium was determined from the P_{H_2} in the gaseous constituents that were evolved on heating a specimen at a rate of $15^\circ\text{C}/\text{min}$ from 25 to 1000°C . The P_{H_2} was determined by a quadrupole, partial-pressure, residual gas analyzer mounted in an ion-pumped vacuum system. The temperature of a specimen during heating was determined with a recording infrared pyrometer. The hydrogen concentration in the lithium-exposed specimens was also determined by the combustion technique in a purified argon environment at Teledyne Wah Chang with a LECO Model RH-1 Hydrogen Determinator with $0.1\text{-}\mu\text{g}$ resolution (Analytical Technique 2, Table 4). Hydrogen analyses were also performed at Argonne National Laboratory using both vacuum fusion and inert gas fusion techniques. In both of the latter analytical techniques, the reference specimens were standardized with National Bureau of Standards calibrations.

RESULTS

Hydrogen in Lithium

Lithium hydride (LiH) is the solid phase in equilibrium with saturated solutions of hydrogen in lithium. As can be seen in Fig. 1, the calculated solubility of hydrogen in lithium [8,14] increases uniformly with temperature.

The high solubility of hydrogen in yttrium can be used to provide an independent determination of the hydrogen concentration in the lithium.

Yttrium samples were exposed to lithium in the loop at temperatures of 408 to 538°C. The concentration of hydrogen in the yttrium specimens, determined by vacuum fusion analysis, was used in conjunction with calculated distribution coefficients to determine the hydrogen concentration in lithium. The concentrations are plotted in Fig. 1 as a function of both the cold-trap temperature and the exposure vessel temperature. The results show that, to a first approximation, the cold-trap temperature had a significant effect in controlling the upper limit of hydrogen in the system. As can be seen in Fig. 1, the hydrogen concentrations determined by yttrium exposure show good agreement with the solubility curve at the temperature of the cold trap for each test (Table 2).

Partitioning of Hydrogen

Hydrogen will fractionate between lithium and various refractory metals as a function of temperature. A distribution coefficient, K_H , can be defined as the ratio of the hydrogen concentration in the metallic alloy to that in the liquid lithium:

$$K_H = C_M / C_{Li} \quad (1)$$

where C_M and C_{Li} are concentrations (wt.%) of hydrogen in the metal and lithium, respectively, at constant P_{H_2} . The calculated distribution of hydrogen among various refractory metals and liquid lithium is shown in Fig 2 as a function of temperature [8,14]. At 500°C, a hydrogen concentration of 100 wppm in lithium will establish hydrogen concentrations of ~3000 wppm in yttrium, 10 wppm in titanium, 0.3 wppm in vanadium, and <0.0001 wppm in chromium.

The experimentally determined hydrogen distribution coefficients from yttrium equilibrations (Fig. 2) exhibit good correspondence with the predicted results. The K_H values for vanadium, shown as open circles in Fig. 2 and as closed circles in Figs. 3-5, exhibit variations that can be attributed to the diversity of specimen types and test conditions. For comparison, distribution coefficients obtained from tests at 600°C [13] are included in Figs. 2-5. The higher values of K_H in tests 8 and 20 can be attributed to the specimen cleaning method observed in test 8 and the short equilibration time in test 20. At temperatures of <400°C, the lithium equilibration period should be $\gg 24$ h.

The K_H values for the V-3Ti-0.5Si alloy at 500°C were based on hydrogen concentrations obtained by both RGA and inert gas fusion techniques (Table 4), and the results are in good agreement.

The results for the ternary V-Cr-Ti system in Table 4 and Fig. 3 from tests 6, 10, 13, 15, and 17 exhibit a fair degree of scatter in the experimentally determined K_H values. The three values in Fig. 3 for the V-15Cr-5Ti alloy from test 6 at temperatures of 538 and 482°C follow the trend of decreasing K_H as the temperature decreases.

An effect of Ti or Cr in the binary V-Ti and V-Cr alloys on K_H is consistent with the calculated curves (Fig. 2), i.e., the value of K_H increases with the concentration of Ti at all temperatures (Fig. 4) and decreases with an increase in the concentration of Cr (Fig. 5).

CONCLUSIONS

1. The results from the hydrogen analyses (Table 4) suggest that the hydrogen isotope inventories in V-Ti, V-Cr, and V-Ti-Cr structural materials would not be substantially different.
2. Because the distribution coefficient for hydrogen in vanadium and vanadium-base alloys is much less than one ($\sim 10^{-2}$), hydrogen embrittlement as a result of somewhat higher hydrogen concentrations in lithium would not be expected.
3. The tritium concentration in lithium of a fusion reactor is expected to be <1 wppm or $<1\%$ of that in our lithium loop (~ 100 wppm) [15], thus the results obtained in this study indicate that tritium pickup by vanadium alloys in the reactor structure will not be significant.
4. The low hydrogen levels in vanadium-base alloys exposed to flowing lithium in this study were shown to produce good residual ductility [1].

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REFERENCES

1. B. A. Loomis, A. B. Hull, and D. L. Smith, in: Proc. 4th Intl. Conf. on Fusion Reactor Materials, Dec. 4-8, 1989, Kyoto, Japan.
2. O. K. Chopra and D. L. Smith, J. Nucl. Mater. 155-157 (1988) 683.
3. O. K. Chopra and A. B. Hull, Fusion Tech. 15, 303-308 (1989).

4. B. A. Loomis, R. H. Lee, D. L. Smith, and J. R. Peterson, *J. Nucl. Mater.* 155-157 (1988) 631.
5. B. A. Loomis, D. L. Smith, and F. A. Garner in: *Proc. 4th Intl. Conf. on Fusion Reactor Materials*, Dec. 4-8, 1989, Kyoto, Japan.
6. B. A. Loomis, B. J. Kestel, B. D. Edwards, and D. L. Smith, in: *Fusion Reactor Materials, Semiannual Progress Report for Period Ending September 30, 1988*, DOE/ER-0313/5, Oak Ridge National Laboratory, Oak Ridge, TN (April 1989), p. 242.
7. B. A. Loomis and D. L. Smith in: *Proc. Proc. 4th Intl. Conf. on Fusion Reactor Materials*, Dec. 4-8, 1989, Kyoto, Japan.
8. A. B. Hull, O. K. Chopra, B. A. Loomis, and D. L. Smith, *Fusion Tech.* 15 (1989) 303.
9. B. A. Loomis, A. B. Hull, O. K. Chopra, and D. L. Smith, in: *Fusion Reactor Materials, Semiannual Progress Report for Period Ending March 31, 1988*, DOE/ER-0313/4, Oak Ridge National Laboratory, Oak Ridge, TN (Aug., 1988), p. 160.
10. O. K. Chopra and D. L. Smith, *J. Nucl. Mater.* 133 & 134, 861 (1985).
11. R. M. Yonco and M. I. Homa, *J. Nucl. Mater.* 138, 117 (1986).
12. L. M. Melnick, L. L. Lewis, and B. D. Holt, *Determination of Gaseous Elements in Metals*, John Wiley and Sons, NY (1974), p. 392.

13. D. L. Smith, R. H. Lee, and R. M. Yonco, Proc. 2nd Intl. Conf. on Liquid Metal Technology in Energy Production, U. S. Dept. of Energy Report CONF-800401-P1 (1980) p. 272.
14. K. Natesan and D. L. Smith, Nucl. Technol. 22, 138 (1974).
15. D. L. Smith, et al., Fusion Reactor Blanket Shield Design Study, Argonne National Laboratory Report ANL/FPP-79-1 (1979).

Table 1. Chemical Composition of Vanadium and Vanadium-base Alloys

Nominal ^a Composition	ANL I.D.	Melt ^b No.	Concentration (wt.%)		Concentration (wppm)						
			Cr	Ti	H	O	N	C	Si	S	Fe
V	BL-19	V6	---	---	<5.0	1101	161	360	-	-	-
V-10Cr	BL-35	ANL 35	9.5	---		340	45	120	<50	-	410
V-15Cr	BL-5	ANL 5	14.1	---	15.0	330	69	200	<50	-	570
V-10Cr-5Ti	BL-43	ANL 206	9.2	4.9	<5.0	230	31	100	340	20	170
V-15Cr-5Ti ₁	BL-23	CAM 834	12.9	5.9	9.0	400	490	280	1230	50	420
V-15Cr-5Ti ₂	BL-24	ANL 101	13.5	5.2	33.6 ^c	1190	360	500	390	<30	520
V-15Cr-5Ti ₃	-	ANL 274	-	-	50.0	810	138	230	-	-	-
V-15Cr-5Ti ₄	V4	ANL 282	14.9	5.25	-	-	-	-	-	-	500
V-15Cr-1Ti	BL-26	ANL 26	14.1	1.0	-	560	86	140	<50	-	650
V-3Ti-0.5Si ₁	BL-42	WI 8505		3.1	65.3 ^c	580	190	140	5400	90	190
V-3Ti-0.5Si ₂	BL-27	ORNL 10837	---	3.1	8.0	210	310	310	2500	120	380
V-5Ti	BL-46	TWC 831		4.6	-	300	53	85	160	10	-
V-15Ti	BL-13	ANL 13	---	14.4	-	1580	370	440	205	-	6300
V-20Ti ₁	BL-15	CAM 832	---	17.7	16.0	830	160	380	480	<10	390
V-20Ti ₂	Inv#144	ANL 215	---	-	-	-	-	-	-	-	-
V-30Ti	Inv#5	-	---	-	-	1300	-	-	-	-	-
V-10Cr-3Fe-1Zr	BL-28	CAM837	9.0	---	-	275	520	640	-	-	32000

^aAnalyses were performed by the Analytical Department of the Teledyne Wah Chang Albany Co.

^bDue to material scarcity, it was not always possible to work with well-characterized material, thus necessitating use of four different melts of V-15Cr-5Ti, for example. In such cases, "-" indicates insufficient information, while "---" indicates element not present.

^cHydrogen analyses were performed by residual gas analysis [9].

Table 2. Lithium Loop Operating Conditions for Various Hydrogen Distribution Tests

Test Run	Loop Temperature (°C)			
	Test Vessel	Equilibration Vessel	Supply Vessel	Cold Trap
6	538	482	410	208
8	482	427	426	213
10	500	452	425	208
13	400	345	350	221
15	482	412	398	202
17	480	403	392	220
20	463	360	355	206
21	545	503	450	215

Table 3. Chemical Composition of Lithium at Time of Test Runs

Test Run	Lithium Flow Age ^a (x 10,000 h)		Nonmetallic Concentration (wppm)								
	Begin Test	Lithium Sample	Nonmetallic			Metallic ^b					
			Nc	Cd	He ^e	Fe	Ca	Cr	Mo	Ti	V
	<i>As Received^f</i>		100	-9	-	10	300	5	-	-	<5
6	4.5617	5.1384	26	11	118	-	-	-	-	-	-
8	5.8800	5.9844	23	55	90	79	50	49	146	80	-
10	6.9756	6.980	167 ^h	119	100	6690	67	1730	78	147	<20
13	7.1040	7.0400	136	84	105	-	-	-	-	-	-
15	7.3835	7.2994	88	57	110	102	310	30	10	40	<5
17	7.8257	7.8229	1912 ⁱ	47	140	44	209	15	<10	64	<10
20	8.4231	8.4088	225	13	120	48	146	<10	<10	108	<10
21	8.4259	8.4088	225	13	135	48	146	<10	<10	108	<10

^aTime since operation of the FFTL-3 loop commenced in 1980.

^bAnalysis by inductively coupled plasma atomic emission spectroscopy.

^cNitrogen in lithium determined by micro-Kjehldal nitrogen combustion technique [12].

^dCarbon in the lithium was determined by the acetylene evolution method [11].

^eHydrogen in lithium in Tests 6 and 8 was determined by H meter and substantiated by yttrium equilibration [8]; in Tests 10-21, hydrogen was determined by the yttrium equilibration method.

^fInformation provided by lithium supplier, LITHCO.

^gThe "-" indicates insufficient information rather than absence of element.

^hIncrease in most elements can be attributed to extended time period at high temperatures (Test 6).

ⁱArgon cover gas purifier (gettering furnace) malfunctioned, and ingress of air into cover gas system caused a high N concentration.

Table 4. Hydrogen Concentration in Vanadium-base Alloys After Exposure to Flowing Lithium

Specimen Identity	Test No.	Exposure Conditions			Hydrogen in Alloy (wppm)	K_H^a	Analytical Method
		Temp (°C)	Time (h)	H in Li ^c (wppm)			
V	6	482	1538	118	3	0.025	3
	8	427	405	90	7	0.078	3
	17	403	234	140	2.8	0.020	2
	20	360	24	120	8	0.067	2
	20	463	24	120	11	0.09	2
	21	503	42	135	4.7	0.035	2
	21	545	42	135	3.4	0.025	2
	21	545	42	135	6	0.044	2
V-10Cr	20	463	24	120	7	0.058	2
V-10Cr-5Ti	21	503	42	135	6	0.044	2
	21	545	42	135	6	0.044	2
	15	482	3400	110	4.3	0.039	1
V-15Cr	17	403	234	140	3.3	0.023	2
	20	463	24	120	5	0.042	2
	21	503	42	135	3	0.022	2
	21	545	42	135	4.7	0.035	2
V-15Cr-1Ti	13	400	72	105	5.8	0.055	3
	17	403	234	140	6	0.043	2
V-15Cr-5Ti ₁ ^d	8	482	1992	90	7	0.078	3
V-15Cr-5Ti ₂	6	538	1384	118	2	0.017	3
	5	482	1618	118	1	0.008	3
	6	538	794	118	3	0.025	3
	10	500	25	100	0.3	0.003	1
	15	482	3400	110	7.7	0.070	1
V-15Cr-5Ti ₃	13	400	24	105	2.2	0.021	1
V-15Cr-5Ti ₄	17	403	234	140	2.2	0.016	2
V-3Ti-0.5Si ₁	10	500	25	100	6.7	0.067	1
	13	400	24	105	3.6	0.034	1
	20	463	24	120	6	0.050	2
	21	503	42	135	7	0.052	2
	21	545	42	135	8	0.044	2
	15	482	3400	110	4.7	0.043	1
V-3Ti-0.5Si ₂	20	463	24	120	4.6	0.038	2
	21	503	42	135	4.3	0.032	2
	21	545	42	135	4.2	0.031	2
V-15Ti	20	463	24	120	6	0.05	2
	21	503	42	135	4.8	0.036	2
	21	545	42	135	3	0.022	2
V-20Ti ₁	6	482	619	118	8	0.068	3
	15	482	3400	110	6	0.054	1
	17	403	234	140	3.2	0.023	2
	17	403	234	140	2.7	0.019	3
V-20Ti ₂	20	463	24	120	9	0.075	2
	21	503	42	135	7	0.052	2
	21	545	42	135	6	0.044	2
	20	463	24	120	18	0.15	2
V-30Ti	21	503	42	135	16	0.1185	2
	21	545	42	135	10	0.074	2
	6	538	590	118	6	0.051	3

^aThe distribution coefficient, K_H , is defined as the ratio of the hydrogen concentration in the Li-exposed alloy to that in the Li [3,14].

^bAnalytical methods are as follows: (1) residual gas analysis [9]; (2) inert gas fusion, Teledyne Wah Chang Co.; and (3) vacuum and inert gas fusion, Argonne National Laboratory Analytical Chemistry.

^cThe uncertainties in the values of the concentration of hydrogen in the lithium, as determined by the hydrogen activity meter and/or yttrium equilibrations, are $\pm 25\%$.

^dRefer to Table 1 for explanation of subscripts 1, 2, 3, 4.

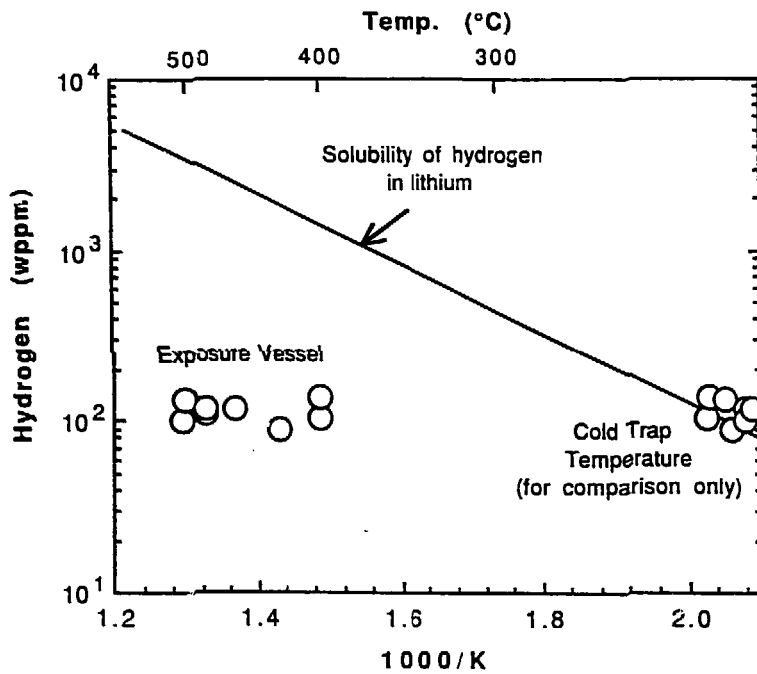


Fig. 1. Solubility of Hydrogen in Liquid Lithium.

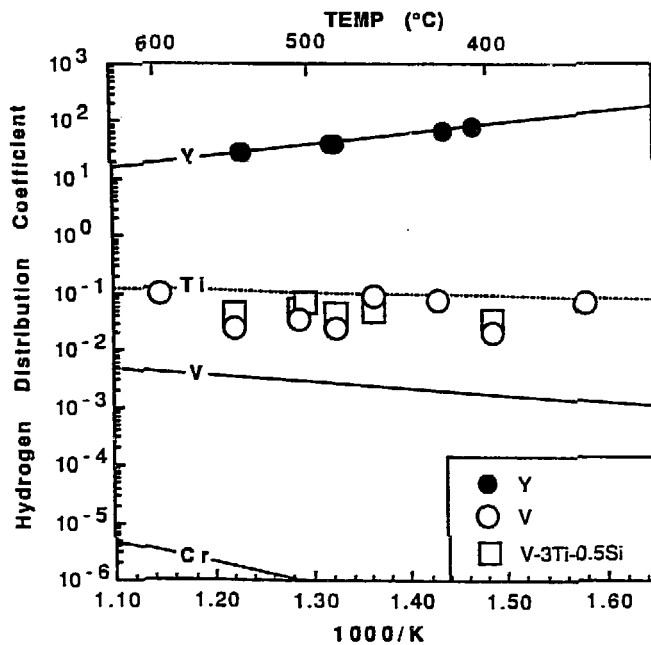


Fig. 2. Temperature Dependence of Equilibrium Distribution Coefficients of Hydrogen between Vanadium and V-3Ti-0.5Si and Lithium. Lines indicate calculated values for different pure metals.

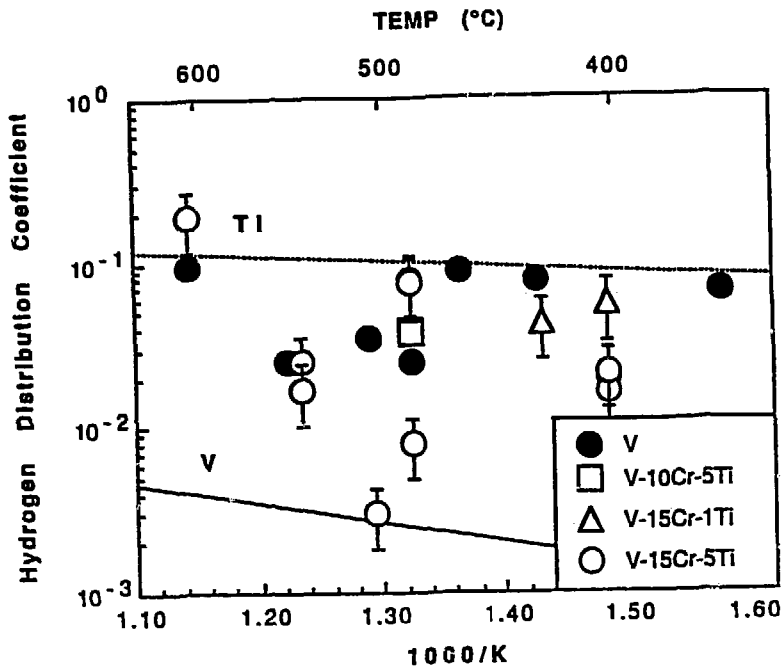


Fig. 3. Temperature Dependence of Equilibrium Distribution Coefficients of Hydrogen between Selected Ternary Vanadium Alloys and Lithium. Lines indicate calculated values for pure metals.

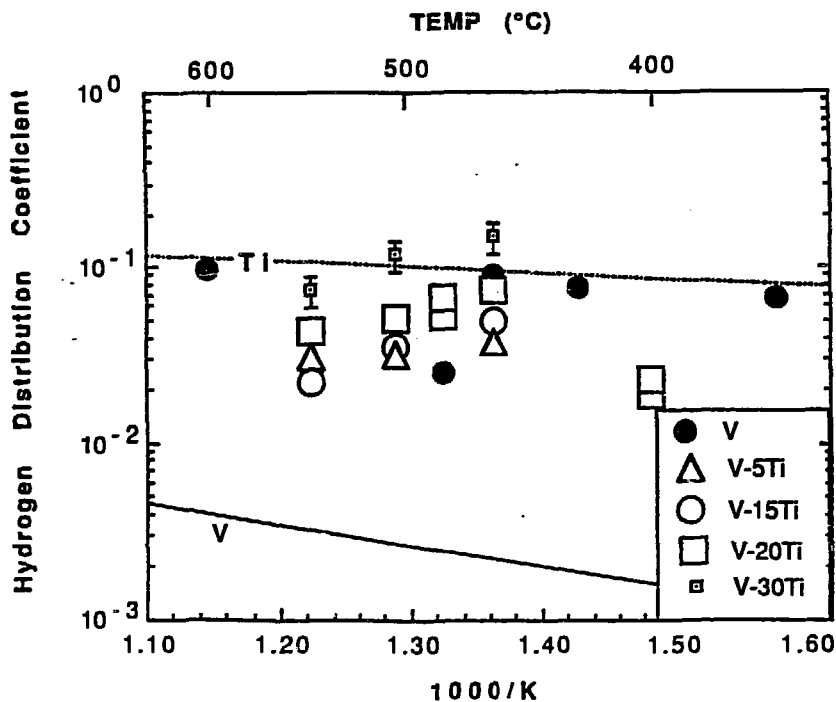


Fig. 4. Effect on Hydrogen Distribution Coefficients of Titanium Concentration in Binary Vanadium Alloys.

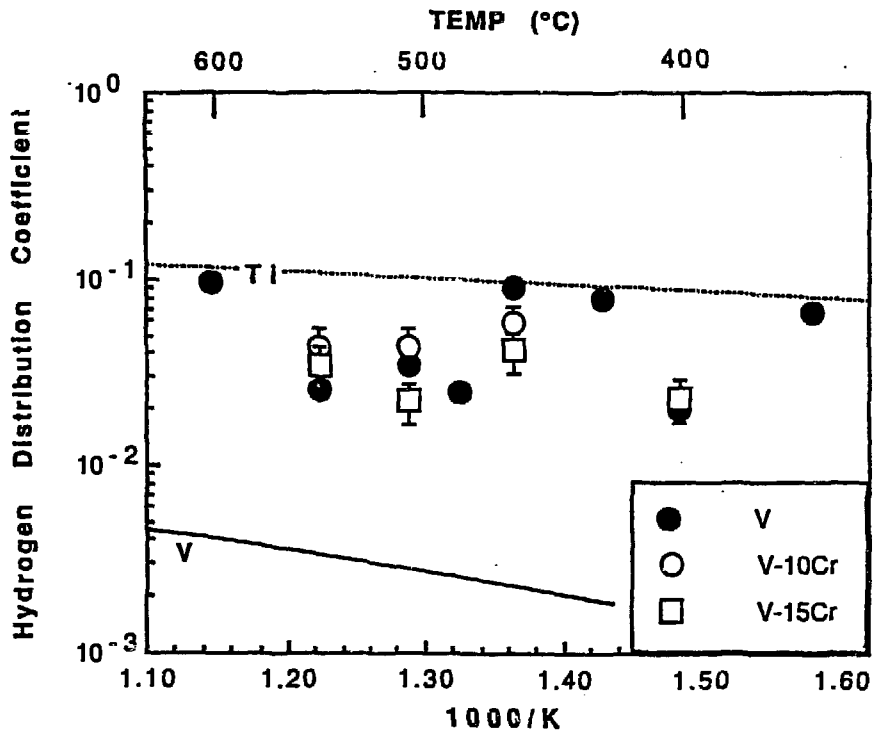


Fig. 5. Effect on Hydrogen Distribution Coefficients of Chromium Concentration in Binary Vanadium Alloys.