Structures and mechanical properties of Nb-Mo-Co(Ru) solid solutions for hydrogen permeation

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A B S T R A C T

The structures and mechanical properties of Nb-Mo-Co(Ru) solid solutions for hydrogen permeation have been investigated by X-ray diffraction (XRD) analysis, pressure-composition-temperature (PCT) measurements, and three-point bending tests. The as-prepared Nb86Mo14, Nb86Mo7Co7, and Nb86Mo7Ru7 samples composed of Nb-based solid solutions with bcc structures were hydrogenated into their corresponding hydrides to give the NbH0.95 phases after hydrotreatment. The largest lattice deformations of the bcc structure and NbH0.95 phase were observed in the Nb86Mo7Ru7 sample. This sample possessed the highest hydrogen-diffusion coefficient value (2.32/10^9 cm/s), the lowest hydride formation enthalpy (∆Hf = 21.4 kJ/(mol H2)), and the maximum force before and after hydrogenation. Overall, these results demonstrate that the addition of Ru improves hydrogen diffusion and enhances the mechanical properties of Nb86Mo14 alloy against hydrogen embrittlement.

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1. Introduction

Membrane reactors that employ dense hydrogen separation and purification alloys are one of the most important components for industrial hydrogen production by the steam reforming of natural gas [1–3]. Recently, the increased demand of ultra-pure hydrogen for various applications like anode reactants of fuel cells, semiconductor fabrication, foodstuff hydrogenation, and production of high-purity chemical feedstock has intensified the metal membrane research [4–6]. Polymer materials have potential to store hydrogen while at low temperatures [7,8]. Pd and its alloys are now widely used for hydrogen separation and purification; the obvious disadvantage of these relatively rare alloys is their high cost. In this respect, Group 5 metals (i.e., vanadium (V), niobium (Nb), and tantalum (Ta)) have generated considerable interests as promising hydrogen separation materials due to their lower price and higher hydrogen permeability than the currently used Pd-based alloys [9–12]. However, their poor resistance to hydrogen embrittlement poses a significant barrier to their practical use [9,10,13,14].

Experimental studies have verified that alloying of metals is an effective way to address this problem [12–15]. Recent theoretical studies by Watanabe et al. have shown that the addition of W could decrease the hydrogen solubility in Nb and therefore improve its resistance to hydrogen embrittlement [12,16]. In addition, Hu et al. found that the addition of W can increase the mechanical properties of Nb16H phases, decrease the structural stability of the...
2.2. Measurement of PCT curves and hydrogen diffusion coefficient

The hydrogen diffusion behavior of the alloy samples was studied by a potentiostatic method using a Solarstat SI1287 potentiostat at a 100% charge state with a potential step and discharge time of +500 mV and 3600 s, respectively. The hydrogen diffusion coefficient (\(D_h\)) can be evaluated according to Eq. (1) [23]:

\[
\log i = \log \left( \frac{6FD}{da^2} (C_0 - C_F) \right) - \left( \frac{a^2}{2.303} \right) \left( \frac{D}{a^2} \right) t
\]

where \(i\) represents the diffusion current density (mA/g); \(F\) is the Faraday constant; \(D\) is the hydrogen-diffusion coefficient (cm²/s); \(d\) is the powder density (g/cm³); \(a\) is the alloy particle radius of the powder (cm), for which an average value of 50 μm was used for the alloy powder sieved by 200 standard screening; \(C_0\) is the initial hydrogen concentration (mol/cm³); \(C_F\) is the hydrogen concentration at the particle surface (mol/cm³); and \(t\) is the discharge time (s). Given Eq. (1), it is clear that the value of \(D\) can be derived from the slope of \(\log i - t\) curves. Before testing, the alloy electrodes were prepared by mixing the alloy powders with carbonyl nickel powders at a weight ratio of 1:3 and then cold pressed into a pellet under 10 MPa.

The electrochemical studies were performed in a half-cell consisting of a working electrode, a sintered Ni(OH)₂/NiOOH counter electrode, and a Hg/HgO reference electrode. The electrolyte was a 6 M KOH solution.

2.3. Mechanical performance of the metallic membranes

A three-point bending test was conducted to measure the bending stress of the alloy membranes of size \(L_b \times b \times h = 18 \text{ mm} \times 6 \text{ mm} \times 0.8 \text{ mm}\). When the membranes were in the elastic range, the maximum bending stress is \(\sigma = Mh/L_b^2\). Here, \(M = Fls/4, W = bh^3/6\) [22,23], \(F\) is the bending force, \(L_b\) is the span length, and \(b\) and \(h\) are the width and thickness of the membrane sample, respectively. Detailed information of this test is provided in the literature [24,25].

3. Results and discussion

3.1. Structure of Nb-Mo-Co(Ru) alloy samples before and after hydrogenation

Refined XRD data of the as-prepared Nb₈₆Mo₁₄, Nb₈₆Mo₇Co₇, and Nb₈₆Mo₇Ru₇ alloy samples are shown in Fig. 1, where the red
and black lines correspond to the experimentally observed and calculated patterns, respectively.

The blue lines indicate the standard patterns, whereas the green lines represent the difference between the observed and calculated patterns. The as-prepared Nb-Mo-Co(Ru) samples are composed entirely of Nb-based solid solutions with a body-centered cubic (bcc) structure, and no new phase is formed. The calculated lattice parameters of these samples are listed in Table 1. Compared with pure Nb, clear lattice deformations can be observed for these Nb-Mo-Co(Ru) alloy samples owing to different atomic sizes of Nb (1.429 Å), Mo (1.362 Å), Co (1.253 Å), and Ru (1.325 Å). Fig. 2 and Table 2 show the refined XRD data of the Nb86Mo14, Nb86Mo7Co7, and Nb86Mo7Ru7 alloy samples after hydrogenation.

The results indicate that these solid solutions are hydrogenated into their corresponding hydrides with the NbH0.95 phase after hydrotreatment under 2 MPa of hydrogen pressure at 653 K. Similar changes in the lattice parameters have also been detected in the hydride samples. Based on the structure analysis before and after hydrogenation, it is suggested that the as-prepared alloys are all Nb-based solid solutions with bcc structures, which can be hydrogenated into Nb-based hydrides with NbH0.95 phases after hydrotreatment. Partial replacement of Nb does not lead to the formation of a new phase, but instead results in the lattice deformation due to different atomic sizes of Nb and the dopants. A larger variation in lattice parameters was observed for the Nb86Mo7Ru7 sample and its corresponding hydride; the degree of variation of the lattice parameters (a, b, c, V) for the bcc structure is 2.57% for a, 2.03% for b, 3.61% for c, and 7.99% for V, and that of the NbH0.95 phase is 2.18%, 1.63%, 2.44%, 6.06%, respectively, as shown in Table 1.

### Table 1
Calculated lattice parameters of Nb-Mo-Co(Ru) solid solutions with BCC structures.

<table>
<thead>
<tr>
<th>Formula</th>
<th>(a) (Å)</th>
<th>(b) (Å)</th>
<th>(c) (Å)</th>
<th>(V) (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb(ICSDB9-5157)</td>
<td>3.300</td>
<td>3.300</td>
<td>3.300</td>
<td>35.973</td>
</tr>
<tr>
<td>NbH0.95(ICSDB0-2282)</td>
<td>3.447</td>
<td>4.860</td>
<td>4.860</td>
<td>81.417</td>
</tr>
<tr>
<td>As-Prepared Nb86Mo14</td>
<td>3.2765(5)</td>
<td>3.2765(5)</td>
<td>3.2765(5)</td>
<td>35.175(7)</td>
</tr>
<tr>
<td>Nb86Mo3,hydride</td>
<td>3.4003(0)</td>
<td>4.8154(9)</td>
<td>4.7798(0)</td>
<td>78.265(0)</td>
</tr>
<tr>
<td>As-Prepared Nb86Mo7Co7</td>
<td>3.2382(3)</td>
<td>3.2382(3)</td>
<td>3.2382(3)</td>
<td>33.956(5)</td>
</tr>
<tr>
<td>Nb86Mo7Co7,hydride</td>
<td>3.3583(2)</td>
<td>4.7613(0)</td>
<td>4.6847(0)</td>
<td>74.908(2)</td>
</tr>
<tr>
<td>As-Prepared Nb86Mo7Ru7</td>
<td>3.2761(6)</td>
<td>3.2761(6)</td>
<td>3.2761(6)</td>
<td>33.163(7)</td>
</tr>
<tr>
<td>Nb86Mo7Ru7,hydride</td>
<td>3.3716(1)</td>
<td>4.7480(9)</td>
<td>4.7413(8)</td>
<td>76.478(8)</td>
</tr>
</tbody>
</table>

Note: the data marked with * is the calculated variation of the lattice parameters relative to ICSD reference data.

### 3.2. Hydrogenation performance of Nb-Mo-Co(Ru) powder samples

To evaluate the structural stability of the Nb-based hydrides, the hydride formation enthalpy (\(\Delta H\)) has been derived from the PCT analysis [26–28]. The PCT curves at three temperatures (573, 613, and 653 K) are shown in Fig. 3(a–c). As seen, the hydriding platform pressure increases with increasing the temperature. The formation enthalpies of the Nb-based hydrides have been calculated using the van’t Hoff equation. As seen in Fig. 3(d), a good linear relation between \(\ln P_{eq}\) and \(1/T\) with a slope of \(\Delta H/k\) (k is the Boltzmann constant) has been derived from the PCT curves. This approach gives the calculated \(\Delta H\) values of 1.84 \(\times\) 10⁻⁹ kJ/(mol·K) for Nb86Mo14, 1.68 \(\times\) 10⁻⁹ kJ/(mol·K) for Nb86Mo7Co7, and 2.32 \(\times\) 10⁻⁹ kJ/(mol·K) for Nb86Mo7Ru7. These results suggest that the addition of Ru leads to an improvement of the hydrogen diffusion behavior of the Nb86Mo14 sample, which can be attributed to the larger lattice deformation and higher formation enthalpy of the corresponding hydride in Nb86Mo14. Similar work has been reported by Iwakura et al. using aMnNi4₆₋ₓAl₃₀₋ₓM₀.₇₅Al₀.₂₅Coₓ alloy sample [29,30]. In that case, hydrogen diffusion in the a-phase was diminished as the cobalt content increased because of the strong attractive interactions between the absorbed hydrogen atoms.

### Table 2
Data of three-point bending test of the Nb-Mo-Co(Ru) alloy membranes before and after hydrogenation.

<table>
<thead>
<tr>
<th>Alloy number</th>
<th>(F) (N)</th>
<th>(L) (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>91.3080</td>
<td>0.44902</td>
</tr>
<tr>
<td>N2</td>
<td>99.9593</td>
<td>0.5030</td>
</tr>
<tr>
<td>N3</td>
<td>113.8878</td>
<td>0.4740</td>
</tr>
<tr>
<td>N4</td>
<td>17.4411</td>
<td>0.1844</td>
</tr>
<tr>
<td>N5</td>
<td>21.6929</td>
<td>0.2022</td>
</tr>
<tr>
<td>N6</td>
<td>22.7722</td>
<td>0.1835</td>
</tr>
</tbody>
</table>

Fig. 4 shows the relationship curves of the hydrogen permeability current density and time, as measured by the potentiostatic method. Based on the spherical electrode diffusion theory, the hydrogen diffusion coefficient (\(D_H\)) can be calculated from the slope of the \(\ln C_0/\ln C_i\) vs. time curves. This approach gives the calculated \(D_H\) values of 1.84 \(\times\) 10⁻⁹ cm²/s for Nb86Mo14, 0.68 \(\times\) 10⁻⁹ cm²/s for Nb86Mo7Co7, and 2.32 \(\times\) 10⁻⁹ cm²/s for Nb86Mo7Ru7. These results suggest that the addition of Ru leads to an improvement of the hydrogen diffusion behavior of the Nb86Mo14 sample, which can be attributed to the larger lattice deformation and higher formation enthalpy of the corresponding hydride in Nb86Mo7Ru7. Similar work has been reported by Iwakura et al. using aMnNi4₆₋ₓAl₃₀₋ₓM₀.₇₅Al₀.₂₅Coₓ alloy sample [29,30]. In that case, hydrogen diffusion in the a-phase was diminished as the cobalt content increased because of the strong attractive interactions between the absorbed hydrogen atoms.
which is caused by its large lattice deformation. However, further work is required to elucidate the underlying mechanism of this process.

3.4. Mechanical properties of Nb-Mo-Co(Ru) alloy membranes before and after hydrogenation

The mechanical properties of the Nb-Mo-Co(Ru) alloy membranes were determined using the three-point bending test as shown in Fig. 5. The results are shown in Fig. 6 and Table 2. The pristine Nb-Mo-Co(Ru) alloy membranes exhibited better mechanical properties than the corresponding hydrogenation-treated samples. The maximum force and maximum displacement of the pristine Nb_{86}Mo_{7}Ru_{7} sample are 113.8878 N and 0.5030 mm, respectively. In contrast, poor mechanical properties were observed for the hydrogenation-treated Nb-Mo-Co(Ru) samples. Such a clear reduction in the mechanical property performance can be attributed to hydrogen embrittlement resulting from the hydrotreatment. However, regardless of whether or not hydrogenation treatment was performed, both the maximum force and maximum
displacement increased in these two double-element doping samples, indicating that the addition of Ru (or Co) can improve the mechanical properties of Nb86Mo14 sample.

Generally, there exists a strong affinity between hydrogen and Groups 4 and 5 elements. The produced brittle hydride after hydrogenation may possibly lead to cracks and their enlargement, resulting in a reduced plasticity or strength of the materials that may not be recoverable. In order to verify the results of the three-point bending test, SEM fractographic analysis of the above-mentioned Nb-Mo-Co(Ru) samples before and after hydrogenation was performed. The corresponding SEM images are shown in Fig. 7. Relative to the pristine Nb-Mo-Co(Ru) membrane samples, obvious hydrogen embrittlement cracks can be observed in the samples after hydrogenation, especially in Nb86Mo14. As can be seen from N5 and N6, the cracks decreased obviously after hydrogen percolation because of the addition of Co and Ru respectively, which effectively suppressed the problem of hydrogen embrittlement, and the addition of Ru was more significant. These results can be attributed to the larger lattice deformation of Nb86Mo7Ru7 due to different atomic sizes of Nb and the dopants. Similar results have also been reported for Mo [23–25], W [23], and Nb [26] metals.

4. Conclusions

In this study, the as-prepared Nb86Mo14, Nb86Mo7Co7, and Nb86Mo7Ru7 alloy samples composed of Nb-based solid solutions with bcc structures were hydrogenated into their corresponding hydrides with NbH0.95 phases after hydrotreatment. Doping treatment leads to the lattice deformations of both the bcc structure and the NbH0.95 phase due to atomic size differences between Nb and the dopant atoms (Mo, Co, and Ru). The largest lattice deformation is observed for the Nb86Mo7Ru7 sample and its hydride. Specifically, the Nb86Mo7Ru7 sample has the highest DH value (2.32 \times 10^{-3} cm^2/s), lowest hydride-formation enthalpy (∆H = -21.4 kJ/(mol H2)), and the maximum force before and after hydrogenation (113.8878 N and 22.7722 N, respectively). Overall, these results indicate that the addition of Ru will improve hydrogen diffusion and enhance the mechanical properties of Nb86Mo14 alloy against hydrogen embrittlement.
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