Irradiation Effects in Ni–17Mo–7Cr Alloy Bombarded with MeV Au Ions

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Received: 24 December 2014 / Revised: 6 February 2015 / Published online: 5 May 2015
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Abstract Irradiation effects in Ni–17Mo–7Cr alloy have been systematically investigated by using 3 MeV Au ions at different fluences ranging from $8 \times 10^{13} \text{ cm}^{-2}$ to $2.3 \times 10^{15} \text{ cm}^{-2}$, corresponding to doses of 1–30 dpa. The results indicated that sample microstrain increased gradually from 0.14 to 0.22% as dose increased from 0 to 30 dpa. Besides, the nanohardness of Ni–17Mo–7Cr alloy increased with irradiation dose until 10 dpa, and then, softening effect became dominant while further increasing dose to 30 dpa. After being irradiated at room temperature, the swelling rate of Ni–17Mo–7Cr alloy was found to be around 0.04% per dpa. These data are helpful in estimating the irradiation resistance of this newly developed Ni–17Mo–7Cr alloy in nuclear energy systems.

KEY WORDS: Ni-base alloy; Swelling rate; Radiation damage; Nanoindentation

1 Introduction

Nickel-base alloys have excellent high temperature performance and corrosion resistance so that they are widely used in advanced nuclear energy systems such as molten salt reactor (MSR) and supercritical water reactor (SCWR) [1]. In these applications, Ni-base alloys will be subjected to harsh work conditions, especially intensive neutron irradiation as high as a hundred displacement per atom (dpa) [2], which can greatly degrade material's mechanic performance.

Therefore, the irradiation resistance of these alloys is crucial for their application in new-generation nuclear systems.

Irradiation can induce many effects in materials, such as hardening, volume swelling, segregation and precipitation, and decrease in thermal conductivity. In particular, radiation-induced swelling and hardening are two most concerned irradiation effects for materials used in nuclear energy systems. A certain amount of work has been done on the irradiation effects in nickel-base alloys. Boothy [3] examined the microstructures and volume changes of Ni-monic PE16, irradiated in fast reactor at the temperature from 394 to 636 °C to different doses up to 74 dpa, and he has found that the volume change of PE16 was <1%. Sencer et al. [4] have investigated alloy 718 irradiated with mixed spectra of high-energy protons and spallation neutrons and found that the yield stress of alloy 718 increases with doses up to ~0.5 dpa and then decreases with further increase in dose. Rowcliffe et al. [5] have investigated the radiation effects in a series of nickel-base alloys, including alloy 718, 706 and PE16, and their results suggested that modifying the composition can mitigate the irradiation effects on the performance of the present commercial nickel-base alloys.

Available online at <http://link.springer.com/journal/40195>

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However, compared with numerous works on austenitic stainless steels and ferritic–martensitic steels, studies on the irradiation effects in nickel-base alloys are rather limited. The lack of experimental data has greatly impeded the effort to explore new type of nickel-base alloys with good resistance to irradiation damage which is crucial for the nuclear facilities in the future. Therefore, it is urgent to investigate irradiation effects in existed or newly developed nickel-base alloys, which is necessary for understanding the irradiation damage process in nickel-base alloys and for designing new alloys with excellent resistance to irradiation damage.

In the present work, we systematically studied a newly developed Ni–17Mo–7Cr alloy, which is intended to be used in China MSR facility. The samples were irradiated with MeV Au ions at different doses up to 30 dpa, and the irradiation effects such as changes of microstrain, radiation-induced swelling and hardening were measured. These data are very helpful in estimating the irradiation resistance of this newly developed nickel-base alloy and in further improving its performance.

2 Experimental

The nominal chemical composition of Ni–17Mo–7Cr alloy is shown in Table 1, and the samples used in our experiments were cut into 5 mm × 5 mm × 2 mm and then polished to a mirror-like surface. In the irradiation experiments, part of the sample's surface was masked to form a boundary between the irradiated and the pristine region where a step will appear after irradiation which could be used to calculate the swelling rate of the irradiated samples. 3 MeV Au²⁺ was adopted to irradiate the samples at ion fluences of $8 \times 10^{13} \text{ cm}^{-2}$, $2.5 \times 10^{14} \text{ cm}^{-2}$, $7.4 \times 10^{14} \text{ cm}^{-2}$ and $2.3 \times 10^{15} \text{ cm}^{-2}$, corresponding to dose of 1, 3, 10 and 30 dpa, respectively. Ion beam current density was kept in a low level (around 15 nA/cm²) to avoid significant increase in the sample temperature during irradiation.

To calculate the irradiation damage level, SRIM [6] was used in the “detailed calculation with full damage cascades” mode and the threshold displacement energy E_d was set to 40 eV [7–9]. With the number of displacements per ion per unit depth in the sample thickness C_i obtained by SRIM, the damage level D_c in unit of dpa can be calculated with the following formula:

$$D_c(\text{dpa}) = \frac{C_i \cdot \phi}{A}$$

where ϕ is the ion fluence and A is the target atomic density. Figure 1 shows D_c as a function of depth when the sample is irradiated at dose of 1 dpa. Dpa distributions of other irradiation doses are similar with that shown in Fig. 1, with the only difference in peak heights. It could be seen that the radiation-damaged region is up to 600 nm from the sample surface and the irradiation damage is not homogeneously distributed in the irradiated region, with a peak at the depth of about 200 nm. The dose mentioned in the following sections refers to the peak value.

The structure of the irradiated samples was determined by grazing incident X-ray diffraction (GIXRD, D8) at a grazing angle of 2° with a CuK α radiation source (the wavelength $\lambda = 0.15406 \text{ nm}$). The surface morphologies and the swelling behaviors were investigated by atomic force microscopy (AFM). Raman spectrometer (JY HR800) was used to characterize the carbon segregation of the ion-irradiated Ni–17Mo–7Cr alloy. The excitation source was a 532 nm Ar-ion laser with power of 12 mW. The radiation-induced hardening effect of the implanted layer was measured by G200 nanoindenter in the continuous stiffness mode [10]. For these tests, the Berkovich diamond indenter tip was used.

3 Results and Discussion

3.1 GIXRD Analysis of the Structure and the Microstrain of Irradiated Samples

First we investigated the structural changes of the irradiated samples with GIXRD, and the results are shown in

Fig. 1 SRIM simulation of damage profiles produced by 3 MeV Au²⁺ ion irradiation to a dose of $8 \times 10^{13} \text{ cm}^{-2}$ in Ni–17Mo–7Cr alloy

Table 1 Nominal chemical composition of the Ni–17Mo–7Cr alloy (wt%)

C	Si	Mn	Fe	Cr	Mo	Ni
0.05	0.5	0.5	4	7	17	Bal.

Fig. 2a. The GIXRD patterns are normalized for comparison. As dose increases from 0 to 30 dpa, intensities of all the diffraction peaks decrease while their widths increase. The decrease tendency in the peak intensities indicates that the crystal structure of the irradiated samples has been disrupted by ion irradiation, thus reducing the extent of the ideal crystal structure.

By measuring the broadening of the diffraction peaks, we can obtain the microstrain in the irradiated samples as the following equation [11].

$$\varepsilon = \frac{\beta(2\theta) - \Delta(2\theta)}{4 \tan \theta}, \quad (1)$$

where $\beta(2\theta)$ is the diffraction broadening, θ is the diffraction angle, and $\Delta(2\theta)$ is the instrumental broadening. The calculated values of the microstrain as a function of dose are shown in Fig. 2b.

Clearly, the microstrain in the irradiated samples increases significantly compared to the pristine one. At the lowest dose of 1 dpa, the microstrain increases quickly to 0.21 from 0.14% of the unirradiated sample. Hereafter, it increases slowly with doses up to 30 dpa. Since the microstrain depends on the distortions of sample's crystal structure, the increase in the microstrain could be attributed to the radiation-induced defects and dislocations. Lee *et al.* [12] have investigated the radiation-induced hardening and microstructural evolution of EC316LN stainless steel and found that the predominant defects were black dots below 1 dpa whose density saturated within a few dpa, followed by the evolution of interstitial loops. Similar phenomena were also observed in other materials [13]. Thus, the

microstrain evolution with ion dose could be interpreted as following: Below 1 dpa, radiation-induced defects in Ni–17Mo–7Cr alloy are mainly small vacancy and interstitial clusters (black dot defects). The density of these defects increases rapidly with ion dose, resulting in dramatic microstrain increase. When ion dose exceeds 1 dpa, black dot defects become saturated and evolve to dislocation loops, and the density of the defects as well as the microstrain saturates or even decreases, as shown in Fig. 2b. This tendency was also found in Zr alloy, in which the microstrain increased quickly at the lowest ion fluence and rather slowly at higher ion doses [14]. Jin *et al.* [15] have found that after 82.5 dpa Ar^+ irradiation, original grains of C-276 transformed into subgrains and the microstrain calculated by GIXRD was about 0.696%. Figure 2b shows that the microstrain in Ni–17Mo–7Cr alloy irradiated at 30 dpa is about 0.22%.

3.2 Swelling Rate of Irradiated Samples

Radiation-induced volume swelling is one of the most concerned irradiation effects for judging material's resistance to irradiation damage, because it not only distorts sample's shape but also influences its thermal conductivity. We estimated the swelling rate of Ni–17Mo–7Cr alloy by measuring the step height near the irradiated–unirradiated interface with AFM. Figure 3a shows the topography near the interface between the irradiated and unirradiated region, and the ion dose is 30 dpa. The topographies of other doses of the samples are similar to that shown in Fig. 3a. We have measured the step height at four different

Fig. 2 Normalized GIXRD patterns **a**, the microstrain **b** of Ni–17Mo–7Cr alloy samples irradiated with 3 MeV Au ions at different doses

Fig. 3 AFM image of the irradiated and unirradiated zone **a**, the measured step height **b** of the Ni-17Mo-7Cr alloy specimen

positions, and at each position three step height data have been collected as shown in Fig. 3b.

The finally averaged step height is about 8 nm. Considering the thickness of the damaged region is 600 nm, the swelling rate of Ni-17Mo-7Cr alloy is around 1.3% at 30 dpa. It is worth mentioning that 30 dpa is the value of the irradiation damage at the damage peak, and thus, the average dose in the sample is smaller than that. In other words, the swelling rate should be larger than 1.3% if the sample was damaged homogeneously at 30 dpa. The swelling rate of PE16, which have the lowest swelling behavior, is <1% after neutron irradiation to 77 dpa at 667–909 K [3, 16], and the swelling rates of alloy 625, Hastelloy X and alloy 800 are found to be <0.6%, (0.6–2.1)% and (0.5–5)%, respectively, after exposure to 5×10^{26} n/m² (~ 30 dpa) at 873–923 K [17]. As vacancy mobility increases with increasing temperature and Dubinko *et al.* [18] have found that the void size and the density in Ni under 1.2 MeV Cr ion irradiation increased with increasing temperature, it is thought to be quite likely that the swelling rate of Ni-17Mo-7Cr alloy would be even larger when irradiated at elevated temperature. Thus, compared to other nickel-base alloys, the resistance to radiation-induced swelling of Ni-17Mo-7Cr alloy may not be so satisfactory.

3.3 Hardness Changes of Irradiated Samples Measured with a Nanoindenter

The nanohardness of the irradiated samples was measured by a nanoindenter, and the near-surface hardness as a function of the contact depth of the indenter tip at different doses is shown in Fig. 4a.

Because the Berkovich diamond indenter tip sampled the hardness in the region extend to about seven times of the indenter's contact depth [19], in order to eliminate the surface effects, the hardness values measured at depth of 100 nm are used in comparing the irradiation hardening effect of the samples irradiated at different doses, as shown in Fig. 4b. Data in the figures are the averaging of ten indents performed from two separate samples, irradiated under identical conditions. Deviation from the mean value for each indent was <0.3 GPa.

The hardness of the pristine sample at 100 nm contact depth is about 5.06 GPa, and it increases to 5.64, 5.69 and 5.77 GPa, corresponding to relative hardening of 11.5, 12.5 and 14%, after being irradiated at dose of 1, 3 and 10 dpa, respectively. However, when ion dose further increases to 30 dpa, a significant softening effect can be observed and the hardness drops down to 5.33 GPa, corresponding to a relative hardening of 5.4%. The initial hardening may be due to the black dot defects appearing at very low dose (~ 0.001 dpa) [20]. The black dot defects can pin dislocations and thus inhibit their motion. The density of these “black dots” increases with ion dose and reaches the saturation at about 1 dpa as mentioned above. At higher doses, loops evolve and continue to produce hardening at a slower rate. What interesting is that the softening effect was observed at the highest dose of 30 dpa, which may be caused by the radiation-induced dissolution of the precipitation in the samples. Similar phenomenon has been observed in previous work. Hunn *et al.* [8] have studied the irradiation hardening behavior of Inconel 718 with a nanoindenter and found that after Fe ions irradiation, the samples with aging treatment

Fig. 4 Near-surface hardness as a function of contact depth **a**, the hardness of the samples as a function of dose at 100-nm contact depth **b**

exhibited softening as the dose increased because of the radiation-induced dissolution of γ' and γ'' precipitation. Wanderka *et al.* [21] investigated a Hastelloy alloy after 10 MeV electron irradiation and found that the irradiation-induced small local chemical changes destabilized the $L1_2$ LRO structure for the unirradiated samples and transformed it to SRO structure. As to Ni–17Mo–7Cr alloy, its nominal chemical composition is quite similar with Hastelloy N in which precipitates were thought to be nickel–molybdenum intermetallic compounds [22]. In our experiment, similar nickel–molybdenum intermetallic

phases may exist in the samples, and the softening phenomenon appeared at 30 dpa probably could be attributed to the dissolution or transformation of these precipitates.

We note that the change tendency of the hardness at different ion fluences is similar to that of microstrain as shown in Fig. 2b, and each of them reaches the maximum value at dose of 10 dpa and then drops at dose of 30 dpa. This means that a larger microstrain causes a higher hardness, and they all result from the defects produced by the incident Au ions.

Fig. 5 Raman spectra of the Ni–17Mo–7Cr alloy samples **a**, areas of D and G peaks at different doses **b**

3.4 Raman Analyses of Carbon Segregation During Ion Irradiation

In order to analyze the radiation-induced segregation of carbon inside the alloy, Raman spectra of the Ni–17Mo–7Cr alloy samples are measured, and the results are shown in Fig. 5a.

Raman spectra show great sensitivity to the detection of the carbon atoms. Although the density of the carbon atoms in the pristine samples is 0.5 wt%, the carbon atoms are dispersed in the samples so that there is no C–C vibration peak observed before irradiation. After ion irradiation, peaks near 1355 and 1580 cm^{-1} appear, which correspond to D-peak and G-peak of the carbon materials, respectively [23–25]. Carbon peaks in the Raman spectra represent the carbon clusters formed by the carbon atoms. We calculated the D-peak area and the G-peak area of the samples at 10 and 30 dpa, and the results are shown in Fig. 5b. It is clear that as the ion fluence increases, the relative Raman intensity of the carbon peaks increases. This is because irradiation induces more atom displacements at higher ion fluence, and thus, the carbon atoms have more chance to segregate. The ratio of the integral intensity of the D-peak and G-peak I_D/I_G also increases with ion fluence, which manifests the defects of the clustered carbon caused by ion irradiation increased and the degree of graphitization decreased during irradiation.

4 Conclusions

After being irradiated with 3 MeV Au^{2+} , irradiation effects in Ni–17Mo–7Cr alloy are investigated. The results showed that the lattice structure of the irradiated samples was disrupted, and a microstrain of 0.22% in Ni–17Mo–7Cr alloy was found at dose of 30 dpa. AFM measurements indicated that the average swelling rate of Ni–17Mo–7Cr alloy was about 1.3% at dose of 30 dpa. Besides, significant hardening was observed when ion dose was lower than 10 dpa, but if ion dose is further increased to 30 dpa, softening behavior was observed.

These results are primary data of this newly developed nickel-base alloy, and further experiments, especially TEM observations, are necessary to clarify questions which have not been solved in this work. Based on the above results, Ni–17Mo–7Cr alloy exhibits averaged resistance to ion irradiation compared with other existed nickel-base alloys, and further efforts are needed to improve its irradiation resistance.

Acknowledgments This work is financially supported by the China-Australia Joint Research Project (Grant No. 2014DFG60230), the Joint Fund of the National Natural Science Foundation of China and the China Academy of Engineering Physics (Grant No. U1230111) and the National Natural Science Foundation of China (Grant No. 91226202).

References

- [1] P. Yvon, F. Carré, J. Nucl. Mater. **385**, 217 (2009)
- [2] T. Allen, J. Busby, M. Meyer, D. Petti, Mater. Today **13**, 14 (2010)
- [3] R.M. Boothby, J. Nucl. Mater. **230**, 148 (1996)
- [4] B.H. Sencer, G.M. Bond, F.A. Garner, M.L. Hamilton, S.A. Maloy, W.F. Sommer, J. Nucl. Mater. **296**, 145 (2001)
- [5] A.F. Rowcliffe, L.K. Mansur, D.T. Hoelzer, R.K. Nanstad, J. Nucl. Mater. **392**, 341 (2009)
- [6] J.P. Biersack, J.F. Ziegler, in *Ion implantation techniques*, ed. by H. Ryssel, H. Glawischnig (Springer, New York, 1982), pp. 122–156
- [7] N. Hashimoto, J.D. Hunn, T.S. Byun, L.K. Mansur, J. Nucl. Mater. **318**, 300 (2003)
- [8] J.D. Hunn, E.H. Lee, T.S. Byun, L.K. Mansur, J. Nucl. Mater. **296**, 203 (2001)
- [9] M.J. Norgett, M.T. Robinson, I.M. Torrens, Nucl. Eng. Des. **33**, 50 (1975)
- [10] W.C. Oliver, G.M. Pharr, J. Mater. Res. **7**, 1564 (1992)
- [11] G. Williamson, W. Hall, Acta Metall. **1**, 22 (1953)
- [12] E.H. Lee, J.D. Hunn, N. Hashimoto, L.K. Mansur, J. Nucl. Mater. **278**, 266 (2000)
- [13] E.H. Lee, J.D. Hunn, G.R. Rao, R.L. Klueh, L.K. Mansur, J. Nucl. Mater. **271–272**, 385 (1999)
- [14] P. Mukherjee, A. Sarkar, P. Barat, Mater. Charact. **55**, 412 (2005)
- [15] S.X. Jin, L.P. Guo, Z. Yang, Z.P. Zhou, D.J. Fu, C.S. Liu, R. Tang, F.H. Liu, Y.X. Qiao, Plasma Sci. Technol. **14**, 548 (2012)
- [16] J. Bates, R. Powell, J. Nucl. Mater. **102**, 200 (1981)
- [17] W.K. Appleby, D.W. Sandusky, U.E. Wolff, J. Nucl. Mater. **43**, 213 (1972)
- [18] V.I. Dubinko, A.G. Guglya, E. Melnichenko, R. Vasilenko, J. Nucl. Mater. **385**, 228 (2009)
- [19] L.E. Samuels, T.O. Mulhearn, J. Mech. Phys. Solids **5**, 125 (1957)
- [20] E.H. Lee, J.D. Hunn, T.S. Byun, L.K. Mansur, J. Nucl. Mater. **280**, 18 (2000)
- [21] N. Wanderka, A. Bakai, C. Abromeit, D. Isheim, D.N. Seidman, Ultramicroscopy **107**, 786 (2007)
- [22] H.E. McCoy, ORNL-TM-1353 (1966)
- [23] G.A. Baratta, M.M. Arena, G. Strazzulla, L. Colangeli, V. Mennella, E. Bussolletti, Nucl. Instrum. Methods Phys. Res. B **116**, 195 (1996)
- [24] B. Elman, M. Dresselhaus, G. Dresselhaus, E. Maby, H. Mazurek, Phys. Rev. B **24**, 1027 (1981)
- [25] S. Mathew, B. Joseph, B.R. Sekhar, B.N. Dev, Nucl. Instrum. Methods Phys. Res. B **266**, 3241 (2008)