Phase Transformation in $\xi$-Al-Ni-Rh Approximant Phase Induced by Electron Irradiation by In-situ TEM

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Abstract. Electron beam irradiation induced phase transition processes were studied on crystalline approximant phase $\xi$-Al-Ni-Rh in Al$_{75}$Ni$_{15}$Rh$_{10}$ alloys. Approximant phase to amorphous transition phase occurred under different density of electron beam irradiation. Phase transition and separation occurred in a comparatively lower density of electron beam due to defects modulation and defects play an important role in this process. Higher density electron beam induces hollow holes with amorphous phase in the rim of the hole in the sample and face centered structure transition phase with parameter of 2.2 Å appears between the amorphous phase and $\xi$-phase. The appearance of the face centered structure indicates that it is the most possible shortest-range order in amorphous phase.

1. Introduction

A central issue asked about quasicrystals (QC) since the quasicrystal discovered in 1984 [1] is why they form [2]. To answer this question, the most important step is to disclose the relationships between the crystalline phases, approximant phases, quasicrystals and amorphous phase. Many techniques have been used to study the structure transition in the solidification process of the liquid metallic alloys which may include the transition of amorphous phase, quasicrystal phase and complex metallic crystalline phase. However, the work done including molecular dynamics calculation [3], in-situ X ray technique [4] cannot give the structure transition in a direct way. In situ transition, electron microscopy (TEM) technique provides a convenient, visualized way to observe the structure transition when external factors on sample which induce phase transition.

Phase transformation in quasicrystals have been intensively studied in the last two decades due to unstable character of some quasicrystals is unstable and in situ structure transition study trigger more researcher’s interesting for the goal of finding the forming mechanism. Electron beam irradiation induced phase transition by in situ TEM is one of the methods which give visualized image during the transformation process. Zhang and Urban have reported the transition from decagonal quasicrystal phase to a CsCl-type phase by electron beam irradiation in Al-Cu-Co alloy [5] and reversed to decagonal phase by in situ annealing at temperature of 600 °C [6]. In other systems such as that in quasicrystal phase forming system Al-V [7] and Al-Mn [8], they found that electron irradiation can induce transformation between quasicrystal phase and amorphous phase and an approximant phase appeared between them.

Structurally complex alloy phases, crystalline phase with giant unit cells comprising up to more than a thousand atoms per cell, is the interesting system due to its special characters of physics and chemistry [9]. Quasicrystalline approximant phases (APPs) are belonging to the structurally complex structure phases and they have characteristics of corresponding quasicrystal and crystalline phases [10].
The study of the crystalline approximant especially defected structure [11] is the bridge that connecting the quasicrystal even amorphous phase and crystalline phases. In situ phase transition study on approximant phase is an effective way to study transition mechanism. Though electron irradiation induced phase transition on quasicrystals and common crystals have been done by many people, there is little work made on approximant phases.

In the following pages, the processes of amorphization and crystallization of ξ-Al-Ni-Rh phases induced by electron beam irradiation have been investigated systematically via changing the electron flux. The effect of defects in ξ-phase will be discussed to find the transition mechanism.

2. Experimental Details

Alloys with nominal compositions of Al$_{75}$Ni$_{15}$Rh$_{10}$ were prepared by melting high purity metals (99.99%) in an arc furnace under an argon atmosphere. In order to achieve homogeneity, each ingot with a weight of only 1 g was flipped over and remelted at least six times. Specimens for transmission electron microscopy (TEM) observations were prepared by dispersing crushed ingot fragments on micro-grids covered with holey carbon films. Different electron microscopes were used to observe the structure variance under different irradiation. One is the JEOL-2010 electron microscope equipped with a single crystal LaB$_6$ filament. The other is JEOL-2010F transmission electron microscopy equipped with a field-emission gun. All experiments were carried out at the voltage of 200 KV. Fast Fourier transform (FFT) and Inverse Fast Fourier transform (IFFT) was made in the Digital Micrograph software. Crystal model was made in Crystalkit software and high-resolution transition electron microscopy simulation was made in Mactempas software.

3. Results

The basic phase is the ξ-phase, which has hexagonal lattice with main parameters of $a = 20.3$ Å, $b = 16.4$ Å and $c = 14.8$ Å, the main building block of the ξ-phase is a hexagon with pseudo Mackay cluster in the vertices of them [12]. Figures 1a and 1b show the high-resolution transition electron microscopy (HRTEM) lattice image of the defected ξ-phase in Al$_{75}$Ni$_{15}$Rh$_{10}$ ribbon before and along [010] direction. The inset images of figures 1a and 1b give corresponding electron diffraction patterns. In this case, microscope of JEOL-2010 was used under 200KV with electron beam flux $5.76 \times 10^{18}$ e$^{-}$cm$^{-2}$s. From these two images, we can see that defected area that appears in the middle of the image becomes obscure after 1800-second irradiation. The diffraction spots after irradiation in corresponding EDPS become comparatively less than that without irradiation. This indicates highly accelerated electrons disturbed ξ-phase especially the defected region. With damage of long-range order of the sample in the real space, some satellite diffraction spots disappear in the reciprocal space. Figure 1b is the initial scene during amorphization and defects is the first part that transformed to amorphous phase under a comparatively lower electron flux. Though, 1800-second irradiation is comparatively long time period compare to Si or SiC or other simple structure crystals, it is common for quasicrystals such as Al-Cu-Co. In this aspect, approximants are similar to quasicrystals.

![Figure 1](image-url)

**Figure 1.** High resolution transition electron microscopy lattice image of the defected ξ-Al-Ni-Rh along (a) the pseudo tenfold axis before and (b) after 1800 s electron irradiation, inset images are corresponding EDPS.
To find the effects of electron beam flux to the amorphization process, another experiment made in the same microscope with electron beam flux is about 5.4×10^{20} e^{-}\cdot cm^{-2}\cdot s^{-1} under voltage of 200 KV in JEOL-2010. Figures 2a-2c give the structure variance of a ξ-Al-Ni-Rh phase region before and after irradiation with the beam diameter about 10 nm which is some larger than the island area irradiated. Figure 2a is a HRTEM image which gives an island grain of completely ξ-phase with some defects on them. 1800-second irradiation can induce amorphization in most regions (bright contrast region in figure 2b. Due to a completely one little grain it belongs to, the variance in contrast cannot be induced by rotary of the grain. While another crystal phase appears in figure 2b which appears as black contrast dot or ribbon and condensed beam electron diffraction pattern indicates that it has another crystal structure that different from that of ξ-Al-Ni-Rh phase. Another 900-second irradiation under same condition makes black contrast region in the middle of the island region becoming obscure and disappear gradually in figure 2c. The structure variance indicate that irradiation induce non-crystallization and phase separation. In order to find the structure change during the irradiation, the corresponding areas in figure 2a that transition to another crystalline phase (black contrast regions in figure 2b) after irradiation are outlined by circles. However, longer time irradiation inducing another change is that part of the black contrast region that appears in the middle part of figure 2b with a ribbon like shape disappears gradually. This change can be seen in figure 2c and we can also find that dot region appeared in the border in figure 2b still retain its contrast. To enhance defected structure in figure 2a, an inversed fast Fourier transform (IFFT) is made in figure 2d by selecting six diffraction spots distributed in the vertices of the flattened hexagons (inset FFT image in figure 2d). Defects can be clearly seen in figure 2d, and it includes two kind of defects, one is phason defect with character of banana-pentagon polygons (B-P) strings distributed in ξ-phase and another is semi-formed quasicrystals in the border of the sample which display as a wheel-like polygons with bright dots distributed in the vertices of them. Comparing the four images in figure 2, we can find that the area that appearing new crystal phase induced by irradiation is just adjacent to the region that include defects. B-P strings transformed to ribbon region with simple crystal structure and wheel like QC transformed to a circle region near it with crystal structure in it. When high energy electrons disturbed the samples, defects aggregation firstly occurred firstly in the defected region and then expanded to the adjacent region. Variance of the component and atoms shifting induce the ribbon like transition crystal phase appears in the middle of the island and then transferred to the border due to decrease of the energy. Due to the high energy generated by the defects or the new phase appeared in the middle of the island, it tends to release its redundant energy by the defects moving to the surface in the following irradiation process.

This approximant (APP) phase to amorphous (A) phase and common crystalline (C) phase transition mode is the first mode report in crystalline approximant system and this transition process is simplified as APP-A+C. Phase transition mechanism is similar to that in quasicrystal which is simplified as QC-A+C [13]. However, Urban did not find effect of defects in phase transition. This defected modulated amorphization mechanism indicate that defects are important factors that control phase transition and defects study is the key step in disclosing mechanism of quasicrystal forming mechanism.

To deep understand the effect of the flux density of the electron beam to the sample, experiment was made in another electron microscope (JEOL-2010F) equipped with a field-emission gun. Figure 3 is a series image of the high-resolution microscopy image along [010] direction of defected ξ-Al-Ni-Rh in Al_{75}Ni_{12}Rh_{10} which give the transition process when a condensed electron beam irradiated on them. In this condition with a beam diameter of about 10 nm the sample were irradiated with a flux of 4.6×10^{21} e^{-}\cdot cm^{-2}\cdot s^{-1}. To enhance the contrast, a smaller aperture was used to get a columnar cluster-based image in which the pseudo Mackay clusters appear as bright balls. Figure 3a gives the formal image without any condensed dose of electron beam irradiation on them (the structure observation flux is about 0.06×10^{20} e^{-}\cdot cm^{-2}\cdot s^{-1}), in which we can see in the border of the sample, flattened hexagons arranged in parallel. In some region of figure 3a, phonons with saw-tooth like polygon can be seen in some places. Figure 3b gives the image 10 seconds later under irradiated with
electron beam flux about $3.19 \times 10^{20} \text{e}^{-1}\text{cm}^{-2}\text{s}^{-1}$. In figure 3b, we can see that a hollow appears in the border of the sample and figure 3c gives another image when the sample shifted to the adjacent region with a same irradiation flux density and a greater hole appears.

**Figure 2.** (a) Original HRTEM image before irradiation, which include $\xi$-Al-Ni-Rh with some defects in them. Circles outlined index the corresponding black contrasts in (b); (b) TEM image of the same region in (a) after 3000 s irradiation; (c) TEM image of the same region in (a) after 4500 s irradiation; (d) Inverse Fast Fourier Transform (IFFT) image by masking other regions except to six diffraction dots in the vertices of flattened hexagons. Two wheel-like polygons are outlined by circles. Inset image shows the corresponding Fourier transverse image masked, six diffraction spots are selected to obtain corresponding IFFT image.

**Figure 3.** (a) HRTEM image of the original samples viewed along [010] direction; (b) HRTEM image of the same region as that in (a) under irradiation of 10 seconds; (c) HRTEM image of the same region as that in (a) under irradiation of another 10 seconds; (d) Structure analyses of (b), in which four different regions were outlined by white squares (indexed as I, II, III, IV) from the upper to the bottom with different phase, and corresponding FFT can be seen from the adjacent left part of the square.

However, structure of the rim of the hole or the transition area between crystal and amorphous is not systematically studied. The study of the transition region between crystal and amorphous plays a key role to understand the transition mechanism. Figure 3d is the enlarged high-resolution microscopy image which gives the clear image of the crystalline approximant phase area, transition region and amorphous phase region. Four different regions with different phases can be discerned in this image from the upper part to the bottom part which is outlined by four white squares. In the upper part of figure 3d is the $\xi$-Al-Ni-Rh phase with little phason defect in them (indexed as part I), this can be seen in the FFT pattern near the square. However, in the lower part of the $\xi$-Al-Ni-Rh, two mixing phase regions exist. Region II is the phase mixing of $\xi$-Al-Ni-Rh phase and a kind of face centered cubic (FCC) phase, while adjacent region III can be expressed as phase mixing of FCC phase and
amorphous phase. On the bottom part (indexed as IV) of figure 3d is the nearest part adjacent to the damaged sample, in which a completely amorphous area can be seen.

![Figure 4](image-url)

**Figure 4.** (a)-(d) Series HRTEM images of the same region during the irradiation under 200KV in the flux of $4.6 \times 10^{21} \text{e}^{-\text{cm}^{-2}\text{s}^{-1}}$ with an electron beam diameter about 10 nm; (b)-(d) are the images that after 5 s, 15 s, 60 s later; (d)-(e) HRTEM images of the recovery process with a flux about $0.92 \times 10^{21} \text{e}^{-\text{cm}^{-2}\text{s}^{-1}}$ with the beam diameter about 1μm; (e) is the image after 5400 s and (f) is the image after 23400 s.

From six images in figure 4, we can see that transition from crystal to amorphous is a gradual process. Figure 5a is the enlarged image from edge of the hole in figure 4d, and in the middle of the image a square is outlined which has a structure that different from $\xi$-Al-Ni-Rh phase. In the square area of figure 5a, eight-layer structures that appear in $\xi$-Al-Ni-Rh phase cannot be seen. Figure 5b is the enlarged image of figure 5a, all the bright contrast dots in it arranged in a close packing form with the shortest distance $d = 2.2$ Å. According to the contrast variance of the image, we can conclude that it should belong to FCC structure. HRTEM simulation indicates that one sheet of $\xi$-Al-Ni-Rh ($b=14.8$ Å, the smallest unit of $\xi$-phase of eight layer) cannot have the same contrast. Though HRTEM simulation image of any layer of the $\xi$-Al-Ni-Rh cannot have the $\xi$-Al-Ni-Rh structure similar to that in figure 5b, part of simulation image from sliced $\xi$-Al-Ni-Rh (see figure 5c) with a thickness of 2-5 Å can have the same contrast as that in figure 5b. These results indicate that it may have recombination when it becomes thinner under irradiation. The close packed structure is the energy lower state in metal and alloys, so the thinned region retains a close packed structure to obtain a low energy state.

To disclose the structure transition of the electron beam damage to the approximant phases and find the transition mechanism, another series HRTEM image are taken along two-fold axis of $\xi$-Al-Ni-Rh phase. Figures 4a-4d are series time-dependent HRTEM images that indicate the variance of irradiation damage to the $\xi$-Al-Ni-Rh along [001] direction with beam diameter of 10 nm and a flux density of $4.6 \times 10^{21} \text{e}^{-\text{cm}^{-2}\text{s}^{-1}}$. From the four images we can see that the amorphization area becomes larger till a 10 nm diameter hole appears with increase of the irradiation time. In the initial of the irradiation, amorphization generate without any hollow appearing five seconds later (see figure 4b). The diameter of the amorphization area becomes larger with the time become longer until a small hole with diameter about 1 nm appears in figure 4c (15 s later) and then become larger in figure 4d (60 s later) about 10 nm in diameter. This phenomenon indicates that non-crystallization is the original process till hole appears. Another phenomenon found interesting in our group is that the irradiation hole damaged can recover by a lower irradiation density in Si by about 10 seconds. This recovery is also effective in our crystalline approximant phase but irradiated by a longer time under same electron beam flux range [14]. Figures 4e and 4f give the HRTEM image of the recovery process with electron
beam diameter about 1×10^{-2} m^2 and the irradiation is about 0.92×10^{21} e^{-1}cm^{-2}s^{-1}. In figure 4e, the damage hole that is about 10 nm in figure 4d in diameter now becomes a hole about 6 nm in diameter (5400 seconds’ later) and in figure 4f the hole is only about 3 nm in diameter (23400 seconds’ later).

Figure 5. (a) Enlarged HRTEM image of the transition area in figure 3d, three phases included in the image, amorphous phase, FCC phase (square region) and ξ-phase. The black square outlined the FCC phase structure and the inset image gives the FFT pattern of the square area; (b) Enlarged HRTEM image of the square area that in (a), and the lattice parameter \( a = 2.2 \text{ Å} \) (the distance between the two black lines); (c) HRTEM simulation of one layer of ξ-phase with a thickness of 2 Å and defocus of -200 Å.

As a special kind of crystalline phase, ξ-Al-Ni-Rh phase is in any way similar to quasicrystal in phase transition under irradiation. Under different electron beam flux from 5.76×10^{18} e^{-1}cm^{-2}s^{-1} to 4.6×10^{21} e^{-1}cm^{-2}s^{-1}, phase transition processes are different. Under lower electron beam irradiation, amorphization process is sluggish. Approximant phase transformed to amorphous phase and a simple structure crystal phase about 30 minutes later. In this case, defects aggregation is the dominate way to transfer to amorphous phase especially to the defected structure such as figures 1 and 2. It is the defected region that firstly amorphization and aggregated and then diffused to other area. Due to in a high energy state the grain border is, a new formed phase will eventually slide or move to the border. In the case of figure 2, new phase emerged in the middle of the grain went to the border. It indicates that the new phase is only a meta stable phase that occurs in the phase transition.

With the increase of the electron beam density and the decrease of the electron beam diameter, local sample was damaged by highly accelerated electrons. In the center of the irradiated area, amorphization region appears at the initial stage and then it grows larger till it becomes hollow. Thickness and phase distribution of the irradiated region and the adjacent areas can be illustrated by figure 6. A volcanic went shape with a hollow in the center and amorphous phase near the hole and a FCC structure phase adjacent to the amorphous phase. This process is similar to that of rapid solidification process to prepare metallic glass thin ribbon which is the most commonly used method to prepare metallic glass. Both of the processes include highly density exterior quick force and thinned samples at last.

The finding of FCC structure in the transition region between the amorphous phase and the original phase important in discover the relationship between the amorphous phase and the crystal phase. There are two kinds of transition mechanism in Zr-based amorphous alloys, and one of them is A(amorphous)-FCC (face centered structure)-C(crystal) process and another is A(amorphous)-QC (quasicrystal)-FCC (face centered structure) & QC-C(crystal) process [15]. Which kind of process undergone in phase transition is decided by many factors such as components, thermal conditions and so on and short-range order in amorphous phase is another important deciding impactor and still a mystery in our system. Many researchers believed that icosahedra polygon is the main structure [16].
and the growth of the short-range icosahedra under special condition will induce quasicrystals with icosahedra as the basic units. From the above experiments, we believed that FCC structure exists in amorphous phase as the shortest-range order but not icosahedra order in the Al-Ni-Rh system. Pseudo Mackay clusters is a comparatively larger cluster which includes the FCC structure in the center of the cluster. In the following crystal growth process in our system, it is the FCC structure firstly and then Mackay cluster form, subsequently cluster-based quasicrystals or approximants give its birth. In all, in situ irradiation study give us more clue about the phase transition especially about this unknown structurally complex crystal. Closed packed structure played the transition phase in phase transition between approximant phase and amorphous phase.

![Figure 6. Cross-section model of thickness and phase distribution of the irradiated region.](image)

4. Conclusion

Electron beam irradiation induced phase transition processes were studied on crystalline approximant phase $\xi$-Al-Ni-Rh in Al$_{75}$Ni$_{15}$Rh$_{10}$ alloys. At a lower electron density, amorphization needs a comparatively longer time. Phase separation occurred due to defects modulation and it indicates that defects play an important role in phase transition. Higher density electron beam induces holes in the sample with amorphous rim in the border and face centered structure transition phase appears between the amorphous phase and $\xi$-phase. The appearance of the face centered structure indicates that it is the most impossible shortest-range order in amorphous phase.

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