# CHEMICAL AND MECHANICAL INTERACTIONS OF INTERSTITIALS IN V-5%Cr-5%Ti -

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## OBJECTIVE

A vanadium alloy structure with liquid lithium is the favored concept for an advanced breeding blanket for ITER. The objective of this task is to determine the kinetics of reactions of vanadium alloys with hydrogen and oxygen as a function of alloy composition and TMT.

## SUMMARY

Gas-metal reaction studies of V-5Cr-5Ti were conducted to determine the kinetics of reactions with $H_2$ and $O_2$, respectively, at 450-500°C. Reaction rates were determined through weight change measurements and chemical analyses, and effects on mechanical properties were evaluated by room temperature tensile tests. Exposures to hydrogen at 450°C and 0.1 torr pressure resulted in a significant loss in room temperature ductility in the case of alloys that had been annealed at 1125°C but not in the case of alloys annealed at 1050°C. Adding oxygen at 500°C at concentrations as low as 200 ppm seriously embrittled V-5Cr-5Ti specimens when the specimens were held for 100h in vacuum at 500°C. A subsequent heat treatment in vacuum at 950°C restored the ductility. Exposure to air at 400°C and a subsequent vacuum heat treatment at 500°C caused ductility decreases similar to those observed after the small oxygen additions, and ductility again was restored by a 950°C vacuum anneal. However, similar heat treatments following air exposures at 450 and 500°C, respectively, resulted in ductility losses that were not recovered by the 950°C anneal. The latter exposures also resulted in the formation of thin oxide films.

## INTRODUCTION

### Materials and Procedures

Interactions of the V-5Cr-5Ti alloy with hydrogen were investigated using an ultra-high vacuum Sievert's apparatus to control the hydrogen pressure and temperature at conditions prototypic of the ITER plasma-first wall interface and the diverter. High purity hydrogen was admitted to the apparatus through a controllable leak valve at the same rate that it was extracted by a turbomolecular pump, and the pressure at the specimen was fixed within the range $10^{-1}$ to $10^{-2}$ torr (13-1.3 Pa). Exposure temperatures were 450 and 500°C with times ranging from 24 to 100 hours. A similar apparatus was used to make controlled oxygen additions to the alloy. In this case the alloy was exposed at 500°C for 4 h to pure oxygen at $2 \times 10^{-6}$ torr ($2.6 \times 10^{-4}$ Pa), and then was heat treated at 500°C under ultra-high vacuum to diffuse the oxygen into the specimen. Some specimens were given a secondary heat treatment in vacuum at 950°C to remove the oxygen from solid solution. Additional exposures were carried out in an air atmosphere at 400, 450, and 500°C, respectively. Subsequent heat treatments were the same as those following the exposures to oxygen at $2 \times 10^{-6}$ torr. In all tests the reaction rates were determined through weight change measurements and chemical analyses, and effects on mechanical properties were evaluated by room temperature tensile tests.

The V-5Cr-5Ti alloy used for these studies was produced by Teledyne Wah Chang Albany and has been given the designation BL-63. The compositions of major components are listed in Table 1. Small tensile specimens (SS-3), nominally 0.76 mm thick with 1.5 mm x 7.6 mm gage sections, were machined or stamped from 40% warm-reduced sheet stock of the alloys. One set of specimens was vacuum annealed for 1 h at 1125°C and a second set for 1 h at 1050°C. Another set of identically-shaped specimens was stamped

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from 0.75 mm sheet that had been autogenously welded using the gas-tungsten arc (GTA) process.[1] The weld bead was positioned laterally at the center of the gage length, and the specimens were not heat treated before testing.

Table 1. Composition of Vanadium Alloy

| Heat # | Concentration wt % | | | Concentration wt ppm | | | |
|---|---|---|---|---|---|---|---|
| | Cr | Ti | Fe | O | N | C | Si |
| WC 832394 (BL63) | 4.2 | 5.4 | <0.045 | 427 | 52 | 40 | <0.031 |

## RESULTS AND DISCUSSION

To evaluate the effects of prior heat treatment on hydrogen embrittlement, specimens annealed at 1050°C and 1125°C, respectively, were exposed side-by side in 0.1 torr hydrogen at 450°C for times of 24 and 100 hours, respectively. As shown in Table 2, room temperature ductilities of specimens annealed at 1050°C were significantly higher than the corresponding ductilities of specimens annealed at 1125°C. Prior to hydrogen exposure, elongations were on the order of 30% irrespective of the heat treatment temperature. Specimens annealed at 1050°C showed only a slight drop in elongation, while specimens annealed at 1125°C showed elongations of only 2-5%.

The embrittlement of the specimens annealed at 1125°C and exposed to hydrogen at 450°C torr was significantly less when the hydrogen pressure was reduced to 0.01 torr than for exposures at 0.1 torr. Room temperature ductilities after exposures at the respective pressures are compared in Table 3. In contrast to the elongations of 2-5% reported above for exposures at 0.1 torr, elongations after exposure at 0.01 torr were all above 14%. However, the latter elongations were still less than elongations of specimens annealed at 1050°C and exposed at 0.1 torr (Table 2).

The weight gains measured in these tests, shown in Tables 2 and 3, generally exceed those which could have accrued from hydrogen pickup alone. Although hydrogen concentrations in these specimens are still being analyzed, based on analyses of earlier tests in hydrogen[2], the bulk of the weight gains over 50 ppm can be attributed to oxygen pickup. As discussed below, ingress of oxygen at 500°C, even at the relatively low levels indicated by the weight changes in these tests, can significantly degrade the room temperature ductility of the V-5Cr-Ti alloy. In the case of the present tests, which were conducted at 450°C, the diffusion rate of oxygen into the specimens is sufficiently slow that the embrittlement resulting from the 24-hour exposures can be assumed to be due primarily to hydrogen effects; however, the further decrease in ductility resulting from the 100-hour exposures probably reflects oxygen ingress more than hydrogen. As discussed below, the effect of prior annealing treatment on elongation in these tests may be associated more with oxygen contamination than with hydrogen effects. A further investigation of the effect of annealing treatment on hydrogen-induced property changes is being carried out under conditions designed to limit oxygen pickup.

Effects of oxygen contamination on the room temperature properties of the reference V-5Cr-5Ti alloy were evaluated in both the welded and unwelded conditions. Specimens were initially exposed to oxygen at $2 \times 10^{-6}$ torr for 4 h at 500°C, resulting in a pickup of approximately 200-250 ppm of oxygen. Part of these specimens were then heat treated under ultra-high vacuum for 100 h at 500°C, and a group of the latter specimens were further heat treated for 4 h at 950°C. Table 4 shows results for specimens that had been welded by the GTA process. The addition of 250 ppm oxygen at 500°C produced a measurable reduction in elongation even in 4 h, but with the additional 100 h anneal in vacuum the elongation was reduced to 2%. A further anneal at 950°C completely restored the ductility to its value in the as-welded condition. These results are quite comparable to results for unwelded specimens of the same heat that were annealed at

1125°C prior to oxygen exposure, as reported earlier.[2] However, as shown in Table 5, very different results were obtained for specimens that were annealed at 1050°C prior to oxygen exposure and subsequent annealing. The latter specimens showed only a small reduction in ductility for a comparable oxygen pickup following the 100-h anneal at 500°C, although again the ductility was fully recovered by the 950°C anneal.

It was previously reported that embrittlement by oxygen under the present test conditions depends strongly on the alloy grain size.[2] The ductility differences between specimens annealed at 1050°C and 1125°C can be attributed to this grain size effect. Specimens having an ASTM grain size of 5 or less, as produced by the 1125°C anneal, suffer a greater reduction in ductility for a given amount of oxygen absorbed at 450-500°C than specimens with ASTM grain size 6-7, as produced by the 1050°C anneal. Since autogenous welding induces even greater grain coarsening, it is not surprising that the welded specimens showed even greater susceptibility to oxygen embrittlement than the specimens annealed at 1125°C. Consistent with these findings is the observation that fractures of the lower ductility specimens tend to be predominantly intergranular, while those of the higher ductility specimens are transgranular. These results all indicate that oxygen ingress in V-5Cr-5Ti at 450-500°C is occurring mainly along grain boundaries.

Table 2. Effect of Annealing Temperature on V-5Cr-5Ti Exposed to $H_2$ at 450 C
(Specimens exposed at a pressure of 0.1 torr)

| Specimen | Annealing Temp. (C) | Exposure Time (h) | Weight Change (ppm) | Yield Strength (MPa) | Ultimate Strength (MPa) | Elong. (%) | Cooling Rate |
|---|---|---|---|---|---|---|---|
| VN 13 | 1050 | 24 | 38 | 404 | 494 | 21.3 | fast |
| VN 10 | 1125 | 24 | 348 | 441 | 476 | 5.6 | fast |
| VN14 | 1050 | 100 | 423 | 414 | 499 | 19.2 | fast |
| VN11 | 1125 | 100 | 231 | 451 | 451 | 1.6 | fast |
| VN 18 | 1050 | 100 | 270 | 430 | 515 | 16.7 | slow |
| VN 09 | 1125 | 100 | 232 | 441 | 462 | 1.8 | slow |

Table 3. Room Temperature Properties of V-5Cr-5Ti after Exposure to $H_2$ at 450 C

| Specimen* | Hydrogen Pressure (torr) | Exposure Time (h) | Weight Change (ppm) | Yield Strength (MPa) | Ultimate Strength (MPa) | Elong. (%) | Cooling Rate |
|---|---|---|---|---|---|---|---|
| VR30 | 0.01 | 24 | 59 | 396 | 469 | 20.7 | fast |
| VN 07 | 0.1 | 24 | 308 | 430 | 494 | 10.0 | fast |
| VR20 | 0.01 | 100 | 58 | 395 | 474 | 21.3 | fast |
| VN11 | 0.1 | 100 | 231 | 451 | 451 | 1.6 | fast |
| VN19 | 0.01 | 100 | 75 | 353 | 465 | 14 | slow |
| VN12 | 0.1 | 100 | 329 | 452 | 470 | 3.8 | slow |

*Specimens annealed at 1125C prior to exposure to $H_2$

Test results for exposures of the reference V-5Cr-5Ti alloy (annealed at 1125°C) to ambient air at 400, 450, and 500°C are shown in Table 4. Exposure to air for 24 h at 400°C resulted in a pickup of approximately 500 ppm oxygen, and the effects on room temperature ductility were similar to those for the exposures in $2 \times 10^{-6}$ torr oxygen, discussed above. The ductility, which dropped only slightly following the 24-h air

Table 4. Oxygen Effects on Room Temperature Properties
(Specimens exposed to 1.0E-6 torr O2 at 500C for 4 hours)

| Specimen | Weight Change (ppm) | Holding Time (C) | Holding Temp. (h) | Yield Strength (MPa) | Ultimate Strength (MPa) | Elongation (%) |
|---|---|---|---|---|---|---|
| | | **Weld Specimens** | | | | |
| VO04 | Control | 100 | 500 | 475 | 578 | 14.5 |
| VO05 | " " | 100<br>4 | 500<br>950 | 335 | 428 | 16.8 |
| VO01 | 250 | As-oxidized | | 467 | 516 | 7.2 |
| VO02 | 250 | 100 | 500 | 494 | 556 | 1.9 |
| VO03 | 242 | 100<br>4 | 500<br>950 | 329 | 436 | 15.6 |
| | | **As Annealed - 1050C** | | | | |
| VN04 | Control | 100 | 500 | 376 | 454 | 26.6 |
| VN05 | " " | 100<br>4 | 500<br>950 | 315 | 416 | 27.8 |
| VN01 | 116 | As-oxidized | | 363 | 452 | 26.7 |
| VN02 | 193 | 100 | 500 | 374 | 481 | 23.9 |
| VN03 | 233 | 100<br>4 | 500<br>950 | 312 | 432 | 28.5 |

Table 5. Effect of Air Exposures on Properties of V-5Cr-5Ti*

| Specimen | Anneal Time (h) | Conditions Temp. (C) | Weight Change (ppm) | Yield Strength (MPa) | Ultimate Strength (MPa) | Elongation (%) |
|---|---|---|---|---|---|---|
| | | **Exposed to air for 24 h at 400C** | | | | |
| VR09 | As-exposed | | 441 | 363 | 442 | 26.2 |
| VR08 | 100 | 500 | 500 | 400 | 425 | 4.0 |
| VR04 | 100<br>4 | 500<br>950 | 500 | 327 | 466 | 27.2 |
| | | **Exposed to air for 25 h at 450C** | | | | |
| VB95 | As-exposed | | 1101 | 375 | 464 | 24.7 |
| VB89 | 100 | 500 | 1420 | 401 | 447 | 19.7 |
| VB92 | 100<br>4 | 500<br>950 | 956 | 362 | 494 | 19.2 |
| | | **Exposed to air for 25 h at 500C** | | | | |
| VB94 | As-exposed | | 1855 | 387 | 481 | 21.0 |
| VB85 | 100 | 500 | 1971 | 401 | 427 | 9.4 |
| VB91 | 100<br>4 | 500<br>950 | 2290 | 401 | 428 | 7.2 |

*Annealed at 1125C

exposure, was substantially reduced following a subsequent heat treatment in vacuum for 100h at 500°C but then was fully recovered by a secondary heat treatment in vacuum at 950°C. Exposures to air for 25 h at 450 and 500°C resulted in substantially greater oxygen pickup than at 400°C, and in this case the effects on ductility were different from the exposures to oxygen and to 400°C air. After the 450°C air exposure, the subsequent heat treatment for 100 h at 500°C lowered the ductility less than after the 400°C air exposure, and the subsequent heat treatment at 950°C had no effect on the ductility. After the 500°C air exposure, the subsequent 500°C vacuum heat treatment reduced the ductility to the same order as had occurred for the 400°C air exposure, but, like the 450°C air exposure, the ductility was not recovered by the subsequent 950°C vacuum heat treatment. One important difference in the 450 and 500°C air exposures from other tests conducted to date was a marked darkening of the specimen surfaces, indicative of the presence of an oxide film. How the morphology and chemistry of this film may have affected the oxygen uptake by the vanadium alloy is still under investigation.

REFERENCES

1. G. M. Goodwin and J. F. King, "Welding Development for V-Cr-Ti Alloys" in *Fusion Reactor Materials Semiannual Progress Report for Period Ending March 31, 1994*, DOE/ER-0313/16, Oak Ridge National Laboratory.

2. J. H. DeVan, J. R. DiStefano, and J. W. Hendricks, "Chemical and Mechanical Interactions of Interstitials in V-5%Cr-5%Ti" in *Fusion Reactor Materials Semiannual Progress Report for Period Ending March 31, 1994*, DOE/ER-0313/16, Oak Ridge National Laboratory.