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TENSILE PROPERTY OF LOW ACTIVATION VANADIUM ALLOY AFTER LIQUID LITHIUM EXPOSURE

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Abstract: A candidate low activation vanadium (V) alloy, V-4Cr-4Ti (NIFS-HEAT-2), was exposed to liquid lithium (Li) at 973 and 1073 K for up to 1963 hr. Contamination by carbon (C) and nitrogen (N) from the Li on the order of thousands of wppm were observed. Oxygen (O) levels were reduced to the several 10 wppm level by Li exposure at 1073 K, but not at 973 K. The Li exposure caused strength degradation as measured by tensile tests at 973 and 1073 K. On the other hand, good ductility was demonstrated after the Li exposure even with the significant contamination of C and N. From microstructural observations, C and N are likely to be scavenged by Ti-C-N type precipitates. Reduction of O was attributed to disappearance of Ti-C-O type precipitates.

Keywords: First wall / blanket materials, impurity effect, mechanical property

1. Introduction

Vanadium alloys are recognized as attractive candidate structural materials for liquid Li cooled blanket for fusion reactors [1][2]. Transfer of impurities occurs between V alloy and liquid Li. Generally, C and N migrate to the V alloy from Li, while O is removed from the V alloy by Li[3]. However, the mechanisms of the transfer, distribution of the impurities after Li exposure, and the effects on mechanical properties have not been clarified. In the present study, a candidate V-4Cr-4Ti alloy, designated as NIFS-HEAT-2, was exposed to liquid Li for durations up to 1963 hr. The impurity transfer, impurity distribution and its effect on tensile properties were investigated.

2. Experimental procedure

Coupon specimens (0.25 x 5 x 25 mm) of the reference low activation V-4Cr-4Ti alloy (NIFS-HEAT-2) annealed at 1273 K for 2 hr [4] were used. The Li exposure temperatures (T_{Li}) and duration were 973 K and 1073 K, and up to 1963 hr, respectively. The detail of the exposure tests has been described elsewhere [5]. After the exposure, Li was chemically removed by liquid ammonia. From the coupons, miniature tensile specimens (gauge: 0.25 x 1.2 x 5 mm), and disks (ϕ3 x 0.25 mm) were punched out. The residual material was chemically analyzed for C, N and O.

Tensile tests were conducted with the initial strain rate of 6.7×10^{-4} s^{-1}. Test temperatures ($T_{Tensile}$) ranged from room temperature (RT) to 1073 K. The atmospheres for the tensile tests at RT and elevated temperature were air and a $<10^{-4}$ Pa vacuum, respectively. Vickers microhardness was measured along the cross section of the coupons with a load of 25 g for 30 s. Microstructural observations were performed with scanning electron microscope (SEM) and transmission electron microscope (TEM) by using the punched disks.

3. Results

Table 1 lists the results of the chemical analysis after the Li exposure. The table also shows the liquid Li batch number. Liquid Li was changed after each 1 or 2 sets of exposure. Impurity concentrations in NIFS-HEAT-2 after Li exposures depended on the batch. Better correlations between exposure time and impurity concentrations are given in some batches as shown in Fig. 1. In these batches, C and N impurity levels were increased with exposure time by contamination from the Li, while O was decreased by scavenging by the Li.

Figure 2 shows the hardness distribution in the cross section along the thickness direction of the coupons exposed to liquid Li at 1073 K (T_{Li}). The 428 hr-exposed specimen exhibited uniform and similar hardness distributions as compared to that before Li exposure. The coupons exposed for 1443 and 1963 hr showed hardening 60 μm from the surface. Fig. 3 and 4 present the tensile parameters obtained for specimens exposed to liquid Li at 1073 K (T_{Li}). From the previous data [6] and the present data at room temperature (943 hr), miniature tensile tests show data scatter of about 40 MPa in strength (YS, UTS) and 10 % in elongation (UE, TE). Considering this scatter the change in UTS after Li exposure at 1073 K (T_{Li}) for 428

Table 1 Impurity concentrations in NIFS-HEAT-2 (V-4Cr-4Ti) before (t_{Li} = 0) and after (t_{Li} > 0) liquid Li exposure

Exposure temperature, T_{Li} / K	Exposure time, t_{Li} / hr	C, C_C / wppm	N, C_N / wppm	O, C_O / wppm	Li batch ID
	0	62	84	158	
973	255	142	342	142	#5
	499	280	1000	171	#6
1073	260	238	884	51	#2
	428	130	143	66	#1
	943	477	2273	29	#2
	1443	505	2317	79	#3
	1963	797	3420	47	#4

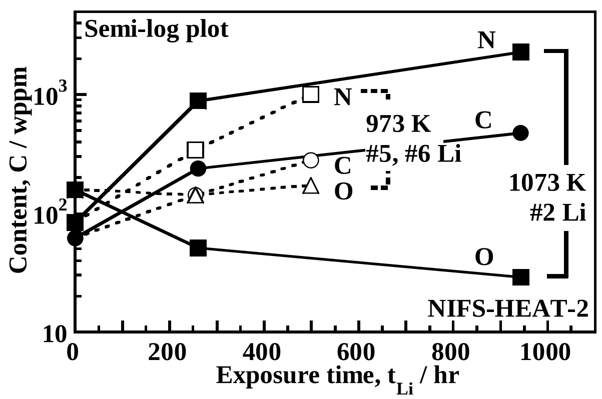


Fig. 1 Change in impurity concentration after the Li exposures at 973 K (Li #5 and 6) and 1073 K (#2).

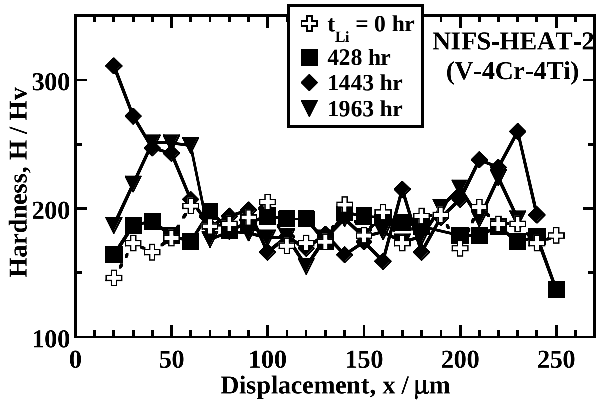


Fig. 2 Hardness distribution in the cross section and along the thickness direction of the coupons after exposure to liquid Li at 1073 K. The surfaces of the coupons are located at 0 µm and 250-270 µm in displacement, x.

and 943 hr was small below test temperatures of 773 K ($T_{Tensile}$). However, the degradation of UTS at 973 and 1073 K ($T_{Tensile}$) was clear, and 50 and 80 MPa, respectively. On the other hand, elongation decrease owing to Li exposure was observed at RT and 773 K ($T_{Tensile}$), but not at higher temperature. However, all the specimens still exhibit higher ductility than 6.5 % in UE and 13 % in TE.

Figure 5 shows the microstructures obtained by SEM. Compared with the specimen before Li exposure, precipitates increased in number and grew in size. The grain boundary was also populated by precipitates after Li exposure. By energy dispersive X-ray (EDX) analysis, Ti, C, N and O segregation were detected for both precipitates in grain interior and at grain boundaries. For the precipitates in the grain interior, Ti-C-N is considered to be the main compound, because it has been reported previously that N doping strongly increased the amount of the precipitates compared with O [7].

However, TEM can detect smaller precipitates than SEM, and Fig. 6 shows TEM images before and after Li exposure. Re-precipitation annealing, such as annealing at 1373 K for 1 hr and again at 973 K for 1 hr, was conducted on a part of specimens. The 1373 K annealing dissolves precipitates smaller than about 100 nm (observed only in TEM), but does not dissolve the above mentioned Ti-C-N type precipitates observed both in TEM and SEM. The 973 K annealing produces re-precipitation in the matrix. The shape of the precipitates before the re-precipitation was not regular, whereas a disk shape was obtained after the re-precipitation, and the diameter of the disk can be determined as the length of precipitate image. More detailed descriptions of the experimental technique and the impurity behavior have been presented elsewhere [7].

The main compound of the small and unstable precipitates is assumed to be Ti-C-O, since C and O were detected in EDX analysis[8], and the number density of the precipitates increased with O concentration in the experiments with model alloys doped with O [7]. Fig. 7 shows the correlation between O concentration and the number density of both the small precipitates (Ti-C-O, < 100 nm) and larger ones (Ti-C-N, > 100 nm) observed by TEM. The Ti-C-O type precipitates decreased with decreasing O concentration during Li exposure. After the re-precipitation annealing, the number density of the Ti-C-O

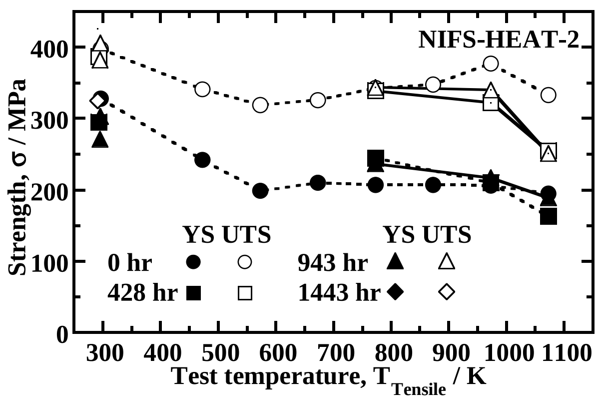


Fig. 3 Tensile test temperature ($T_{Tensile}$) dependence of yield strength (YS, 0.2 % proof stress) and UTS (UTS) of NIFS-HEAT-2 before and after the Li exposures at 1073 K (T_{Li}).

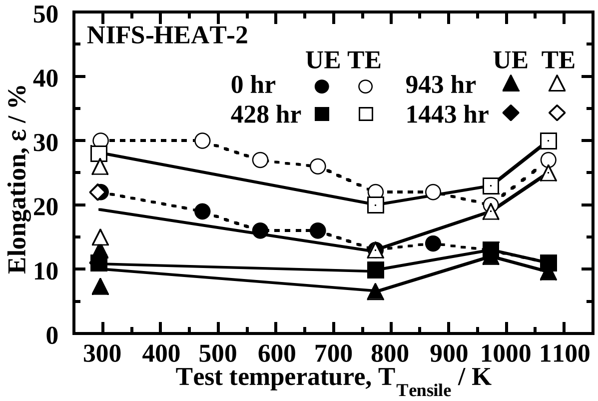


Fig. 4 Tensile test temperature ($T_{Tensile}$) dependence of uniform elongation (UE) and total elongation (TE) of NIFS-HEAT-2 before and after the Li exposures at 1073 K (T_{Li}).

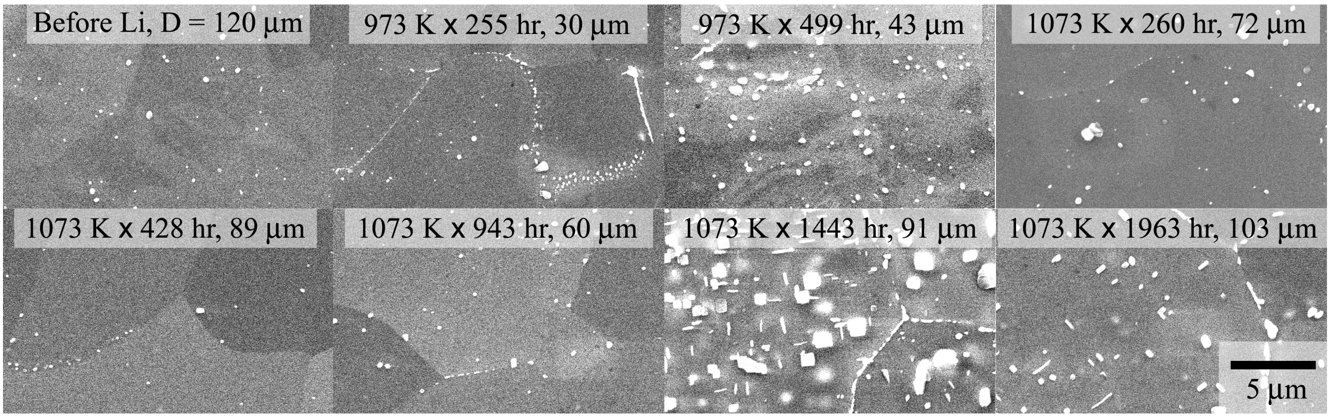
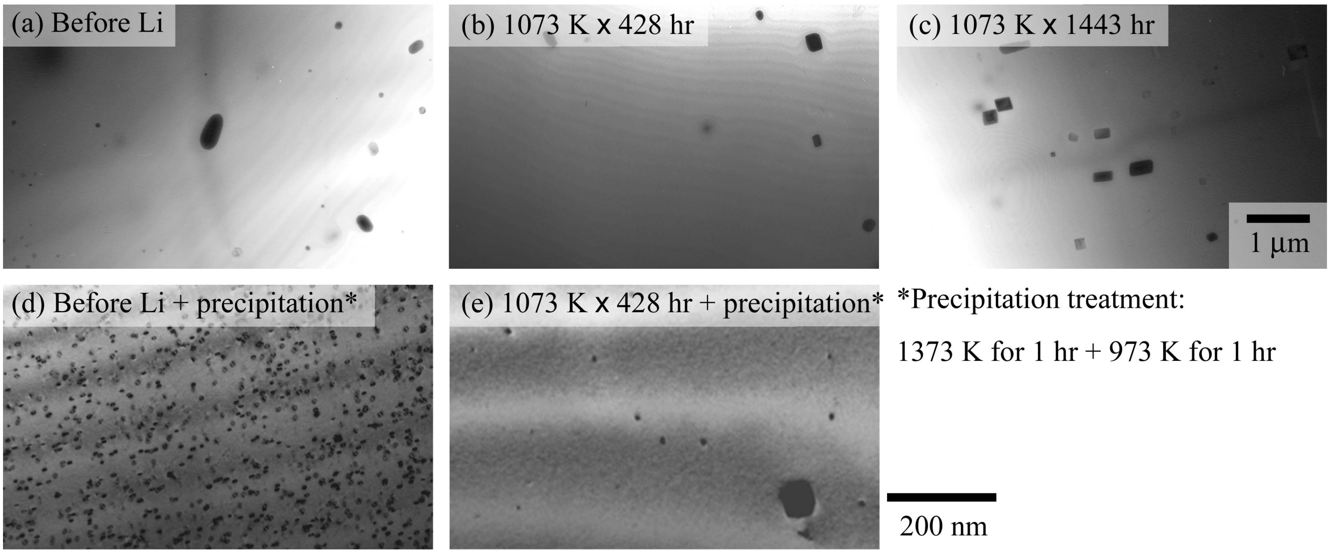


Fig. 5 SEM images before and after the Li exposure. The exposure temperature and time are indicated. Observation depth from the coupon surface, D, is also indicated.



*Precipitation treatment:

1373 K for 1 hr + 973 K for 1 hr

Fig. 6 TEM images (a) before and (b), (c) after the Li exposure at 1073 K. Small precipitates were dissolved by an annealing at 1373 K, and then (d), (e) homogeneous re-precipitation was introduced at 973 K. In TEM analysis, observation depth is expected at the center of the specimen, which is about 130 μm from the surface.

type precipitates after Li exposure was much smaller than that before exposure.

4. Discussion

4-1. Impurity transfer

From Fig. 1, it is apparent that C and N impurities were introduced by Li exposure at both 973 K and 1073 K (T_{Li}). For example, the N concentration in the Li before melting prior the exposure was measured as 161 and 171 wppm for batch #1. During melting of Li prior to the exposure tests, the concentration can change, because melted Li was considered to uptake impurities from the atmosphere. From Table 1, C and N contaminations in batch #1 are much smaller than the other batches. This was expected since this batch was already re-used once and thus purified by previous exposure tests by using vanadium alloys. C and N contamination can be controlled by a management of Li purity. C and N are strong hardening agents if they are dissolved into interstitial positions. From Fig. 2 the hardening region was limited to near the surface. From SEM observation after the exposure at 1073 K (T_{Li}) for 1443 hr and 1963 hr, as shown in Fig. 5, the increase in the amount of Ti-C-N type precipitates was observed at 91 and 103 μm from the surface, where no hardening was detected in Fig. 2. This means that C and N diffused into the center of the specimens, but were scavenged out from solid solution state by the production of Ti-C-N precipitates at grain interior and at grain boundaries.

On the other hand, the O concentration in the V-alloy, as shown in Fig. 1, was reduced by Li exposure for 500 hr at 1073 K (T_{Li}), but not at 973 K (T_{Li}) . The diffusion coefficient of O has been obtained in a previous study on V-4Cr-4Ti alloy [9].

$$D = D_0 \exp(Q / RT) \qquad \text{(Eq. 1)}$$

$$D_0 = 4.02 \times 10^{-6}\ \mathrm{m^2\ s^{-1}}$$

$$Q = 1.30 \times 10^{5}\ \mathrm{J\ mol^{-1}}$$

D: Diffusion coefficient, D_0: Constant, R: gas constant = 8.3144 J mol^{-1} K^{-1}, T: temperature

The diffusion range during Li exposure, R_{Li}, can be estimated by following.

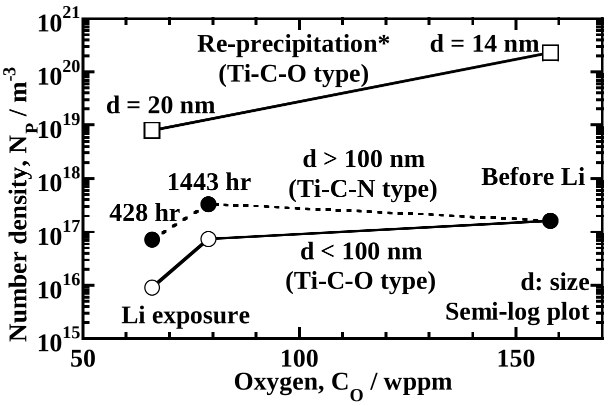


Fig. 7 Correlation between O concentration and number density of the precipitates observed by TEM for the specimens after Li exposure at 1073 K. In order to estimate the amount of the small and unstable precipitates, the precipitates smaller than 100 nm (Ti-C-O type) and larger ones (Ti-C-N type) were counted separately. Here the size, d, means the maximum length of precipitate image. *Re-precipitation heat treatment: 1373 K x 1 hr + 973 K x 1hr

$$R_{Li} = \sqrt{D\, t_{Li}} \qquad \text{(Eq. 2)}$$

The diffusion ranges for 500 hr exposures at 973 K and 1073 K are calculated as 871 and 1840 μm, respectively. Even 871 μm for 973 K is large enough for O to diffuse out from the 260 μm thick specimen. At 973 K, Ti-C-O type precipitates are considered stable [7] and effective to hold the O in the material. At 1073 K, a part of the Ti-C-O precipitates is thought to decompose and dissolve, then the O diffused out to Li. Fig. 7 shows evidence of the reduction of small precipitates with decreasing O concentration after Li exposure. The difference in the number density of the precipitates after re-precipitation treatment is clear. On the other hand, no softening after the exposure for 428 hr at 1073 K (T_{Li}), as shown in Fig. 2, suggests that the amount of O in solid solution state was not significantly different between before and after Li exposure. Assuming that (1) the difference in the number density of the precipitates after re-precipitation reflects the amount of Ti-C-O precipitates dissolved during the Li exposure, and (2) the Ti-C-O precipitates re-produced are disks with d in diameter and the same thickness, t_P, then the residual O as Ti-C-O precipitates after the 428 hr exposure can be estimated.

$$\frac{(N_P\, \pi\, (d/2)^2\, t_P)_{428\ hr}}{(N_P\, \pi\, (d/2)^2\, t_P)_{Before\ Li}} =$$

$$\frac{8.0 \times 10^{18}\ m^{-3} \times (20\ nm)^2}{2.3 \times 10^{20}\ m^{-3} \times (14\ nm)^2} = 7.1\ \% \qquad \text{(Eq. 3)}$$

From this result, the O concentration before Li exposure, 158 wppm, could be decomposed into 99 wppm in the Ti-C-O precipitates and 59 wppm in other states, such as solid solution state, or large precipitates at grain boundary. 7.1 % of the Ti-C-O precipitates, 7 wppm, and the other component, 59 wppm, remained, resulting in 66 wppm in total.

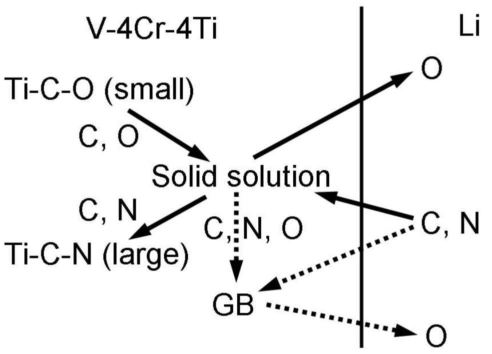


Fig. 8 Impurity transfer between V-4Cr-4Ti alloys and liquid Li. Arrows with solid line are discussed in the present study. Flow to grain boundary (GB) is remaining to be studied (dashed lines).

From the above discussions, a diagram for impurity transfer is suggested in Fig. 8. In the present study, transfer between liquid Li, solid solution state and two types of precipitates (solid lines) was discussed. Impurities are considered to be released or absorbed by the two types of the precipitates in V-4Cr-4Ti alloys. On the other hand, flow to the grain boundary (dashed line) could be considerable. This impurity flow is remaining to be studied to complete the quantitative analysis for impurity transfers.

4-2. Effect of Li exposure at 1073 K (T_{Li}) on tensile property

The ultimate tensile strength at 973 K and 1073 K ($T_{Tensile}$) decreased after the Li exposures. C and N contamination of the order of thousands of wppm indicated in Table 1 did not introduce significant hardening in either hardness or tensile tests. The C and N impurities were thought not to induce solid solution hardening, since they were, as mentioned above, absorbed by the Ti-C-N precipitates.

Possible mechanisms of the 80 MPa softening at 1073 K ($T_{Tensile}$) with impurity reduction are (1) loss of precipitation hardening by Ti-C-O precipitates and (2) loss of hardening by solid solution O. Another mechanism independent of O reduction is (3) change of grain boundary condition. Assuming Orowan-type strengthening [10] for case (1), even the initial contribution to deformation stress of the Ti-C-O precipitates before Li exposure is less than 5 MPa. This is a worst-case estimation using 1.6×10^{17} in number density in Fig. 7, 100 nm in precipitate size and 1 as interaction coefficient between dislocations and the precipitates. Such a small contribution is consistent with the fact that no significant softening is observed at room temperature. For case (2), hardening by dynamic strain aging induced at >773 K ($T_{Tensile}$) can be reduced in low oxygen specimen[11], however this effect is considered not significant at 1073 K ($T_{Tensile}$). On the other hand, the softening would be partly explained, if Ti-C-O precipitates before Li exposure release O into the matrix during tensile tests at 1073 K ($T_{Tensile}$). O in pure V is completely in the solid solution state. The hardening coefficient of O at RT has been reported as 0.057 Hv / wppm [12]. The estimated amount of O for Ti-C-O is 99 wppm before Li exposure, whereas 7 wppm after the exposure. The reduction of O, 92 wppm is equivalent to 5.2 Hv, which can be roughly converted into about 16 MPa in the reduction of the deformation stress [10]. This contribution of the impurity should decrease at higher temperature and is still much smaller than the UTS decrease at 1073 K ($T_{Tensile}$), indicating another mechanism should be considered. Case (3) is the effect of the precipitates covering the grain boundaries. Enhancement of grain boundary slip and local fracture of the precipitates are possible. Further investigation of these processes at 1073 K is ongoing.

From Fig. 4, the NIFS-HEAT-2 maintained large enough ductility after Li exposure for up to 1443 hr, even though significant C and N contamination occurred. For this reason, Li exposure is not expected to induce fatal embrittlement on V-4Cr-4Ti alloys. From the practical viewpoint, the thickness of V alloy plate in fusion blanket is expected to be about 5 mm[13]. The scavenging effect is controlled by O diffusion, and gradually reduces in the deeper regions, therefore the thicker plate probably shows smaller change in tensile properties.

5. Conclusions

NIFS-HEAT-2 maintained large ductility after Li exposure at 1073 K, while it showed degradation of high temperature tensile strength. Li exposure caused large contamination with C and N. Reduction of O occurred at 1073 K, but not at 973 K for exposures up to 500 hr. The C and N contamination lead to the formation of course Ti-C-N type precipitates, but did not cause hardening. O is considered to be released from Ti-C-O type precipitates and scavenged out to the liquid Li.

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