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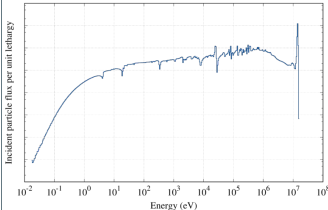

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Graphical Abstract

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Research and development on vanadium alloys for fusion breeder blanket application		 UK Atomic Energy Authority
Radiation environment <p>Mechanical properties are controlled by Ti-based precipitates and nonmetallic impurities. Previous experiments have used fission test reactor experiments and different ion irradiation. Testing under a fusion reactor neutron flux (below) is needed.</p>	Other environments <p>Evaluating the corrosion of the alloy under lithium and combined lithium/radiation is needed.</p> <p>Testing magnetohydrodynamic effects under a magnetic field and flowing lithium in future would also be useful, to simulate fusion reactor magnets.</p> <p>The diffusion of hydrogen isotopes (i.e. tritium) and helium into the alloy, and subsequent embrittlement, is of special interest for fusion reactors.</p>	Conclusion: <p>Further research into the combined effects of high-energy fusion neutron radiation and liquid lithium is required. Understanding the behaviour of precipitates and impurities in the alloy is needed to understand how the alloys would evolve in a fusion reactor</p>
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Highlights

Research and development on vanadium alloys for fusion breeder blanket application

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- The status of research on vanadium alloys for fusion breeder blankets is reviewed.
- This focuses on the microstructure of the alloy after different irradiations.
- The effects of a liquid lithium environment on the alloy are also detailed.
- Combined fusion neutron irradiation and lithium is needed to evaluate performance.

Research and development on vanadium alloys for fusion breeder blanket application

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Abstract

The status of research and development on vanadium alloys and on their application as a structural material in the breeder blanket of a fusion power plant are reviewed. Emphasis has been placed on irradiation experiments and the effects of neutron and ion irradiation on the microstructure of the current reference alloy, V-4Cr-4Ti. The effects of a liquid lithium environment and the exchange of carbon, nitrogen, and oxygen impurities between the alloy and application-relevant environments are also reviewed. The dependence of microstructural features on irradiation experiment parameters are examined, with a summary on magnetohydrodynamic effects and mechanical properties of the alloy. The relationship between the ductility and the alloy chemistry and the irradiation test temperature are analysed. Review of the state of the art indicates that further developments of facilities simulating a realistic fusion radiation and liquid lithium environment are fundamental to advancing fusion reactor breeder design.

Keywords: Vanadium, Irradiation, Blanket, Lithium, Chromium, Titanium

1. Introduction

V-4Cr-4Ti is a candidate structural material for the conceptual liquid lithium or lithium-lead eutectic breeder blanket in a magnetic confinement fusion power plant [1, 2]. A lithium breeder blanket is designed to breed tritium fuel for the reactor using high-energy neutrons from the initial deuterium-tritium fusion reaction. The International Thermonuclear Experimental Re-

actor (ITER) will test four ‘Test Blanket Module’ (TBM) breeder families: liquid lithium-lead, liquid lithium, water-cooled ceramic/beryllium, and helium-cooled ceramic/beryllium [3]. Lead and beryllium are neutron multipliers, increasing the number of neutrons which can then react with the lithium to produce tritium in the blanket. The candidate structural materials for the ITER blanket designs are either reduced-activation ferritic/martensitic (RAFM) steels or the V-4Cr-4Ti alloy [3]. Successful TBM designs will be employed in Demonstration-class (DEMO) reactors as fully-fledged working breeder blankets, which will be required to demonstrate tritium breeding and electricity production [4]. Designs for DEMO reactors will employ structural materials with the maximum amount of data available on degradation in a fusion environment, as reactor safety is of critical importance [3]. Many established research efforts have focused on water cooled breeder blanket designs using reduced activation ferritic martensitic steels [5]. However, with no tritium breeder blanket ever built and tested, and various designs proposed for future reactors, further research into V-4Cr-4Ti is essential to ensure design processes can be flexible and adaptable.

The predicted fusion power plant neutron energy spectrum is dominated by 14 MeV neutrons [6]. Without a fusion power plant to test materials in, irradiation experiments must utilise alternative methods. Historically, fission test reactors have been used to create test neutron environments. However these neutrons typically have energies of 0.1-1 MeV, and will cause different damage compared to 14 MeV neutrons [7]. To simulate the dose rate from fusion reactor irradiation with low-energy neutrons, very long irradiation times are also required. To this end, high-energy ion-irradiation has been employed in recent years as individual ion damage in materials is greater than that of individual fission neutrons [7]. This allows one to simulate the radiation dose exposed to a material over a reactor lifetime in a much shorter length of time.

Research into the production and fabricability of vanadium alloys has been extensively reviewed [8, 9, 10, 11], as has the effect of neutron irradiation on mechanical properties [12] and alloy compatibility with fusion reactor environments [13, 14, 15]. This review will summarise the current status of research on V-4Cr-4Ti for use in a breeder blanket environment with emphasis instead on the effects of different irradiation methods, liquid lithium environments and nonmetallic impurities on the alloy microstructure. Areas requiring further research, such as the formation and growth of precipitates

under fusion neutrons, are highlighted.

2. Background of the alloy system

2.1. Development of the V-4Cr-4Ti reference alloy

The fusion breeder blanket concept is similar to the fast breeder fission reactor concept, which was designed to breed fission fuel in a blanket using the fission neutrons emitted from the reactor core [16]. As part of the fast breeder cladding program during the 1960s, research into vanadium alloys was conducted at Argonne National Laboratory, Westinghouse Electric Company and Karlsruhe Institute of Technology [13]. Based on this research, vanadium-based alloys are suitable candidates for fusion breeder blankets as they have a higher operating temperature than most RAFM steels [3] and exhibit good corrosion resistance in liquid metals [13]. The use of V-Cr-Ti ternary alloys for this application was investigated further as chromium addition was shown to improve creep strength and resistance to oxidation, and titanium can be added to improve fabricability and radiation-swelling resistance [13]. The V-15Cr-5Ti alloy was initially considered the reference composition for fusion-relevant vanadium alloys as it exhibited superior creep and fatigue properties compared to other alloys [13, 17]. However, studies showed that V-15Cr-5Ti alloys exhibited higher susceptibility to irradiation hardening compared to V-3Ti-1Si and V-20Ti alloys [18]. Separately, yield and ultimate tensile strengths were measured to increase with Cr concentration after neutron irradiation, leading to an increase in irradiation hardening [19, 20]. Lower irradiation hardening is desirable for a nuclear structural alloy to retain higher ductility after irradiation, reducing the probability of brittle fracture under increased stress [18]. Chromium addition above 9wt% in V-Cr-Ti alloys also exaggerates irradiation swelling, from observation of lower density changes in V-Cr-Ti alloys with lower Cr content after irradiation [21]. For these reasons, V-Cr-Ti alloys with high Cr content were dismissed as suitable fusion structural material candidates.

Addition of 1-5wt% titanium to V-Cr binary alloys promotes the formation of Ti-based precipitates to form homogeneously after thermal annealing from 950°C to 1125°C [21, 19, 22]. This increases hardening, as the precipitates disturb the diffusion of defects in the material [22]. These precipitates coarsen under irradiation at higher temperatures [19]. The precipitates also reduce irradiation swelling as they provide a sink for vacancies, transmutant

helium and voids. Figure 1 shows that voids can be seen in the the V-4Cr-0.1Ti and V-4Cr-0.3Ti micrographs after neutron irradiation, but not in the V-4Cr-1Ti and V-4Cr-4Ti micrographs. This indicates that only titanium addition above 1wt% suppresses voids [22]. The DBTT of vanadium alloys has been reported to increase with excessive Ti concentration, as summarised in figure 3 [19]. This is likely due to an increase in the size of the Ti-based precipitates in the alloy, which reduce ductility in the alloy by providing initiation points for brittle fracture [23, 24]. These results indicated V-Cr-Ti alloys with 1-5wt% Ti were ideal candidates for fusion application, as they suppress voids without compromising ductility.

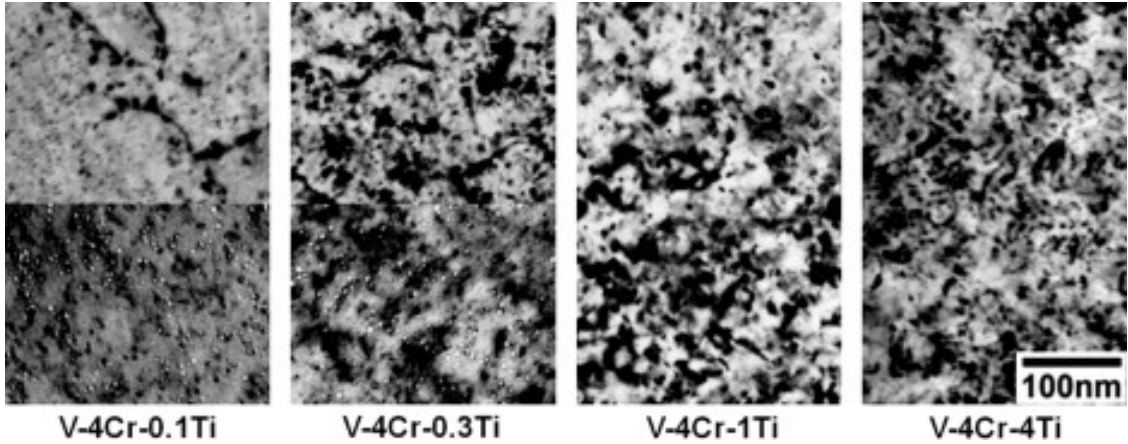


Figure 1: TEM microstructures of V-4Cr-xTi (where $x=0.1, 0.3, 1$ and 4) after neutron irradiation at 425°C in the HFIR (High Flux Isotope Reactor) [22]. The suppression of void formation by Ti addition above 1wt% Ti can be observed (voids are the bright spots in the lower images).

The ductile-brittle transition temperature (DBTT) of V-Cr-Ti alloys with the combined Cr and Ti contents of below 10wt% is approximately -196°C [19]. Increasing the combined Cr and Ti content to 20wt% leads to the DBTT of the alloy increasing to approximately 25°C [19], as displayed in figure 3. Increasing the Cr content above 10wt% has been observed to increase the DBTT of V-Cr-Ti alloys, believed to be due to high flow stress caused by solid-solution hardening of chromium [23]. However the size of the Ti-based precipitates present in the alloy increase with Cr concentration as well as Ti concentration, which may worsen ductility by the mechanism of providing

points for brittle fracture [23, 24]. The relationship between Cr concentration and DBTT for V-Cr-5Ti alloys is displayed in figure 2. Comparison of DBTT values after irradiation at 520°C and 420°C indicates a decrease in ductility after lower temperature irradiation for alloys with over 4wt% Cr. The DBTT of alloys with a low Cr content does not change with irradiation temperature, which has led to the reference composition of V-(4-5)Cr-(4-5)Ti [19]. It is important to note that annealing temperature also increases DBTT dramatically, with annealing at 1100°C increasing the Charpy DBTT of V-4Cr-4Ti from approximately -196°C to near room temperature [25]. Recent studies show that precipitate size also increases with annealing, which may offer an explanation [12, 24].

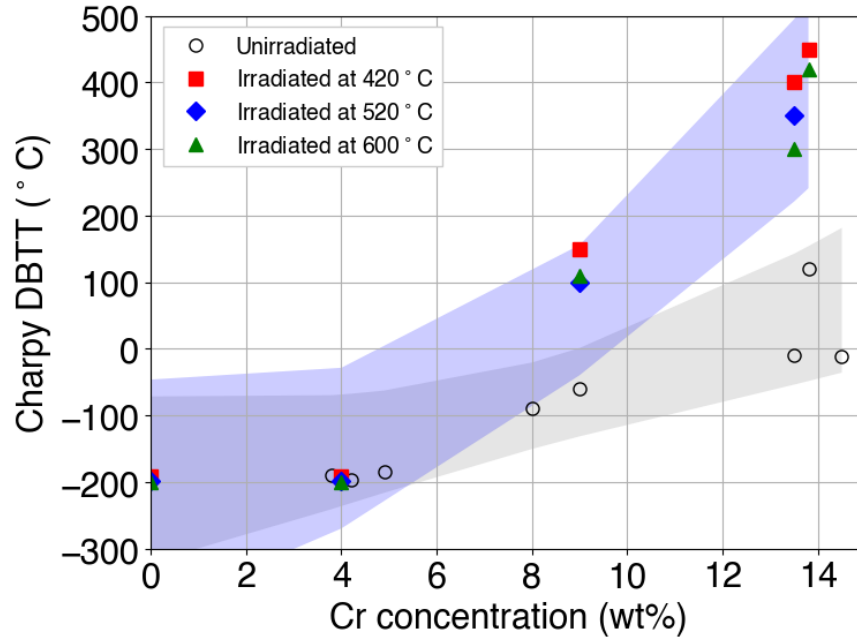


Figure 2: Effect of Cr concentration and irradiation temperature on the DBTT of V-Cr-5Ti. Samples were annealed at 1050°C before neutron irradiation to 24-43 dpa in the Fast Flux Test Facility (FFTF) [19].

A high creep strength up to 650-700°C makes V-4Cr-4Ti an ideal reactor structural material [13, 20]. The stress-rupture behaviour of V-4Cr-4Ti has been measured in a vacuum at 600°C: at a Larsen-Miller parameter of 21 P/1000, the stress is approximately 400 MPa [26]. This is superior to that

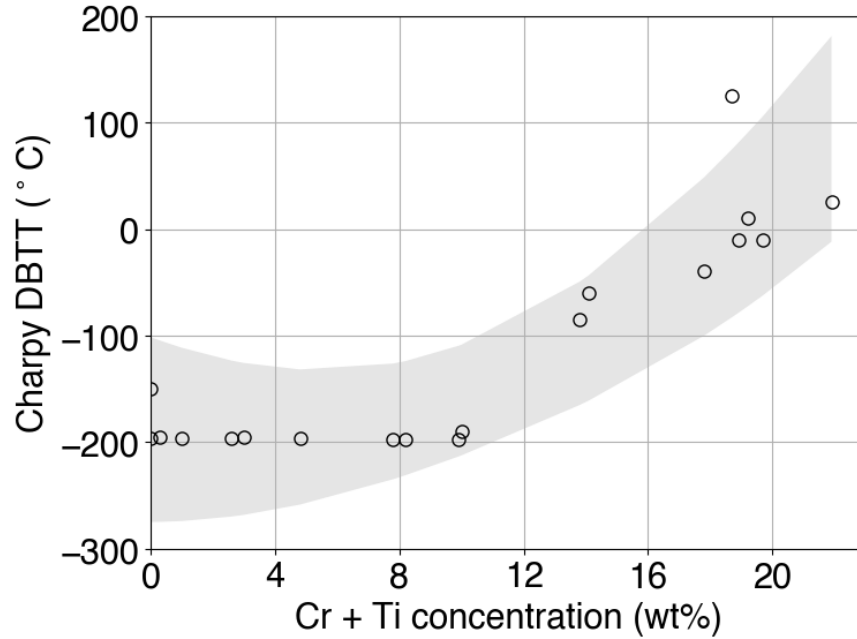


Figure 3: Effect of combined Cr and Ti concentration on the DBTT of unirradiated Charpy specimens of V, V-Ti, V-Ti-Si and V-Cr-Ti alloys annealed at 1050°C [19].

of HT-9 (≈ 130 MPa), Type 316 SS (≈ 150 MPa) and V-20Ti (≈ 300 MPa) but marginally inferior to V-(10-15)Cr-5Ti (≈ 450 MPa) [13, 26]. Higher chromium concentration therefore appears to improve the creep strength of V-Cr-Ti alloys [13]. The higher creep strength of V-Cr-Ti alloys compared to the ferritic/martensitic and austenitic steels is more significant at higher temperatures and longer experiment times: both steels approach rupture much more quickly compared to the vanadium alloys [26].

2.2. Minor alloying elements and nonmetallic impurities

Nonmetallic impurities in the unirradiated alloy (i.e. C, N, O) strongly influence the precipitation behaviour and the mechanical properties. Purified refractory metals are highly resistant to corrosion by liquid alkali metals (i.e. lithium), but the presence of these impurities in the system can change this drastically [27]. The Ti-based precipitates formed in the alloy after thermal annealing are normally Ti(CNO) precipitates of 300-500 nm size for combined C, N and O concentration over 400 wppm [19, 23, 28]. These precipitates

assume a NaCl type structure and are stable during neutron irradiation at 420-600°C [28]. Combined carbon, nitrogen and oxygen impurity concentration should be kept below 1000 wppm to control the number of precipitates in the alloy [19]. The precipitates have previously been identified as titanium oxides by diffraction analysis [23]. However Sakai et al. [23] have suggested that the oxygen in the TiO precipitates can be replaced by carbon and nitrogen atoms because TiN, TiC and TiO assume the same crystal structure with similar lattice parameters [23]. For a solid metal in a liquid lithium environment, mass transfer of nitrogen and carbon into the metal and transfer of oxygen into the lithium is common [27]. This is because the distribution coefficient of oxygen in lithium is low for most metals [27, 29]. Ti-based precipitates are therefore more likely to be carbides and nitrides than oxides after liquid lithium exposure.

The concentration of carbon, nitrogen, oxygen or hydrogen impurities increase the DBTT of vanadium from observation of bend tests [13]. The DBTT of vanadium is approximately -110°C [30]. Increasing the concentration of hydrogen from 0 to 0.05wt% induces the most rapid DBTT increase to approximately 125°C. Increasing oxygen or nitrogen content from 0wt% to 0.1wt% increases the DBTT to approximately -25°C. Finally, increasing carbon concentration by the same amount only increases DBTT to -75°C [13]. Nonmetallic elements cause embrittlement by diffusing into metals and sitting at vacancies or interstitials in the matrix, preventing matrix atoms from moving as freely when stress is applied [27]. Lighter elements (i.e. hydrogen) can diffuse into much smaller spaces (such as interstitials) and so have a greater impact on ductility. These results are valuable in determining impurity embrittlement in vanadium alloys, and are especially relevant in a lithium environment where nonmetallic impurity transfer is common [13, 27]. Hydrogen embrittlement is of particular interest given how fusion neutrons transmute helium and hydrogen in materials, and breed tritium in lithium [31].

Yttrium addition of 0.2wt% reduces the number of precipitates under irradiation and controls impurity levels by means of the scavenging effect [32, 33, 34]. After 2.4 MeV copper ion irradiation, it was found this effect reduced oxygen concentration in the alloy below 7.5 dpa, but not at 12 dpa. Subsequently, the growth of Ti-rich precipitates in vanadium alloys was suppressed for doses below 12 dpa, but the number density of the precipitates

was only reduced for doses below 7.5 dpa [33]. The control of oxygen pickup by yttrium therefore appears to only be effective for reducing the number density rather than size of the precipitates. No explanation for the ineffectiveness of controlling oxygen pickup at higher irradiation doses was offered, however this could be related to a higher rate of radiation enhanced diffusion (RED) for oxygen at higher doses [35]. Yttrium addition was also ineffective at controlling oxygen pickup at 300°C compared to 600°C after neutron irradiation to 0.45 dpa [33]. This result is likely related to the difference in alloy microstructure at low temperatures, where dislocations rather than precipitates are the dominant feature. However no explanation has yet been proposed. As well as affecting the Ti-rich precipitates in the alloy, yttrium addition of 0.3wt% has led to the observation of yttrium oxide precipitates with STEM-EDX [32].

Vanadium-base precipitates are rare in the V-4Cr-4Ti alloy, but can be formed in alloys with high levels of impurities such as Cl, Ca and Li [19]. A more recent study by Peng et al. [32] on V-4Cr-4Ti annealed at 1150°C observed precipitates on grain boundaries with enrichment of oxygen, nitrogen and carbon but not titanium or chromium, and so considered these to be V(C,O,N) compounds. Similar vanadium-base precipitates were imaged after Fe¹⁰⁺ ion at the Chinese Academy of Science, but these were randomly distributed in the alloy [36]. Precipitation of vanadium carbides or oxides has also been observed in unalloyed vanadium after neutron irradiation at the FFTF, as there was no titanium present to form Ti-based precipitates [25].

2.3. Thermal properties

The maximum temperature range for the structural materials in fusion blanket designs is 500-700°C [3]. The materials are likely to be continually exposed to such temperatures over the lifetime of the component, so good high-temperature thermal properties are key to maximising the material lifetimes. The thermal conductivity of V-Cr-Ti alloys is higher than ferritic or austenitic stainless steels [37]. The thermal expansion coefficient of V-4Cr-4Ti is approximately $10.3 \times 10^{-6} \text{ K}^{-1}$: superior to that of 316SS ($18 \times 10^{-6} \text{ K}^{-1}$) and ODS Eurofer-97 ($11.9 \times 10^{-6} \text{ K}^{-1}$) [1]. These are significant as they will reduce the thermal stress on the alloy when heated, which should extend the lifetime of the material and the associated reactor component [13]. Available data shows the lower operating temperature limit for V-4Cr-4Ti due to

low temperature hardening embrittlement is around 400-450°C [10, 38]. This is a disadvantage, as this is higher than the low-temperature limit for most ferritic/martensitic and austenitic structural candidate steels [39]. Multiple ITER blanket designs involve the use of liquid breeders at temperatures below 400°C, which may exclude V-4Cr-4Ti as a candidate [3]. The high-temperature limit of V-4Cr-4Ti is around 600-650°C, which is higher than the respective limits of most ferritic/martensitic and austenitic steels [3, 39]. This is because high-temperature limits are generally enforced by thermal creep effects for candidate structural alloys [39]. The performance of V-4Cr-4Ti at high temperatures compared to RAFM steels makes the alloy an ideal candidate for blanket designs involving temperatures of 600-700°C.

3. Effects of irradiation

3.1. Microstructural properties

3.1.1. Neutron irradiation

The Ti(CNO) precipitates formed in vanadium alloys after annealing have been observed to coarsen under irradiation [19, 25, 28]. Under neutron irradiation, N and O atoms can replace C atoms in these precipitates due to radiation-induced segregation (RIS) [33]. Fast neutron irradiation in both the Dynamic Helium Charging Experiment (DHCE) and the HFIR has also been observed to form TiO precipitates at 420-600°C [22, 25]. The TiO precipitates initially suppress swelling at low irradiation in V-4Cr-4Ti by acting as a sink for defects in alloys, and they coarsen as irradiation continues [25, 32]. The suppression of irradiation swelling is attributed to a large interface area between the matrix and the precipitates which can act as a sink for vacancies, transmutant gas and dislocations [19, 21]. Future research into the chemistry of Ti(CNO) precipitates under fusion radiation and lithium exposure is necessary to understand the mechanism of nonmetallic impurities into and out of the alloy. Under both radiation and lithium exposure, the presence of TiO precipitates observed by Fukumoto et al. [22, 25] due to RIS of O atoms [33] could directly oppose the diffusion of O atoms from the alloy to the lithium reported by Natesan et al. [27]. Characterising the structure of these precipitates before and after exposure to these environments would help to offer an explanation of this process.

The inclusion of 500-1000 wppm silicon also suppresses irradiation swelling in V-4Cr-4Ti as the precipitation of titanium silicide (Ti_5Si_3) occurs un-

der neutron irradiation [19, 20, 26]. This effect is responsible for increased swelling resistance in Si-containing V-4Cr-4Ti at 520-600°C. The dense formation of dislocation loops under neutron irradiation is responsible for swelling resistance below 420°C, as Ti_5Si_3 precipitates are negligible [26]. By trapping transmuted helium, the precipitates can suppress grain boundary embrittlement [32]. They are stable under irradiation at 420-600°C [19]. In silicon-containing ternary alloys, titanium oxide precipitates and coarsens as the irradiation continues. Subsequently, Ti_5Si_3 precipitates develop and grow slowly, taking over the role of cavity suppression as radiation continues [25].

Fusion neutrons are expected to generate helium bubbles on grain boundaries in V-4Cr-4Ti, blocking the movement of dislocations and leading to embrittlement [28]. This effect is of serious concern if the alloy is employed in a fusion reactor, and it limits the upper operating temperature of the material [40]. Helium embrittlement is more significant at higher temperatures because its mobility is high enough that it can be transported to grain boundaries, causing grain boundary embrittlement [40]. To investigate the effect, neutron irradiation of V-4Cr-4Ti has been performed in the FFTF at 420, 520 and 600 °C from 18 to 31 dpa using the DHCE [19, 41, 28]. The DHCE simulates a fusion-relevant helium-to-dpa ratio by immersing a tritium-doped vanadium-alloy in controlled quantities of enriched lithium [19]. Helium is generated from tritium decay and transmutation of the lithium by reactor neutrons. Without the availability of an ideal fusion neutron source to test materials, experiments such as the DHCE are critical to understanding the effects of helium embrittlement. Another approach to simulating fusion gas production is the ‘tritium-trick’, where tritium gas is admitted to the specimen container and left to decay into helium and diffuse from interstitial sites to grain boundaries [40]. It should be noted that the concentration of helium bubbles generated in the tritium-trick experiment is more significant than in the DHCE: helium bubbles are observed continuously at all grain boundaries and in a higher number density [28]. This is generally regarded as an overestimate of the helium content which would actually be induced by fusion neutrons.

DHCE irradiation of V-4Cr-4Ti to ≈ 18 dpa at 500-600°C with a helium generation of ≈ 0.4 -4.2 appm He/dpa produced a limited number of voids and He-bubbles in the interface between the grain and the Ti(CNO) precipitates, and no voids or bubbles elsewhere in the matrix. Both Ti(CNO) and

radiation-induced ultrafine Ti_5Si_3 precipitates were observed after this irradiation. This indicated that the dynamically produced helium atoms were trapped in the matrix without bubble growth occurring. Helium bubbles were negligible in specimens irradiated to 18 dpa at 425°C [28]. DHCE specimens of V-4Cr-4Ti irradiated to 31 dpa at 425°C (He generation 0.4-0.73 appm He/dpa) contained He-bubbles of ≈ 5 nm diameter evenly distributed primarily in the grain matrix, with some bubbles on grain boundaries. Microvoids were also observed. Coalescence of bubbles was prevented as most of the bubbles were trapped in the grain matrix, possibly by the precipitates. This contrasted with alloys irradiated in tritium-trick experiments, which displayed coalescence of He-bubbles on all grain boundaries [26, 41]. Ultrafine Ti_5Si_3 precipitates were not observed at this temperature and irradiation [28]. Irradiation-induced density changes for DHCE and non-DHCE specimens of V-4Cr-4Ti were low, and therefore consistent with the negligible number density of voids or He-bubbles observed. Density change after irradiation was slightly higher for DHCE specimens irradiated at 425°C compared to other temperatures [19, 41]. In unalloyed vanadium, a limited number of high-density He-bubbles were observed uniformly in the grain matrix and at grain boundaries after irradiation in the DHCE at 425°C to approximately 31 dpa [19].

Further FFTF-DHCE neutron irradiation experiments have been performed at 420, 520, 600°C from 15 to 27 dpa [25]. Dislocation density in V-4Cr-4Ti was higher than in pure vanadium, V-5Ti, and V-3Ti-1Si after the irradiation [25]. No cavities were observed in V-4Cr-4Ti in this study and the high density of precipitates observed were concluded to be titanium oxides (Ti_2O or TiO). These precipitates grew in size and density with an increase in irradiation temperature. Ti_5Si_3 precipitates were only observed in V-3Ti-1Si irradiated at 600°C , but cavity suppression was still observed in V-4Cr-4Ti after irradiation. It was concluded that both types of precipitates act as a sink for point defects and suppress cavity formation/swelling. In vanadium alloys containing silicon, titanium oxide precipitates appear to suppress cavity formation in the early stages of irradiation before titanium silicide precipitates take over in the latter stages [25].

Small dislocation loops are formed in V-4Cr-4Ti under low-temperature neutron irradiation to 0.1-0.5 dpa below 300°C , and Ti-rich precipitates are only observed at temperatures above 300°C . As temperature increases, dislo-

cation loop density decreases and the precipitates form, which reduces irradiation hardening outside the low-temperature regime [12]. Neutron irradiation in the Experimental Breeder Reactor (EBR-II) X530 experiment to 4.5 dpa at approximately 400°C produced fine Ti-rich precipitates and no significant density of dislocation loops or network dislocations [42]. This corroborated other low-temperature neutron irradiation results [12]. Diffraction analysis of the precipitates was inconclusive in determining their structures [42]. Further fast neutron irradiation to ≈ 4 dpa at 390°C in the EBR-II X530 experiment resulted in the formation of point-defect clusters and dislocation loops, which can be seen in figure 4(c). Cleared dislocation channels were also identified in samples irradiated at 200-400°C after deformation with a nanoindenter [12, 43, 44]. Dislocation channelling is common in BCC and FCC metals irradiated at low temperatures, as the defects produced are more easily annihilated by dislocations during deformation than defects produced at high temperatures [12]. This is a driving force of radiation embrittlement, as the channels localise strain in the material [43].

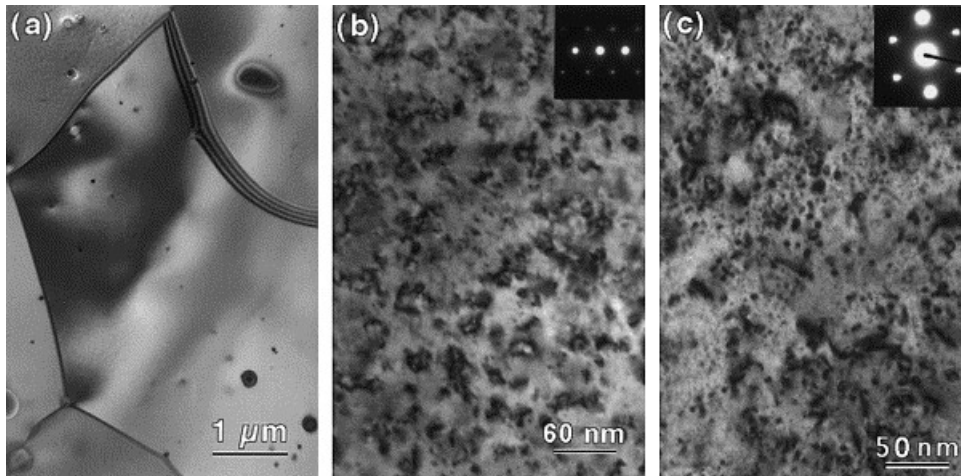


Figure 4: Microstructure of V-4Cr-4Ti after (a) annealing for 1 hour at 1050°C, (b) 4.5 MeV Ni^{2+} ion irradiation to 5 dpa at 350°C, and (c) neutron irradiation to 4 dpa at 390°C [43].

The HFIR was used as part of the JUPITER-II project to irradiate vanadium alloys to 3.7 dpa in lithium-filled capsules at 425 and 598°C. The study found that the primary sources of irradiation hardening are voids in V-Cr-Ti

alloys with Ti wt% <1 , and precipitates otherwise [22]. Whilst ductility of the alloy is not an issue at intermediate temperatures, it is important to remember that the coarsening of the precipitates at high temperatures can provide brittle fracture initiation points [24]. V-4Cr-4Ti and V-4Cr-4Ti with additions of 0.1Si-0.1Al-0.1Y and 0.1Si-0.1Al-0.3Y were irradiated in capsules at JOYO (Japanese sodium-cooled fast reactor) to 1.7 and 7.4 dpa at 450°C. The results indicated that yttrium controls the impurity levels in the alloy through the scavenging effect, however no microstructural characterisation was performed [34]. Another irradiation experiment at 400-600°C showed that Y-doping suppresses the growth of radiation-induced Ti(CNO) precipitates in the reference alloy [33]. This would reduce the radiation-induced hardening caused by larger precipitates [24].

Table 1 shows a summary of the features induced in V-4Cr-4Ti by neutron irradiation. Point defects including dislocation loops were observed in all experiments. At low temperatures ($<350^\circ\text{C}$), dislocation loops are the dominant feature which affect mechanical properties. Above this temperature regime, Ti-rich precipitates are induced by neutron irradiation and the density of dislocation loops decreases [12, 44]. These precipitates are generally identified as Ti(O), Ti₂O or Ti₅Si₃ by diffraction analysis, but efforts to precisely identify the Ti(CNO) precipitates has been inconclusive [42]. The dislocation loops formed at low temperatures undergo loop unfauling around 300°C, allowing them to move and form dislocation complexes which act as sinks [44]. Rice et al. [44] observed such defect clusters enriched in Ti after 0.1-0.5 dpa neutron irradiation at $\approx 400\text{-}500^\circ\text{C}$, and theorised that these were precursors to the Ti-rich precipitates present after higher-dose irradiation. The mechanism behind the formation of these Ti-rich precipitates is not fully understood, but increasing temperature is a driving force: they are formed by thermal annealing or high-temperature irradiation. The increased mobility and interaction of dislocations due to higher temperatures or RED from high-dose irradiation may explain their formation. The final column of table 1 shows that voids and He-bubbles have not been observed outside of DHCE experiments, and are only significant at high irradiation levels. This means that helium charging is required to induce these effects at lower levels of neutron irradiation damage. Irradiation experiments using higher doses of fusion neutron irradiation are required to establish the dose at which He-bubbles can be induced without the support of helium-charging.

Table 1: Summary of microstructural features induced in V-4Cr-4Ti by neutron irradiation experiments.

Irradiation temperature	Test reactor	Peak dpa	Dislocation loops	Precipitates	Voids/He-bubbles
420°C [26]	FFTF	18-31	✓	-	-
500-600°C [26]	FFTF	18-31	✓	Ti ₅ Si ₃	-
425°C [26]	FFTF (DHCE)	18-31	✓	-	✓*
500-600°C [26]	FFTF (DHCE)	18-31	✓	Ti ₅ Si ₃	✓**
430-600°C [25]	FFTF (DHCE)	15-27	✓	Ti(O)/Ti ₂ O	-
110-275°C [44]	HFBR	0.1-0.5	✓	-	-
390-410°C [44]	HFBR	0.1-0.5	✓	Ti-rich defect clusters	-
390-400°C [42, 43]	EBR-II (X530)	4-4.5	✓	Ti(CNO)	-
425-598°C [22]	HFIR	3.7	✓	TiO	-
400-600°C [33]	JMTR	0.45	✓	Ti(CNO)	-

* Only after 31 dpa

* Limited helium atoms trapped in the grain matrix without bubble nucleation

3.1.2. Ion irradiation

Ion irradiation provides a surrogate for neutron irradiation in lieu of a test reactor. The main advantage of this technique is the higher level of damage

caused by ions in a shorter space of time, which provides the opportunity for thorough materials tests at lower costs relative to a neutron test reactor campaign. Lifetime damage rates to reactor materials can be achieved in much shorter timescales [45]. However, ion irradiation damage produces a physically different damage cascade to neutron irradiation damage: the average energy of the primary knock-on atoms (PKAs) is lower, and the energy range of these PKAs is broader. These differences affect the formation of defects in the material [7, 45].

One of the earliest ion beam experiments on V-4Cr-4Ti was performed using the Argonne Tandem Accelerator: single ion irradiation using 4.5 MeV Ni^{2+} and dual ion beam irradiation using 350 keV He^+ with 4.5 MeV Ni^{2+} [43]. Uniform formation of high densities of point-defect clusters and dislocation loops were observed after both irradiation experiments [43]. Figure 4 shows the microstructure after the 4.5 MeV Ni^{2+} irradiation compared to an unirradiated sample and a neutron-irradiated sample. Both ion irradiation methods caused the formation of dislocation loops and point-defect clusters. Slip dislocation channels propagating through the matrix were observed in samples plastically deformed by nanoindentation after the ion irradiation. These channels were also observed in the neutron-irradiated samples deformed by Vickers indentation and tensile deformation [43]. The channels confine slip dislocations and therefore localise plastic strain: prompting an early onset of necking [43].

Irradiation of V-4Cr-4Ti with 550 keV Fe^{10+} ions at 500°C produced voids and dislocation loops. Randomly-oriented vanadium carbide (VC) precipitates were observed and confirmed by diffraction analysis, but the mechanism behind their formation was not explained [36]. 2.4 MeV copper ion irradiation in a vacuum at 600°C has also been performed on V-4Cr-4Ti and Y-doped V-4Cr-4Ti alloys [33]. The microstructure of the irradiated alloy is again controlled by Ti(CNO) precipitates. Yttrium addition suppresses the growth of Ti(CNO) precipitates at lower doses (<4 dpa), but not at higher doses (12 dpa). It also increases precipitate number density at doses <8 dpa, but not at 12 dpa [33]. Neutron irradiation on the same alloys to 0.45 dpa at 400-600°C also showed suppression of precipitate growth [33]. Further research into oxygen pickup and oxidation kinetic of V-4Cr-4Ti under high-dose irradiation is required to determine why irradiation suppresses precipitate growth.

80 keV He-ion irradiation and combined He + H ion irradiation (at 80 and 50 keV respectively) of the V-4Cr-4Ti alloy at room temperature and 300°C were performed to investigate hardness. At room temperature, vacancies and interstitials of high number density appear in the alloy. At 300°C, dislocation loops and bubbles are dominant. No microstructural differences were observed between the two irradiation methods [46]. This was likely due to the limited damage caused by low-energy hydrogen ions relative to the helium ions.

Table 2: Summary of microstructural features induced in V-4Cr-4Ti by ion irradiation experiments.

Irradiation temperature	Ions	Peak dpa	Dislocation loops	Precipitates	Voids/He-bubbles
200-420°C [43]	4.5 MeV Ni ²⁺	0.5-5	✓	-	-
200-420°C [43]	4.5 MeV Ni ²⁺ + 350 keV He ⁺	0.5-5	✓	-	-
600°C [33]	2.4 MeV Cu	0.75-12	✓	Ti(CNO)	-
500°C [36]	550 keV Fe ¹⁰⁺	20	✓	VC	✓
20°C [46]	80 keV He	0.75-12	✓	-	-
20°C [46]	80 keV He + 50 keV H	0.75-12	✓	-	-
300°C [46]	80 keV He	0.75-12	✓	-	✓
300°C [46]	80 keV He + 50 keV H	0.75-12	✓	-	✓

Table 2 shows the features induced by different ion irradiations on V-4Cr-4Ti. As with neutron irradiation, point defects including dislocation loops were observed in all experiments. The positive correlation between the development of precipitates as the dominant microstructure and increased

irradiation temperature also seems to hold true: irradiation-induced precipitates were only observed after irradiation at temperatures above 400°C. Voids were present after He-ion irradiation at 300°C, but not after irradiation at room temperature. This indicates that the helium bubbles caused by ion implantation is only significant above room temperature. It also supports the conclusion from neutron-irradiation results that He-charging or He-ion irradiation are necessary to induce bubbles in the material. Further research into irradiation with higher neutron fluxes and higher neutron energies is needed to induce gas production without the need for He-charging or He-ions.

The results of heavy ion irradiation experiments at high doses [33, 36] also indicated that heavy ions are responsible for higher levels of damage in the material and possibly precipitate development, whereas helium ions are responsible for void/bubble formation. This would support the established theory that the neutron damage cascade can be understood as a summation of the resulting PKA cascades it induces, which include light and heavy ions of varying energies [6, 45]. Further research into He-ion irradiation at higher temperatures in combination with further heavy-ion irradiation (including self-ions) would help to explore these ideas further. This is key to improving ion-irradiation experiments, as if one understands the effects of different ions then one can design experiments which better simulate reactor environments. This will lead to more valuable experimental irradiation results.

Throughout the literature, levels of irradiation dose are generally compared using the dpa metric. Whilst it is useful for describing radiation dose to a material, dpa does not fully describe the microstructural effects induced by different particles: for instance, comparing light-ion damage to heavy-ion damage. Using the effects of different radiation methods is a much more accurate representation, but inconvenient. Computational methods to develop metrics which more accurately and conveniently capture the effects induced by different particles continue to be developed by IGCAR and UKAEA [6, 47].

3.2. Mechanical properties

3.2.1. Neutron irradiation

Fully characterising the mechanical performance of V-4Cr-4Ti after neutron irradiation is especially important to determine if structural components

could withstand a fusion radiation environment over a reactor lifetime. The ductility of V-4Cr-4Ti under irradiation is a strength of the alloy. Irradiation in the FFTF in a non-DHCE environment for 24-34 dpa at 420°C, 520°C and 600°C did not increase the DBTT of V-4Cr-4Ti above -196°C at any dose [19, 21]. After DHCE experiments with implantation of 0.3-4.2 appm helium/dpa, the DBTT only increased to -150°C [26]. In tritium-trick experiments [40], ductility at room temperature and at 700-800°C was lower than ductility at 500-600°C because of susceptibility to intergranular cracking from grain-boundary He-microcavity formation. By comparison, DHCE helium simulation at 23-600°C was not observed to affect tensile properties at any irradiation dose [19]. As tritium-trick experiments are known to induce a higher helium bubble concentration than DHCE experiments [28], this result is expected due to extra helium embrittlement. These results indicate that helium embrittlement under fusion neutrons should not impact the ductility of the alloy at these doses - however further mechanical testing after fusion neutron irradiation is necessary to observe He-bubble generation in this environment.

The properties of V-4Cr-4Ti at lower temperatures are of special interest. In multiple ITER blanket designs, blanket structural materials directly face molten lithium and lithium-lead flowing at temperatures between 300°C and 500°C [3]. The operating windows of structural materials must include this temperature range for them to be used in these designs. A key property of unirradiated V-4Cr-4Ti is the insensitivity of yield/tensile strength to temperatures of 300-700°C [20, 26]. However, neutron irradiation to 18-34 dpa at 425-600°C is reported to increase yield and tensile strength [26]. This effect is more exaggerated at lower temperatures due to the effect of low temperature hardening embrittlement (LTHE). LTHE in V-4Cr-4Ti is generally assumed to be driven by the dislocation channelling observed by Gazda et al. [43]. Tensile ductility of the alloy decreases as irradiation temperature decreases due to LTHE, although ductility still remains reasonable even at 420°C [19]. This is shown by the relationship between tensile elongation and irradiation temperature displayed in figure 5, which supports the continued use of V-4Cr-4Ti at operating temperatures of 400-600°C. The effect of LTHE is also present in vanadium alloys with higher Cr concentration, which is displayed in figure 2 [19]. The increase in ductility of the alloy with irradiation temperature has been corroborated by Fukumoto et al [22] with neutron irradiation experiments at 425°C and 598°C. These results also showed that irradiation

hardening in the higher-purity V-4Cr-4Ti alloy is lower compared to other V-Cr-Ti alloys and V-5Ti and V-5Cr alloys [22]. This is expected given how increased concentrations of Cr, Ti or nonmetallic impurities are reported to reduce the ductility of the alloy [13].

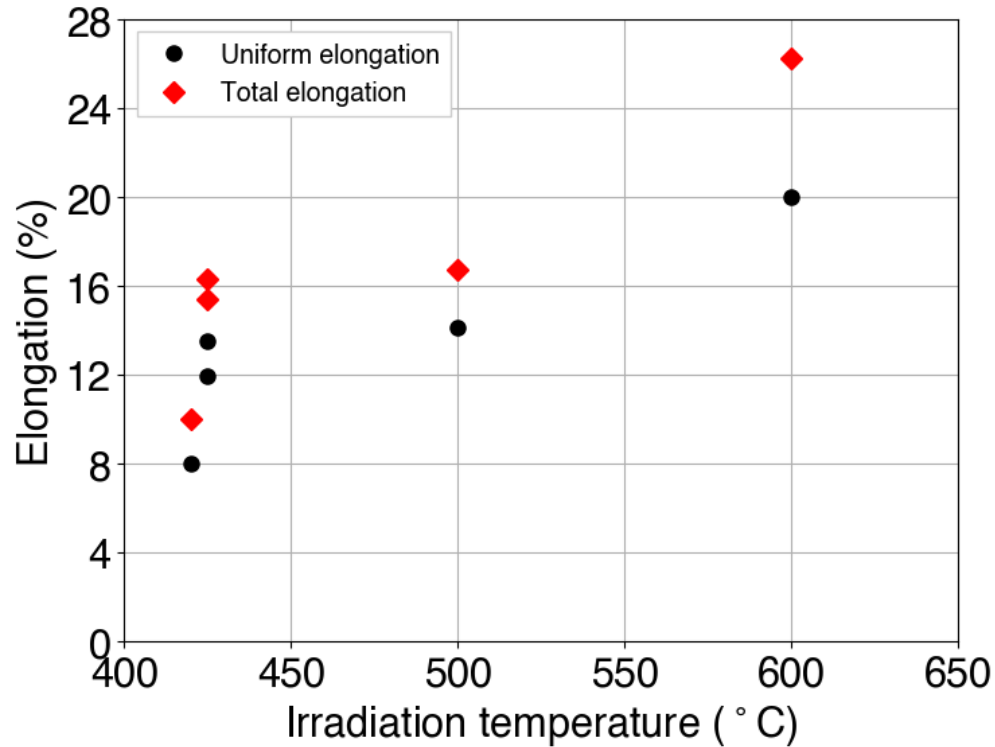


Figure 5: Uniform and total elongation for V-4Cr-4Ti after neutron irradiation at different temperatures. The data for 420°C was taken from Chung et al. (1996) [19]: samples were irradiated to 28-34 dpa. The data for 425-600°C was taken from Chung et al. (1995) [26]: samples were irradiated to 18-31 dpa in the DHCE. All tests were performed at room temperature.

Whilst ductility of the alloy remains at an acceptable level for 400-600°C, the results reported by Chung et al. [19, 26] do not show results for irradiation below 400°C. This low-temperature range is directly relevant to the temperature of the flowing breeder, however irradiation data at these low temperatures is limited [3, 12]. Alloy performance is severely affected at low temperatures: irradiation hardening has been observed in V-4Cr-4Ti after

neutron irradiation at as low as 0.1 dpa below 400°C [48]. Yield strength of V-(4-5)Cr-(4-5)Ti is also affected more strongly by irradiation at 100-330°C than irradiation at temperatures above 430°C due to dislocation channelling [12]. To investigate reduced alloy performance after neutron irradiation at low temperatures, heats of V-(4-5)Cr-(4-5)Ti alloys including V-4Cr-4Ti were irradiated in different test reactors at 200-500°C [38]. The ATR-A1 experiment involved testing capsules containing the alloy with high-purity lithium to a peak damage of 4.7 dpa at 200°C and 300°C. The Fusion-1 BOR-60 experiment placed samples in a lithium-bonded stainless steel capsule irradiated to 17-19 dpa at 320±20°C. The HFIR experiment used gas-bonded capsules irradiated to a peak damage of 6 dpa at 500°C. Low-temperature irradiation in the ATR-A1 led to a marked increase in the DBTT for V-4Cr-4Ti, rising from ≈-190°C to 50-200°C. The ductility of the alloys was also reduced to <1% (elongation). Yield strength and ultimate tensile strength of the alloys increased by a factor of approximately 3-4 under identical radiation damage in the ATR-A1 and BOR-60 Fusion-1 experiments at 200°C and ≈300°C respectively [38]. These results confirm that there is an increase in irradiation hardening in the alloy at low temperatures, and support the restriction of the operating temperature window to 400-600°C.

The effect of irradiation hardening appears to saturate at a dose of ≈5 dpa and an irradiation temperature of 330°C. Yield strength of V-4Cr-4Ti at these parameters is ≈900 MPa, and it decreases after irradiation to 18 dpa [12]. The irradiation hardening of V-4Cr-4Ti at 44-114 dpa was studied in the FFTF at 425°C, 520°C and 600°C. At each of these temperatures, V-Cr-(4-5)Ti alloys were found to undergo greater irradiation hardening at ≈40 dpa irradiation than at >50 dpa [19]. However all V-4Cr-4Ti yield strength values reported here were lower than yield strength values after 4-6 dpa irradiation at 250-350°C, which suggests that the maximum irradiation hardening due to dose is at ≈5 dpa [12]. This correlation between irradiation dose and yield strength also appears to hold true for temperatures inside the required ITER test blanket range, and is displayed in figure 6. As data at very high neutron irradiation doses is limited, this relationship is not yet fully explained. Further neutron irradiation data at doses above 5 dpa, and investigation into the behaviour of the precipitates at these doses, is required to explore this relationship further. In contrast, the total elongation of V-Cr-(4-5)Ti alloys decreases with dose up to ≈30 dpa but does not decrease after higher irradiation doses [19]. V-4Cr-4Ti shows the lowest levels of irradiation

swelling compared to other V-Cr-(4-5)Ti alloys at all temperatures, peaking at 30 dpa at 600°C and 35 dpa at 420°C [19]. This indicates that irradiation temperature is still a major factor affecting hardening at these high doses, and so should be well controlled in any investigation into the effect of dose on irradiation hardening.

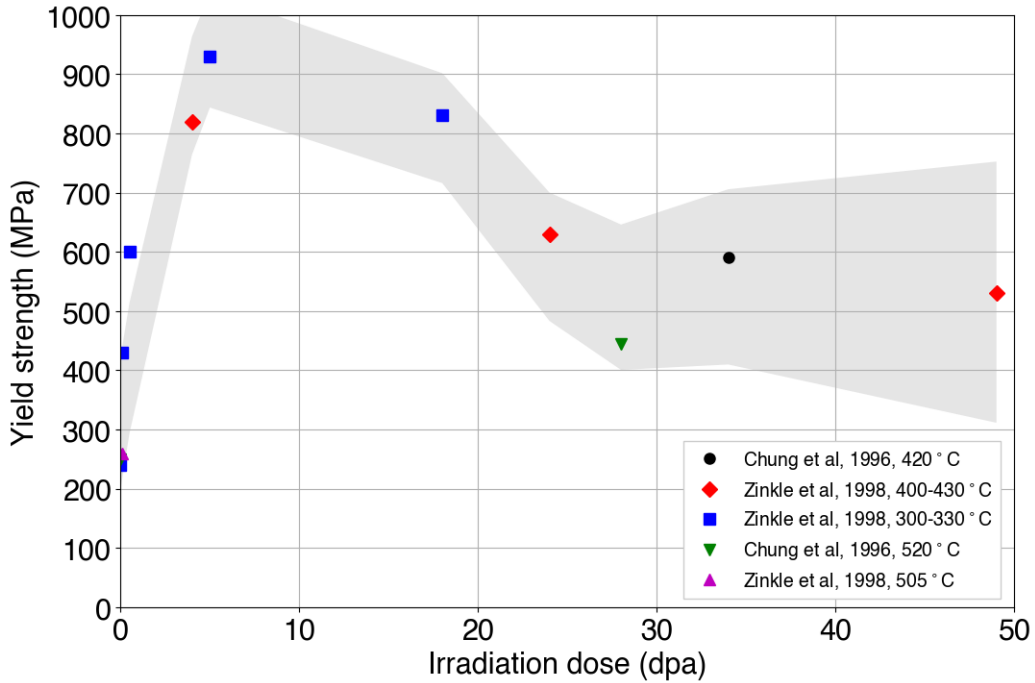


Figure 6: Yield strength of V-4Cr-4Ti for different neutron irradiation doses at irradiation temperatures comparable to ITER TBM liquid lithium working temperatures [12, 19].

This dependence of hardening on irradiation temperature at high doses has been reported after non-DHCE FFTF neutron irradiation experiments to 24-34 dpa [26]. The yield strength of the V-4Cr-4Ti alloy was measured as about 600 MPa at 420°C, about 450 MPa at 500°C and about 380 MPa at 600°C [26]. A similar temperature dependence was also observed for the ultimate tensile strength of the alloy after an identical irradiation. Separate results report an increase in the yield strength of the VM9401-heat V-4.3Cr-4.3Ti-0.12Si from 310 MPa to over 900 MPa after neutron irradiation to 3.5-4.3 dpa at 200-300°C [49].

Yttrium addition has been reported to improve alloy ductility after neutron irradiation [32]. Results from JOYO neutron-irradiation experiments showed that the addition of Si-Al-Y to V-4Cr-4Ti decreased yield strength from 625 to 530 MPa at 1.7 dpa, but had a negligible difference on yield stress at 7.4 dpa. The addition of 0.1Si-0.1Al-0.1Y to the alloy increased the ultimate tensile strength from 700 MPa to 730 MPa at 1.7 dpa [34]. This ineffectiveness at doses around 7 dpa is consistent with how yttrium addition fails to suppress the number density of Ti-based precipitates [33]. These results support the theory that precipitation behaviour is the driving force behind irradiation hardening.

Neutron irradiation of two different V-4Cr-4Ti samples in HFIR at 425°C has been performed to examine the effect of annealing on irradiation hardening [22]. One sample was annealed at 950°C and the other at 1000°C. The DBTT of the irradiated samples were -150°C and -80°C for annealing at 950°C and 1000°C respectively. This is likely because increasing annealing temperature increases the size of the Ti-based precipitates [24], which has been reported by Sakai et al. [23] to increase the DBTT of vanadium alloys through brittle fracture initiation. Annealing at 1100°C has also been shown to increase the Charpy DBTT of V-4Cr-4Ti from approximately -196°C to near room temperature, supporting this correlation [25].

3.2.2. Ion irradiation

Nanoindentation has been used to measure hardness in the V-4Cr-4Ti alloy after irradiation at room temperature and 300°C. Alloy hardness was greater after He + H irradiation than after solely He-ion irradiation. Macroscopic hardness, calculated by excluding indentation size effect (ISE), was measured to be higher at room temperature than at 300°C as the migration of point defects is slower and they are not absorbed by any bubbles formed under irradiation [46]. This is consistent with the low-temperature hardening embrittlement model developed from characterising irradiation hardness after neutron irradiation. 2 MeV He-ion irradiation to 0.5 dpa at 500°C and 700°C of 15 different types of V-(4-8)Cr-(0-4)Ti alloys has been performed to investigate the effects of Cr and Ti addition. Irradiation hardening was observed in all the alloys at both temperatures, and was greatest in the V-4Cr-1Ti alloy at 500°C [50]. The explanation provided for this was the higher density of small Ti(CON) precipitates formed in the alloy, which disturb defect diffusion more than coarser, more sparse precipitates formed at higher

temperatures and higher concentrations of Ti [22, 24]. This corroborates the established relationship between hardening and irradiation temperature.

The data collected after He and H ion irradiation experiments shows that irradiation hardening is induced by all types of irradiation, and is not exclusive to neutrons. Further comparison of mechanical testing data after neutron and ion irradiation would be beneficial to determine how well different ions mimic neutron damage in the alloy. Comparing the effects of self-ions, He and H ions, and fusion neutrons of appropriate energies taken from PKA cascade analysis would provide valuable data on how PKAs affect materials on a larger scale [6].

4. Effects of relevant environments

4.1. Liquid lithium environment

Interaction between liquid alkali metals and structural metals leads to embrittlement, mechanical degradation, liquid-metal penetration and corrosion [27]. Nonmetallic element transfer between liquid lithium and structural metals depends on the distribution coefficient of the nonmetallic elements. A large solid-metal/liquid-metal distribution coefficient increases the probability of impurities diffusing into the solid metal from the liquid metal. This results in embrittlement from increased interstitial concentration and compound formation. A low coefficient results in reduced mechanical strength as interstitials escape, and grain-boundary penetration by the liquid metal [27]. Whilst good corrosion resistance of different vanadium alloys has been measured, redistribution of nonmetallic elements between unalloyed vanadium and a lithium environment has also been observed [13, 27]. Specifically, the loss of oxygen from unalloyed vanadium to lithium due to the low solid/liquid distribution coefficient of oxygen and the pickup of nitrogen and carbon [27]. The scavenging effect of lithium for oxygen can lead to grain-boundary penetration by lithium as the oxides at the grain boundaries are not stable. Structural metals are expected to carburise in a liquid lithium environment due to high carbon activity in lithium, and nitridation has also been observed due to high solubility of nitrogen in lithium [27].

The exchange of oxygen with carbon and nitrogen has been observed minimally in V-4Cr-4Ti after lithium exposure at 700°C [29]. Continued removal

of oxygen could result in the loss of high-temperature strength, and continued pickup of N and C could cause embrittlement from increasing impurity concentration at interstitials [27, 29]. Lithium exposure has been observed to increase the strength and decrease the ductility of V-4Cr-4Ti when interstitial impurity concentration was increased - implying the increase in C and N is the dominant mechanism. Depletion of oxygen in V-4Cr-4Ti did not occur after significant nitrogen pickup from lithium at 700°C and 800°C, supporting this conclusion [29]. A separate experiment exposing V-4Cr-4Ti to 2–3 cm/s flowing lithium at a maximum of 700°C for 2355 hours also showed an increase in hardness and decrease in ductility consistent with uptake of N and C from the lithium [51]. Evidence of matrix interstitial solute scavenging by precipitates was observed; and after lithium exposure at 700°C, plate-shaped Ti(CNO) precipitates were observed in the matrix and globular precipitates were observed at grain boundaries. After lithium exposure at 800°C, globular precipitates at grain boundaries were observed [29]. These precipitates have the same composition as the Ti-rich precipitates observed in the annealed alloy, which have been observed to change under neutron irradiation due to radiation-induced segregation [33]. Further research into the combined effects of radiation and lithium environment on these precipitates and nonmetallic-element redistribution in V-4Cr-4Ti is necessary, as the mechanisms for both are not well understood. Understanding these mechanisms is key to evaluating the irradiation hardening and swelling performance of V-4Cr-4Ti in a fusion breeder blanket environment, as they control these mechanical effects.

Immersion of V-4Cr-4Ti in static lithium at 650°C for 248 hours also resulted in the strengthening of V-4Cr-4Ti alloys [52]. Precipitation hardening from C and N therefore likely contributed more than the decrease in solid solution hardening due to oxygen loss from the alloy. In contrast, pure vanadium was softened by the exposure as the loss of oxygen is the dominant mechanism [52]. Titanium has been separately observed to trap nitrogen in V-4Cr-4Ti from a lithium environment, causing hardening in the alloy and TiN precipitates to form [10]. This corroborates the previous results and provides a possible explanation for why V-Cr-Ti alloys strengthen and pure vanadium hardens after lithium exposure.

4.2. Other environments

In a fusion reactor, V-4Cr-4Ti may also be exposed to common coolants for nuclear reactors (such as pressurised water, helium gas) or air. Research into alloy properties after exposure to different levels of oxygen pressure has been carried out to explore if vanadium alloys are usable in a helium transport system (where very low oxygen pressures are impossible) [13]. Exposure of V-4Cr-4Ti to low-pressure oxygen at 10^{-2} - 10^{-4} Pa at 400-500°C resulted in low penetration of oxygen into the alloy after 10-25 hours [53]. The rate of uptake was higher when tested in air at 1 atm [53]. Exposure led to a reduction in tensile ductility, as one would expect from an increase in interstitial impurities [27]. Use of vanadium alloys in a helium-cooled system therefore seems unrealistic due to excessive oxidation occurring and causing embrittlement [13]. Vanadium also reacts with air and oxygen at elevated temperatures, and so should be protected from air exposure inside a reactor [13]. Under pressurised water environments, vanadium alloys were initially found to exhibit excessive corrosion [13]. More recent research has shown that the addition of chromium reduces the corrosion rate of vanadium alloy in pressurised water [54]. However these results generally indicate that vanadium alloys are not best suited for coolant transport. Future reactor designs could incorporate this by using vanadium alloys for breeder-facing components, and using other structural candidates for coolant-facing components.

The permeation of hydrogen isotopes into vanadium is high compared to austenitic and ferritic steels, potentially due to the higher lattice parameter of vanadium relative to iron [13, 55]. This is undesirable as one objective of a breeder blanket is to maximise the retention of tritium so it can be extracted for fuel. Therefore tritium permeation into a structural blanket material should be as low as possible. This is a major issue with the vanadium and molten salt LiF-BeF₂ blanket design, where tritium solubility is high [15]. It is of less concern in a liquid lithium blanket, however further research into the diffusion of tritium under fusion radiation is critical to maximising tritium output from a blanket. Titanium in V-4Cr-4Ti has not been observed to trap hydrogen and form hydride precipitates, so hydrogen permeation is unlikely to affect embrittlement in the same way as C, N and O impurities. However, hydrogen embrittlement from hydrogen atoms diffusing into interstitials in the alloy could be a factor.

4.3. Magnetohydrodynamic effects

Magnetohydrodynamic (MHD) effects are a concern for the design of liquid-metal blankets in a magnetic confinement fusion reactor [15]. A flowing conducting liquid metal in a magnetic field will induce a Lorentz force, which causes a drop in pressure, and makes the pumping of the breeder fluid more energy intensive as the required pressure is not maintained [15, 56]. One possible solution is the formation of electrically insulating coatings on the inside of the structural alloy pipe to prevent MHD currents from passing through the materials and into the liquid metal. Calcium oxide was initially selected for experimentation as it is thermodynamically stable in liquid lithium, has a high electrical resistivity, and can form in-situ. The coating was formed by charging V-4Cr-4Ti with oxygen and exposing the alloy to lithium with 2.8at% calcium additions [57]. Initial research showed CaO coatings exhibited good electrical resistance during lithium exposure for 435°C for over 200 hours [12, 15]. Park’s study on CaO coatings also theorised that the CaO coating could act as a barrier to C and N impurities from a lithium environment to the alloy, which would be significant for preventing embrittlement [57]. However, CaO was later shown to have poor stability at high temperatures and Er_2O_3 was investigated as another candidate coating. Static tests were performed but flowing liquid lithium experiments are required to verify results, and these are challenging to design [15]. Combining a magnetic field with flowing lithium is critical to understanding how MHD effects change the required breeder pressure in a reactor environment. It is also necessary to determine how high-pressure flowing lithium affects materials compared to static lithium. This may impact the penetration of lithium into the alloy, or change the mechanical properties after impurity exchange.

5. Issues requiring further research

Further understanding of the effect of high-dose fusion neutron irradiation of all structural fusion materials including the V-4Cr-4Ti alloy is key. This will rely on the development of true fusion neutron test sources such as ITER [3] or IFMIF-DONES [58]. The further development of alternative methods such as ion-irradiation to better simulate the damage caused by fusion neutrons will also be necessary [6]. This could include the use of heavy ion and light ion irradiation to observe their effects independently, and correlate the results to the expected damage by neutron irradiation. However this requires careful analysis of the changes in microstructural and mechanical

properties after different types of irradiation, and it is difficult to normalise this for different structural materials.

For the V-4Cr-4Ti alloy specifically, further research is required to determine the high temperature limit. This should primarily test helium embrittlement and alloy strength under high radiation doses. Precisely determining the low temperature limit under high radiation dose is even more important, as this low-temperature range is more relevant to liquid-metal facing structural materials [10]. Research into the combined effects of liquid lithium immersion and fusion-relevant irradiation on the mechanical and microstructural properties of the alloy is of particular importance. Alloy embrittlement in this system is controlled by the mechanisms of nonmetallic impurities and precipitates, all of which are affected differently by irradiation and a lithium environment. A complete understanding of the formation and development of the Ti-rich precipitates in breeder blanket conditions is key, as these control irradiation hardening in the alloy. Understanding the effects of lithium and fusion neutrons is paramount to establishing how the alloy will evolve in a fusion power plant. Future experiments should include neutron irradiation with flowing lithium to determine how a fusion radiation environment will affect lithium-metal interactions, and whether ion-irradiation experiments can be used to emulate these effects [22, 25]. Another key area of research is the diffusion of light nonmetallic elements (such as oxygen and tritium) into structural alloys. This is only possible by designing experiments combining fusion radiation and lithium, to breed tritium and reproduce conditions inside a fusion breeder blanket.

6. Conclusions

Detailed research into the mechanical effects of V-4Cr-4Ti under test reactor neutron irradiation has been undertaken over the past few decades, showing that the ductility of V-4Cr-4Ti is minimally affected by irradiation and helium implantation under irradiation. The microstructural behaviour of the alloy under different neutron irradiation doses is also well documented, and the corrosion effects of interstitial impurities and lithium exposure have previously been studied. In the past few years, ion-irradiation experiments on the alloy have been carried out, with similar mechanical property results to neutron irradiation. Further comparison of the microstructural evolution of

the alloy under ion and neutron irradiation is needed to correlate ion damage to neutron damage. Further irradiation of V-4Cr-4Ti with heavy ions and light ions would be beneficial to understanding how the different PKAs induced by the fusion neutron spectrum damage the material. Developing more realistic fusion breeder-blanket experiments, and analysing the combined microstructural effects of lithium exposure and fusion neutron irradiation are essential for validating breeder blanket designs.

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