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Mechanism of radiation damage reduction in equiatomic multicomponent single phase alloys

F. Granberg
Department of Physics, P. O. Box 43, FIN-00014 University of Helsinki, Finland

K. Nordlund
*Department of Physics, P. O. Box 43, FIN-00014 University of Helsinki, Finland**

M. W. Ullah
Department of Physics, P. O. Box 43, FIN-00014 University of Helsinki, Finland and
Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

K. Jin
Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

C. Lu
Department of Materials Science and Engineering,
University of Michigan, Ann Arbor, MI 48109-2104, USA

H. Bei
Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

L. M. Wang
Department of Nuclear Engineering and Radiological Sciences,
University of Michigan, Ann Arbor, MI 48109-2104, USA

F. Djurabekova
Helsinki Institute of Physics, P. O. Box 43, FIN-00014 University of Helsinki, Finland and
Department of Physics, P. O. Box 43, FIN-00014 University of Helsinki, Finland

W. J. Weber
Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA and
Department of Materials Science and Engineering,
University of Tennessee, Knoxville, TN 37996, USA

Y. Zhang
Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA†

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Recently a new class of metal alloys, of single-phase equiatomic multicomponent composition, have been shown to exhibit promising mechanical, magnetic and corrosion resistance properties, in particular, at high temperatures. These features make them potential candidates for components of next-generation fusion and fission reactors, that will involve high temperatures combined with corrosive environments and extreme radiation exposure. In spite of a wide range of recent studies of many important properties of these alloys, their radiation tolerance at high doses remains unexplored. In this work, a combination of experimental and modeling efforts reveals a substantial reduction of damage accumulation under prolonged irradiation in single-phase NiFe and NiCoCr alloys compared to elemental Ni. This effect is explained by reduced dislocation mobility, which leads to slower growth of large dislocation structures. Moreover, there is no observable phase separation, ordering or amorphization, pointing to a high phase stability of this class of alloys.

The accelerated development of new technologies for efficient energy production demands new materials that are tolerant to extreme environments and can operate reliably at high temperatures. Operating thermal power plants – whether conventional or nuclear – at higher temperatures is, from a principal point of view, a simple way to increase energy efficiency, but requires in practice materials that can withstand the increased operation window. Many of the new energy production concepts considered, such as concentrated solar energy and several Generation-IV nuclear concepts, include components with flowing liquid salts or metals, posing serious

corrosion challenges [1–3]. Both electric power generators and nuclear fusion power plants involve high magnetic fields [4], adding a further class of materials properties that needs to be considered. With respect to these requirements on the materials, a recently developed class of metal alloys shows high promise to exhibit greatly improved properties. Most traditional metal alloys involve one principal element alloyed by much lower concentrations of others, or mixtures of several different phases. Systematic synthesis and study of alloys with multiple elements at equal (called "equiatomic" or, in case they contain at least 5 elements, "high-entropy" alloys) or roughly equal concentrations in a single phase structure has, however, started only recently [5, 6]. Intense recent work has revealed that these alloys have the ability to maintain good mechanical properties both at cryogenic conditions [7] and up to very high temperatures (~ 1000°C), as well as a good corrosion resistance [8]. Hence they are strong candidates to resolve many challenges imposed by extreme environments. However, in the particular case of nuclear reactors, there is the additional complication of radiation damage. In particular, realization of new "Generation IV" fission reactor concepts [9, 10], that will have many improved features (e.g. the capability to burn used nuclear fuel), as well as tokamak-like fusion power plants [10, 11], both will subject materials in the reactors to very high neutron irradiation loads. Hence, to realize the great potential of equiatomic and high-entropy alloys in nuclear environments, it is crucial to consider also radiation damage and its buildup in these materials. Recently, preliminary estimations of the possible reduction of radiation damage in Ni equiatomic alloys were done based on analysis of formation of point defects and initial damage structure [12]. However, the issue of damage build up or its mechanisms, crucial for practical applications, has not been yet addressed.

Even though some classes of steels and other metal alloys are known to have high radiation tolerance, their properties do start to change immediately after the onset of irradiation [10, 13]. This has motivated an intense ongoing search for new classes of materials with improved radiation hardness. New materials, shown to have high radiation tolerance include nanocrystalline materials [14–16], multilayered nanomaterials [17] and nanofoams [18, 19]. Although all of these are promising for some applications, the high fraction of surface or interface, which are thermodynamically unstable, makes nanostructures in general unreliable for long operational times at elevated temperatures. For such conditions, typical for nuclear reactors, it is very valuable to find homogeneous and stable materials with improved radiation tolerance, and equiatomic or high-entropy alloys could become such a class of materials.

In this Letter, we examine the radiation tolerance of single-phase equiatomic alloys of two and three components: NiFe and NiCoCr, by experiments and molecular dynamics computer simulations, with particular emphasis on the damage buildup effects. We show that the multi-elemental composition of the equiatomic materials slows down dislocation motion in them, leading to a strong (factor of $\sim 2-3$) reduction in radiation damage. Understanding of the actual mechanisms of reduction of radiation damage in the equiatomic metal alloys will allow for focused search of other combinations of alloying metals with even more improved radiation tolerance.

For our study, we chose the NiFe and NiCoCr alloys since they could be synthesized experimentally as high-quality single crystals [20], while maintaining a completely random atom arrangement within a well-defined face-centered cubic (FCC) crystal. (see Methods in the Supplementary information). Moreover, interatomic potentials for the same alloy composition were readily available [21–23] We investigated the radiation response in these materials in comparison to pure Ni, which has the same crystal structure. We emphasize that the outcome of radiation in these materials is by no means *a priori* clear: while in elemental metals the damage levels saturate at relatively low defect concentration, around 1 % [24], some metal alloys are known to amorphize under irradiation [25], indicating a major increase in damage production.

The experimental pure Ni and equiatomic alloy samples were irradiated with Ni and Au ions with the energies 1.5 MeV and 3 MeV, respectively, producing damage in the dense cascades similar to those produced by neutron recoils in nuclear reactors [24]. The damage was analyzed by Rutherford backscattering/channeling (RBS/C, see Methods in the Supplementary information). The results in Fig. 1 show that there is a major (a factor 2 - 3) reduction in the damage in the NiFe and NiCoCr equiatomic alloys, as compared to the pure element Ni. Moreover, the three elemental NiCoCr alloy shows still lower damage level than the two elemental NiFe.

Our cross-sectional transmission electron microscopy (TEM) analysis of Ni and NiFe irradiated by 3 MeV Au ions to 2×10^{13} and 1×10^{14} ions/cm^2 at room temperature show that the depth distribution of defect clusters strongly depends on the ion fluence and the composition of the material, Figs. 2 and 3. As expected from previous works showing that dislocations have a crucial role in irradiated metals [26–31], we observe typical features of dislocation loops and vacancy-type stacking fault tetrahedra (SFT) in all investigated samples. However, comparison of the NiFe micrographs with the Ni ones shows clearly that there is less damage in NiFe, and the feature sizes are smaller. This is confirmed by quantitative comparison of the defect cluster sizes (Fig. 2 c and Fig. 3

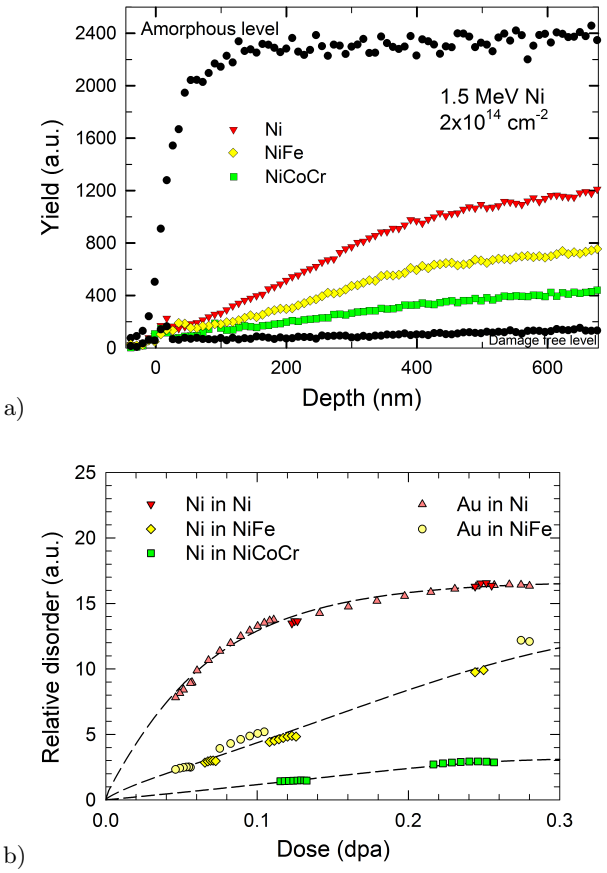


FIG. 1. Comparison of irradiation-induced damage in elemental Ni and equiatomic alloys. a) Rutherford backscattering spectra showing different irradiation response. Higher damage level is observed in the order of Ni, NiFe and NiCoCr after 1.5 MeV Ni to a fluence of 2×10^{14} cm^{-2}. b) Relative disorder in the alloys. Irradiations response in the model systems were investigated under 1.5 MeV Ni and 3 MeV Au irradiations. While there exists large uncertainty ($\sim 20\%$) due to the SRIM predictions and channeling analysis, the data clearly shows that under these irradiation conditions, much less damage is produced in the NiFe and NiCoCr equiatomic alloys. The dashed lines are curve fits to the data to guide the eye.

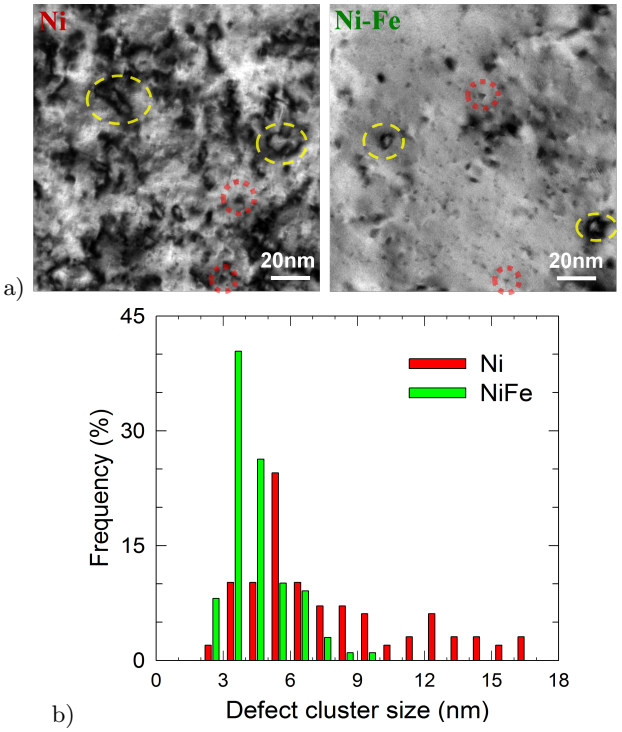


FIG. 2. Defect cluster distributions in Ni and NiFe at low fluence. a) High magnification bright-field images of Ni and NiFe samples irradiated using 3 MeV Au ions to a fluence of 2×10^{13} cm^{-2} (Peak dose at 155 nm is ~ 0.1 dpa) under two beam condition, g=[200], and (b) size distribution of defect clusters. Interstitial-type dislocation loops are indicated by the dashed circles, and small triangles marked by the dotted circles are characterized as SFTs. The scale bar is 20 nm.

b). Moreover, no signs phase separation or ordering is observed even at the highest doses studied.

To establish the origin of the damage reduction and reason for a strong dislocation signal, we turn to molecular dynamics (MD) computer simulations, a method widely used to examine radiation damage production in metals [26, 32, 33] (see Methods in the Supplementary information). We carried out simulations of radiation collision cascades consecutively in the same simulation cell to reach the high doses of about 0.57 displacements-per-atom (dpa[34]) that can be compared with the experiments. The simulations were carried out by running 1500–1800 recoils at a typical subcascade energy of 5 keV in a segment of material far from the surface, to mimic damage production at the experimental depths of hundreds of nanometers.

The MD results of damage production under prolonged irradiation show three results of direct relevance to interpret the experiments. First, the point defect damage level saturates with dose at about 0.3 dpa, consistent with previous experiments in elemental metals [24]. The results up to the same dose as in the experiments (see Fig. 4 a) demonstrate, in agreement with the TEM and RBS measurements, that equiatomic alloys are well resistant to amorphization and do not show any signs of segregation or ordering. Second, the defect clustering analysis showed that after the cascade damage started to overlap with pre-existing defects, recombination effects [35, 36] tended to remove point defects, while defect clusters grew in size and started to form ordered defect structures known as (partial and perfect) dislocation loops. These can be visually seen Fig. 4 c, and their growth and interactions are illustrated in the Sup-

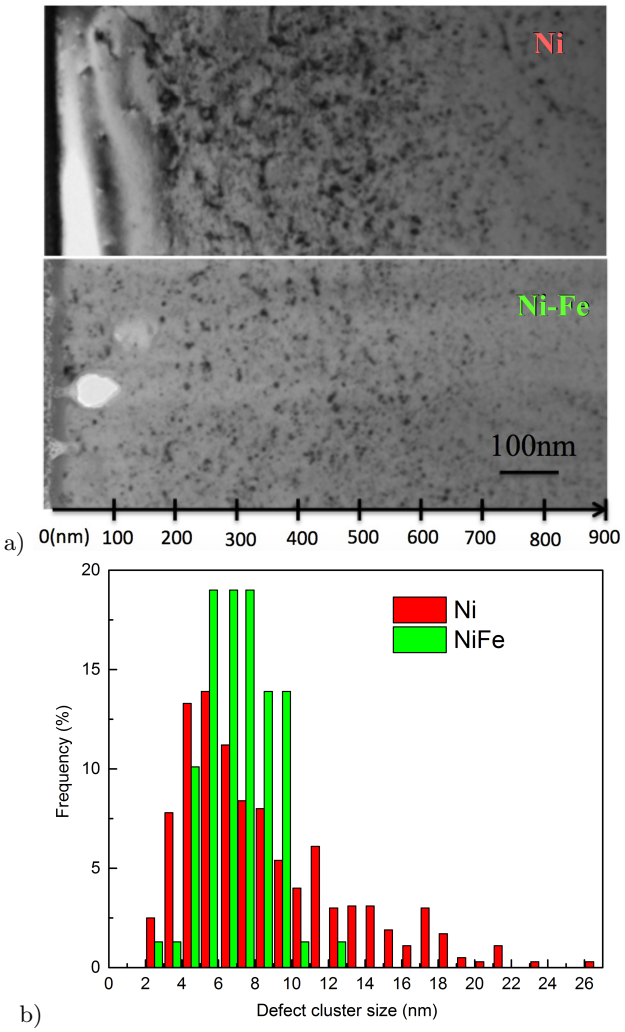


FIG. 3. Defect cluster distributions in Ni and NiFe at high fluence. Bright-field cross-sectional TEM images (g=[200]) showing the overall irradiated region in Ni and NiFe (a) samples after 3 MeV Au ion irradiation to 1×10^{14} cm^{-2} (Damage peak at 155 nm is equivalent to 0.57 dpa). (b) Size distribution of defect clusters.

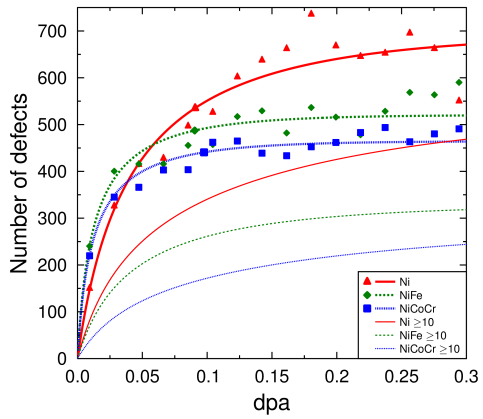
plementary movies. Third, the analysis of damage distribution in clusters showed that the crucial difference between NiFe and NiCoCr compared to Ni is that in the alloys, the fraction of damage in large clusters is smaller (Fig. 4 b). Since the TEM method cannot detect point defects, this result on large defect clusters is the most suitable for comparison with the experiments. The reduced fraction of damage in large ($\geq$ 10 defects) dislocation structures was observed with two different MD interatomic potentials used (see Methods in the Supplementary information), and is fully consistent with the experimental observations on the differences between the materials. The diameter of the defects are also smaller in the alloys than in pure Ni, see Fig. 4 b inset, and has a similar size distribution peaked stronger at small cluster sizes for the alloys NiFe and NiCoCr. Thus, we conclude that the reason for the damage reduction in the equiatomic alloys (Fig. 4 a) is that the dislocation structures are in these materials smaller than in the elemental material.

To determine the mechanism by which the dislocation structures observed in the simulations are smaller in NiFe and NiCoCr compared to Ni, we separately analyzed the mobility of edge dislocations in these materials, following the approach in Ref. 37. Lattice distortions caused by the different atomic types in equiatomic alloys can be expected to affect the dislocation mobility in these materials. We found that the edge dislocation in NiCoCr is indeed less mobile than that in NiFe, which in turn is less mobile than that in Ni. The difference in dislocation mobility in the alloys and pure Ni depended on the strain rate used, but was clearly at least a factor of 2. The onset stress for movement is also much higher for the alloys compared with that in the pure element. Hence we conclude that distortion of the crystal lattice structure in the equiatomic alloying materials is able to hinder the dislocation movement, resulting in smaller damage structures in NiFe and NiCoCr, making them also less likely to grow. This deduction is further supported by the movies provided in the Supplementary material, which show visually that the damage evolution involves extensive discontinuous motion of different dislocation structures, all induced by the radiation condition. The velocity v of a dislocation, once it becomes mobile, depends on an external macroscopic stress σ as[38]

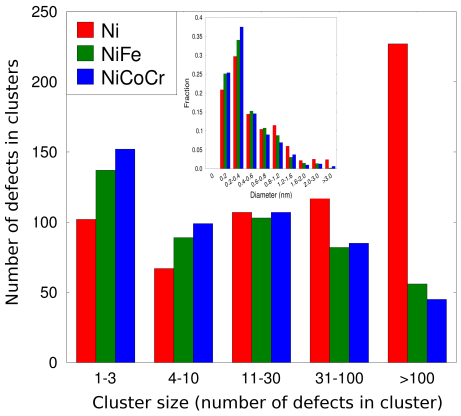
$$v = M_d b \sigma \tag{1}$$

where M_d id the dislocation mobility constant and b the Burgers vector of the dislocation. Our results show that the mobility of dislocations in equiatomic alloys, M_d^{ea} are smaller than those in pure elements M_d^{el}. Because permanent deformation of metals is driven by dislocation motion $\propto v$ in metals, Eq. 1 implies that equiatomic alloys can be expected to able to withstand higher macroscopic stresses σ than the corresponding pure elements.

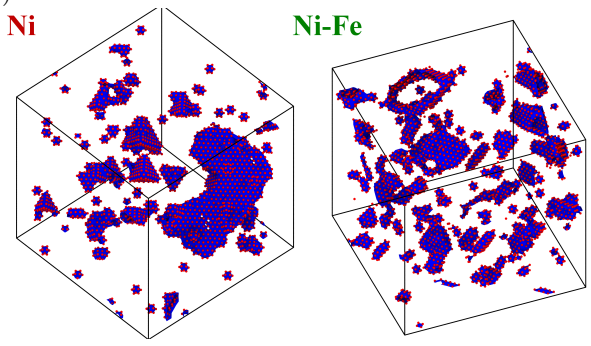
We note that the simulated dose rate is orders of magnitude higher than the experimental one due to the limited time scale available for conventional MD simulations. In particular, at experimental dose rates, there would be much more time for point defects to move between the subcascade events. However, most of the point defects would be absorbed by the dislocations, and hence the effect of practically all defects being in damage clusters would be achieved at even lower doses than in the simulations. Hence the main conclusion of the difference in damage production at higher doses ($\gtrsim 0.1$) being due to different dislocation sizes and mobility is not affected by the underestimation of point defect migration in the MD simulations.



a)



b)



c)

FIG. 4. Molecular dynamics results of damage production in Ni, NiFe and NiCoCr. a) Buildup of total number of defects and number of defects in clusters larger than 10, divided into point defects and defect clusters. The lines are fits of a function to the data points to guide the eye. The individual data points show fairly large fluctuations since individual dislocation recombination reactions (see text) can cause large changes in the defect numbers. b) Average cluster size distribution at the dose from ~ 0.4 dpa to the end. The inset shows the same distribution grouped by cluster diameter. c) Defect structures in Ni and NiFe at a dose of 0.5 dpa. The atoms shown are filtered by removing the perfect structured FCC atoms according to an adaptive common neighbor analysis, to show only atoms that are part of a defective structure.

To summarize, our combined experimental and simulation results show consistently that equiatomic metal alloys may be more resistant to radiation damage than the corresponding pure elements. Moreover, our analysis of the underlying mechanism established that alloy effects on dislocation mobility is a generic one and not specific to the current choice of materials. On the other hand, the difference between the NiFe and NiCoCr results shows that a reduction will depend on material choice, and suggests that there may be alloys with even larger damage reduction than the currently observed one – especially in more chemically disordered alloys with increasing number of principal elements at significant concentrations (not necessary at an equiatomic concentrations), where the number of possible element combinations and alloy compositions are practically limitless.

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Author Contributions:

K. N. wrote the first draft of the paper, and guided the setup of the simulations. Y.Z. initiated the project, guided and coordinated experimental work. F. D. initiated the simulation project and guided the defect clustering analysis. F. G. carried out the simulations with the Zhou *et al* potential, and M. U. the simulations with the Bonny *et al* potential. H. B. grew the high-quality crystals. Y. Z. and W. J. W. supervised ion irradiation experiments and data analysis. K. J. performed ion irradiation and ion channeling measurements, as well as analyzed spectrum. C. L. and L.W. carried out the microstructural characterization. All authors contributed to writing the paper.

Additional information

Supplementary information is available in the online version of the paper. Correspondence and requests for materials should be addressed to K.N. and Y.Z.

* kai.nordlund@helsinki.fi; Corresponding author
† Zhangy1@ornl.gov

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