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Journal of Nuclear Materials 276 (2000) 41–49

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Similarity and difference between fcc, bcc and hcp metals from the view point of point defect cluster formation

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Abstract

In order to obtain an overall understanding of the similarity and difference in the point defect reactions between different types of crystallographic structure of metals, the formation of point defect clusters by a variety of experimental treatments, such as quenching from high temperatures, electron irradiation in high-voltage electron microscopes, irradiation with energetic particles, and high-speed and/or heavy plastic deformation, is reviewed. Not only the simple comparison of the variation of point defect cluster formation, but also the consideration of the variation of underlying point defect reactions with the kind of materials and with experimental parameters are made. The behavior of vacancies is found to be very similar in all fcc metals and behavior of self-interstitial atoms appears to be very similar in fcc and bcc metals. However, the behavior of vacancies in bcc metals, especially in α-iron, is entirely different from that in fcc metals.

1. Introduction

In general, the formation of point defect clusters occurs via various types of reactions of point defects. These reactions start from the generation of supersaturated point defects and ends with their disappearance. Here, one of the important ways for obtaining an overall understanding of the similarity and difference between different crystal structure of metals, which is the major concern of the present workshop, is to compare the point defect cluster formation behavior in different metals.

In this paper, based on long years of research experience of the present author, point defect cluster formation behavior during a variety of experimental treatments is reviewed, placing major interest on extracting the similarity and the difference between fcc, bcc and hcp metals. The production of defect clusters under the following experimental conditions are considered:

1. Quenching from high temperatures.
2. Electron irradiation with high-voltage electron microscopes.
3. Irradiation with energetic particles such as neutrons and ions.
4. High-speed and/or heavy plastic deformation.

2. Quenching from high temperatures

Supersaturated vacancies introduced in aluminum by quenching from high temperature were first reported to aggregate to form loops of perfect dislocation [1,2]. Because of the high stacking fault energy of aluminum, it was logical at that time to accept these loops to be perfect. However, later the loops were found to contain stacking fault, forming Frank sessile loops on {1 1 1} planes as shown in Fig. 1 [3]. This early evidence emphasized that the importance lies in the point defect reaction processes during the early stages of the clustering process and not in the energy of the final form of point defect clusters [4]. Variation of the number density of dislocation loops by changing suddenly the aging temperature during the loop formation showed that the nucleation does not occur at any definite stage of the cluster formation [5]. An early computer simulation to solve the hierarchy type of the set of equations of the number of each size of vacancy clusters [6], which

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PII: S0022-3115(99)00167-1

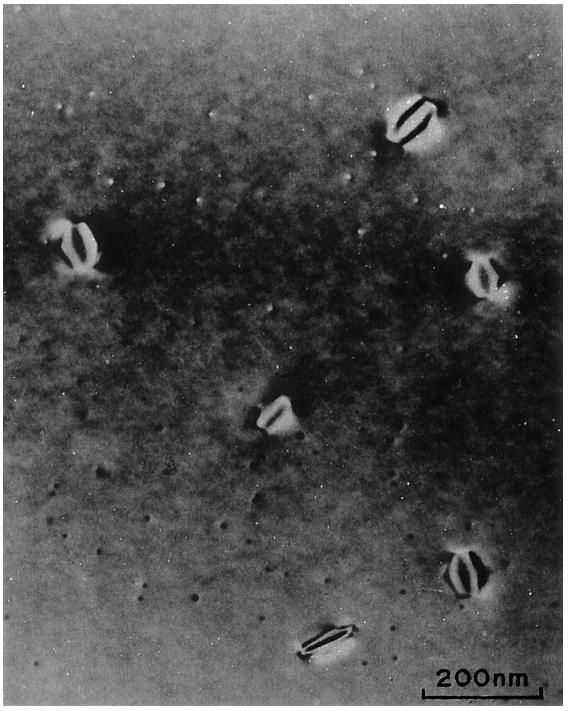

Fig. 1. Vacancy clusters in aluminum introduced by quenching from a high temperature. Hexagonal dislocation loops on {1 1 1} planes contain stacking fault [3]. Small black and white square dots on each side of an equal thickness fringe are octahedral voids [10].

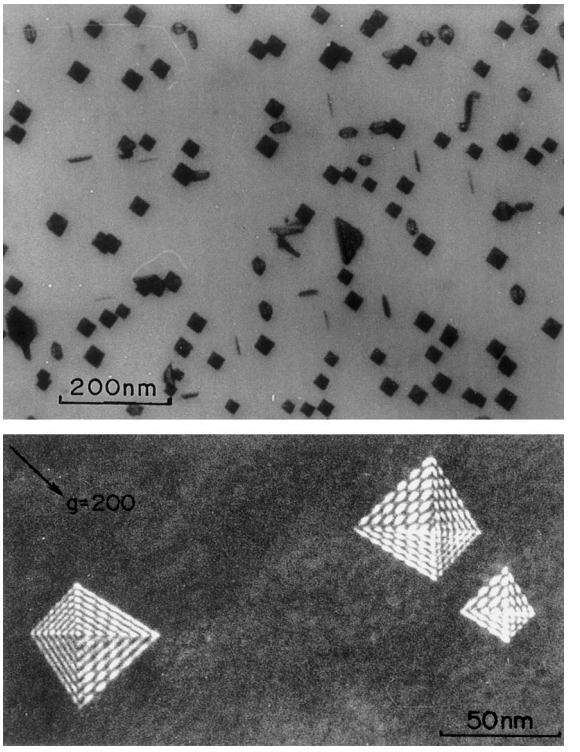

Fig. 2. Stacking fault tetrahedra introduced in gold by quenching from a high temperature. Observed along near [1 0 0] direction (top) [8]. A weak beam dark field picture of large stacking fault tetrahedra is also shown (bottom) [9].

satisfactorily explained the observed experimental results, led to confirm that the nucleation and growth are continuously and interdependent processes.

Defect clusters produced by supersaturated quenched-in vacancies in copper and gold are in the form of stacking fault tetrahedron (SFT) as shown in Fig. 2 [7]. Defect clusters in these metals were often very small depending on the quenching and aging condition as well as the specimen purity. They were called black spot defects [10], but they were all accepted to be small SFT from the later high-resolution observation. Here again, the energy considerations of defect clusters, e.g. lower energy for smaller clusters in the shape of SFT and lower energy for larger clusters in the shape of faulted loops, failed to explain the observed results. Systematic experimentation of the variation of the number density of SFT with experimental parameters led to the conclusion that the nucleation of SFT occurs at a definite stage of their formation, which is very different from the poorly defined border between nucleation and growth of dislocation loops [11].

Observation of small cavities in quenched aluminum as in Fig. 1 was almost the first finding of this type of point defect clusters [12], generally called voids. Later, the presence of dissolved hydrogen atoms was found to be essential to nucleate this type of vacancy clusters in aluminum [13].

Extensive effort was made to observe vacancy clusters in quenched body-centered-cubic metals, especially in α-iron. At this time, not a single reliable report is available. There was a report on voids in quenched tungsten, but the number of voids were so small that they are not accepted to be general.

3. Electron irradiation with high-voltage electron microscopes

The most common point defect clusters produced in metals by high-energy (e.g. 1 MeV) electron irradiation in high-voltage electron microscopes are interstitial clusters in the shape of dislocation loops [15], with no exception of crystallographic structures. They are faulted dislocation loops on {1 1 1} planes in fcc metals [16], perfect dislocation loops on {1 0 0} planes in iron [14] (on {1 1 1} planes in molybdenum [17]), and faulted loops on basal plane in hexagonal zinc [18], as shown in Fig. 3. Point defect reaction kinetics during the nucleation and growth of interstitial type dislocation loops are well understood for all types of metals [15].

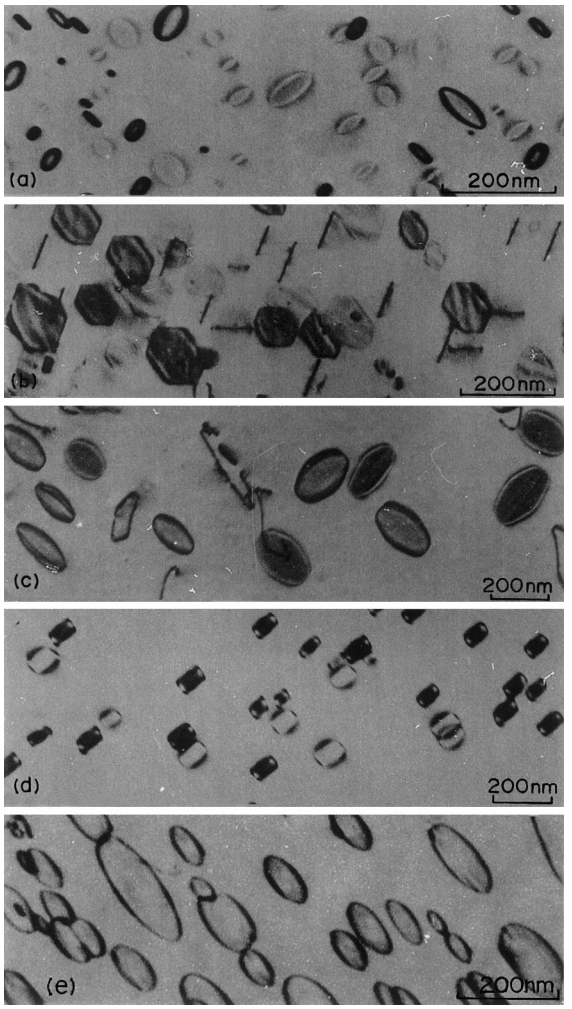

Fig. 3. Interstitial type dislocation loops produced in various metals by electron irradiation at temperatures above the recovery stage III [15]. Faulted loops on {1 1 1} planes in (a) Aluminum, (b) copper, and (c) nickel. Perfect loops on {1 0 0} planes in (d) iron, and loops on basal plane in (e) zinc.

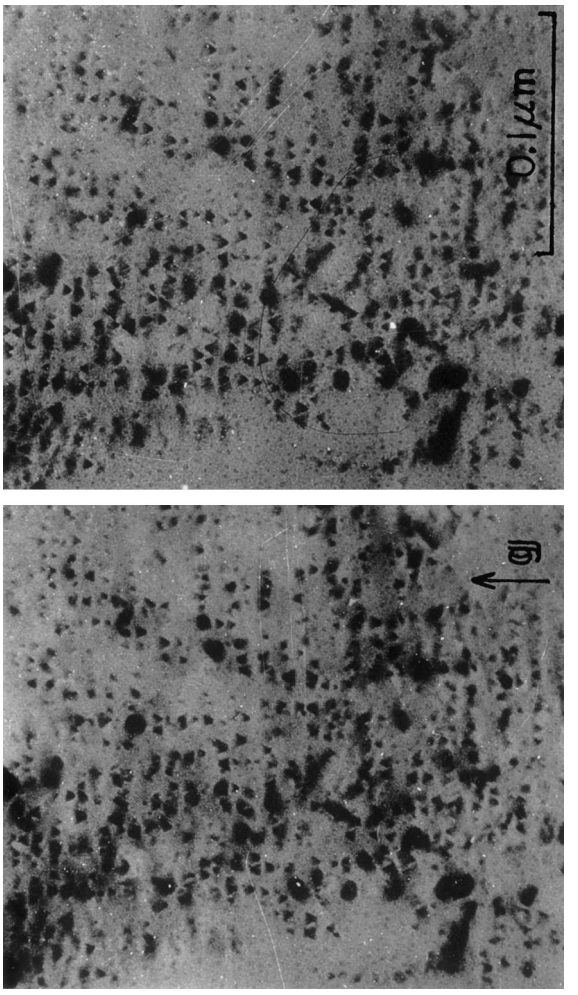

Fig. 4. Stereoscopic pair micrographs of vacancy clusters in the shape of stacking fault tetrahedra in copper electron irradiated at 310 K [26]. All SFT are located within a thin layer beneath the electron incident surface. This is considered to be due to the enrichment of vacancies along the surface caused by the transport of interstitials into the deeper position from the surface.

Nucleation of interstitial clusters under high production rate of point defects ($\sim 10^{-4}$/s in concentration unit in high-voltage electron microscopes) is understood to occur during an initial transient increase of the concentration of interstitial atoms. The temperature dependence of the nucleation (i.e. of cluster density) yields the interstitial mobility [19,20]. Here, the number density of interstitial clusters continuously increases in fcc metals at lower temperatures (close to liquid helium temperature), but in bcc-iron the increase stops at around liquid nitrogen temperature, because the interstitials in this metal lose their mobility by thermal activation below this temperature. Below this temperature, the number density of the interstitial clusters in α-iron is maintained at the same level, because the motion of interstitials is caused by the electron radiation induced diffusion which is temperature independent [21]. Modification of point defect processes by small amounts of solutes gives rise to a stronger temperature dependence of the nucleation of interstitial clusters in the medium temperature range. This is due to the dissociation reaction of interstitials from solute impurities with a larger activation energy than that of free migration of interstitial atoms [22].

Choosing suitable combinations of irradiation conditions (temperature and irradiation dose rate), high number density of small interstitial loops can be nucleated. The motion of these loops is along straight lines in

a wide variety of fcc and bcc metals without exception [23,24]. The direction of the motion is along $\langle 1\,1\,0\rangle$ in fcc and along $\langle 1\,1\,1\rangle$ in bcc metals. They often move repeatedly back and forth between neighboring loops. These observations initiated the idea of one-dimensional easy motion of small interstitial clusters. Examples of the effect of this easy one-dimensional motion of interstitials in the microstructure development will be explained in Section 4 of neutron irradiation.

Point defect reactions under steady electron irradiation at high temperatures (i.e. above the recovery stage III) are understood to be controlled by the motion of vacancies, the slower species of point defects. The temperature dependence of the growth rate of loops yielded the activation energy of vacancy motion [16,25]. Again the small amount of solute atoms modify the growth of loops. For example α-iron, of less purity (RRR < 500), gives higher activation energy of motion (~1.2 eV) and α-iron of higher purity (RRR > 2000) gives smaller activation energy for vacancy motion (~0.6 eV) [26]. For these low and high purity iron, the starting temperature of vacancy motion is known to be around 200°C and 200 K, respectively.

Vacancy clusters, in the form of stacking fault tetrahedra in electron irradiated fcc metals, appear under the circumstances of local enrichment of vacancies as the result of the behavior of interstitials atoms. An example is shown in Fig. 4 in which stacking fault tetrahedra are formed near the electron incident surface as the result of vacancy enrichment due to transport of interstitial atoms to the deeper position by replacement collision sequences [26]. Another example is shown in Fig. 5 in which vacancy clusters are formed along the growth paths of interstitial type dislocation loops [26].

In addition to the vacancy clusters in the form of SFT, sometimes voids appear in fcc metals by electron irradiation as shown in Fig. 6 [27], but they are known to appear due to the influence of solute addition. Addition of slight amounts of solute is believed to change the stability of small-vacancy-cluster solute complex at the beginning stage of the vacancy cluster formation [28,29].

It should be clearly stated here that there is no evidence for the formation of vacancy clusters in bcc metals during electron irradiation.

4. Fission and fusion neutron irradiation

Systematic investigation of point defect cluster formation by fusion neutron irradiation was performed with a fusion neutron source RTNS-II at Lawrence Livermore National Laboratory [30,31]. The same line of irradiation by fission neutron irradiation was performed with a fission reactor JMTR (Japan Materials Testing Reactor, JMTR) installing temperature controlled irradiation rigs [32]. From these experiments, relevant results are quoted in this paper.

Highly localized high concentrations of vacancies are produced by collision cascades started from the transfer of a large amount of energy from incident neutrons to a constituent atom of the target material. Large collision

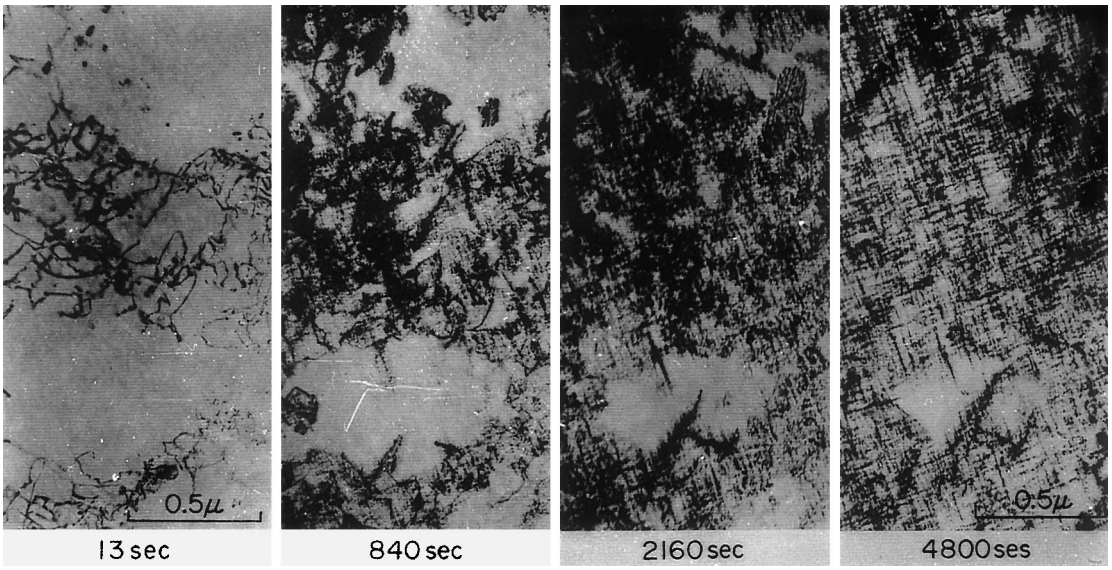

Fig. 5. Formation of vacancy clusters (all the small dots are staking fault tetrahedra) along the climb path of edge dislocations during electron irradiation of copper [26]. Two thousand keV, 3×10^{23} e/m^{2}s at 300 K. They develop into aligned arrangements (so-called self-organization).

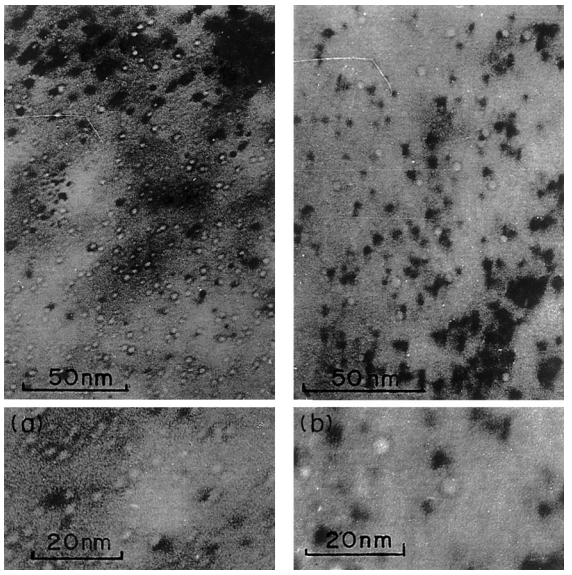

Fig. 6. Voids in electron irradiated gold dilute alloys [27]. Irradiation at 310 K. Observation with under-focus condition, and dark dots are stacking fault tetrahedra. (a) 0.05 at.% Sb and (b) 0.05 at.% Sn. Voids do not appear in pure gold.

cascades are divided into smaller groups of dense collisions, called collision subcascades. In fcc metals, small vacancy clusters are formed one for each subcascade, the majority are in the form of stacking fault tetrahedron with faulted loops mixed. In heavier fcc metals, we observe vacancy clusters forming closely spaced groups as in Fig.7(c) in silver [33]. This is unique direct evidence for subcascades. In fcc metals with lighter weight as Fig. 7(d) of nickel, the vacancy clusters cannot be identified to belong to each subcascade group [35], because of the distance between the subcascades, consequently the distance between vacancy clusters, is too large to be identified as a family [34].

In aluminum, though with the same fcc structure as others mentioned above, vacancy clusters have never been observed to be formed from collusion cascades. The reason for this absence of vacancy clusters is sought in the less dense collisions in cascades. Vacancy clusters in aluminum are dislocation loops in the case of quenching from high temperature, which have an unstable stage during nucleation, contrary to the vacancy clusters in the form of stacking fault tetrahedra in other fcc metals, which have a definite stage of the formation of stable nucleus. This difference of the stability of vacancy cluster nucleus might explain the absence of vacancy clusters in aluminum from collision cascades. However, this is not decisive when we consider the formation of stacking fault tetrahedra in the material by thin foil deformation explained in Section 5.

Even after extensive efforts of the irradiation of bcc metals by the irradiation with fission and fusion neutrons, there were no vacancy clusters which can be

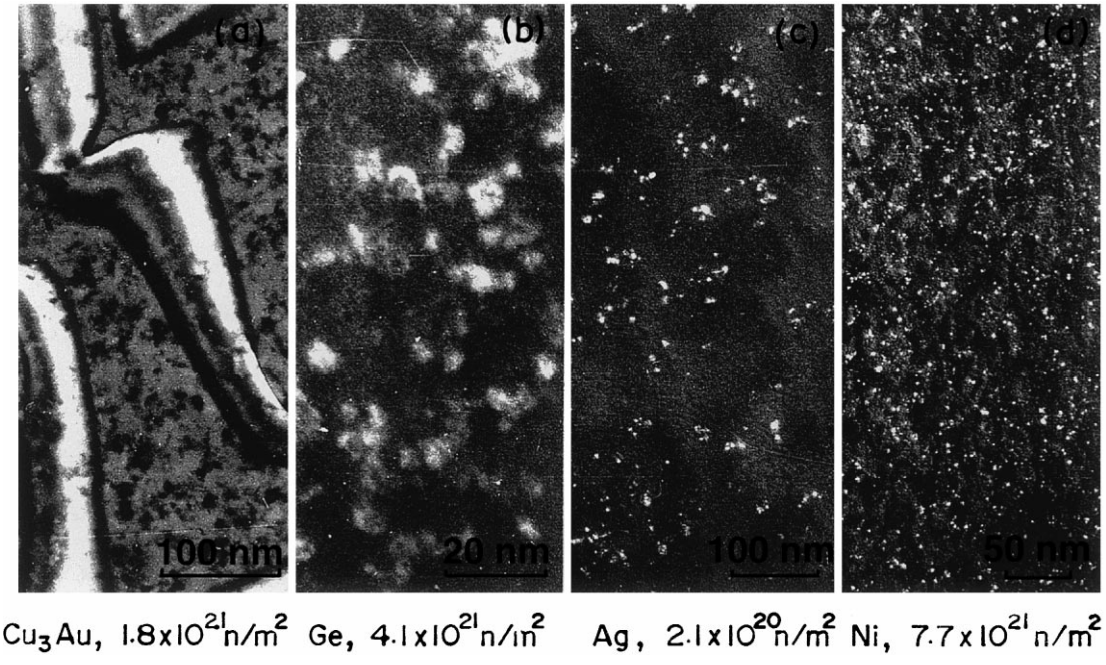

Fig. 7. Defects produced by collision cascades in D–T fusion neutron irradiated materials. (a) Disordered zones in ordered Cu_3Au, (b) amorphous zones in Ge, (c) vacancy cluster groups in Ag, and (d) dispersed vacancy clusters in Ni [33]. All irradiated at 300 K.

confidently identified to be formed from collision cascades. Collisions in cascades should not be much different between fcc and bcc metals if we compare metals of comparable weight. The difference in the point defect cluster formation should be sought in the difference in the interaction and reaction of point defects.

Voids appear after the consumption of an appreciable amount of interstitials to develop dislocation structure as in Fig. 8 [32]. Factors that influence the formation of voids are so complex that their description is beyond the scope of this short paper.

Interstitial clusters in the shape of dislocation loops are commonly formed both in fcc and in bcc metals by neutron irradiation. They are thought to be nucleated at small interstitial clusters generated at collision cascades, and their growth is the result of freely migrating interstitials released from the cascades [35]. Enhancement of interstitial cluster formation on one side of edge dislocations as shown in Fig. 9 are commonly observed [36–38]. This enhancement can be understood as the result of the directional flow of interstitials along the gradient of dilatational strain field of dislocations.

There are several excellent observations of the interstitial cluster formation which clearly indicate the effect of one-dimensional motion of interstitials and/or small interstitial clusters during neutron irradiation [39]. One example is shown in Fig. 10 in which entirely different microstructures are observed on two sides of a grain boundary. The specimen was irradiated as a thin foil observable with an electron microscope. The crystal grain on one side had such an orientation as to have all the directions of easy one-dimensional motion intersect with surface by short distance, and there is no dislocation structures from the interstitial loop growth. Another side of the crystal grain had an orientation with some direction of easy motion parallel to the foil surface, and dislocation structure developed from interstitial type dislocation loops are observed. In the former, all the small interstitial clusters had escaped to the surfaces, and voids appeared from an efficient accumulation of vacancies. In the latter, some interstitials and interstitial clusters stayed within the foil and subsequently developed into dislocation loops. Another example of the effect of easy one-dimensional motion of interstitials was found in the population of interstitial loops on each orientation. Not all the populations of interstitial loops on equivalent crystallographic planes are equivalent. It is much less for the loops whose easy direction of motion is facing towards the specimen surfaces. This observation was possible after an additional

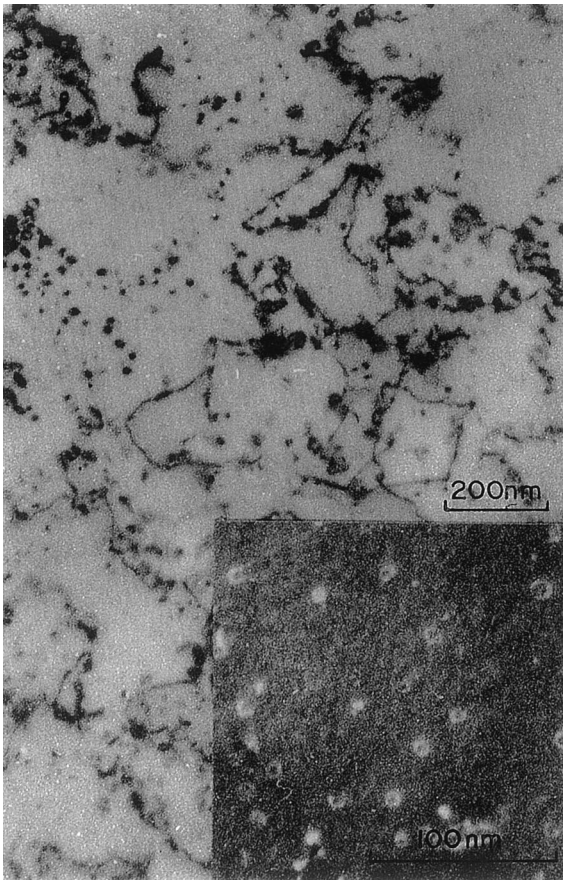

Fig. 8. Defect microstructures in fission neutron irradiated Ni [32]. Interstitial atoms were consumed to form interstitial clusters and spent for the climb of dislocations. In the background, voids are formed as in the insert micrograph. Irradiated for 24 days at 573 K up to 6×10^{23} n/m^2 (>1 MV).

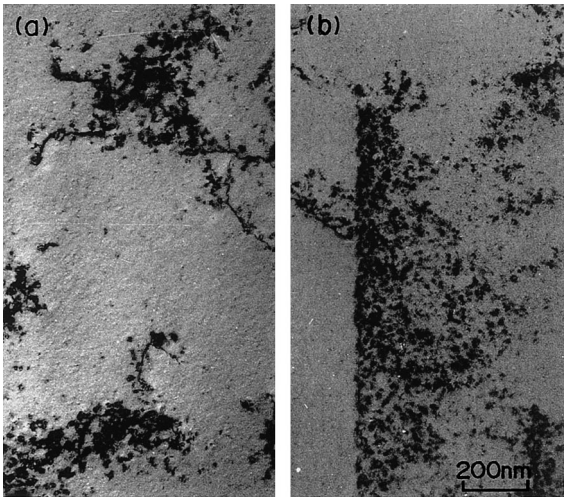

Fig. 9. Interstitial cluster formation in (a) Cu and (b) Cu–0.3at.% Ge alloy on one side of edge dislocations [36]. This kind of decoration occurs commonly in fcc and bcc metals. This never occurs during electron irradiation (see Fig. 5).

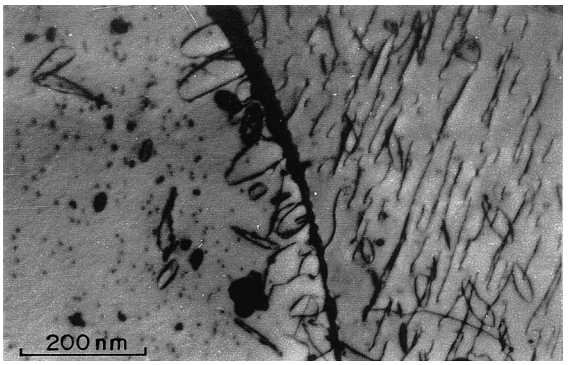

Fig. 10. Entirely different defect microstructures in two adjacent crystal grains in neutron irradiated Ni [39]. Irradiated in the form of thin foil suitable for TEM at 673 K to 9×10^{23} n/m^2 (>1 MV). Left side: voids (black dots) but no dislocations. Right side: dislocations but no voids.

irradiation by electrons to make the loops larger in a high-voltage electron microscope after neutron irradiation.

5. Plastic deformation

It has been long known that point defects are generated through the several types of reactions of glide dislocations during plastic deformation, and they sometimes form point defect clusters. Recently, heavy plastic deformation of fcc metal thin foils to fracture has been found to produce an unexpectedly high density of point defect clusters [40], and the comparison with bcc metals will be made as the last case of the various experimental treatments in this paper.

Tremendously high number density of vacancy clusters are formed in fcc metals when their thin foil (~50 μm) are deformed in elongation to fracture. At the final stage, at which both ends of an elongated foil come apart, the tip of the foil becomes so thin (~50 nm) that the part can be observed by transmission electron microscopy without any additional thinning treatment, and it is there that these vacancy clusters were observed. All vacancy clusters are in the form of SFT, and examples are shown in Fig. 11 for aluminum, gold, copper and nickel. Astonishingly enough, the vacancy clusters in aluminum are also stacking fault tetrahedra as shown in Fig. 12. This has never been observed in any other experimental treatment, such as quenching from high temperature, irradiation with various energetic particles and normal plastic deformation. Dependence of these vacancy cluster formations on deformation speed and deformation temperature, together with the change of point defect clusters by the annealing after the deformation, led to an understanding of the vacancy cluster formation from the dispersed vacancies or small invisible vacancy complexes, not directly by the plastic deformation. No dislocation nor the indication of the operation of dislocations was observed in the area of high density of vacancy clusters, and a plastic deformation mechanism without dislocation which results in the generation of high density of point defects has been proposed [41].

The shape and thickness of the fractured tip of bcc metals such as iron and vanadium were no different from

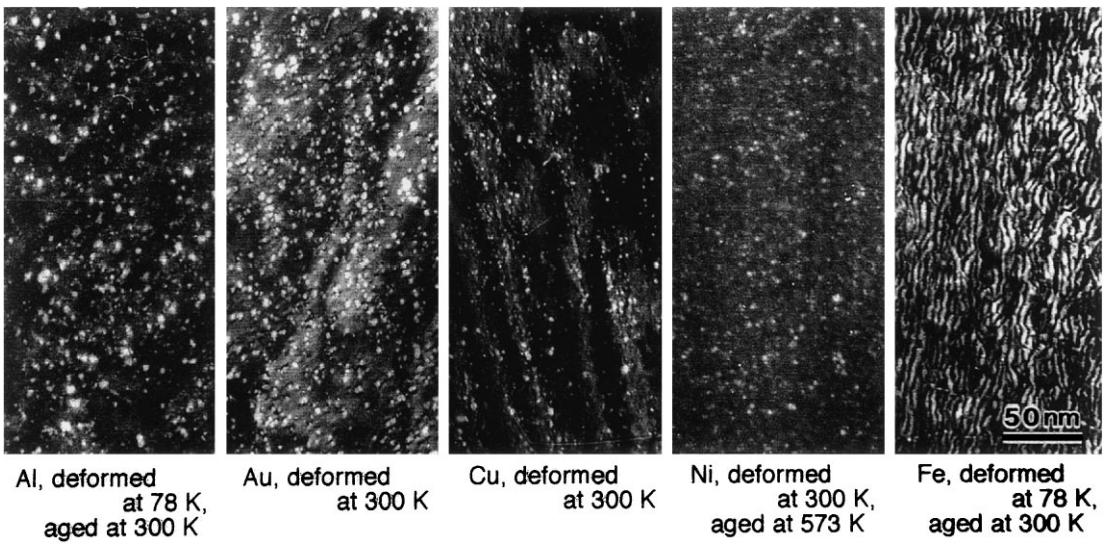

Fig. 11. High number density of small vacancy clusters formed in very thin part of fractured tips of fcc metal thin foils (a–d) [40]. Vacancy clusters are all in the form of stacking fault tetrahedra. Highly distorted part of α-iron (e).

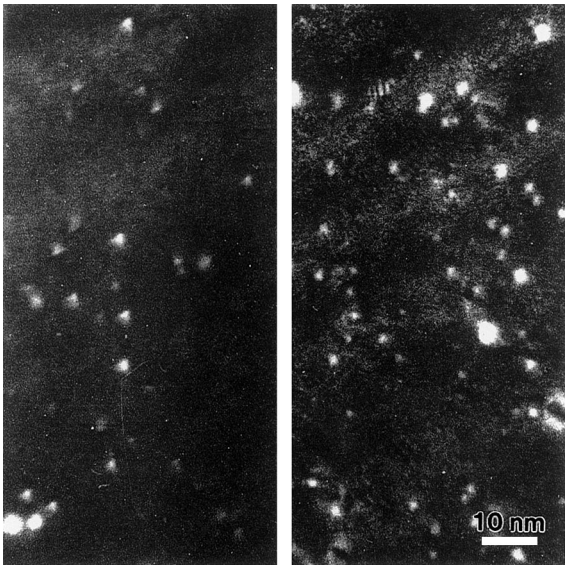

Fig. 12. Stacking fault tetrahedra observed in aluminum 'for the first time'. Introduced in a very thin part (<50 nm) of fractured tips. (a) Observation along [1 1 0], and (b) along [1 0 0].

those of fcc metals, but point defect clusters were not observed. Here, the large distortion of lattice detected in electron diffraction spots may be important, indicating the existence of high concentration of microscopically invisible point defects and small point defect clusters.

6. Concluding remarks

Point defect reactions related to point defect cluster formation have been reviewed for different types of crystallographic structure of metals and for a wide variety of experimental treatments of their production. Some concluding remarks on the characteristic similarities and differences among different metals are summarized below.

The author had thought that there was a noticeable difference even among metals with the same crystallographic structure. Typically in fcc metals, aluminum was thought to be different from other fcc metals in terms of vacancy cluster formation. However, the recent finding of the same type of vacancy clusters as those in other fcc metals taught us that this difference may be only quantitative but not qualitative.

As for the question of vacancy cluster formation, bcc metals (especially α-iron) are entirely different from fcc metals in all of the cases studied experimentally. Further research is needed to elucidate experimentally the state of supersaturated vacancies in this metal and understand theoretically as to why these vacancies do not form clusters that can be resolved in the TEM.

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