

预辐照对钨及钨-镍-铁合金中氘滞留与脱附行为的影响

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摘要 钨-镍-铁合金(W-Ni-Fe 合金)具有较好的耐高温性能,被认为是具有较大潜力的聚变堆结构材料,然而复杂服役环境下辐照缺陷对其氘滞留与脱附行为的影响机理尚不明确。本工作通过铁(Fe)离子预辐照 W-Ni-Fe 合金(97W-2Ni-1Fe)与纯钨(W),随后注入低能等离子体氘,模拟中子辐照产生的离位损伤对氘滞留和脱附行为的影响。实验采用正电子湮没谱学技术、热脱附质谱和电镜等方法表征样品中辐照产生空位缺陷的深度分布、缺陷结构类型及热脱附行为。结果表明,纯钨及 97W-2Ni-1Fe 合金中预辐照缺陷捕获大量氘形成氘-空位复合体和氘泡,氘捕获量随预辐照损伤程度而增大,但增加速率逐渐减小。相比于纯钨,97W-2Ni-1Fe 合金低剂量和高剂量预辐照情况下氘滞留量分别减少了 65.0% 和 55.8%。

关键词 重离子辐照, 氘滞留, 热脱附, 辐照损伤, 微观缺陷

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The effect of pre-irradiation on deuterium retention and desorption behavior in tungsten and tungsten alloys

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Abstract [Background] Tungsten (W) and tungsten alloys, such as 97W-2Ni-1Fe, are critical materials for nuclear fusion reactors due to their excellent thermal conductivity and high melting point. However, the performance of these materials can be significantly affected by irradiation-induced defects and deuterium (D) retention, which is crucial for maintaining material integrity and minimizing fuel retention in fusion environments. [Purpose] This study aims to investigate the influence of pre-irradiation defects on deuterium retention and desorption behavior in W and tungsten-nickel-iron (W-Ni-Fe) alloys. [Methods] Firstly, pure W and 97W-2Ni-1Fe alloy samples were irradiated with Fe^{13+} ions at doses of $5 \times 10^{14} \text{ Fe} \cdot \text{cm}^{-2}$ and $3 \times 10^{15} \text{ Fe} \cdot \text{cm}^{-2}$ using the heavy ion accelerator at Lanzhou University, and SRIM simulations were conducted to model the defect and Fe ion distribution in the samples. Subsequently, D plasma irradiation was performed at Hefei University of Technology for 1 h at a constant plasma flow of $4 \times 10^{16} \text{ D} \cdot \text{cm}^{-2}$ with 50 eV. Finally, the D retention and desorption behaviors were studied using Thermal Desorption Spectroscopy (TDS), Doppler-broadening Spectroscopy (DBS) of Positron Annihilation, Transmission Electron Microscopy (TEM), and Scanning Electron Microscopy (SEM). SRIM simulations were also conducted to model the defect and D atom distributions in the materials. [Results] Observational findings show that Fe^{13+} ion irradiation induces significant vacancy-type defects in both materials, with higher defect concentrations in pure W compared to the alloy. D retention is observed to be higher in pure W, with desorption occurring at approximately 250 °C and 700 °C. In contrast, the 97W-2Ni-1Fe alloy shows reduced D retention, with desorption peaks at 200 °C and 700 °C. The TDS results reveal that pure W retained 2~3 times more D than the alloy. Pre-irradiation with Fe^{13+} ions further enhances D retention, especially in pure W. TEM analysis results confirm the formation of D bubbles in the defect regions, especially under high-dose irradiation. Compared to pure tungsten, the deuterium retention of the 97W-2Ni-1Fe alloy decreases by 65.0% and 55.8% under low and high dose pre-irradiation conditions, respectively. [Conclusions] The 97W-2Ni-1Fe alloy demonstrates superior performance in minimizing D retention, with significantly lower D desorption and reduced bubble formation compared to pure W, hence is a more favorable material for applications where minimizing D retention and associated damage is critical, such as in fusion reactors. The results highlight the importance of material composition and defect structure in controlling D behavior under irradiation and plasma conditions, offering valuable insights into the design of next-generation plasma-facing materials.

Key words Heavy ion irradiation, Deuterium retention, Thermal desorption, Radiation damage, Microstructural defects

纯钨因其优异的热导率、耐高温和低溅射率等特性,被认为是理想的面向等离子体壁材料,然而,纯钨存在室温塑性差、脆性大等问题,很难直接应用于核聚变系统。相比于纯钨,钨重合金(W-Ni-Fe合金)不仅具有纯钨以上优点,还展现出较好的室温塑性和良好的抗辐照性能,有望成为聚变反应堆中纯钨的潜在替代材料^[1-2]。在托卡马克装置的偏滤器中,研究采用钨重合金替代纯钨进行热冲击实验,成功解决了纯钨板的开裂问题^[2-4]。尽管如此,钨重合金在服役环境中将承受高剂量的氘氚(DT)等离子体和高能中子的双重辐照^[5-8],要实现其商业化仍需经受其他考验。比如,高能中子不仅会造成直接离位损伤,还会与材料中的易活化靶原子发生核嬗变反应,从而引入大量的氢和氦气体原子,高浓度气体原子与级联碰撞产生的微观缺陷相互作用,导致材料起泡、肿胀^[9-10],影响其热传导性能和力学性

能^[11-14],威胁核能系统安全运行。

氘氚作为核聚变反应的重要燃料,减少其在钨合金等壁材料中的滞留是保证氘氚反应持续发生的重要因素,因此,研究氘氚等离子体与壁材料的相互作用、滞留/脱附行为具有重要意义。氘氚聚变会产生大量的高能中子(14.06 MeV)^[15-16],这些高能中子“轰击”偏滤器材料产生的大量辐照缺陷为氘氚滞留提供了重要场所^[17-20],这将严重影响聚变堆的氘氚自持反应。为探究以上氘氚滞留问题,实验中通常采用重离子预辐照和低能等离子体注入等方法在材料中诱导缺陷模拟中子辐照产生的微观缺陷捕获氘氚^[21-24],研究缺陷与氘氚的相互作用及辐照缺陷对氘氚滞留的影响。Wang等^[25]实验结果表明,重离子辐照可诱导产生大量的空位型缺陷,空位型缺陷加速氘向材料内部扩散,导致辐照后氘的滞留率显著提升。Zhang等^[26-27]发现铁离子预辐照缺陷会显著

增加氙在纯钨中的滞留量,而通过元素Re合金化(W-Re合金)能够明显降低氙的滞留量。纪富豪等^[28]通过使用重水充氙和热脱附实验研究了钨合金中氙的滞留行为,并建立了预测合金中氙滞留的扩散模型。尽管学者针对钨中氙滞留行为开展了大量的研究工作,但钨重合金中的预辐照缺陷对氙滞留行为影响机制尚不明确。本研究将通过正电子湮没谱学技术和热脱附质谱技术探究重离子辐照微观缺陷(空位、氙-空位复合体等)的形成与深度分布及氙的滞留行为,进而评估钨重合金抗辐照性能和氙滞留性能,为推进钨重合金的聚变堆商业化应用提供实验数据支撑。

1 实验材料及方法

实验采用纯钨(纯度为99.95%)和97W-2Ni-1Fe(质量百分比)合金为研究对象,实验材料购于厦门钨业。纯钨和97W-2Ni-1Fe合金首先线切割成5 mm(*l*)×5 mm(*w*)×1 mm(*h*)的片状方块,使用机械抛光和电化学抛光消除表面杂质。电化学抛光过程中,采用质量分数为2%的NaOH溶液作为电解液,并使用液氮维持低温。抛光电压设定为15 V,抛光时间为30 s,以确保去除表面杂质。在1 200 °C真空(10^{-6} Pa)退火炉中保温2 h,然后随炉缓慢冷却至室温,以消除应力。随后在室温条件下,采用能量为3.5 MeV Fe¹³⁺离子辐照纯钨和97W-2Ni-1Fe合金样品,引入辐照缺陷,吸收剂量分别为 5×10^{14} Fe·cm⁻²、 3×10^{15} Fe·cm⁻²,重离子辐照实验在中国科学院近代物理研究所重离子加速器上完成。为研究预辐照缺陷对氙的滞留与脱附的影响,重离子辐照后样品在室温下进行氙等离子注入,等离子体流强恒定为 4×10^{16} D·cm⁻²·s⁻¹,能量为50 eV,注入时间为1 h,氙离子累计注量为 1.4×10^{20} ions·cm⁻²($\Phi = J \times t$, Φ 为累计注量, J 为等离子体流强, t 为注入时间)。氙等离子注入后样品进行热脱附质谱(Thermal Desorption Spectroscopy, TDS)实验,脱附实验中温度以速率为1 °C·s⁻¹从室温(Room Temperature, RT)升高至1 260 °C且在高真空(10^{-8} Pa)环境下进行,脱附释放气体采用高分辨率四极杆质谱仪进行检测。

实验采用扫描电镜(Scanning Electron Microscopy, SEM, JEOL JSM 7200F)对未辐照样品、辐照后样品及热脱附后样品表面微观形貌进行分析。基于正电子对材料内开体积缺陷的灵敏性^[29],采用慢正电子束多普勒展宽谱学(Doppler-broadening Spectroscopy of Positron Annihilation, DBS)技术对样品内部缺陷浓度和缺陷类型进行表征。样品内部的辐照损伤(位错、位错环等)与氙在

材料内部的分布及演化行为通过透射电镜(Transmission Electron Microscopy, TEM, FEI Tecnai G2 F20)和TDS进行深入分析与研究。

2 结果与讨论

2.1 SRIM模拟结果

退火处理后的纯钨和97W-2Ni-1Fe合金在室温下进行铁离子辐照实验,并使用SRIM软件对铁离子在材料中的注入过程进行模拟。铁离子辐照引起的离位损伤和铁离子浓度分布随深度的变化如图1所示。纯钨和97W-2Ni-1Fe合金的损伤峰值深度均约为660 nm,当两组样品辐照剂量为 3×10^{15} Fe·cm⁻²时,对应的离位损伤分别为2.61 dpa(displacement per atom)和2.72 dpa,铁离子浓度的峰值大约在880 nm深度处。模拟结果表明,在相同能量和剂量的铁离子辐照下,粒子在两种材料中的入射深度和离位损伤程度无明显差异。

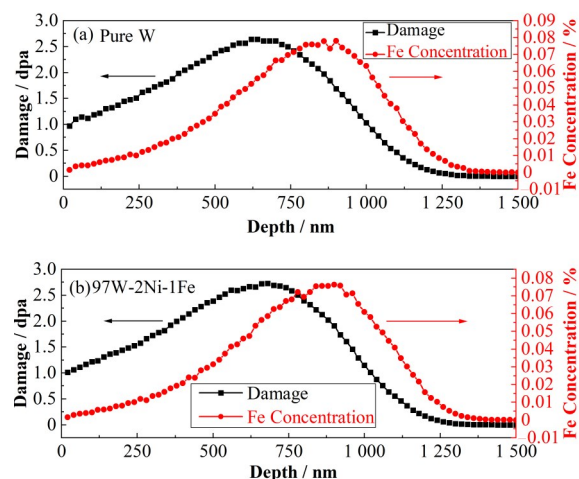


图1 SRIM模拟3.5 MeV铁离子辐照纯钨(a)和97W-2Ni-1Fe合金(b)的离位损伤分布和铁离子分布(彩图见网络版)

Fig.1 Displacement damage distribution and Fe ion distribution in pure W (a) and 97W-2Ni-1Fe alloy (b) under 3.5 MeV Fe ion irradiation simulated by SRIM software (color online)

2.2 SEM结果

图2和图3展示了不同辐照条件及热脱附处理后,纯钨与97W-2Ni-1Fe合金的表面微观形貌SEM表征结果。辐照前,两组样品表面平整,97W-2Ni-1Fe合金表面可见明显的Ni-Fe弥散相(图2(a)、(d))。经过低剂量铁离子(5×10^{14} ions·cm⁻²)预辐照处理后,纯钨表面出现肿胀(图2(b)),97W-2Ni-1Fe合金表面未见明显变化(图2(e))。高剂量铁离子(3×10^{15} ions·cm⁻²)预辐照条件下,纯钨和97W-2Ni-1Fe合金样品表面均观察到凹坑现象,但97W-2Ni-

1Fe合金中凹坑密度相对较低(图2(c)、(f)所示)。值得注意的是,未经过预辐照处理的纯钨与97W-2Ni-1Fe合金在氦等离子体注入后表面均出现起泡现象(图3(a)、(b)),这是因为低能等离子体(50 eV)克服表面吸附势垒(1.41~2.08 eV)^[30-32],通过自由扩散进入材料表层^[33],导致表面起泡,实验现象与Arshad等的研究结果一致^[27,34]。铁离子预辐照后氦等离子体注入使得纯钨表面出现不规则的凹坑(图3(b)、(c)),随着预辐照剂量的增加,纯钨表面不规则

凹坑的尺寸和密度均增大,而97W-2Ni-1Fe合金表面未见明显变化(图3(e)、(f))。高剂量铁离子辐照在材料表面形成了明显的损伤(图2(c)),氦等离子体注入加剧了表面损伤程度(图3(c)),该实验结果反映了铁离子辐照后能够在材料内形成大量辐照缺陷(如空位、空位团簇、位错和位错环等),这些缺陷为氦原子的扩散和聚集提供了大量通道和形核位点^[35],随着氦原子在缺陷处聚集成泡,最终破裂从而形成表面凹陷^[36]。

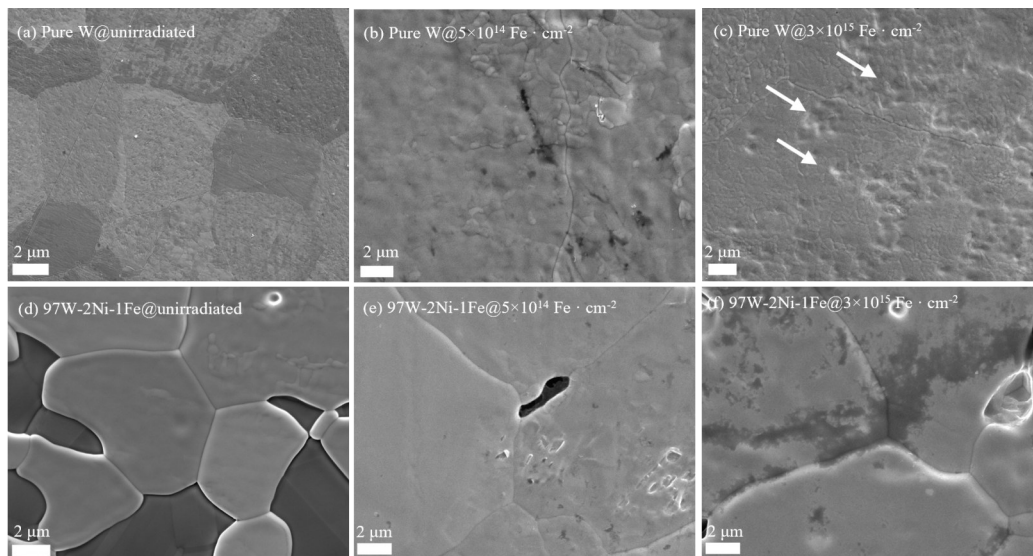


图2 纯钨和97W-2Ni-1Fe合金样品表面形貌SEM表征结果

(a) 纯钨未辐照样品表面形貌, (b) 纯钨低剂量($5 \times 10^{14} \text{ Fe} \cdot \text{cm}^{-2}$)铁离子辐照后样品表面形貌, (c) 纯钨高剂量($3 \times 10^{15} \text{ Fe} \cdot \text{cm}^{-2}$)铁离子辐照后样品表面形貌, (d) 97W-2Ni-1Fe合金未辐照样品表面形貌, (e) 97W-2Ni-1Fe合金样品低剂量($5 \times 10^{14} \text{ Fe} \cdot \text{cm}^{-2}$)铁离子辐照后样品表面形貌, (f) 97W-2Ni-1Fe合金样品高剂量($3 \times 10^{15} \text{ Fe} \cdot \text{cm}^{-2}$)铁离子辐照后样品表面形貌

Fig.2 SEM characterization of surface morphologies for pure tungsten and 97W-2Ni-1Fe alloy samples

(a) Surface morphology of unirradiated pure W, (b) Surface morphology of pure W after low-dose Fe ion irradiation ($5 \times 10^{14} \text{ Fe} \cdot \text{cm}^{-2}$), (c) Surface morphology of pure W after high-dose Fe ion irradiation ($3 \times 10^{15} \text{ Fe} \cdot \text{cm}^{-2}$), (d) Surface morphology of unirradiated 97W-2Ni-1Fe alloy, (e) Surface morphology of 97W-2Ni-1Fe alloy after low-dose Fe ion irradiation ($5 \times 10^{14} \text{ Fe} \cdot \text{cm}^{-2}$), (f) Surface morphology of 97W-2Ni-1Fe alloy after high-dose Fe ion irradiation ($3 \times 10^{15} \text{ Fe} \cdot \text{cm}^{-2}$)

2.3 正电子表征探测结果

为深入探讨铁离子预辐照样品中内部空位缺陷与氦相互作用及演化过程,实验进一步采用了正电子湮没谱学技术对辐照后样品内缺陷类型进行定性分析^[37],以揭示辐照诱导缺陷与氦相互作用机制以及氦滞留行为。慢正电子束流技术表征结果如图4所示,其中 S 参数反映正电子与低动量电子的湮灭过程,对空位型缺陷较为敏感;而 W 参数表示正电子与高动量电子(芯电子)的湮灭过程,可反映湮灭位点的化学环境。未辐照的纯钨和97W-2Ni-1Fe合金样品的 S - E 曲线随着正电子注入深度的增加迅速降低,最终趋于平稳,表明退火后样品中几乎无缺陷。铁离子辐照后纯钨和97W-2Ni-1Fe样品 S 参数相较于未辐照样品显著升高, W 参数降低,这是由于辐照诱导产生缺陷,导致正电子与低动量电子发生

湮没的概率增加^[38]。当铁离子辐照剂量从 $5 \times 10^{14} \text{ Fe} \cdot \text{cm}^{-2}$ 增加到 $3 \times 10^{15} \text{ Fe} \cdot \text{cm}^{-2}$,纯钨样品的 S 参数随着剂量而升高,而97W-2Ni-1Fe合金的 S 参数变化较小,表明97W-2Ni-1Fe合金样品中空位缺陷浓度随辐照剂量增加不明显。此外,通过对比相同辐照剂量条件下两组样品的 S 参数,发现纯钨样品的 S 参数较高,表明97W-2Ni-1Fe合金内产生的缺陷浓度低于纯钨。结合图4中 S - E 与 W - E 参数曲线结果,铁离子预辐照后注入氦等离子体,纯钨和97W-2Ni-1Fe合金的 S 参数均明显下降,同时 W 参数升高,这是由于缺陷捕获了氦原子,使正电子与高动量电子发生湮没概率增加,从而导致 W 参数升高^[39]。

为定性分析铁离子预辐照后氦等离子体注入对样品缺陷类型的影响,本文通过分析 S - W 参数,揭示不同辐照条件下样品内部缺陷的变化及其对氦滞留

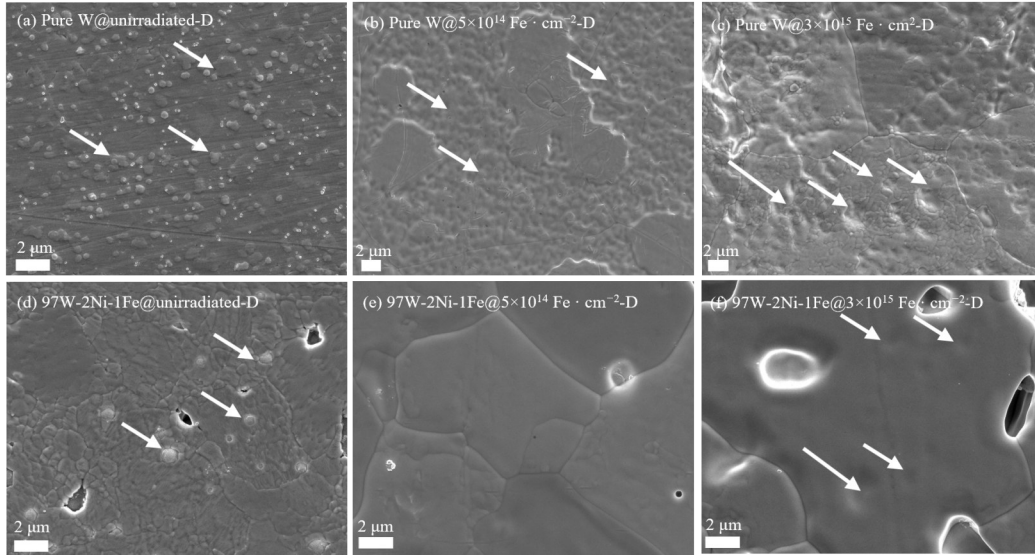


图3 纯钨和97W-2Ni-1Fe合金样品氘等离子体注入表面形貌SEM表征结果

(a) 纯钨氘等离子体注入样品表面形貌, (b) 纯钨低剂量($5 \times 10^{14} \text{ Fe} \cdot \text{cm}^{-2}$)辐照后再注入氘等离子体样品表面形貌, (c) 纯钨高剂量($3 \times 10^{15} \text{ Fe} \cdot \text{cm}^{-2}$)辐照后再注入氘等离子体样品表面形貌, (d) 97W-2Ni-1Fe合金氘等离子体注入样品表面形貌, (e) 97W-2Ni-1Fe合金样品低剂量($5 \times 10^{14} \text{ Fe} \cdot \text{cm}^{-2}$)辐照后再注入氘等离子体样品表面形貌, (f) 97W-2Ni-1Fe合金样品高剂量($3 \times 10^{15} \text{ Fe} \cdot \text{cm}^{-2}$)辐照后再注入氘等离子体样品表面形貌

Fig.3 SEM characterization of surface morphologies for pure tungsten and 97W-2Ni-1Fe alloy samples after deuterium plasma injection (a) Surface morphology of pure tungsten after deuterium plasma injection, (b) Surface morphology of pure tungsten after low-dose Fe ion irradiation ($5 \times 10^{14} \text{ Fe} \cdot \text{cm}^{-2}$) followed by deuterium plasma injection, (c) Surface morphology of pure tungsten after high-dose Fe ion irradiation ($3 \times 10^{15} \text{ Fe} \cdot \text{cm}^{-2}$) followed by deuterium plasma injection, (d) Surface morphology of 97W-2Ni-1Fe alloy after deuterium plasma injection, (e) Surface morphology of 97W-2Ni-1Fe alloy after low-dose Fe ion irradiation ($5 \times 10^{14} \text{ Fe} \cdot \text{cm}^{-2}$) followed by deuterium plasma injection, (f) Surface morphology of 97W-2Ni-1Fe alloy after high-dose Fe ion irradiation ($3 \times 10^{15} \text{ Fe} \cdot \text{cm}^{-2}$) followed by deuterium plasma injection

的影响。如图4(e)和(f)所示,未辐照的纯钨和97W-2Ni-1Fe合金的 S - W 参数曲线均呈一条直线,表明退火后两组样品中无缺陷^[40]。经过不同剂量的铁离子预辐照后,纯钨样品的 S - W 参数斜率发生了变化(图4(e)),表明材料内部缺陷类型由单一空位型缺陷转变为更大尺寸的空位团簇^[40]。纯钨样品在不同剂量铁离子预辐照后再注入氘等离子体, S - W 参数发生了变化,其中低剂量辐照下 S - W 曲线表现为 S 参数点的聚集,随着辐照剂量的增加, S - W 曲线出现转折(图4(e)中绿色与蓝色曲线),斜率发生变化,表明氘等离子体的注入使材料内微观缺陷类型发生改变,形成了氘-空位复合体($D_m V_n$)^[41-42]。与纯钨样品相比,97W-2Ni-1Fe合金的 S - W 曲线斜率变化较小(如图4(f)所示),氘等离子体注入后,97W-2Ni-1Fe合金的 S - W 参数点出现了聚集,但未发现明显斜率变化,表明97W-2Ni-1Fe合金样品中存在较为单一类型的缺陷如氘-空位复合体^[41-42],该结果说明97W-2Ni-1Fe合金对辐照缺陷的产生具有较好的抑制作用,减少了缺陷对氘的捕获和聚集行为。

2.4 透射电子显微镜结果分析

为揭示预辐照缺陷与氘原子相互作用机理,尤其是氘在缺陷周围聚集以及氘泡的形成过程,本研

究采用透射电子显微镜(Transmission Electron Microscope, TEM)对样品的微观结构进行直观表征。TEM表征结果如图5和图6所示,图5(a)、(b)为 $3 \times 10^{15} \text{ Fe} \cdot \text{cm}^{-2}$ 高剂量铁离子辐照样品表层区域(30~280 nm)的TEM表征结果,此区域与DBS探测深度一致。结果显示,该区域内观察到大量位错,辐照产生的位错导致此区域的电子密度降低^[43],正电子湮没结果中表现为 S 参数增加。图5(c)、(d)为高剂量铁离子预辐照后氘等离子体注入样品180 nm深度附近的TEM表征结果,可见少量氘泡形成,结合正电子探测表征结果,推测此处形成了 $D_m V_n$ 复合体。图6(a)和(b)展示了铁离子预辐照后两组样品在650~950 nm损伤峰区域的TEM结果,合金中辐照产生的位错环密度低于纯钨,表明该区域内97W-2Ni-1Fe合金的辐照缺陷浓度显著低于纯钨。图6(c)、(d)为氘等离子体辐照样品880 nm深度损伤峰附近的TEM结果,样品内存在氘泡并均匀分布(如箭头所示)。这一现象表明,辐照缺陷为氘原子的聚集提供了形核点,氘原子逐渐在缺陷处聚集并形成氘泡。

2.5 热脱附分析

为研究预辐照缺陷对氘脱附行为的影响,实验

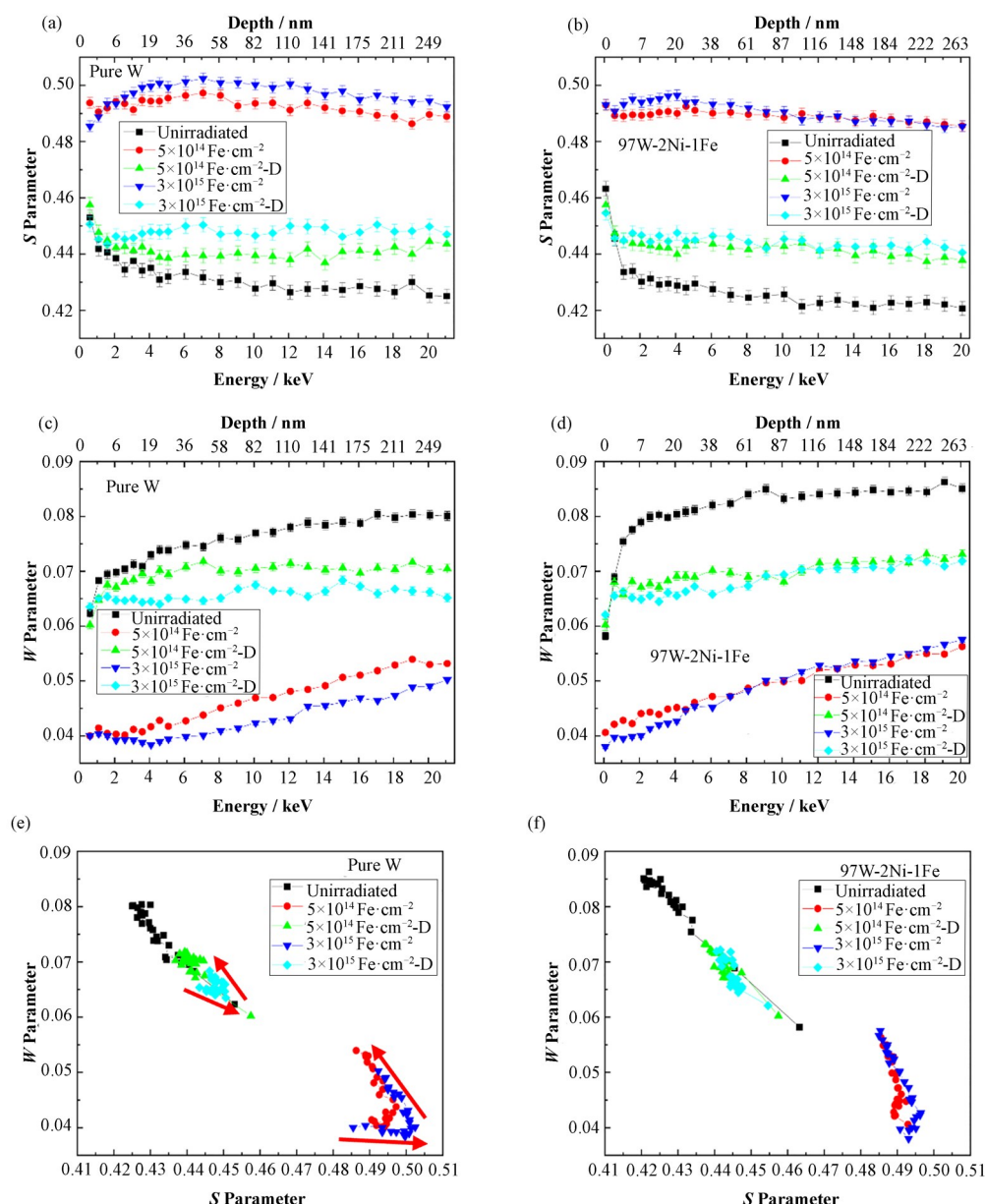


图4 纯钨及97W-2Ni-1Fe合金分别在不同辐照条件下的 S - E 、 W - E 及 S - W 参数(彩图见网络版)
(a~b) 未辐照、铁离子辐照和氘等离子体辐照的 S - E 参数,(c~d) 未辐照、铁离子辐照和氘等离子体辐照的 W - E 参数,(e~f) 未辐照、铁离子辐照和氘等离子体辐照的 S - W 参数

Fig.4 S - E , W - E , and S - W parameters for pure W and 97W-2Ni-1Fe alloy under different irradiation conditions (color online)
(a~b) S - E parameters of unirradiated, Fe ion irradiated, and deuterium plasma irradiation, (c~d) W - E parameters of unirradiated, Fe ion irradiated, and deuterium plasma irradiation, (e~f) S - W parameters of unirradiated, Fe ion irradiated, and deuterium plasma irradiated

采用 TDS 对不同辐照条件下处理的纯钨和 97W-2Ni-1Fe 合金样品进行表征。通过热脱附过程分析氦在材料中的脱附特性,并探讨不同缺陷类型对脱附过程的影响。图 7 和图 8 为不同剂量铁离子预辐照的两组样品在氦等离子体注入热脱附处理后扫描电镜表征结果和热脱附谱图结果。图 7(a)为低剂量铁离子预辐照纯钨样品在热脱附后表面的微观形貌,结果显示热脱附后纯钨表面形成了坑洞和白

色颗粒结构,并且坑洞尺寸随着预辐照剂量的增加进一步增大(图 7(b)),表明铁离子预辐照诱导的缺陷浓度随着辐照剂量而增大,这些缺陷为氦的聚集和扩散提供了形核位点和扩散通道,加剧了氦-空位复合体或氦泡的形成。在热力学作用下,氦从材料内部扩散至表面并脱附,导致表面形成坑洞,表面损伤越严重则反映其内部氦滞留量越大。图 7(c)、(d) 为 97W-2Ni-1Fe 合金热脱附后的表面微观形貌表征

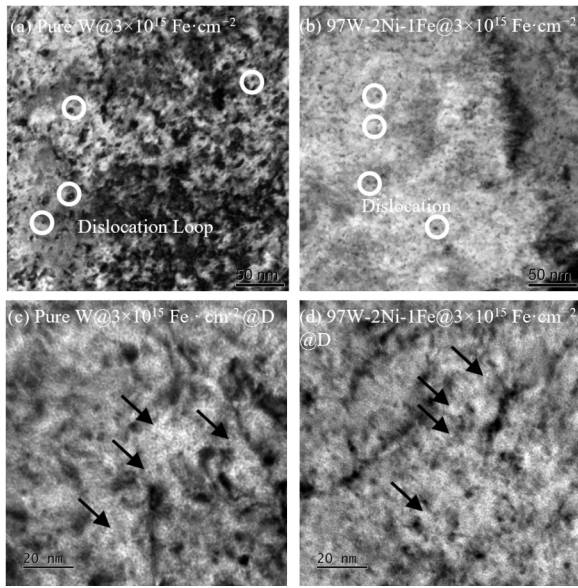


图5 $3 \times 10^{15} \text{ Fe} \cdot \text{cm}^{-2}$ 铁离子预纯钨(a)和97W-2Ni-1Fe合金(b)在30~280 nm深度区域TEM图,以及预辐照处理氘等离子体注入后纯钨(c)和97W-2Ni-1Fe合金(d)在180 nm深度附近的TEM图

Fig.5 TEM images of pure W (a) and 97W-2Ni-1Fe alloy (b) after Fe ion pre-irradiation at $3 \times 10^{15} \text{ Fe} \cdot \text{cm}^{-2}$, showing the 30~280 nm depth region, TEM images of pure W (c) and 97W-2Ni-1Fe alloy (d) pre-irradiated samples after deuterium plasma injection, focusing on the region around 180 nm depth

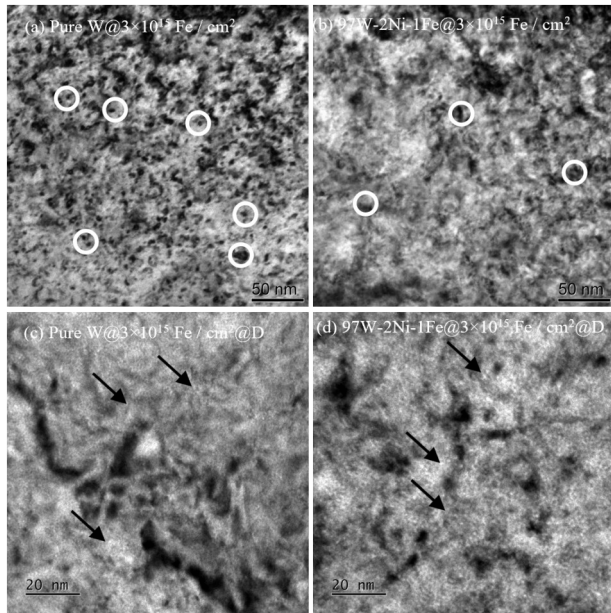


图6 $3 \times 10^{15} \text{ Fe} \cdot \text{cm}^{-2}$ 铁离子预辐照纯钨(a)和97W-2Ni-1Fe合金(b)在650~950 nm深度区域TEM图,以及预辐照处理氘等离子体注入后纯钨(c)和97W-2Ni-1Fe合金(d)在800 nm深度附近的TEM图

Fig.6 TEM images of pure tungsten (a) and 97W-2Ni-1Fe alloy (b) samples after Fe ion pre-irradiation at $3 \times 10^{15} \text{ Fe} \cdot \text{cm}^{-2}$, showing the 650~950 nm depth region, and TEM images of pre-irradiated pure tungsten (c) and 97W-2Ni-1Fe alloy (d) samples after deuterium plasma injection, focusing on the region around 800 nm depth

结果,相较于纯钨,其表面未形成坑洞,仅存在白色珊瑚状结构。这一结构在课题组之前的研究结果中进行了详细阐述^[42],这是由于在热力学作用下氦-空位复合体吸收更多的氦原子,氦泡尺寸进一步增大,氦泡扩散到样品表面时,氦逃逸形成的。在97W-2Ni-1Fe合金样品表面未见坑洞形成,表明在97W-2Ni-1Fe合金中未形成较大尺寸的氦-空位复合体,从而导致其内部氦原子滞留量相对较少。

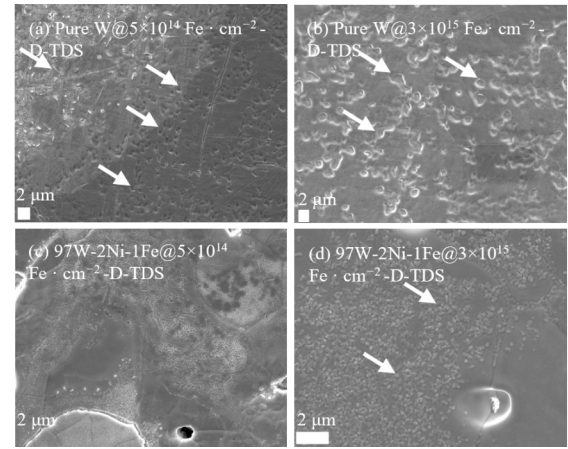


图7 纯钨样品低剂量($5 \times 10^{14} \text{ Fe} \cdot \text{cm}^{-2}$)(a)与高剂量($3 \times 10^{15} \text{ Fe} \cdot \text{cm}^{-2}$)(b)辐照后再注入氘等离子体样品热脱附后表面形貌,以及97W-2Ni-1Fe合金样品低剂量($5 \times 10^{14} \text{ Fe} \cdot \text{cm}^{-2}$)(c)与高剂量($3 \times 10^{15} \text{ Fe} \cdot \text{cm}^{-2}$)(d)辐照后再注入氘等离子体样品热脱附后表面形貌

Fig.7 Surface topographies of pure tungsten specimens subsequent to low-fluence ($5 \times 10^{14} \text{ Fe} \cdot \text{cm}^{-2}$) (a) and high-fluence ($3 \times 10^{15} \text{ Fe} \cdot \text{cm}^{-2}$) (b) irradiation and subsequent deuterium plasma implantation, as observed post-thermal desorption, surface characteristics of 97W-2Ni-1Fe alloy specimens after being subjected to low-fluence ($5 \times 10^{14} \text{ Fe} \cdot \text{cm}^{-2}$) (c) and high-fluence ($3 \times 10^{15} \text{ Fe} \cdot \text{cm}^{-2}$) (d) irradiation and subsequent deuterium plasma treatment, as examined post-thermal desorption

图8(a~b)中黑色曲线为两组样品未预辐照注入氘后的热脱附谱图结果,热脱附谱中的横坐标为温度,纵坐标为氦原子的热脱附速率。实验结果表明,退火后纯钨样品在注入氘等离子体后,氦的初始脱附温度约为100 °C,只存在一个脱附峰。基于脱附能与温度的经验关系式^[44-45]: $E = 0.0029 \cdot T_p$, E 为热脱附激活能, T_p 为脱附温度。计算得到该脱附峰对应的氦脱附能为1.28 eV,低于钨中单空位与氦的结合能($(1.56 \pm 0.06) \text{ eV}$)^[46]。考虑到氦与钨的结合能较低($1.0 \sim 1.4 \text{ eV}$)^[47-48],并在约290 °C时完成脱附,对应的脱附能为1.63 eV。推测在未预辐照的纯钨样品中,脱附的氦主要来源于表层区域的间隙氦原子。未预辐照97W-2Ni-1Fe的初始脱附温度相对较高(150 °C),脱附峰较宽,推测是氦通过与金属形成氢化物或在晶界处聚集,从而表现出稍强的束缚作用^[49]。

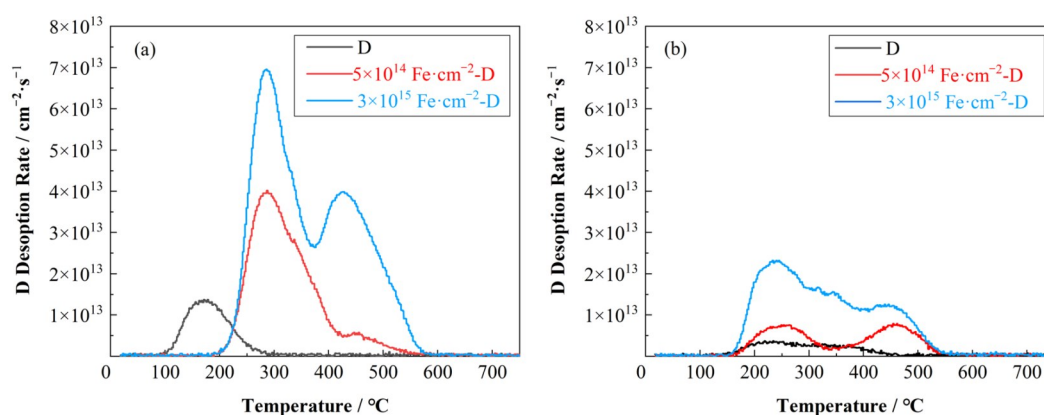


图8 不同剂量铁离子预辐照纯钨(a)及97W-2Ni-1Fe合金(b)再注入氘等离子体的热脱附谱(彩图见网络版)
Fig.8 Thermal desorption spectroscopy of pure W (a) and 97W-2Ni-1Fe alloy (b) after deuterium plasma injection following Fe ion pre-irradiation at different doses (color online)

图8(a~b)中红色曲线和蓝色曲线分别为纯钨和97W-2Ni-1Fe合金两组样品在低剂量和高剂量铁离子预辐照后注入氘的热脱附谱图。由图2(d)可知97W-2Ni-1Fe合金是一种两相复合材料,NiFe以第二相的形式存在于基体相中。现有研究表明:镍铁元素的加入能够有效抑制晶内偏析、脆性相的形成和气体原子的迁移^[50-53]。不同元素对氘的溶解能力存在显著差异。例如氢同位素原子在铁中的溶解能约为0.275 eV,在镍中的溶解能约为0.237 eV^[54],在钨中的溶解能约为1.095 eV^[55],这导致H原子优先与Ni、Fe结合形成H-金属化合物,从而将氘原子钉扎在合金中某个特定的位置,减少钨中氘原子的聚集。除了溶解能,空位与氢的结合能对氘滞留起着关键作用。Ni中空位与氢的结合能为0.37~1.05 eV^[56-57],铁中空位与氢的结合能约为0.5 eV^[58],钨中空位与氘的结合能为 (1.56 ± 0.06) eV^[46]。此外,有研究表明合金元素能够减小H与空位的结合能^[58]。热脱附谱图数据表明,在相同铁离子预辐照剂量下,纯钨和97W-2Ni-1Fe合金两组样品的热脱附曲线趋势相同,均出现了两个脱附峰,但脱附峰对应的温度不同,表明辐照后样品内存在不同类型的缺陷。不同铁离子辐照剂量下纯钨样品的初始脱附温度为190 °C,第一个脱附峰的温度均约为290 °C,对应氘的脱附能为1.63 eV,这与研究者计算值相吻合,说明氘-单空位复合体主要为氘从单空位缺陷中逸出所致。热脱附速率下降的温度区间在低剂量组与高剂量组存在差异,低剂量组热脱附速率在290~425 °C逐渐降低,高剂量组热脱附速率在290~370 °C逐渐降低,表明不同剂量的辐照导致缺陷浓度和缺陷类型存在差异,如不同尺寸大小的空位、团簇和不同几何形状的位错^[59],从而影响氘原子的俘

获和脱附行为。纯钨样品中第二个峰的形成主要与氘-空位团簇复合体相关,低剂量组在425 °C起峰并在450 °C达到峰值;高剂量组在370 °C开始起峰,在425 °C达到峰值,此温度下对应的氘的脱附能为2.038 7 eV,推测此处为大尺寸的 D_mV_n 复合体或氘-缺陷团簇开始分解,大量氘原子逃逸导致氘脱附速率升高。不同铁离子辐照剂量下的97W-2Ni-1Fe合金开始脱附的温度均为160 °C,略低于纯钨,第一个脱附峰温度均为240 °C,氘的脱附能为1.48 eV,略低于纯钨。第二个脱附峰温度均为465 °C,氘的脱附能2.140 2 eV,在540 °C时脱附完成。不同铁离子辐照剂量下97W-2Ni-1Fe合金的氘脱附速率一致,由此推测不同铁离子预辐照在97W-2Ni-1Fe合金产生的缺陷类型与纯钨一致,且形成的氘-空位复合体类型相似,但由于缺陷浓度差异,导致脱附峰值存在差异。97W-2Ni-1Fe合金中第一个脱附峰温度与纯钨的第一个脱附峰温度接近,表明该温度条件下氘-单空位复合体先分解后脱附,更高温度脱附峰为 $D_mV_nX_y$ 复合体分解后脱附(X为镍、铁)^[60-62]。众所周知,空位-杂质复合体的形成能抑制空位的形成^[63],镍、铁作为一种合金元素,能有效抑制钨中的空位的形成。

为进一步对两组样品中氘脱附进行了定量分析,图9数据表明未预辐照、低剂量铁离子辐照、高剂量铁离子辐照三组样品中纯钨的氘脱附量分别为97W-2Ni-1Fe合金的1.81、2.86和2.26倍。相比于纯钨,97W-2Ni-1Fe合金在低剂量和高剂量预辐照情况下氘滞留量分别减少了65.0%和55.8%。实验数据显示,同等辐照条件下纯钨样品中氘的脱附量更大,反映出纯钨中氘原子滞留率高于97W-2Ni-1Fe合金,表明高剂量铁离子辐照导致纯钨内微观缺陷

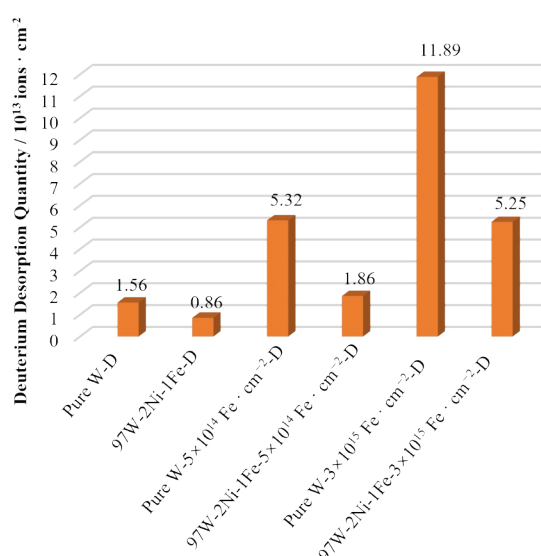


图9 氘等离子体注入纯钨、97W-2Ni-1Fe合金和铁离子预辐照纯钨、97W-2Ni-1Fe合金再注入氘等离子体热脱附处理后脱附量计算结果

Fig.9 The calculated results of deuterium desorption after thermal desorption treatment for pure W, 97W-2Ni-1Fe alloy, and for pure tungsten and 97W-2Ni-1Fe alloy that were pre-irradiated with iron ions and then re-injected with deuterium plasma

浓度迅速增大, $D_m V_n$ 复合体浓度相应增加, 因此氘滞留量相应增大。而 97W-2Ni-1Fe 合金中镍和铁元素的加入有效抑制了空位形成, 降低了氘滞留量。此外, 97W-2Ni-1Fe 合金中氘的初始脱附温度 (160°C) 低于纯钨 (190°C), 进一步表明镍和铁元素的加入不仅降低了氘的滞留, 还降低了氘的脱附温度。

3 讨论

在本研究中, 通过铁离子预辐照与氘等离子体注入实验, 对纯钨与 97W-2Ni-1Fe 合金的辐照行为进行了深入探究。SEM 结果显示 97W-2Ni-1Fe 合金表面损伤相较于纯钨有所减轻, 纯钨表面出现更多的微观缺陷, 而合金表面表现出较少的大尺寸微观缺陷。正电子湮没表征结果显示 97W-2Ni-1Fe 合金和纯钨辐照后, S 参数显著升高, 97W-2Ni-1Fe 合金样品的 S 参数低于纯钨, 表明 97W-2Ni-1Fe 合金样品中空位缺陷浓度低于纯钨。TEM 结果中观察到氘泡存在, 表明铁离子辐照产生的缺陷为氘原子聚集提供进入通道和形核位点。热脱附结果揭示了辐照后的纯钨和 97W-2Ni-1Fe 合金内存在不同类型的缺陷, 低温度条件 ($190\sim 370^\circ\text{C}$) 下脱附的是结合能较低的氘-空位复合体中的氘原子, 较高温度 ($370\sim 580^\circ\text{C}$) 脱附的是 $D_m V_n (m>n)$ 和 $D_m V_n X_y$ 中的氘原子,

且 $D_m V_n X_y$ 复合体中氘原子需要更高的脱附温度。综合上述实验结果表明铁离子辐照引入的微观缺陷 (如空位、位错) 是氘原子滞留与氘泡形成的主要原因, 相比于 97W-2Ni-1Fe 合金, 纯钨中辐照缺陷浓度高, 易形成 $D_m V_n$ 复合体和氘泡, Ni/Fe 相抑制了辐照缺陷产生, 进而阻碍了氘的聚集和氘泡的形成, 并能降低氘的脱附温度。

4 结语

本文通过铁离子和氘等离子体辐照实验, 结合 SRIM 模拟结果, 采用正电子湮没谱学技术、热脱附谱学技术和电镜表征技术, 系统探讨了重离子辐照纯钨和 97W-2Ni-1Fe 合金辐照损伤机理, 深入探讨了辐照微观缺陷与氘相互作用的过程, 最后综合分析了氘在样品中的滞留与脱附行为。实验结果表明, 铁离子辐照引起的空位型缺陷能够有效捕获氘原子, 形成 $D_m V_n$ 复合体, 最终聚集形成氘泡。对比两种材料的辐照行为, 纯钨样品表面损伤较为显著, 氘等离子体辐照后使表面损伤进一步加剧, 97W-2Ni-1Fe 展现出了更优的抗辐照能力, 其表面损伤明显减轻, 且氘滞留行为受到抑制。通过热脱附谱仪分析, 纯钨的氘脱附量为 97W-2Ni-1Fe 的 2~3 倍, 表明纯钨中氘的滞留程度较高, 导致较大的氘脱附量, 形成了 $D_m V_n$ 复合体和氘团簇。相比之下, 97W-2Ni-1Fe 合金表现出较低的氘滞留和较低的脱附温度, 这使其在聚变堆环境中具有更好的稳定性和耐辐照性能。未来研究可进一步优化合金成分, 探讨多元素合金化对抗辐照性能的提升机制, 并结合更复杂的中子辐照实验, 深入揭示氘-缺陷相互作用机理。

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