



HOKKAIDO UNIVERSITY

Title	Growth of oxide particles in FeCrAl- oxide dispersion strengthened steels at high temperature
Author(s)	Oono, N.H.; Ukai, S.; Hayashi, S. et al.
Citation	Journal of nuclear materials, 493, 180-188 https://doi.org/10.1016/j.jnucmat.2017.06.018
Issue Date	2017-09
Doc URL	https://hdl.handle.net/2115/75319
Rights	© 2017. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/
Rights(URL)	https://creativecommons.org/licenses/by-nc-nd/4.0/
Type	journal article
File Information	manuscript(revised clean).pdf



Growth of Oxide Particles in FeCrAl- Oxide Dispersion Strengthened Steels at High Temperature

N. H. Oono^{1,a}, S. Ukai^{1,b}, S. Hayashi^{2,c}, S. Ohtsuka^{3,d}, T. Kaito^{3,e}, A. Kimura^{4,f}, T. Torimaru^{5,g}, K. Sakamoto^{5,h}

¹Faculty, Graduate School and School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

²School of Materials and Chemical Technology, Tokyo Institute of Technology, Meguro-ku 152-8550, Japan

³Japan Atomic Energy Agency, Oarai 311-1393, Japan

⁴Institute of Advanced Energy, Kyoto University, Uji 611-0011, Japan

⁵Nippon Nuclear Fuel Development, Co., LTD., Oarai 311-1313, Japan

^an-oono@eng.hokudai.ac.jp, ^bs-ukai@eng.hokudai.ac.jp, ^chayashi@eng.hokudai.ac.jp,

^dohtsuka.satoshi@jaea.go.jp, ^ekaito.takeji@jaea.go.jp, ^fkimura@iae.kyoto-u.ac.jp,

^gtorimaru@nfd.co.jp, ^hkan.sakamoto@nfd.co.jp

Corresponding author: Naoko Hori OONO

Faculty, Graduate School and School of Engineering, Hokkaido University, Kita 13, Nishi 8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan

e-mail: n-oono@eng.hokudai.ac.jp

Tel.: +81 11 706 6356

Abstract

The growth of oxide particles in FeCrAl- oxide dispersion strengthened steel (ODSS) considering an accident condition of the light-water reactor at above 1500 K was studied by using a high-temperature annealing. Oxide particles grew from 9nm to more than 50nm as maximum at 1623K for 27h, with decreasing their number density in two orders of magnitude. Most of the oxide particles in 15Cr-7Al were identified as YAM or YAP, while the oxide particles in 15Cr-7Al-0.4Zr were identified trigonal $Y_4Zr_3O_{12}$. Zr addition to 15Cr-7Al ODSS accelerated the growth of the oxide particles, which is quite contrary to the effect of Zr addition during sintering as suggested in the literature. The kinetics of coarsening was characterized by an equation of Ostwald ripening. The diffusion activation energies obtained in the present materials were quite larger than the conventional diffusion activation energy of Y in alpha-iron. Gibbs free energy of oxides should be considered to discuss the coarsening.

1. Introduction

According to the reports of the Fukushima Daiichi Nuclear disaster, the oxidation of the Zircaloy cladding began above 1173 K and causes accelerated hydrogen generation above 1500 K [1, 2]. To remove the potential threat of hydrogen explosion in the severe accident condition, alternating the Zircaloy with other oxidation-resistant materials is very important. FeCrAl-alloy is one of the most suitable candidates for the accident-tolerant fuel cladding of the light-water reactors, because they form a protective Al_2O_3 scale under high temperature steam oxidation conditions [3, 4]. However, applying FeCrAl-alloy to the cladding requires reducing the wall thickness to almost half of that of Zircaloy to maintain neutron economy [4]. To overcome the deterioration of strength to be caused by the thickness reduction of the cladding, we have developed FeCrAl-based oxide dispersion strengthened steels (ODSS), which have not only oxidation resistance at high temperature, but also strength and irradiation resistance [5]. We added Zr into Fe-Cr-Al ODSS to improve the high-temperature strength by forming the fine Y-Zr complex oxide particles instead of the coarse Y-Al complex oxide particles [6, 7, 8, 9, 10, 11]. There have been reported the relationship between the type of oxide and the size of oxide particles by observing the as-fabricated materials [12, 13, 10, 14]. However, in a specific accident scenario, FeCrAl-alloy is exposed to high temperature at approximately 1500-1600K for more than several ten hours in the absence of any cooling [3]. The stability of oxide particles at such a high temperature has yet to be clarified, even though the coarsening of oxide particles could significantly reduce the mechanical integrity. In the present study, we discuss the coarsening of oxide particles in FeCrAl-ODSS and FeCrAl-ODSS with Zr addition at elevated temperatures.

2. Experimental

The target compositions of the material in this study were Fe-15Cr-7Al-0.5Ti-0.5Y₂O₃ (in wt. %) without and with 0.4wt. % Zr. We call the former 15Cr-7Al and the latter 15Cr-7Al-0.4Zr. FeCrAl- pre-alloyed powder, Cr and Zr metal powder, Y₂O₃ powder and Fe₂O₃ powder to control the excess amount of oxygen were mixed together and mechanically-alloyed (MAed) by using an attritor in Ar atmosphere, with a rotation speed of 220rpm, for 48h. The MAed powder was then canned in a capsule and extruded at 1433K. The chemical compositions of the extruded bars are described in Table 1.

Table 1. Chemical composition of the extruded bars in wt. % (Ex. O: excess oxygen).

Specimen	Fe	Cr	Ti	Al	Y ₂ O ₃	Zr	Ex. O
15Cr-7Al	bal.	14.18	0.51	6.44	0.470	<0.01	0.120
15Cr-7Al-0.4Zr	bal.	14.76	0.50	6.40	0.470	0.37	0.220

The extruded bars were cut into several pieces (we call them “as-extruded” pieces). The pieces were annealed in a vacuum furnace at a vacuum $\sim 1 \times 10^{-4}$ Torr, to coarsen oxide particles. The annealing temperature and time ranged from 1473 K to 1623 K and from 3 h to 200 h, respectively, as listed in Table 2. The temperature increase and decrease rates were 5 K/min. The as-extruded and annealed pieces were punched into 3 mm ϕ disc specimens and electro-polished for TEM observation. Some TEM specimens were fabricated by focused ion beam (FIB) with a subsequent low-energy ion milling to remove the damages induced by FIB. Three types of transmission electron microscopes (TEM) were applied for microstructure observation: JEOL JEM-2010 (200kV) to observe the mean size and distribution, JEM-2010F

(200kV) to analyze the lattice structure and FEI Titan (300kV) to analyze the chemical elements of the oxide particles. Micro-Vickers hardness test was applied for all specimens before and after annealing, with a load of 0.98N and a holding time of 30 second.

Table 2. Annealing temperature and time.

Temperature (K)	Time (h)		
1473	27	81	200
1543	3	27	81
1623	3	9	27

3. Results

Fig.1 shows TEM micrographs of the oxide particles before and after high temperature annealing. The initial average sizes of oxide particles were 8nm and 9nm in 15Cr-7Al and 15Cr-7Al-0.4Zr, respectively. In both alloys, the oxide particles after annealing for 27 h at 1623 K were more than three times larger than those before annealing. Some particles taken from an appropriate crystal orientation (for example, $1\sim 2g^*$ on the systematic reflection) show a strain-contrast originated from the coherent precipitate or misfit moiré fringes originated from the semi-coherent precipitates (pointed by red arrows). The average size and the number density of oxide particles after annealing are plotted in Fig. 2a, 2b, 2d and 2e. Each value was derived from 168 particles in average. The number of particles in each specimen and their size distribution are shown in Supplemental data 1 and 2. The results of 9Cr ODSS [15] are also shown in Fig. 2c and f. The oxide particles in the present work were coarsen more significantly

than those in 9Cr ODSS. Notably, the size of the oxide particles in the 15Cr-7Al-0.4Zr after annealing at 1623 K for 27 h became larger than those of the other alloys. After annealing at 1623 K for 27 h, the number densities of the oxide particles in FeCrAl-ODSS decreased almost two orders of magnitude as compared to those before annealing, while the number density of 9Cr ODSS after the annealing at 1623K for 27h decreases just one order of magnitude as compared to that before annealing. The size of oxide particles after annealing increased with decreasing their number density, indicating that the oxide particles coarsened by Ostwald ripening.

Fig. 3 shows STEM-EDS mapping of the oxide particles in 15Cr-7Al after annealing at 1623K for 27h. In the HAADF image, oxide particles appeared as the dark spheres, pointed by red arrows. The small black area in adjacent to the oxide particles are Ar bubbles induced during the MA. Y, Al and O are distributed on the oxide particles, indicating that most of the oxide particles are Y-Al complex oxides. Fig. 4 shows the magnified images of a coarse oxide particle in 15Cr-7Al after annealing at 1623K for 27h. The large oxide particle had a core-shell structure; the core contained Al, Y and O, while the shell contained additionally Fe and Cr. Ti were distributed at the surface of the shell. Fig. 5 shows STEM-EDS mapping results of the oxide particles in 15Cr-7Al-0.4Zr after annealing 1623K for 27h. Most of the oxide particles did not clearly appear in the HAADF images except for the particles pointed by the red arrows. However, there were many areas where Y and Zr are concentrated, indicating that the Y-Zr oxides exist in the specimen.

Fig. 6 and 7 show a series of the HRTEM analyses of the oxide particles in 15Cr-7Al and 15Cr-7Al-0.4Zr after annealing at 1623 K for 27 h, respectively. The right images of Fig. 6a, 6b, 7a and 7b show the simulated diffraction patterns of the oxide particles, based on the lattice information of the literature displayed in a database [16, 17, 18, 19] and the simulating software [20]. Most of the oxide particles in 15Cr-7Al were indexed as monoclinic $Y_4Al_2O_9$ (YAM: $P2_1/c$,

No. 14, $a = 0.73752$ nm, $b = 1.04621$ nm, $c = 1.11102$ nm, $\alpha = \gamma = 90^\circ$, $\beta = 108.575^\circ$) [16] or orthorhombic YAlO_3 (YAP: P_{nma} , No. 62, $a = 0.5184$ nm, $b = 0.5317$ nm, $c = 0.7368$ nm, $\alpha = \beta = \gamma = 90^\circ$) [17]. Based on the orientation relationship proposed by Dou et al. [14], the particle shown in Fig. 6a is measured 34nm and semi-coherent to the matrix, referred as $(\bar{1}\bar{2}4)_{\text{YAM}} \parallel (\bar{1}10)_{\alpha\text{-Fe}}$ and $[253]_{\text{YAM}} \parallel [111]_{\alpha\text{-Fe}}$. The lattice misfit $\delta = (d_p - d_m)/d_p$ is 17.0% using the lattice constant of the Fe-Cr alloy $d_{\text{Fe-Cr}} = 0.2876$ nm [10]. The particle shown in Fig. 6b is measured 23nm also semi-coherent to the matrix, referred as $(2\bar{2}1)_{\text{YAP}} \parallel (\bar{1}10)_{\alpha\text{-Fe}}$ and $[432]_{\text{YAP}} \parallel [111]_{\alpha\text{-Fe}}$. The lattice misfit δ is -2.1%. Almost all the oxide particles in 15Cr-7Al-0.4Zr were indexed as trigonal $\text{Y}_4\text{Zr}_3\text{O}_{12}$ (R-3, No. 68, $a = b = 0.9738$ nm, $c = 0.9115$ nm, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$). The particles shown in Fig. 7a is measured 27nm and semi-coherent to the matrix, referred as $(\bar{1}\bar{2}4)_{\text{Y}_4\text{Zr}_3\text{O}_{12}} \parallel (\bar{1}10)_{\alpha\text{-Fe}}$ and $[2\bar{1}0]_{\text{Y}_4\text{Zr}_3\text{O}_{12}} \parallel [111]_{\alpha\text{-Fe}}$. The lattice misfit δ is -9.7%. The particles shown in Fig. 7b is measured 27nm and coherent to the matrix, referred as $(\bar{2}3\bar{2})_{\text{Y}_4\text{Zr}_3\text{O}_{12}} \parallel (\bar{1}10)_{\alpha\text{-Fe}}$, $(\bar{4}20)_{\text{Y}_4\text{Zr}_3\text{O}_{12}} \parallel (\bar{1}01)_{\alpha\text{-Fe}}$ and $[122]_{\text{Y}_4\text{Zr}_3\text{O}_{12}} \parallel [111]_{\alpha\text{-Fe}}$. The smallest lattice misfit δ is 16.5% for $(\bar{2}3\bar{2})_{\text{Y}_4\text{Zr}_3\text{O}_{12}} \parallel (\bar{1}10)_{\alpha\text{-Fe}}$. There were also ZrO_2 to some extent in 15Cr-7Al-0.4Zr (photo not shown).

Fig. 8 shows the results of Vickers hardness test of 15Cr-7Al and 15Cr-7Al-0.4Zr. Before annealing, the hardness of 15Cr-7Al-0.4Zr is harder than that of 15Cr-7Al, whereas after annealing at 1623K for 27h, the hardness of 15Cr-7Al-0.4Zr significantly decreases and lower than that of 15Cr-7Al. The tendency of the hardness-decrease roughly agrees with that of the coarsening of the oxide particles.

4. Discussion

4.1. Type of oxide particles in the present specimens

In the present work, most of the oxide particles in 15Cr-7Al were YAM or YAP. They are likely to have been formed by internal oxidation of Y and Al during sintering. Based on the literature

[21], the reactions leading to these oxides are summarized as follows: $2Y_2O_3 + Al_2O_3(\gamma) \rightarrow YAM$ (~1273K), $Al_2O_3(\gamma) + YAM \rightarrow 4YAlO_3$ (Hexagonal: YAH, 1273-1373K), $YAH \rightarrow YAP$ (1373-1473K). Dou et al. [14] suggested in their analysis of the oxide particles in 15.5Cr-4Al ODSS that the formation occurs due to the affinity of oxygen with different solute atoms, and concluded that the oxide particles in their specimen could be transformed to YAH because of their very low concentration of Ti, i.e., 0.1wt. %. In the present work, the concentration of Ti is quite high, i.e. ~0.5wt. %, which would retard the diffusion of oxygen by forming TiO^{2+} ions and leave YAM in the as-received specimen. Once YAH could be formed in our specimen as a consequence of the high temperature annealing, it should be transformed to YAP at 1623K. On the other hand, almost all particles in 15Cr-7Al-0.4Zr were $Y_4Zr_3O_{12}$. Because Zr has a slightly higher affinity to oxygen than Al [22], Y-Zr complex oxides are formed instead of Y-Al complex oxide. In the literature, several phases of zirconium oxide have been identified in Zr-added ODSS: Yu et al. [11] have found cubic $Y_2Zr_2O_7$ particles in Fe-16Cr-4Al-2W-0.35Y₂O₃ with 0.6Zr, while Dou et. al. [10] have found tetragonal $Y_4Zr_3O_{12}$ particles in Fe-15Cr-2W-0.1Ti-4Al-0.35Y₂O₃ with 0.63Zr (in mass. %). The phase diagram for the ZrO_2 -YO_{1.5} system suggests that $Y_4Zr_3O_{12}$ are possible at the temperature range from 1473K to 1623K [23], while no interpretation or existence of $Y_2Zr_2O_7$ is shown. The present result agrees with P. Dou et. al. and is reasonable according to the phase diagram.

4.2. Kinetics of the particle coarsening

Given the kinetic relationship for precipitate coarsening thorough Ostwald ripening [24]:

$$r^n - r_0^n = k \cdot \exp(-Q/RT) \cdot t \quad (1)$$

where r and r_0 are precipitate radius after and before annealing, respectively, k is the rate constant for a specific temperature and diffusive process, Q is the diffusion activation energy, R is the gas constant, T is the temperature, t is the annealing time, and the exponent n is the

value restricted by the mechanisms of diffusion: $n = 3$ for lattice diffusion, $n = 4$ for grain-boundary diffusion and $n = 5$ for dislocation 'pipe' diffusion. Taking logarithm for eq. (1), it gives:

$$\ln(r^n - r_0^n) = A + \ln t \quad (2)$$

where $A = -(Q/RT) + \ln k$, is a constant at given temperature. Fig. 9a shows an example of the corresponding plot of $\ln(r^n - r_0^n)$ versus $\ln t$ ($n = 5$ for 15Cr-7Al), and Table 3 shows the values of the slope of the line fits for all n and at all annealing temperatures. The slope of the fits becomes nearest to 1, when $n = 5$ for 15Cr-7Al at 1473K and when $n = 4$ for 15Cr-7Al-0.4Zr. For 15Cr-7Al, the corresponding slopes at 1543K and 1623K are much lower than 1. The slopes of the fits for 15Cr-7Al at 1543K and 1623K become nearest to 1 when $n = 8$ and $n = 9$, respectively. The higher values of n than $n = 5$ indicate that certain diffusion mechanism faster than pipe diffusion mechanism would be applied. However, the mechanism faster than pipe diffusion mechanism, e.g. surface diffusion, is difficult to be considered because the oxide particles distributed in a solid material. The change in the slope at higher temperature is similar to that of Alinger for MA956 [24]. He suggested that, at higher temperature, a transformation of the nano-clusters to nearer to equilibrium oxide type phases should be considered as well as a possible change in coarsening mechanism from pipe diffusion. However, in the present work, the transformation from YAH to YAP could occur at all annealing temperatures from 1473K to 1623K, as mentioned in the section 4.1. We think that it is too early to draw a conclusion without any further examination with longer annealing time, because the growth of oxide particles does not appear to be saturated in Fig. 2 at 1543K and 1623K. So far, we apply $n = 5$ (pipe diffusion) for 15Cr-7Al because the oxide particles in annealed specimen associate with dislocations (see Fig. 1 at 1623K, 27h).

Table 3. The values of the slope of the line fits.

15Cr-7Al

Temperature [K]	n=3	n=4	n=5	n=6	n=7	n=8	n=9
1473	0.60	0.76	0.93	1.10	1.28	1.46	1.64
1543	0.39	0.50	0.61	0.73	0.85	0.97	1.09
1623	0.34	0.45	0.56	0.67	0.78	0.90	1.01

15Cr-7Al-0.4Zr

Temperature [K]	n=3	n=4	n=5
1473	0.62	0.75	0.90
1543	0.76	0.95	1.15
1623	0.81	1.05	1.31

Substituting $\alpha = k \cdot \exp(-Q/RT)$ in eq. (1) and taking logarithm for the equation:

$$\ln \alpha = -Q/RT + \ln k = -Q/R \cdot (1/T) + \ln k \quad (3)$$

For 15Cr-7Al, for instance, applying $n = 5$ to eq. (1), the t versus $r^5 - r_0^5$ curve can be plotted as shown in Fig. 9b. The value of α can be obtained by the fit to the data $r^5 - r_0^5$ and t in Fig. 9b. Fig. 9c shows the corresponding fit to the $\ln \alpha$ versus $1/T$ in eq. (3) with the values of α obtained by the fits in Fig. 9b. The slope of the fit in Fig. 9c yields the values of k and Q . Table 4 shows the values of k and Q for the present materials. The values for 9Cr ODSS are also shown as a reference [15].

Table 4. The rate constant (k) for a specific temperature and the diffusion activation energy (Q).

Material	k [$\text{m}^n \cdot \text{s}^{-1}$]	Q [$\text{kJ} \cdot \text{mol}^{-1}$]	n
15Cr-7Al	1.3×10^{20}	480	5 (pipe)
15Cr-7Al-0.4Zr	1.4×10^{28}	747	4 (grain-boundary)
9Cr ODSS [15]	2.8×10^{33}	891	5 (pipe)

The value of Q for 15Cr-7Al is much lower than those for 15Cr-7Al-0.4Zr and 9Cr ODSS due to the small values of the slope at 1543K and 1623K in Table 3 which are already discussed above. The value of Q for 15Cr-7Al-0.4Zr is lower than that for 9Cr ODSS, which indicates that the diffusion of the dispersion species is faster in 15Cr-7Al-0.4Zr than that in 9Cr ODSS. The interpretation agrees with the present results of coarsening (see Fig. 2). In any case, the values of Q obtained in the present work and the past work for 9Cr ODSS are remarkably higher than that of the impurity diffusion of Y atom in alpha-iron ($299 \text{ kJ} \cdot \text{mol}^{-1}$ [25]). The present values of Q should contain the contributions of both the diffusion activation energy and the effective activation energy controlling the solubility of the key solutes at a dislocation or a grain-boundary [24]. Then, we distinguish the superficial activation energy during Ostwald ripening of oxide particles, as $Q = Q_{sup}$, from the real diffusion activation energy of the elements, as Q_d . The most effective contribution to Q_{sup} should be from the bonding energies of oxides. We do not interpret that the bonding energy can be inserted directly into the equation (1). However, note that Gibbs free energy (G_0) of the oxides is very large negative even at high

temperature. For example, G_0 of Y_2O_3 at 1623K becomes -2218kJ/mol according to the thermodynamic function of ref [26].

4.3. Coarsening of the oxide particles at a high temperature

Al is the element which coarsens oxide particles by forming incoherent Y-Al complex oxides [6-8], while Zr is the element which prevent coarsening oxide particles in Al added ODSS by forming coherent trigonal $Y_4Zr_3O_{12}$ [10] or pyrochlore $Y_2Zr_2O_7$ [11]. In the present study, however, the oxide particles in the 15Cr-7Al-0.4Zr become more than 10 nm coarser than those 15Cr-7Al after annealing at 1623 K for 100 h. Our result agrees with the previous study of Sawazaki et al. [27]. Here we discuss the result in more detail.

Considering the equation of Ostwald ripening, eq. (1) is rewritten as following equation [24]:

$$r^n - r_0^n = a \{ (DC_0\gamma(V_m)^2)/(RT) \} t \quad (4)$$

where a is the coefficient depending on the morphology of the diffusion path, D is the diffusivity of the dispersion species which is the slowest moving, C_0 is the solubility of the elements which compose the oxide particles. γ is the interface energy of the oxide particle/matrix, and can be calculated based on the Read–Shockley equation of the well-established dislocation model of grain-boundaries [28]. V_m is the molar volume of the oxide particles. In eq. (4), D , C_0 and γ depend on the type of oxide. Fig. 10 shows the calculated γ against the size of the oxide particle observed in the specimen annealed at 1623K for 27h (the list of oxide particles and corresponding γ are shown in supplemental data 3). To calculate γ , we used the equation of shear modulus for alpha-iron [29]. There is no correlation seen between the size of the oxide particles and γ . The values of C_0 for the dispersion species at 1623 K [30, 31, 32, 33] are shown in Table 5. Considering the diffusion coefficient D , eq. (4) is expanded as follow:

$$r^n - r_0^n = a \{ (DC_0\gamma(V_m)^2)/(RT) \} t = a \{ (C_0\gamma(V_m)^2)/(RT) \} \cdot D_0 \exp(-Q_d/RT) \cdot t \quad (5)$$

where D_0 is pre-exponential factor and Q_d is the diffusion activation energy as defined in the section 4.2. We calculated the volume diffusion coefficient at 1623K by using the values of D_0 and Q_d in ref. [25, 35, 34, 36] and show in Table 5 (we applied the volume diffusion coefficient instead of the short-circuit diffusion coefficients used when $n = 4$ or $n = 5$, because of lack of the data). According to Fig. 10 and Table 5, there is no sufficient reason for the acceleration of coarsening of oxide particles in 15Cr-7Al-0.4Zr at 1623K.

Table 5. The physical property of the dispersion species at 1623K.

Element	C_0 [wt. %]		D [$\text{m}^2 \cdot \text{s}^{-1}$]	
Y	<1	[30]	2.4×10^{-15}	[25]
Al	>20	[31]	2.3×10^{-14}	[35]
Zr	1~2	[32]	3.7×10^{-14}	[34]
Ti	~7	[33]	7.6×10^{-11}	[36]

In the section 4.1. we discussed the kinetics of Ostwald ripening and distinguished the superficial activation energy during Ostwald ripening of oxide particles, as $Q = Q_{sup}$, from the real diffusion activation energy of the elements, as Q_d . Now we re-write the equation (5) as follows:

$$r^n - r_0^n = a \{(C_0 \gamma (V_m)^2) / (RT)\} \cdot D_0 \exp(-Q_{sup}/RT) \cdot t \quad (6)$$

Table 6 shows the values of G_0 of oxide particles which are expected to exist in the present materials at 1623 K. The values are calculated being based on the thermodynamic functions described in ref. [26, 37, 23, 38]. According to Table 6, the stability of oxide is in order of YAM

$> \text{Y}_2\text{Ti}_2\text{O}_7 > \text{Y}_2\text{O}_3 > \text{YAP} > \text{Y}_4\text{Zr}_3\text{O}_{12}$. The order of stability roughly agrees with the coarsening of oxide particles, except for the result of YAM. Note that, the value of G_0 for $\text{Y}_4\text{Zr}_3\text{O}_{12}$ is significantly lower minus than those of the other oxides. According to the phase diagram of $\text{ZrO}_2\text{-Y}_2\text{O}_3$, $\text{Y}_4\text{Zr}_3\text{O}_{12}$ decomposes above 1660K [23], while the other oxides are stable far above the temperature [26, 37, 38]. So far, we conclude that, for the oxide particle at high temperature, the stability of oxide is most effective on Ostwald ripening.

Table 6. Gibbs free energy of the typical oxides in Al, Zr, Ti-added ODS alloys at 1623K.

possible oxide	G_0 [kJ·mol ⁻¹]	
$\text{Y}_2\text{O}_3(\text{cubic})$	-2218	[26]
YAlO_3 (YAP)	-2080	[37]
$\text{Y}_4\text{Al}_2\text{O}_9$ (YAM)	-6515	[37]
$\text{Y}_4\text{Zr}_3\text{O}_{12}$	-275.8	[23]
$\text{Y}_2\text{Ti}_2\text{O}_7$	-4515	[38]

5. Conclusion

The growth of oxide particles in FeCrAl-ODSS considering an accident condition of the light-water reactor at above 1500 K was studied by using a high-temperature annealing. Oxide particles in 15Cr-7Al and 15Cr-7Al-0.4Zr became more than three times larger at 1623K for 27h than those of before annealing, while decreasing their number density by two orders of magnitude. Most of the oxide particles in 15Cr-7Al were identified as YAM or YAP, while the oxide particles in 15Cr-7Al-0.4Zr were identified trigonal $\text{Y}_4\text{Zr}_3\text{O}_{12}$. 0.4w. % Zr addition to 15Cr-

7Al accelerated the growth of the oxide particles, which is quite contrary to the effect of Zr addition which refines oxide particles during sintering as suggested in the literature. The kinetics of coarsening were characterized by an equation of Ostwald ripening and the diffusion activation energies of the coarsening were estimated. The diffusion activation energies obtained in the present materials were quite larger than the conventional diffusion activation energy of Y in alpha-iron. The large diffusion activation energies and the coarsening acceleration of $Y_4Zr_3O_{12}$ at higher temperature could be explained by the stability of oxides, so far Gibbs free energy.

References

- [1] F. Tanabe, "Analyses of core melt and re-melt in the Fukushima Daiichi nuclear reactors," *J. Nucl. Sci. Tech.*, vol. 49, pp. 18-36, 2012.
- [2] C. Allison, J. K. Hohorst, B. S. Allison, D. Konjarek, T. Bajs, R. Pericas, F. Reventos and R. Lopez, "Preliminary Assessment of the Possible BWR Core/Vessel Damage States for Fukushima Daiichi Station Blackout Scenarios Using RELAP/SCDAPSIM," *Science and Technology of Nuclear Installations*, vol. 2012, p. 646327, 2012.
- [3] K. Terrani, S. J. Zinkle and L. L. Snead, "Advanced oxidation-resistant iron-based alloys for LWR fuel cladding," *J. Nucl. Mater.*, vol. 448, pp. 420-435, 2014.
- [4] N. George, K. A. Terrani, J. Powers, A. Worrall and I. Maldonado, "Neutronic analysis of candidate accident-tolerant cladding concepts in pressurized water reactors," *Annals of Nuclear Energy*, vol. 75, p. 703–712, 2015.
- [5] S. Ukai, N. Oono, S. Ohtsuka, T. Kaito, K. Sakamoto, T. Torimaru, A. Kiimura and S. Hayashi, "Development of FeCrAl-ODS Steels for ATF Cladding," *Proc. Light Water Reactor (LWR) Fuel Performance Meeting (TOP FUEL) 2016*, 2016.
- [6] A. Kimura, R. Kasada, N. Iwata, H. Kishimoto, C. H. Zhang, J. Isselin, P. Dou, J. H. Lee, N. Muthukumar, T. Okuda, M. Inoue, S. Ohnuki, T. Fujisawa and T. F. Abe, "Development of Al added high-Cr ODS steels for fuel cladding of next generation nuclear systems," *J. Nucl. Mater.*, vol. 417, pp. 176-179, 2011.
- [7] C. Zhang, A. Kimura, R. Kasasda, J. Jang, H. Kishimoto and Y. Yang, "Characterization of the oxide particles in Al-added high-Cr ODS ferritic steels," *J. Nucl. Mater.*, vol. 417, pp. 221-224, 2011.
- [8] L. Hsiung, M. Fluss, S. Tumey, B. Choi, Y. Serruys, F. Willaime and A. Kimura, "Formation mechanism and the role of nanoparticles in Fe-Cr ODS steels developed for radiation tolerance," *Phys. Rev. B*, vol. 82, p. 184103, 2010.
- [9] R. Gao, T. Zhang, X. Wang, Q. Fang and C. Liu, "Effect of zirconium addition on the microstructure and mechanical properties of ODS ferritic steels containing aluminum," *J. Nucl. Mater.*, vol. 444, pp. 462-468, 2014.
- [10] P. Dou, A. Kimura, R. Kasasda, T. Okuda, M. Inoe, S. Ukai, S. Ohnuki, T. Fujisawa and F. Abe, "TEM and HRTEM study of oxide particles in an Al-alloyed high-Cr oxide dispersion strengthened steel with Zr addition," *J. Nucl. Mater.* 444, pp. 441-453, 2014.
- [11] C. Yu, H. Oka, N. Hashimoto and S. Ohnuki, "Development of damage structure in 16Cr–4Al ODS steels during electron-irradiation," *J. Nucl. Mater.* 417, pp. 286-288, 2011.

- [12] I. Kim, B. Choi, C. Kang, T. Okuda, P. Maziasz and K. Miyahara, "Effect of Ti and W on the Mechanical Properties and Microstructure of 12% Cr Base Mechanical-alloyed Nano-sized ODS Ferritic Alloys," *ISIJ International*, vol. 43, no. 10, pp. 1640-1646, 2003.
- [13] S. Ukai, S. Mizuta, M. Fujiwara, T. Okuda and T. Kobayashi, "Development of 9Cr-ODS Martensitic Steel Claddings for Fuel Pins by means of Ferrite to Austenite Phase Transformation," *J. Nucl. Sci. Tech.*, vol. 39, no. 7, pp. 778-788, 2002.
- [14] P. Dou, A. Kimura, T. Okuda, M. Inoue, S. Ukai, S. Ohnuki, T. Fujisawa and F. Abe, "Polymorphic and coherency transition of Y–Al complex oxide particles with extrusion temperature in an Al-alloyed high-Cr oxide dispersion strengthened ferritic steel," *Acta Mater.*, vol. 59, pp. 992-1002, 2011.
- [15] N. Oono, K. Nakamura, S. Ukai, T. Kaito, T. Torimaru, A. Kimura and S. Hayashi, "Oxide particle coarsening at temperature over 1473 K in 9CrODS steel," *Nucl. Mater. Energy*, vol. 9, pp. 342-345, 2016.
- [16] H. Yamane, K. Ogawara, M. Omori and T. Hirai, "Phase Transition of Rare-Earth Aluminates (RE₄Al₂O₉) and Rare-Earth Gallates (RE₄Ga₂O₉)," *J. Am. Ceram. Soc.*, vol. 78, pp. 2385-2390, 1995.
- [17] T. Adylov, G. Voronov, E. Mansurova, L. M. Sigalov and E. Urazaeva, "The Y₂O₃-Al₂O₃ System Above 1473 K," *Russ. J. Inorg. Chem.*, vol. 33, pp. 1062-1063, 1988.
- [18] Materials Database Group, "Inorganic Material Database (AtomWork)," National Institute for Materials Science, 6 2010. [Online]. Available: http://crystdb.nims.go.jp/index_en.html. [Accessed 2016].
- [19] L. Lopato, V. Red'ko, G. Gerasimyuk and A. Shevchenko, "Synthesis and properties of M₄Zr₃O₁₂ and M₄Hf₃O₁₂ compounds (M-rare earth element)," *Inorg. Mater.*, vol. 27, pp. 1445-1449, 1991.
- [20] T. Kogure, "Geometry of Electron Diffraction and Its Calculation," *Microscopy (Japanese)*, vol. 50, no. 1, pp. 1-5, 2015.
- [21] X. Li, J. Li, Z. Xiu, D. Huo and X. Sun, "Transparent Nd:YAG Ceramics Fabricated Using Nanosized α -Alumina and Yttria Powders," *J. Am. Ceram. Soc.*, vol. 92, no. 1, pp. 241-244, 2009.
- [22] J. Hoffmann, M. Rieth, R. Lindau, M. Klimenkov, A. Möslang, H. Ricardo and Z. Sandim, "Investigation on different oxides as candidates for nano-sized ODS particles in reduced-activation ferritic (RAF) steels," *J. Nucl. Mater.* 442, pp. 444-448, 2013.

- [23] Y. Du, Z. Jin and P. Huang, "Thermodynamic Assessment of the ZrO₂-Y₂O₃ System," *J. Am. Ceram. Soc.* **74**, pp. 1569-1577, 1991.
- [24] M.J. Alinger, "On the Formation and Stability of Nanometer Scale Precipitates in Ferritic Alloys during Processing and High Temperature Service," University of California Santa Barbara, California, 2004.
- [25] C. Hin, B. Wirth and J. Neaton, "Formation of Y₂O₃ nanoclusters in nanostructured ferritic alloys during isothermal and anisothermal heat treatment: A kinetic Monte Carlo study," *Phys. Rev. B*, vol. 80, p. 134118, 2009.
- [26] M. Zinkevich, "Thermodynamics of rare earth sesquioxides," *Prog. Mater. Sci.*, vol. 52, pp. 597-647, 2007.
- [27] Y. Sawazaki, S. Ukai, Y. Sugino, S. Hayashi, N. Oono, K. Hamajima and A. Niwa, "Development of 15CrODS ferritic steels for over 1273 K service," *J. Nucl. Mater.*, vol. 442, pp. S169-S172, 2013.
- [28] N. Oono, Q. Tang and S. Ukai, "Oxide particle refinement in Ni-based ODS alloy," *Mater. Sci. Eng. A*, vol. 649, pp. 250-253, 2016.
- [29] G. Ghosh and G. Olson, "The isotropic shear modulus of multicomponent Fe-base solid solutions," *Acta Mater.*, vol. 50, p. 2655-2675, 2002.
- [30] W. Zhang, G. Liu and K. Han, "Fe-Y (Iron-Yttrium)," in *Binary Alloy Phase Diagrams Vol. 2. Fe-Ru to Zn-Zr*, Metals Park, Ohio, American Society for Metals, 1986, pp. 1793-1794.
- [31] U. Kattner, "Al-Fe (Aluminum-Iron)," in *Binary Alloy Phase Diagrams Vol.1*, Metals Park, Ohio, American Society for Metals, 1986, pp. 147-148.
- [32] H. Okamoto, "Fe-Zr (Iron-Zirconium)," *J. Phase Equilib. Diff.*, vol. 27, pp. 543-544, 2006.
- [33] J. Murray, "The Fe-Ti (Iron-Titanium) System," *Bulletin of Alloy Phase Diagrams*, vol. 2, no. 3, pp. 320-322, 1981.
- [34] D. Murali, B. Panigrahi, M. Valsakumar and C. Sundar, "Diffusion of Y and Ti/Zr in bcc iron: A first principles study," *J. Nucl. Mater.*, vol. 419, pp. 208-212, 2011.
- [35] J. Hirvonen and J. Räisänen, "Diffusion of aluminum in ion-implanted alpha iron," *J. Appl. Phys.*, vol. 53, pp. 3314-3316, 1982.
- [36] P. Klugkist and C. Herzig, "Tracer diffusion of titanium in α -iron," *Phys. Stat. Sol. (a)*, vol. 148, p. 413, 1995.

- [37] O. Fabrichnaya, H. Seifert, T. Ludwig, F. Aldinger and A. Navrotsky, "The assessment of thermodynamic parameters in the $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ system and phase relations in the Y-Al-O system," *Schand. J. Metall.*, vol. 30, pp. 175-183, 2001.
- [38] T. Schaedler, O. Fabrichanaya and C. Levi, "Phase equilibria in the $\text{TiO}_2\text{-YO}_{1.5}\text{-ZrO}_2$ system," *J. Europ. Ceram. Soc.*, vol. 28, pp. 2509-2520, 2008.

Captions of the figures

Figure 1. TEM micrographs of the oxide particles in 15Cr-7Al and 15Cr-7Al-0.4Zr before and after high temperature annealing.

Figure 2. (a, b) Sizes and (d, e) number densities of the oxide particles in 15Cr-7Al and 15Cr-7Al-0.4Zr against annealing time. The data of 9Cr-ODSS from ref. [14] is also shown in (c, f).

Figure 3. STEM-EDS mapping of the oxide particles in 15Cr-7Al after annealing at 1623K for 27h. In the HAADF image, oxide particles appeared as the dark spheres, pointed by red arrows. The small black area in adjacent to the oxide particles are Ar bubbles induced during the MA. The scale bars measure 100nm

Figure 4. Magnified images of a coarse oxide particle in 15Cr-7Al after annealing at 1623K for 27h. The scale bars measure 3nm.

Figure 5. STEM-EDS mapping results of the oxide particles in 15Cr-7Al-0.4Zr after annealing at 1623K for 27h. The scale bars measure 200nm.

Figure 6. HRTEM images (left), their FFT image (middle) and simulated diffraction patterns (right) of the oxide particles in 15Cr-7Al.

Figure 7. HRTEM images (left), their FFT image (middle) and simulated diffraction patterns (right) of the oxide particles in 15Cr-7Al-0.4Zr.

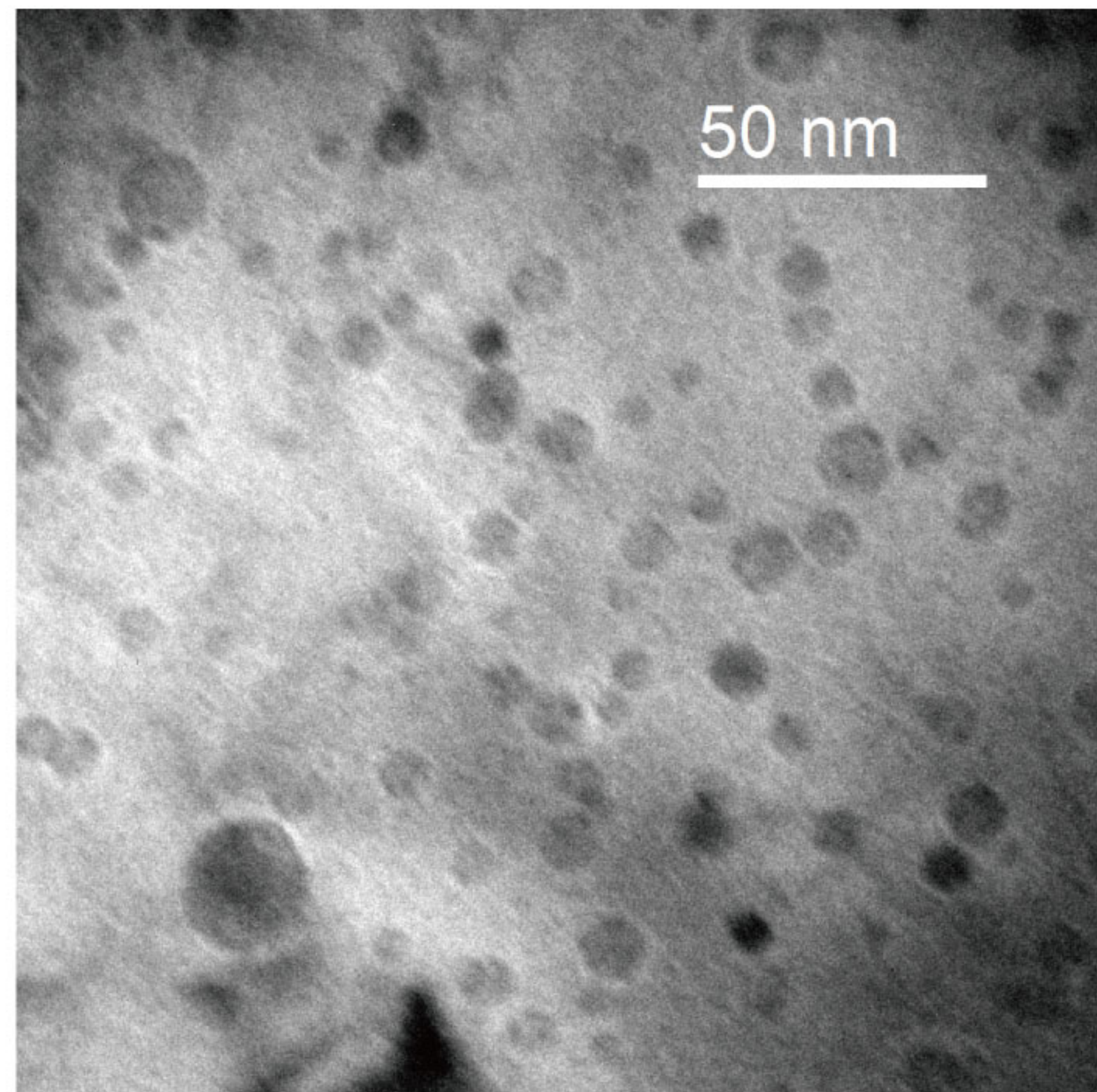
Figure 8. Vickers hardness of the specimens before and after annealing against the annealing time.

Figure 9. (a) $\ln t$ versus $\ln(r^5 - r_0^5)$, (b) t versus $r^5 - r_0^5$ curve for oxide particles in 15Cr-7Al and (c) the corresponding fit to the $\ln \alpha$ versus $1/T$ with the values of α obtained by the fits in Fig. 8a.

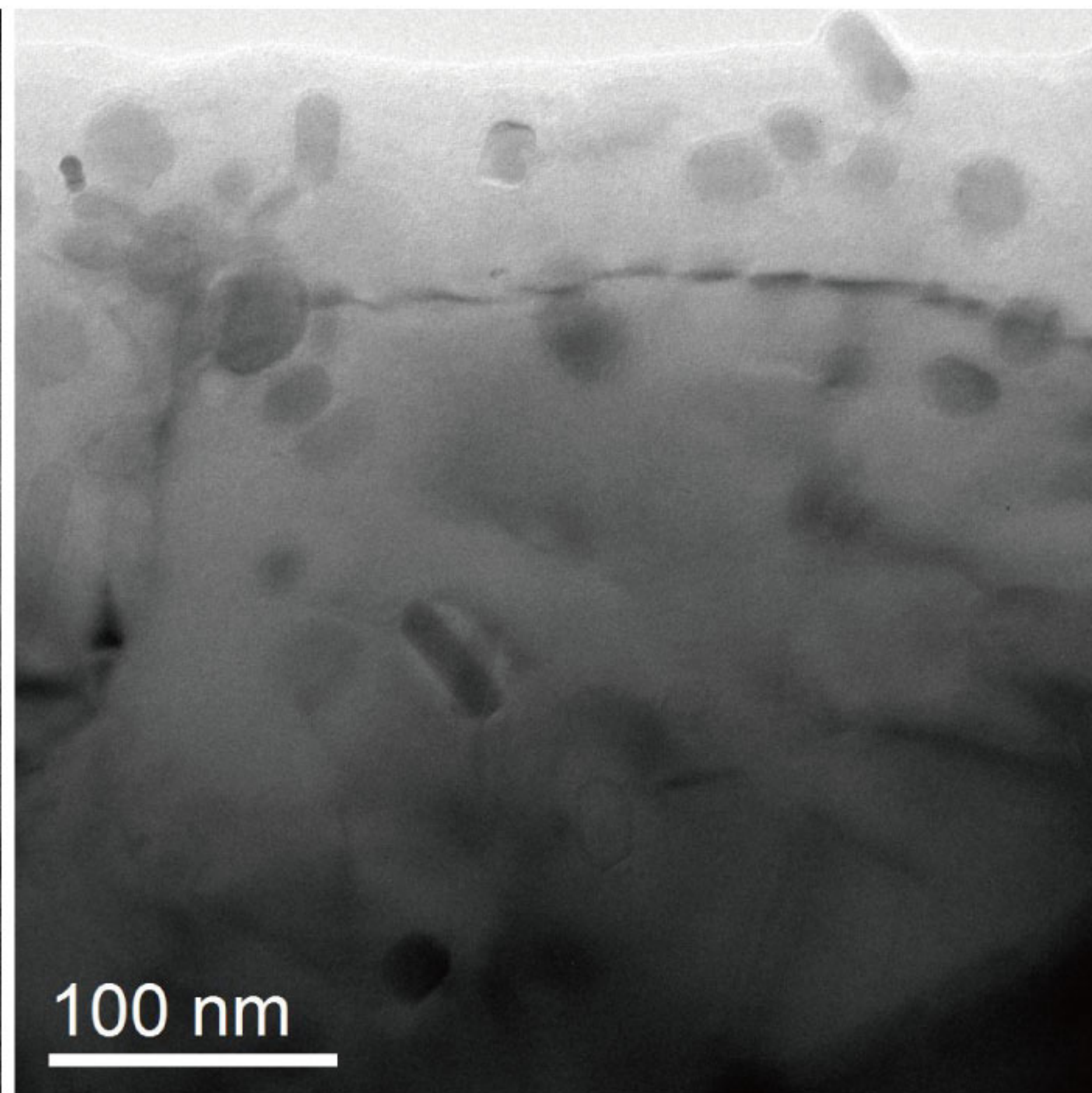
Figure 10. Calculated interfacial energy based on the lattice misfit (γ) against the size of the corresponding oxide particles.

15Cr-7Al

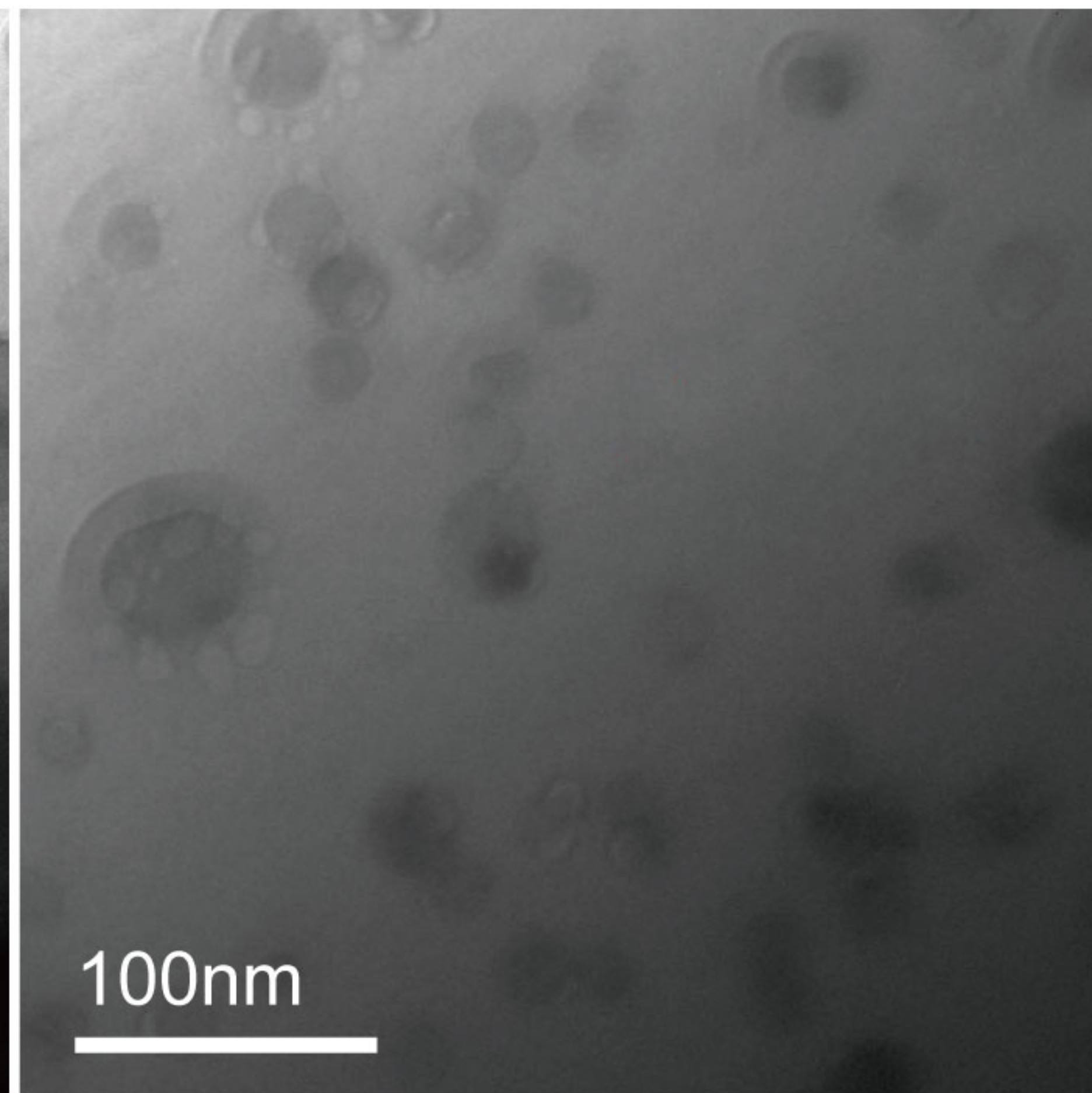
as-extruded



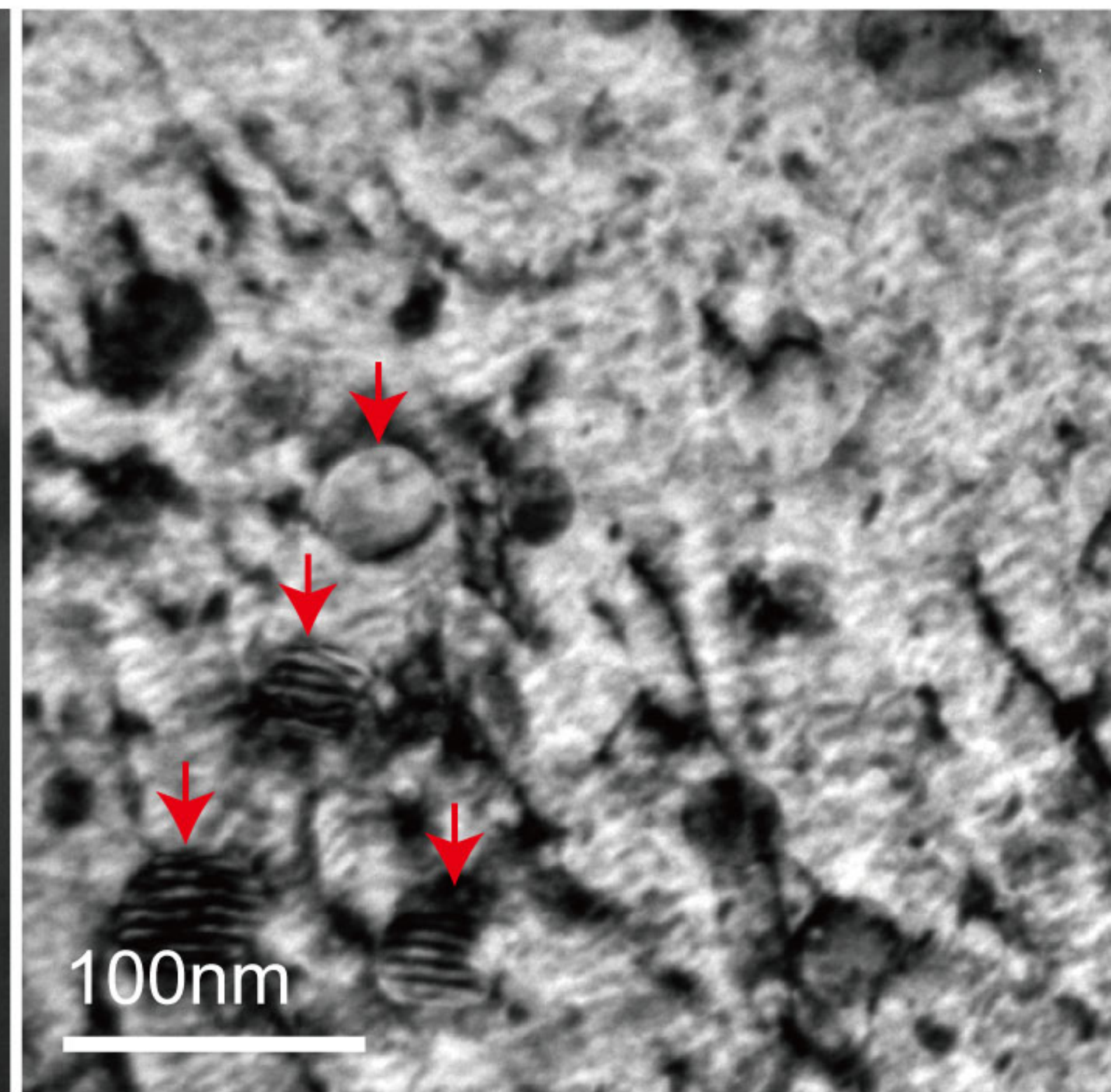
1473K, 200h



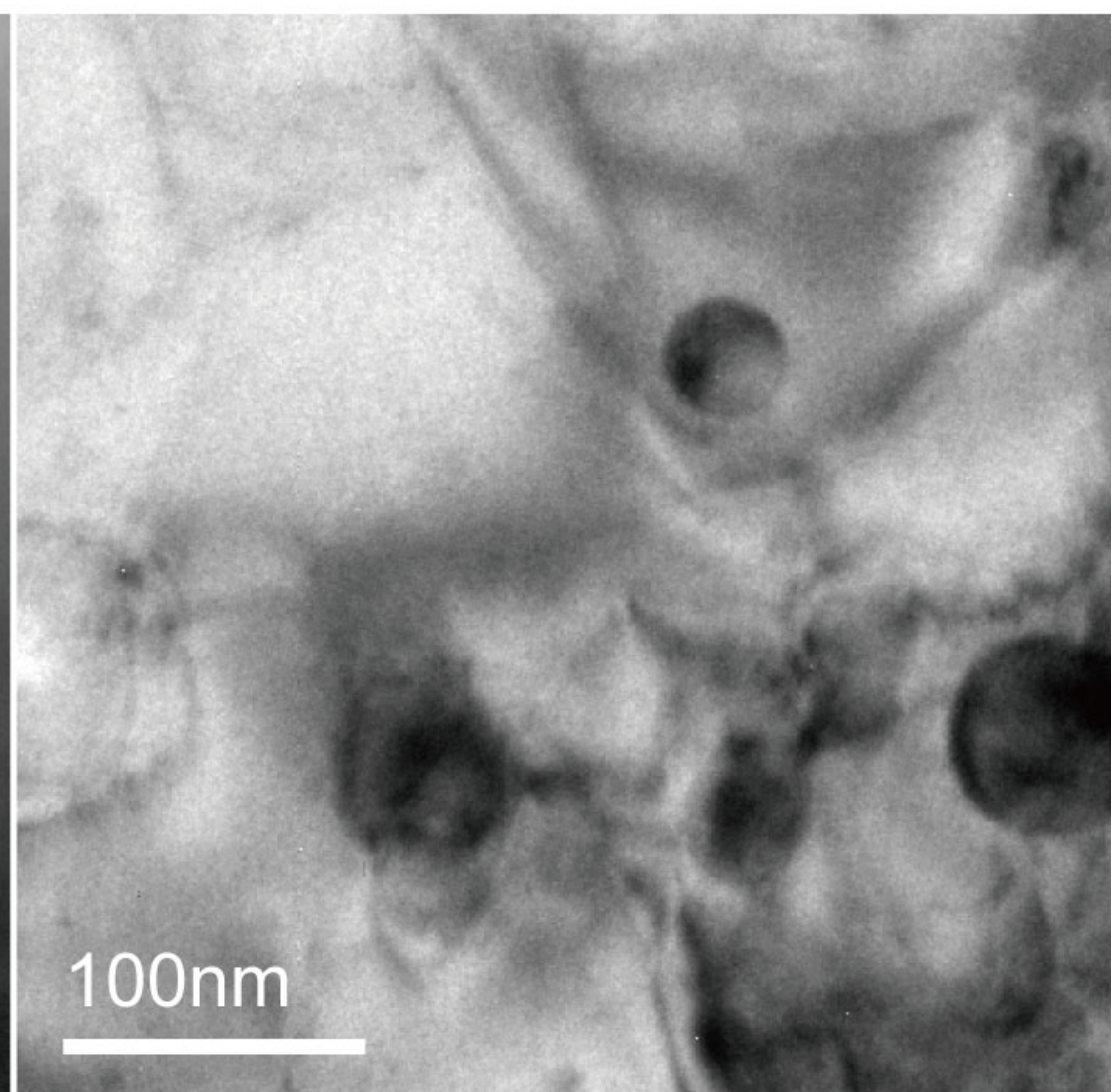
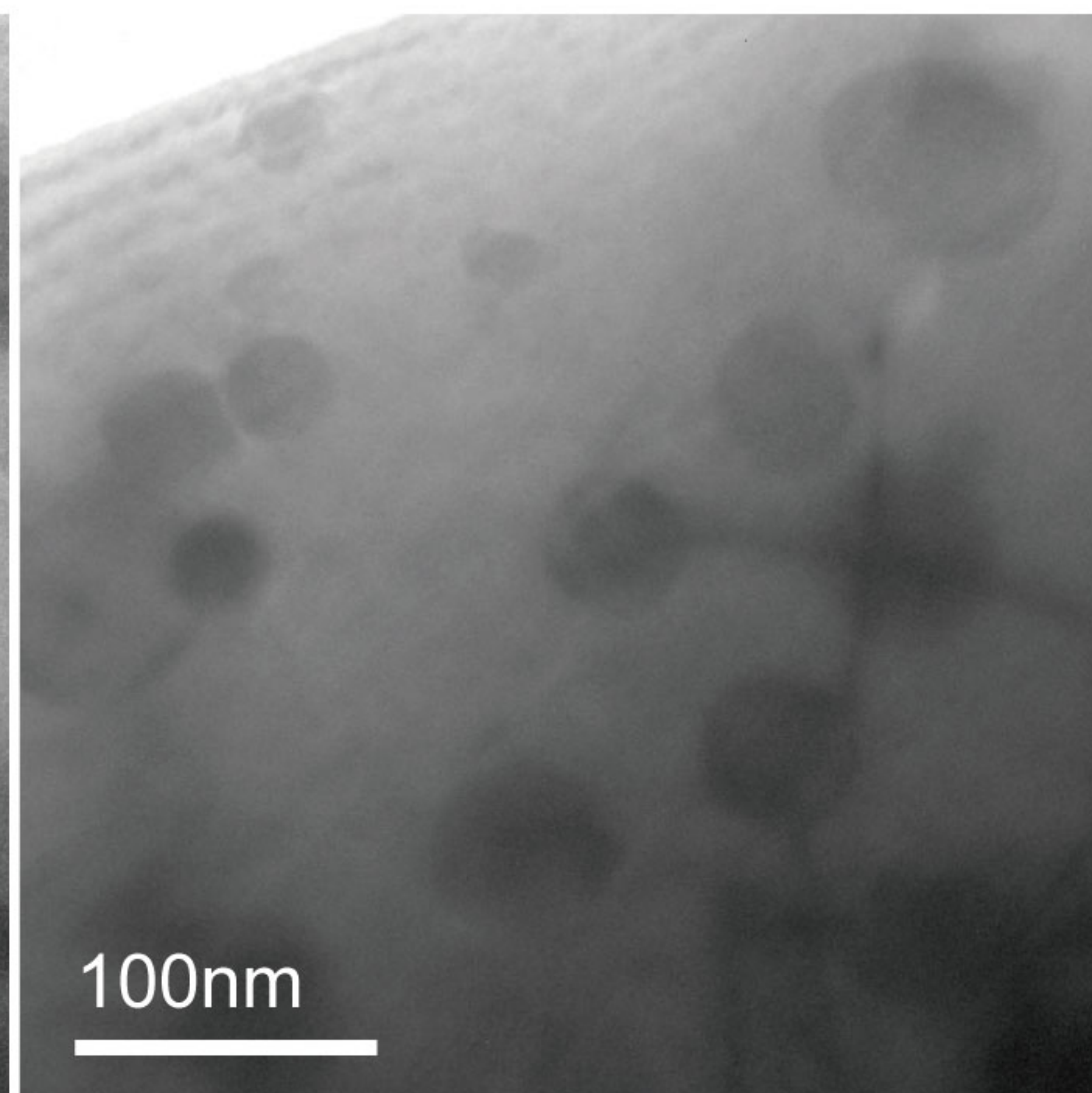
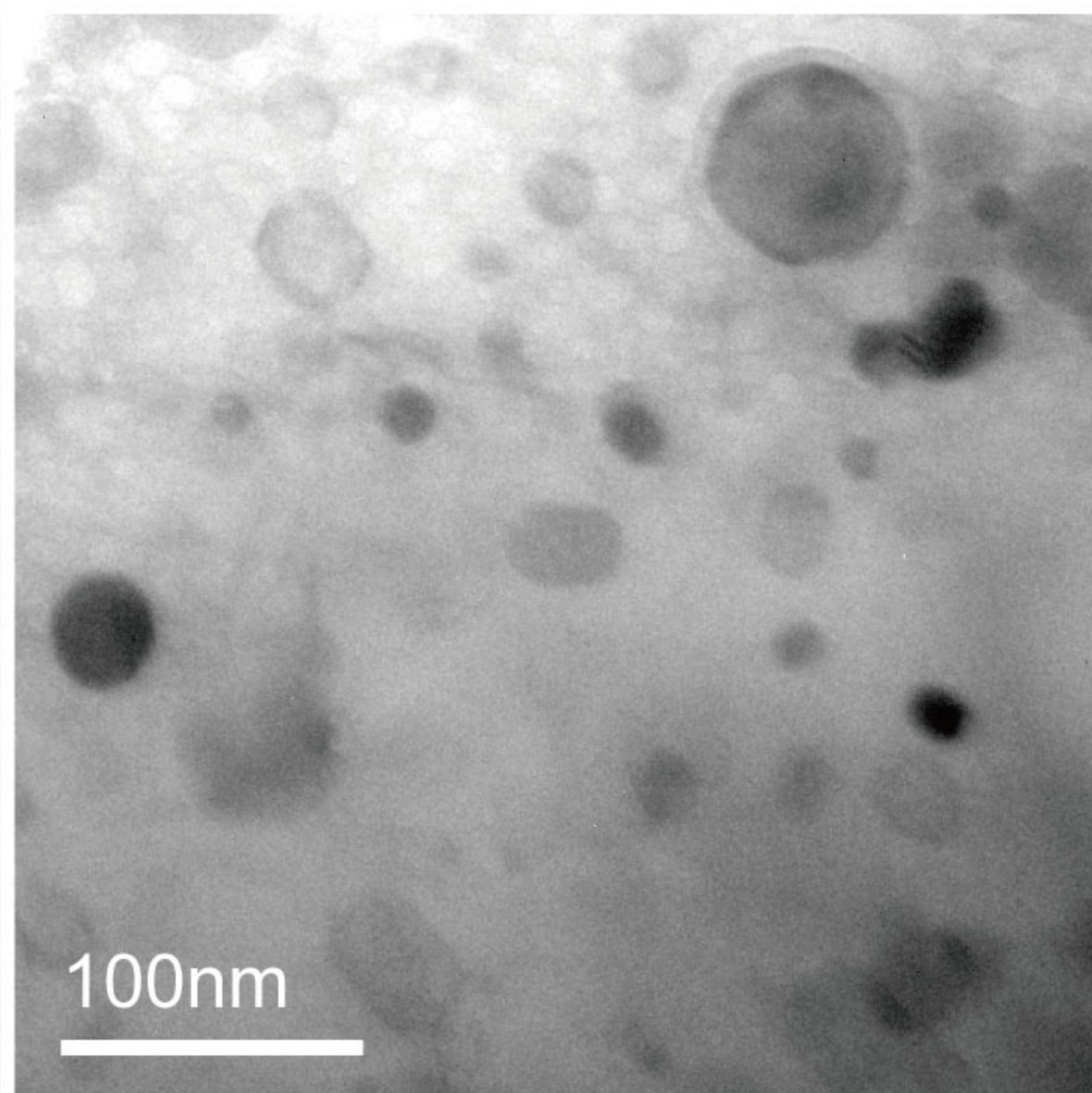
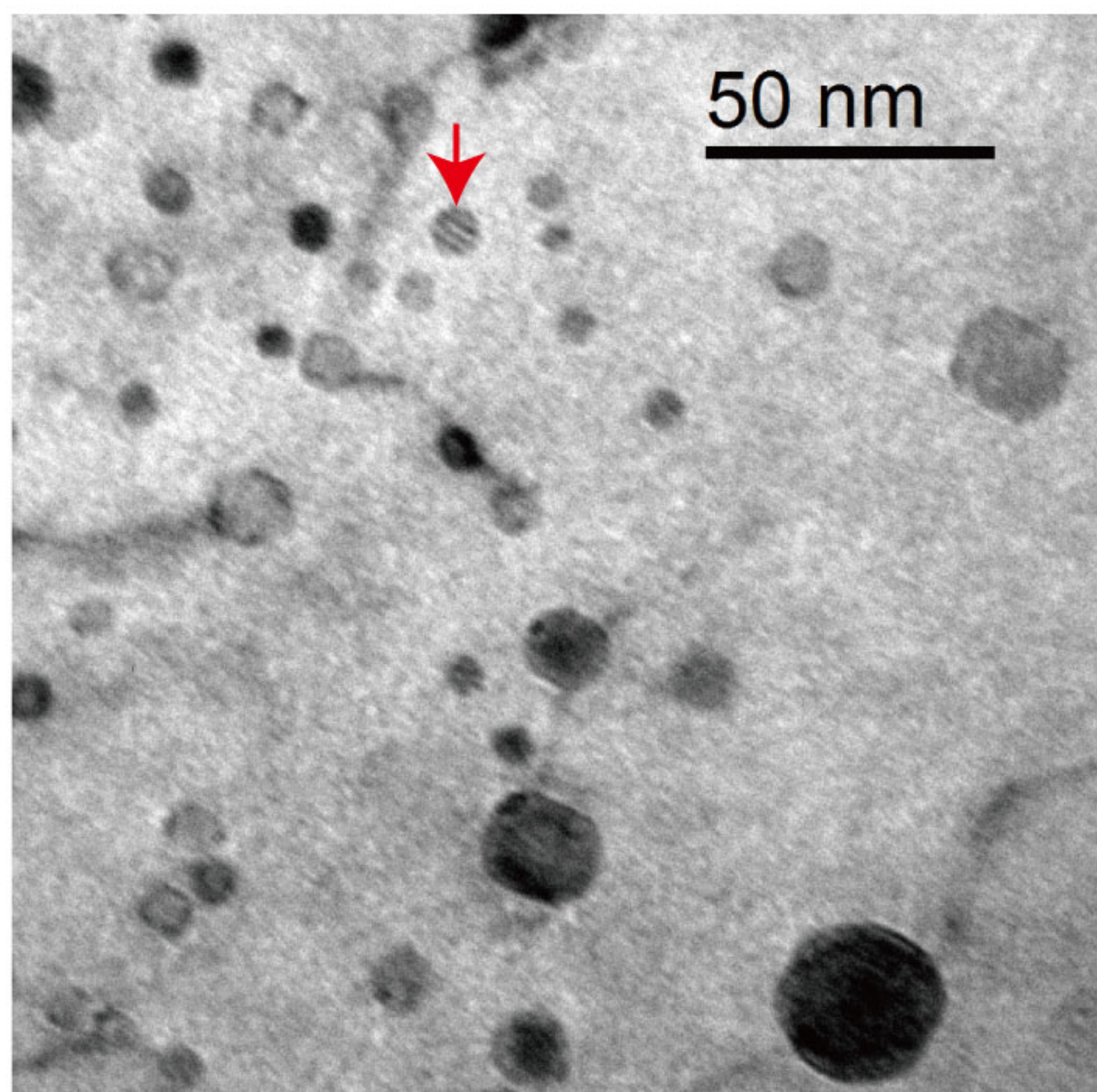
1543K, 81h

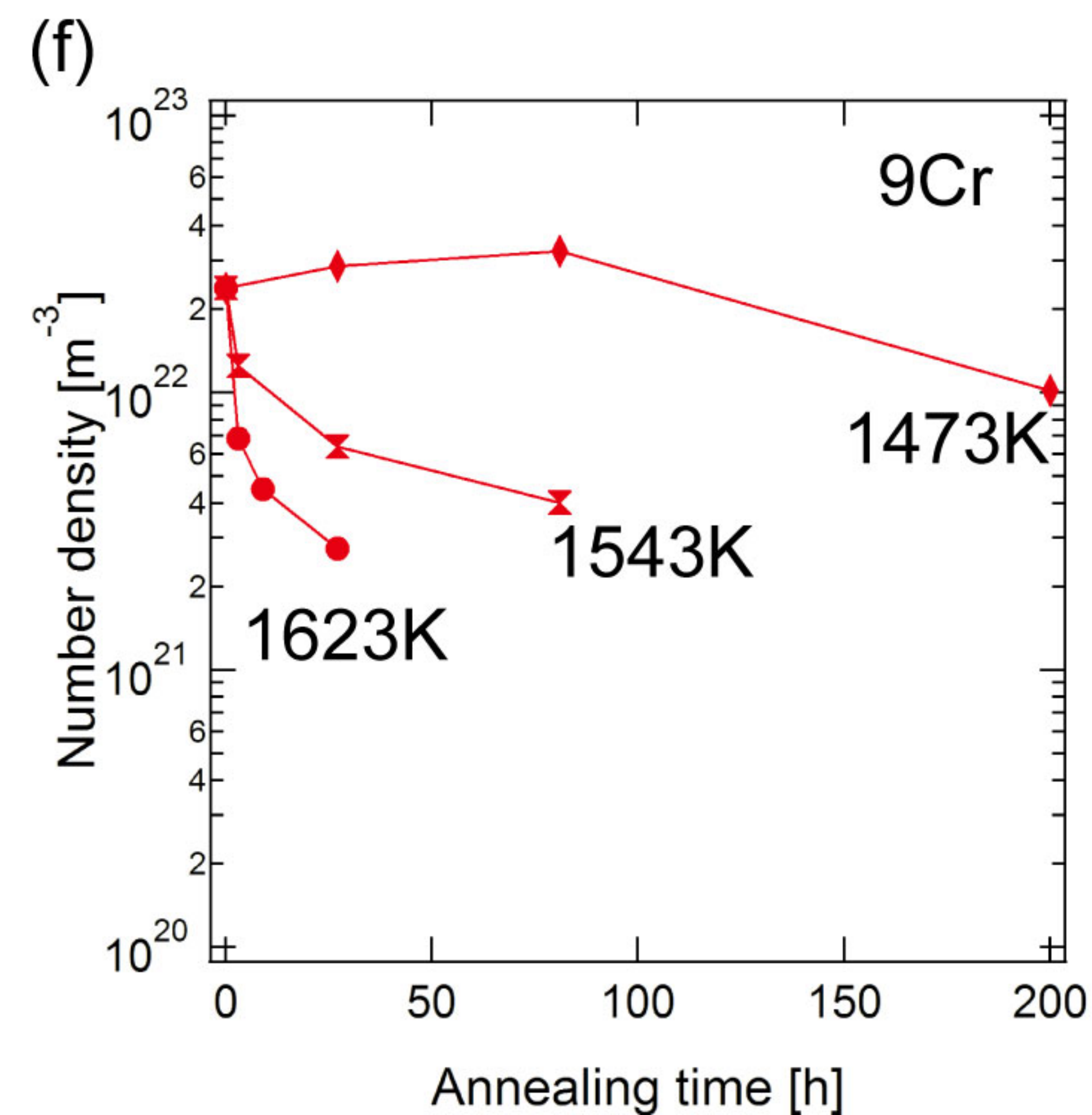
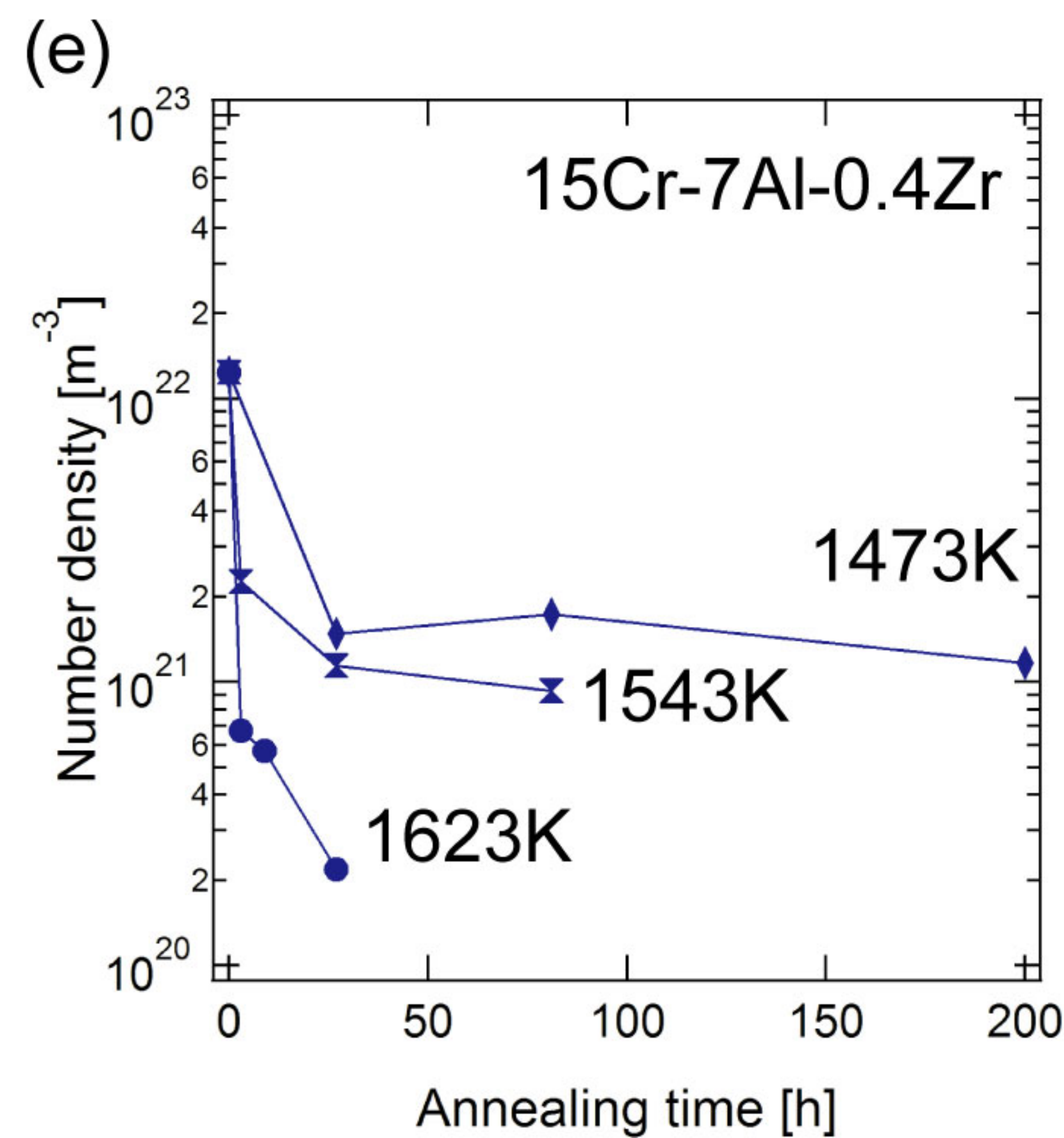
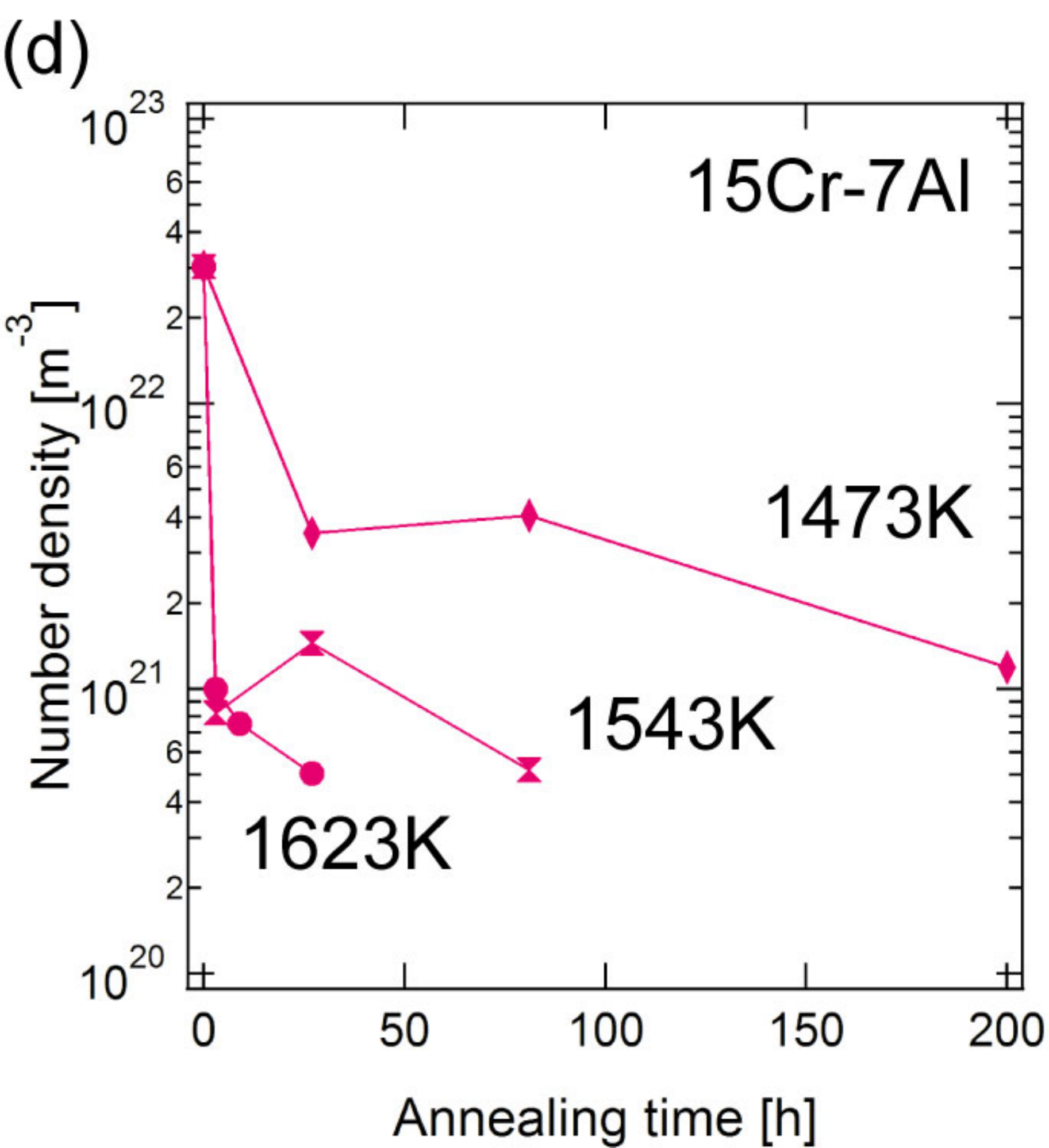
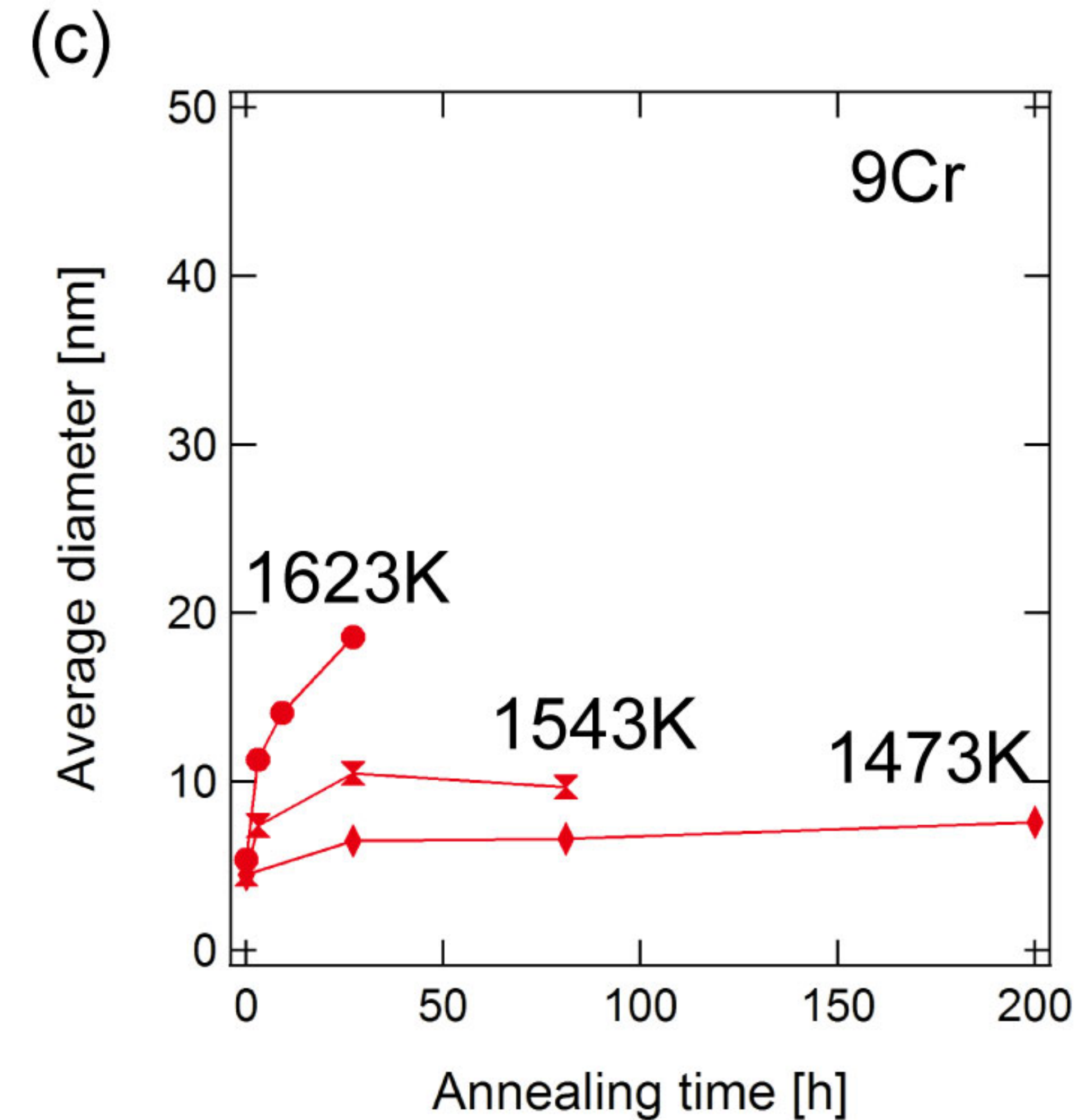
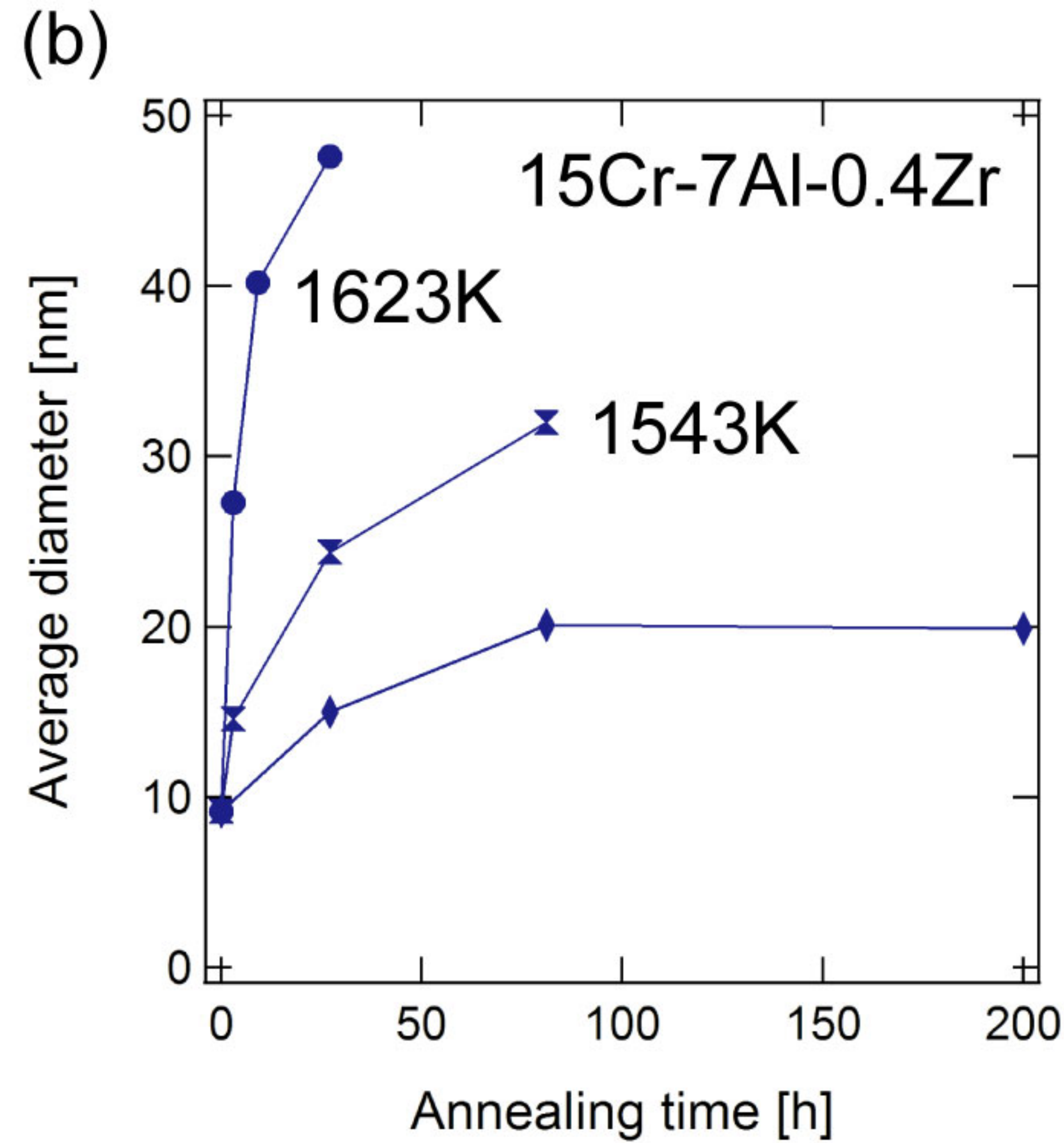
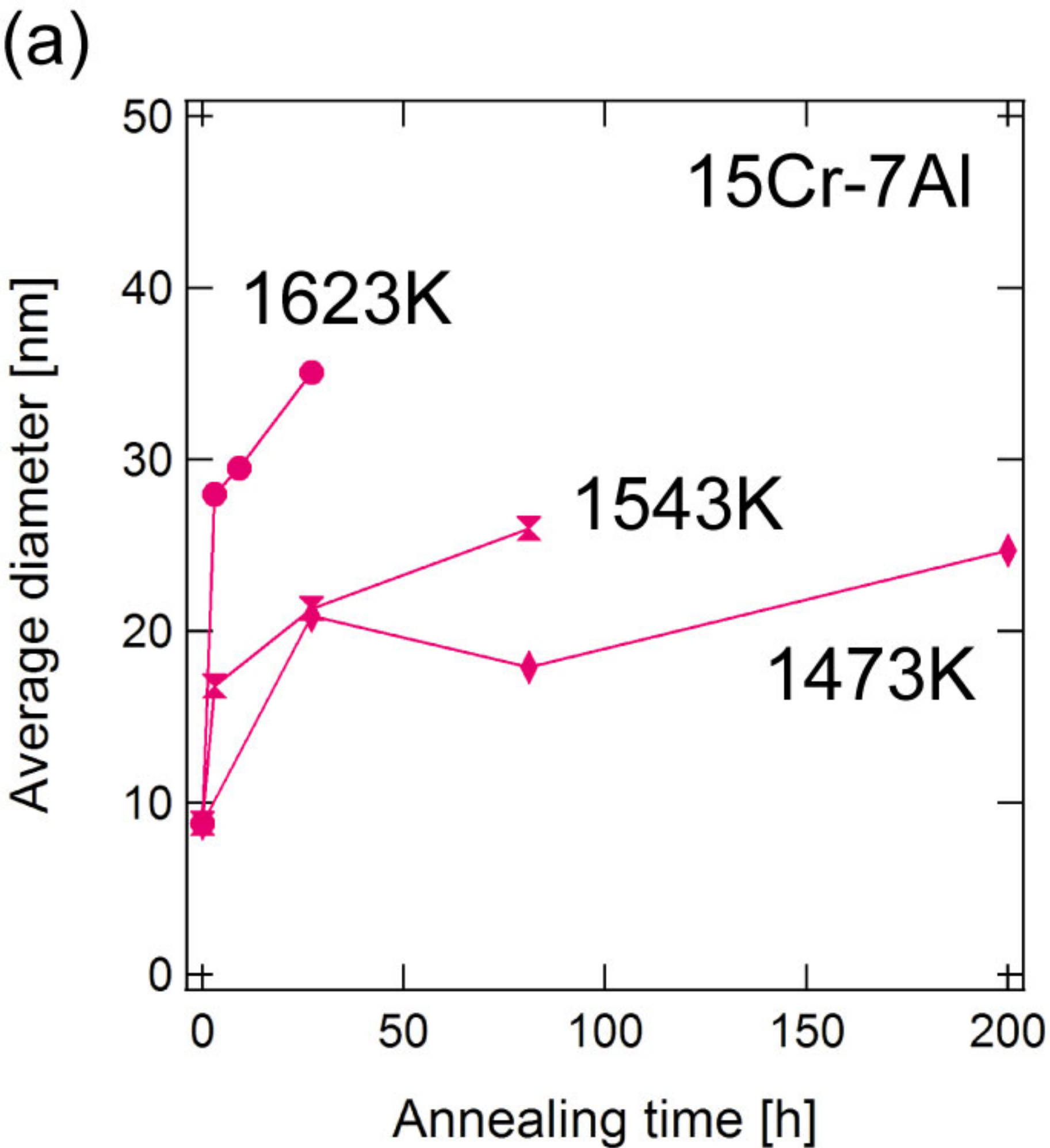


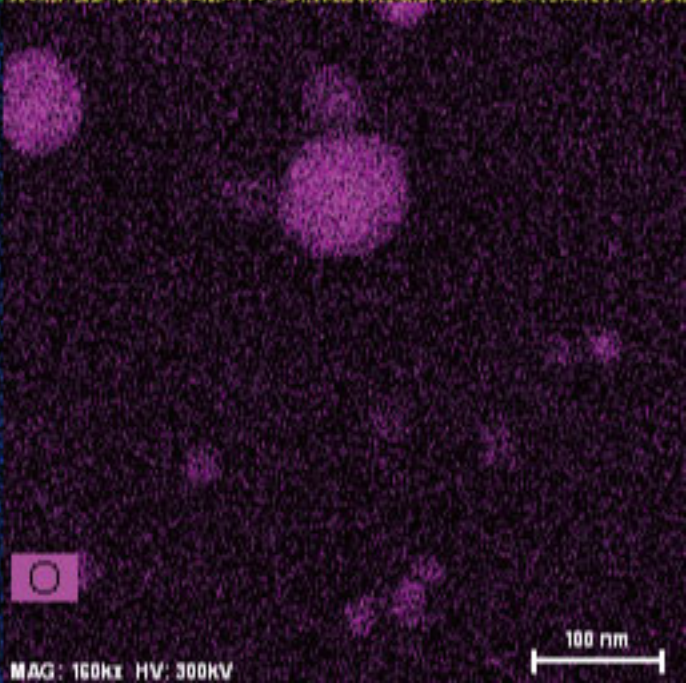
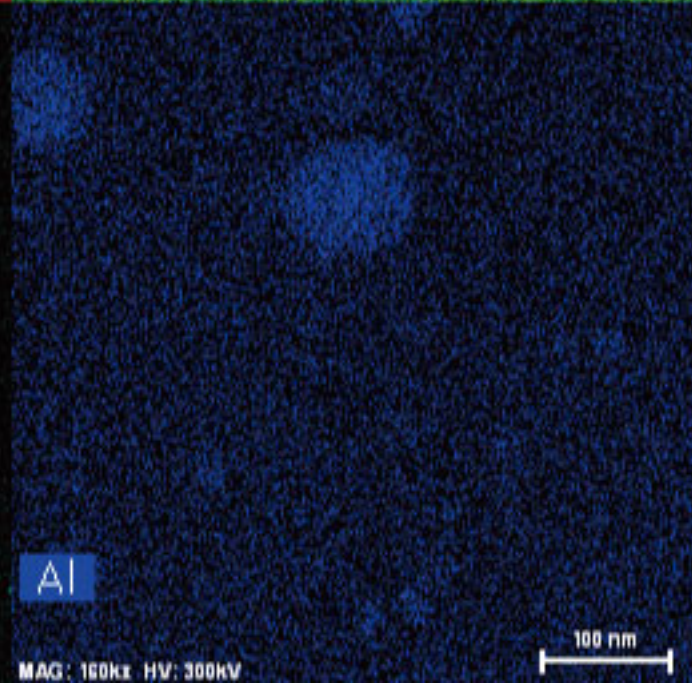
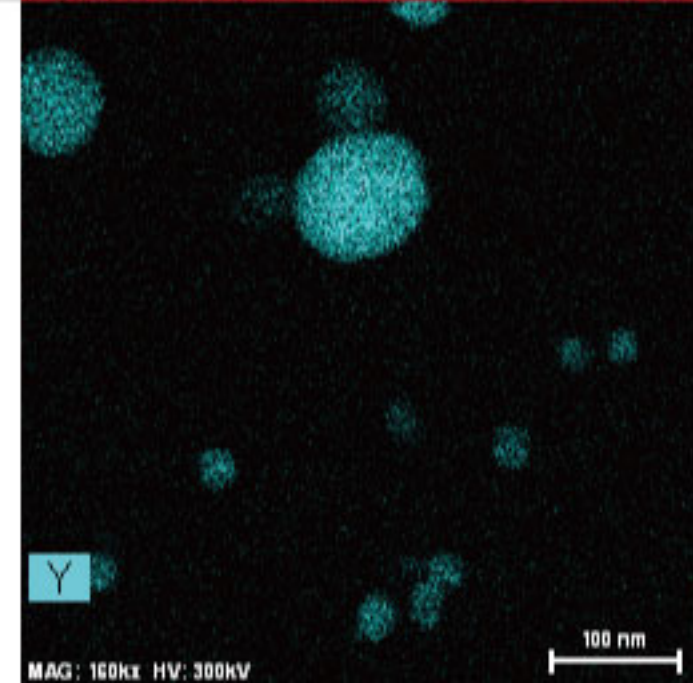
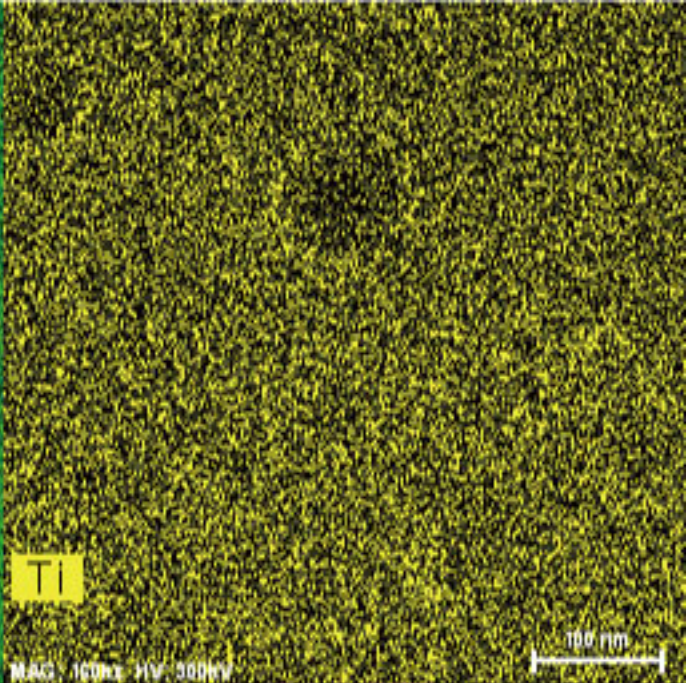
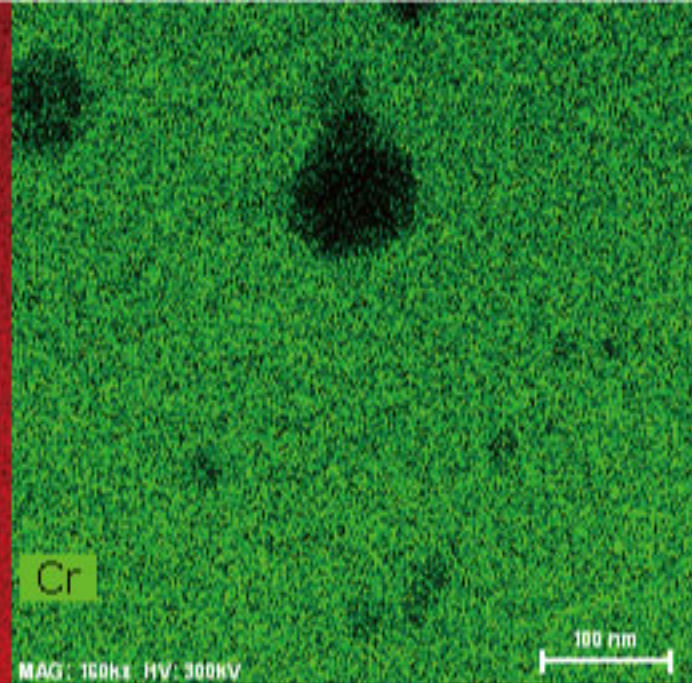
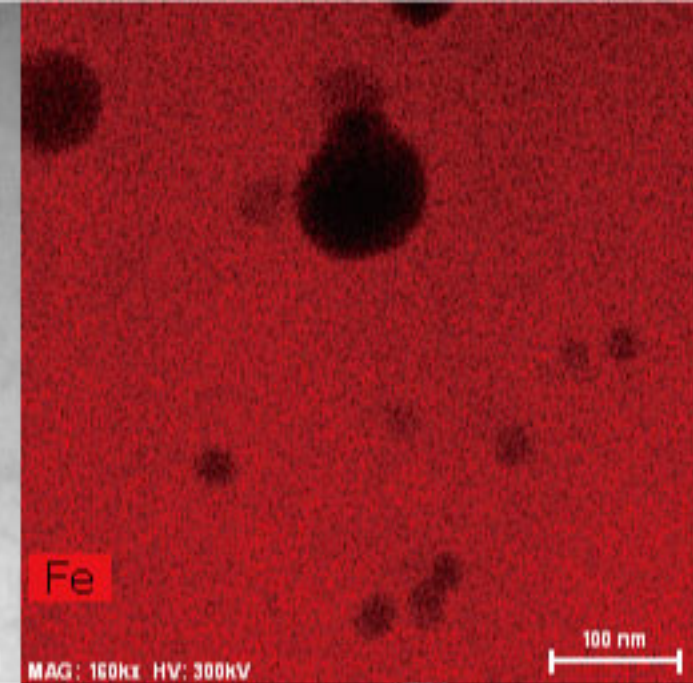
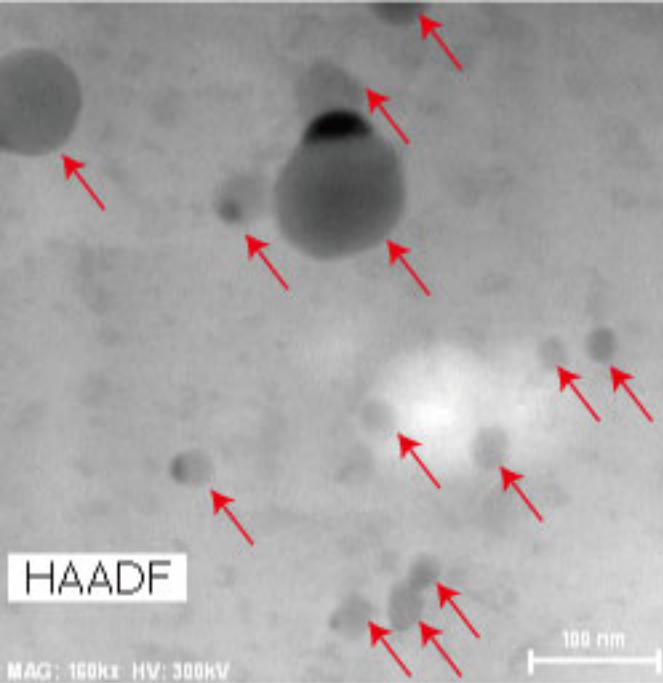
1623K, 27h

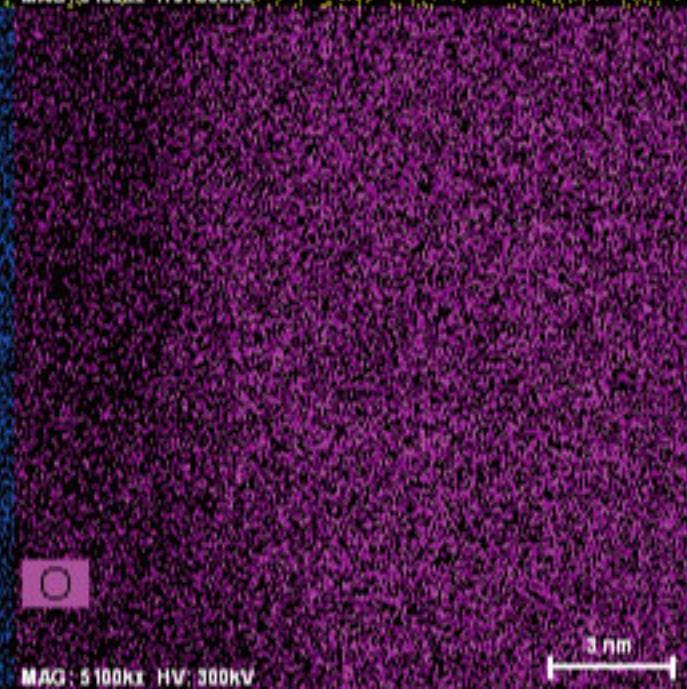
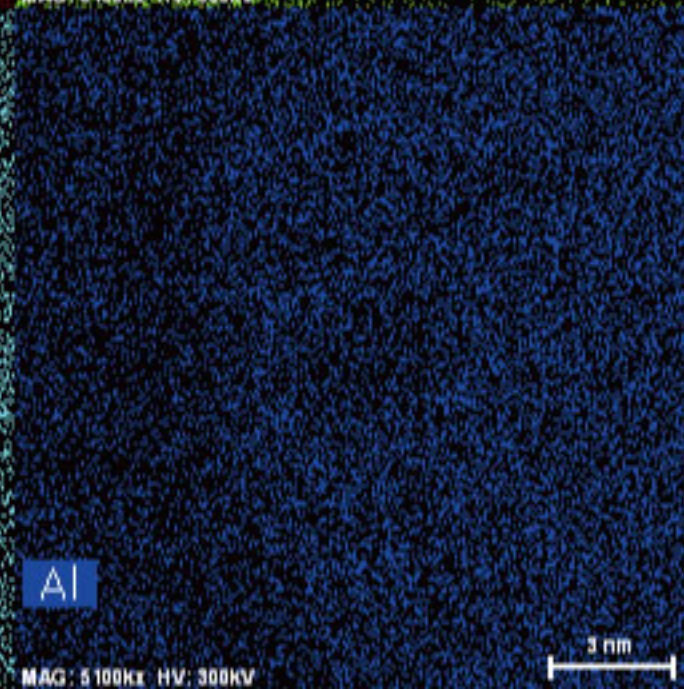
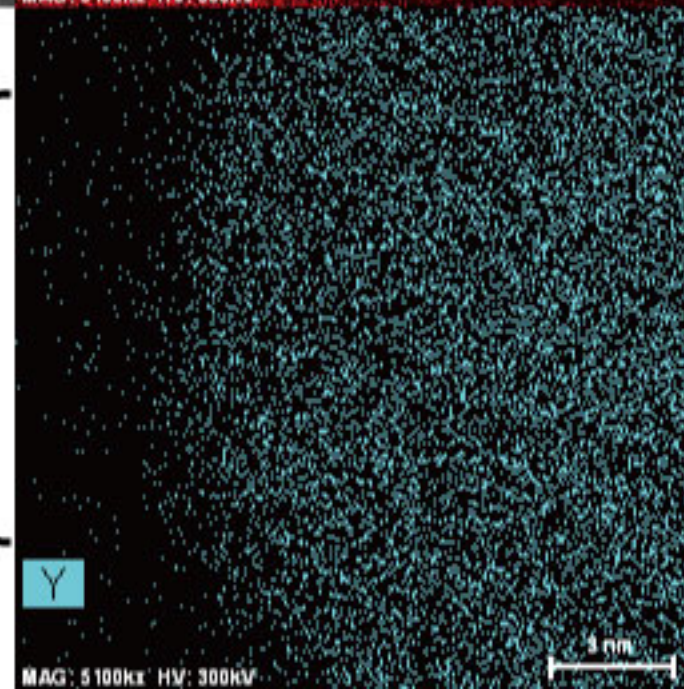
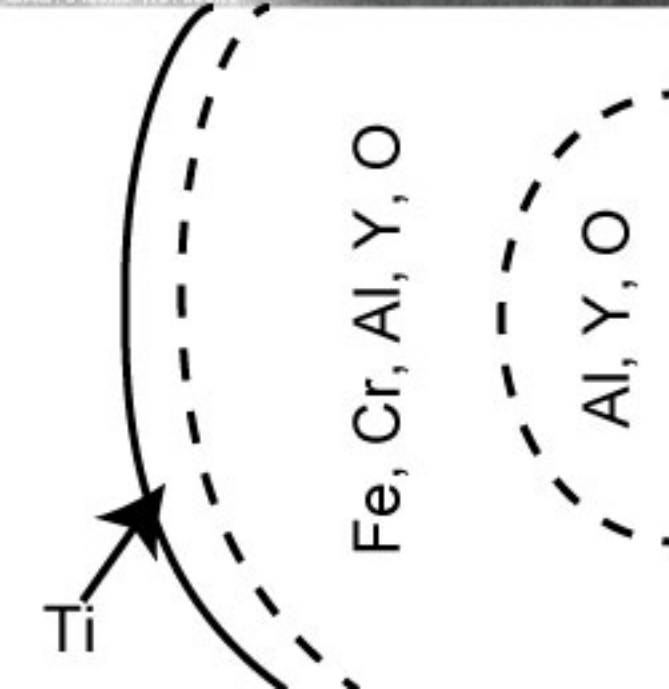
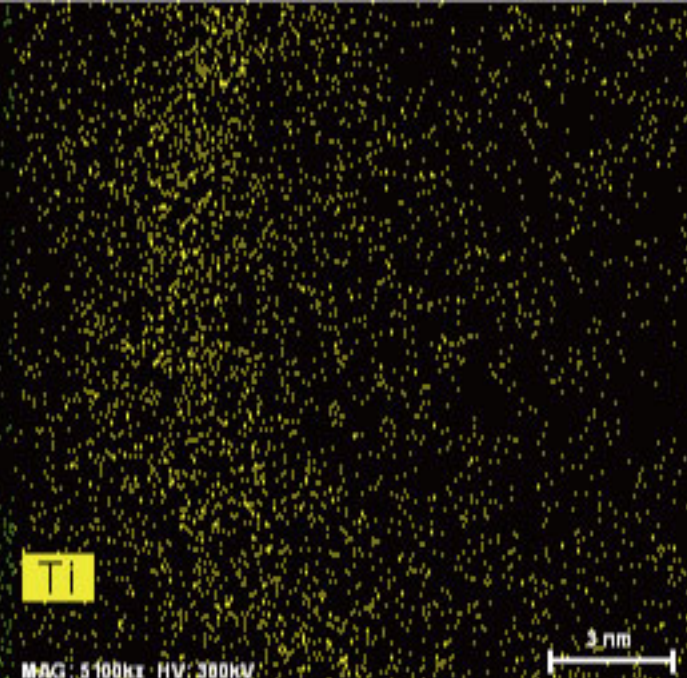
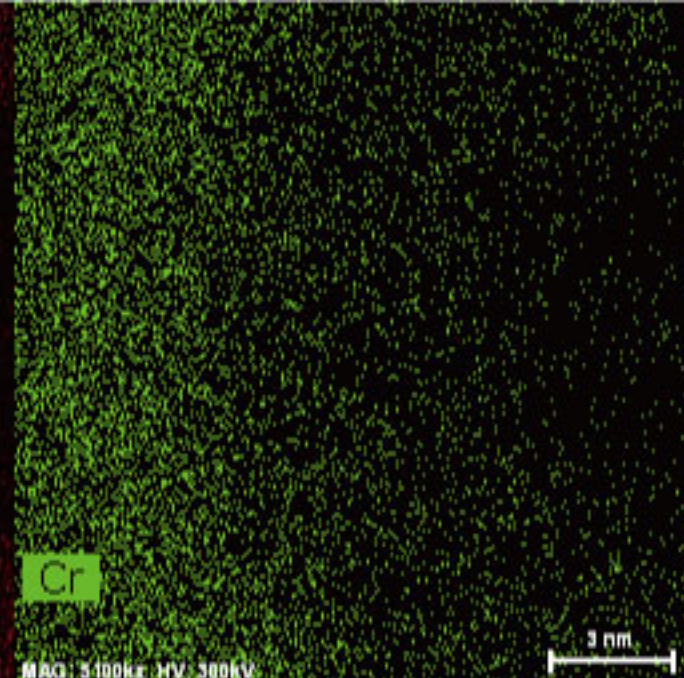
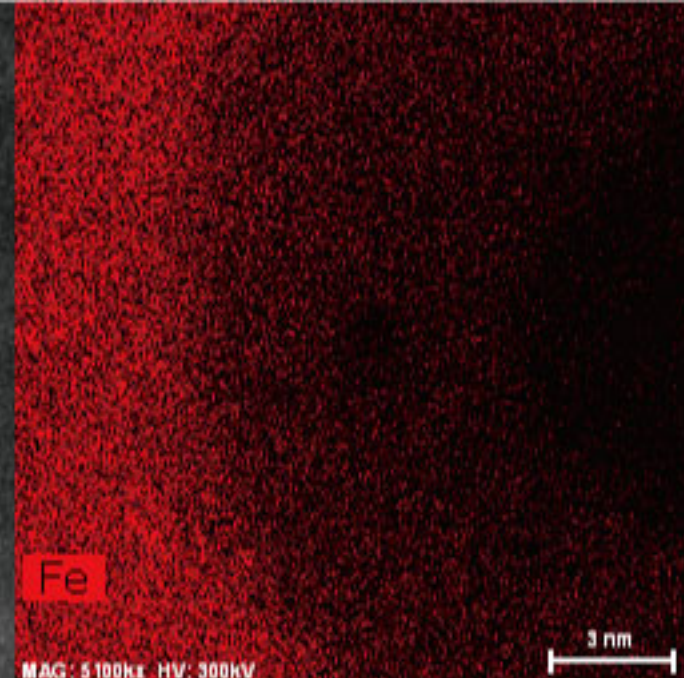
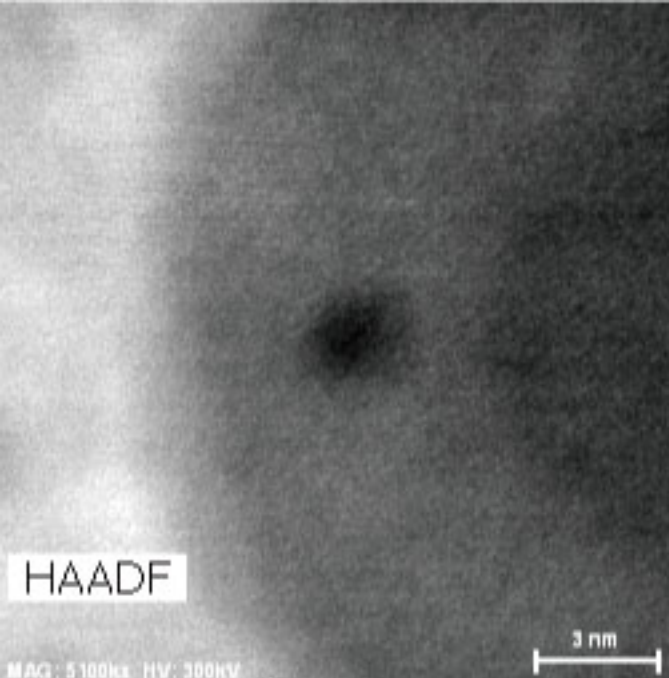


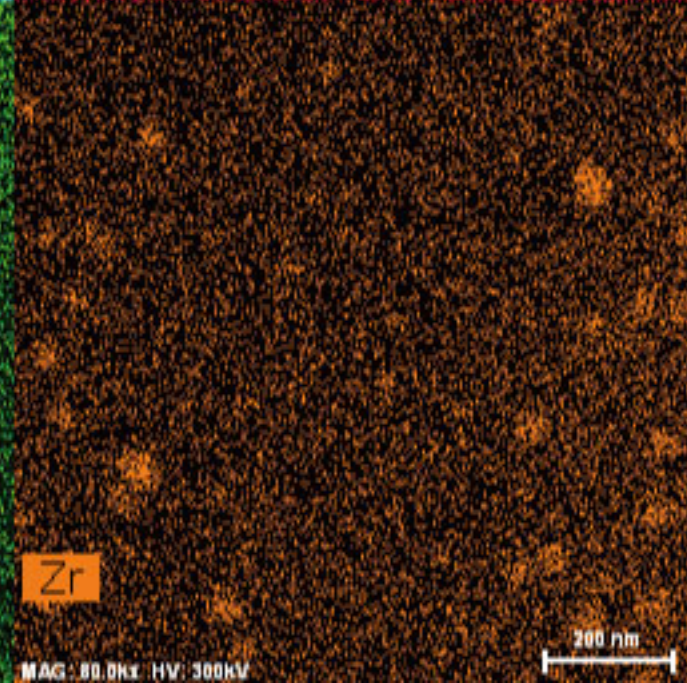
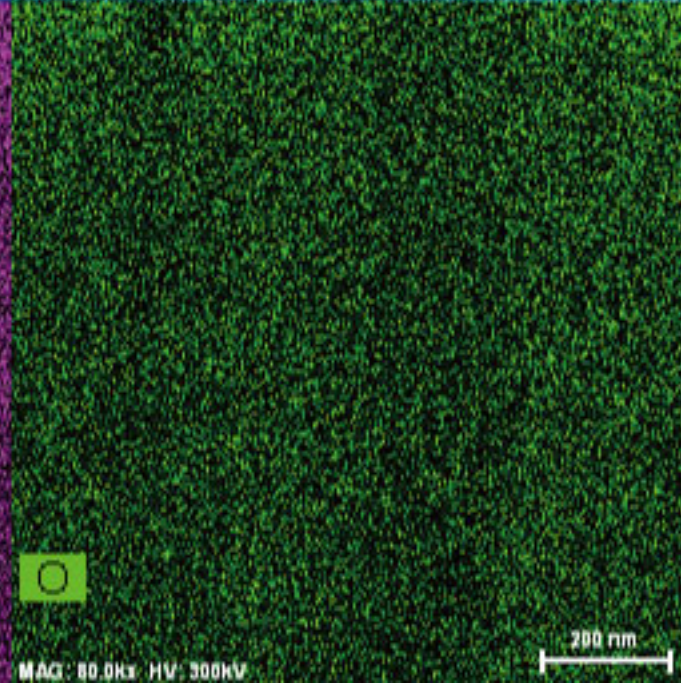
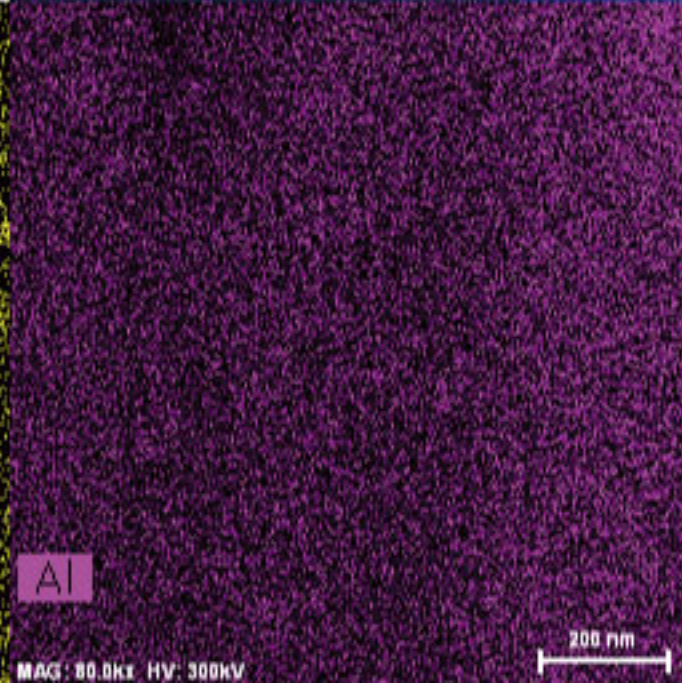
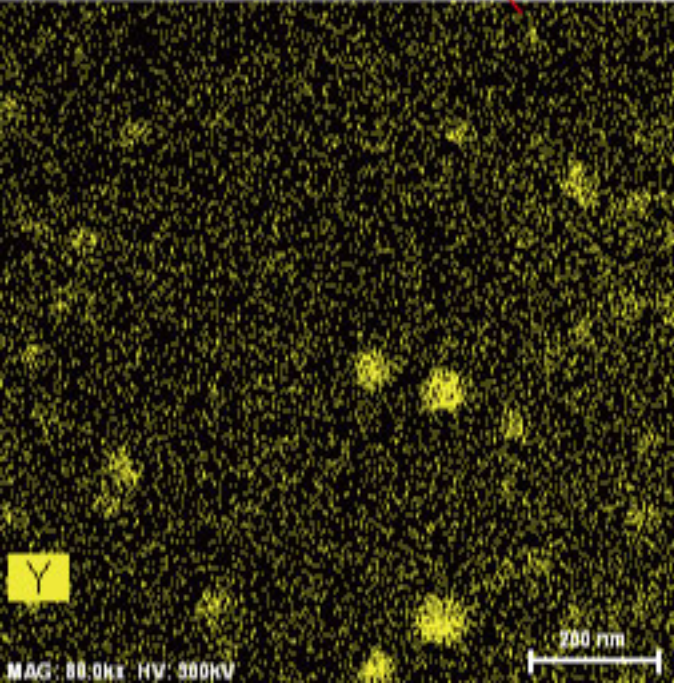
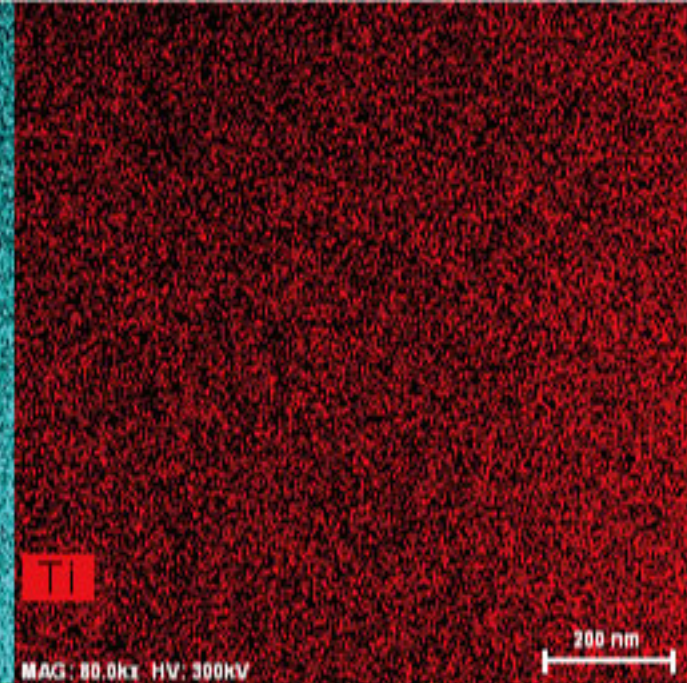
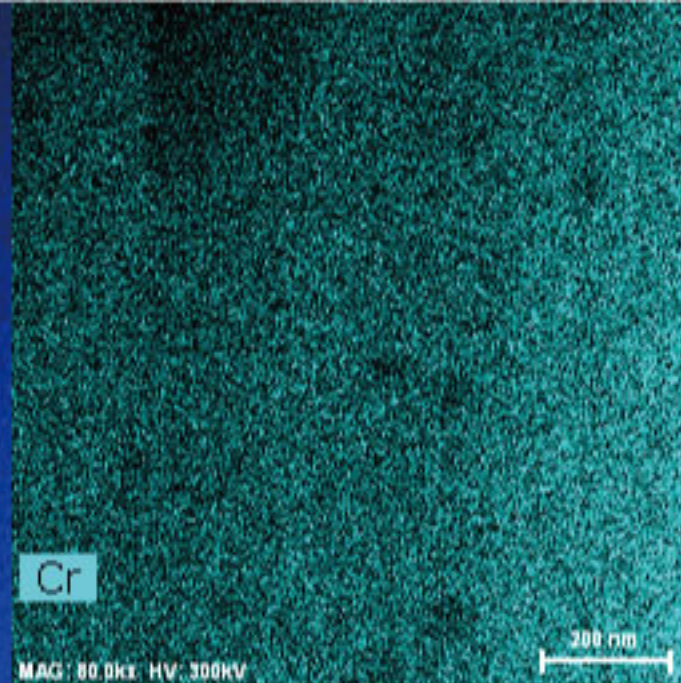
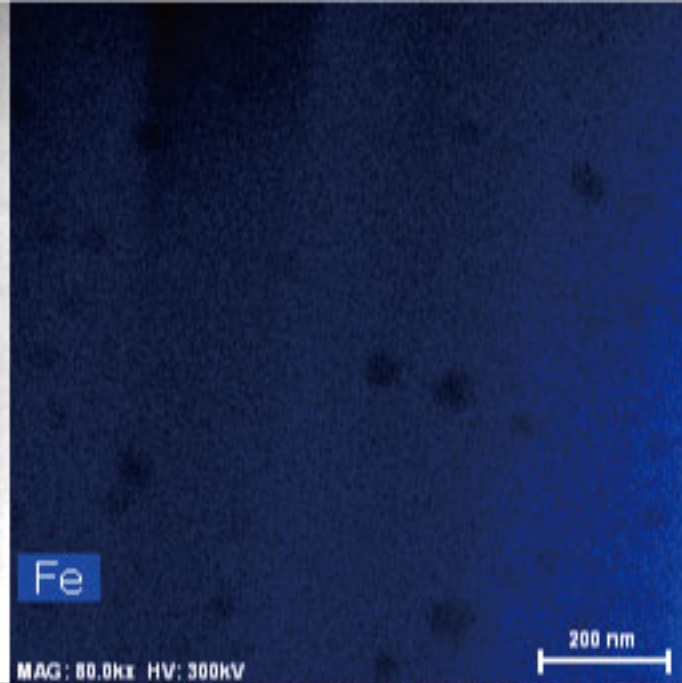
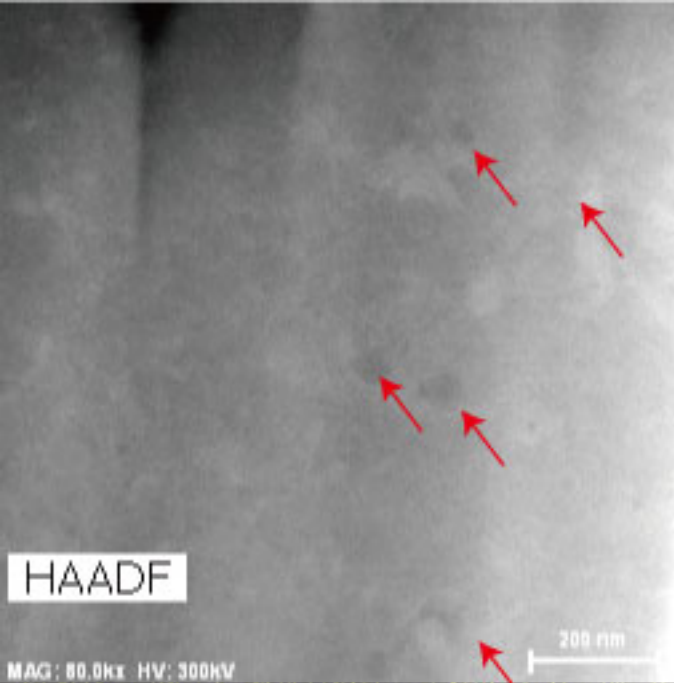
15Cr-7Al-0.4Zr



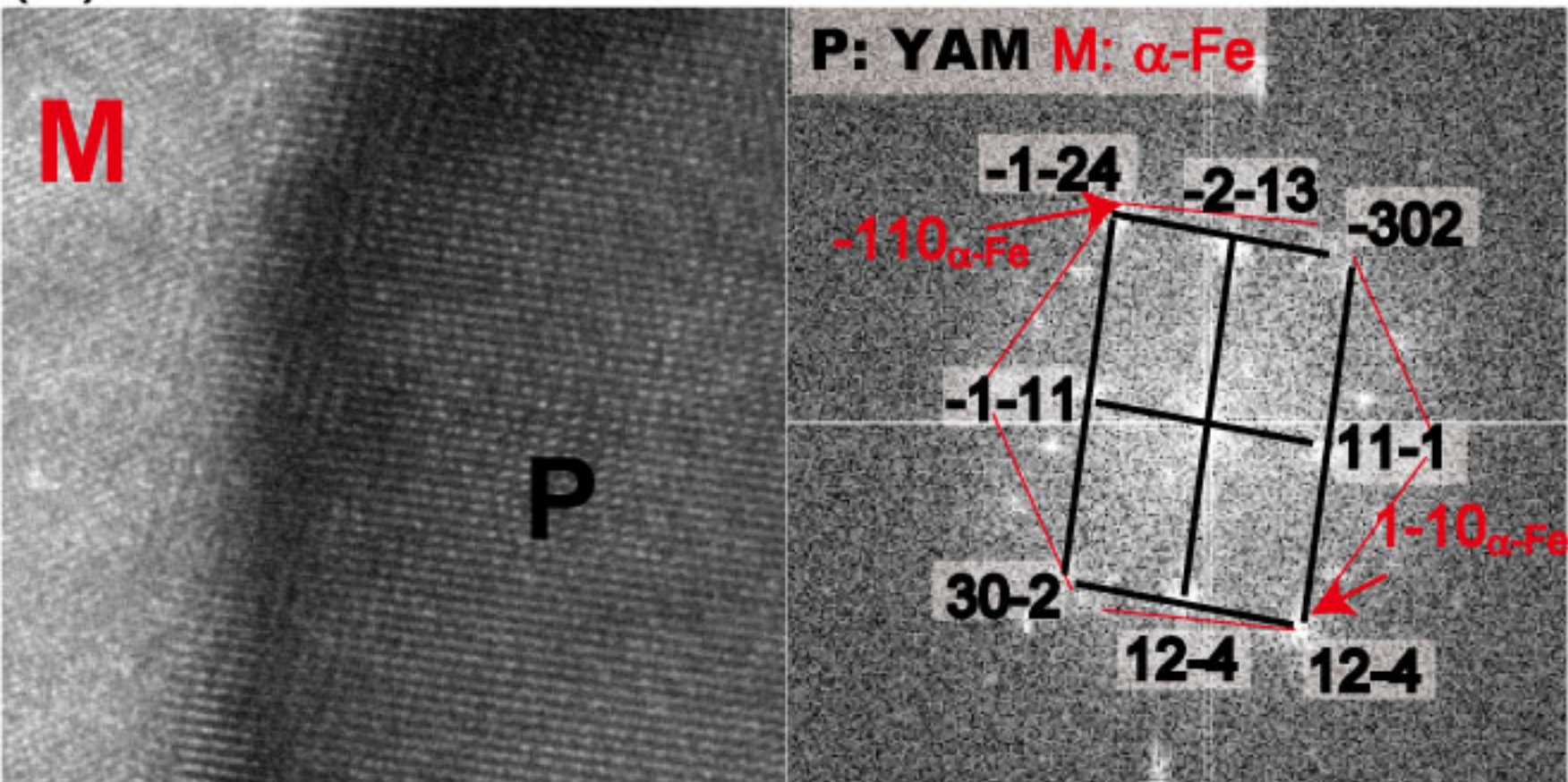




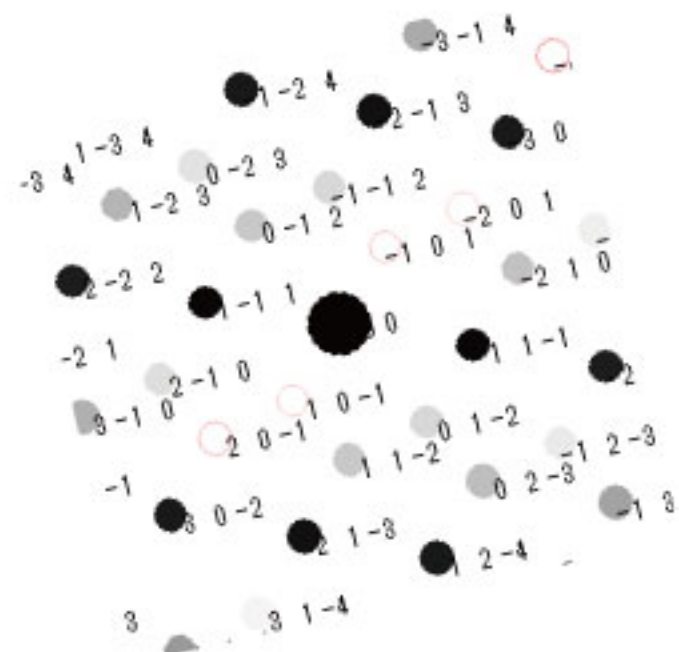




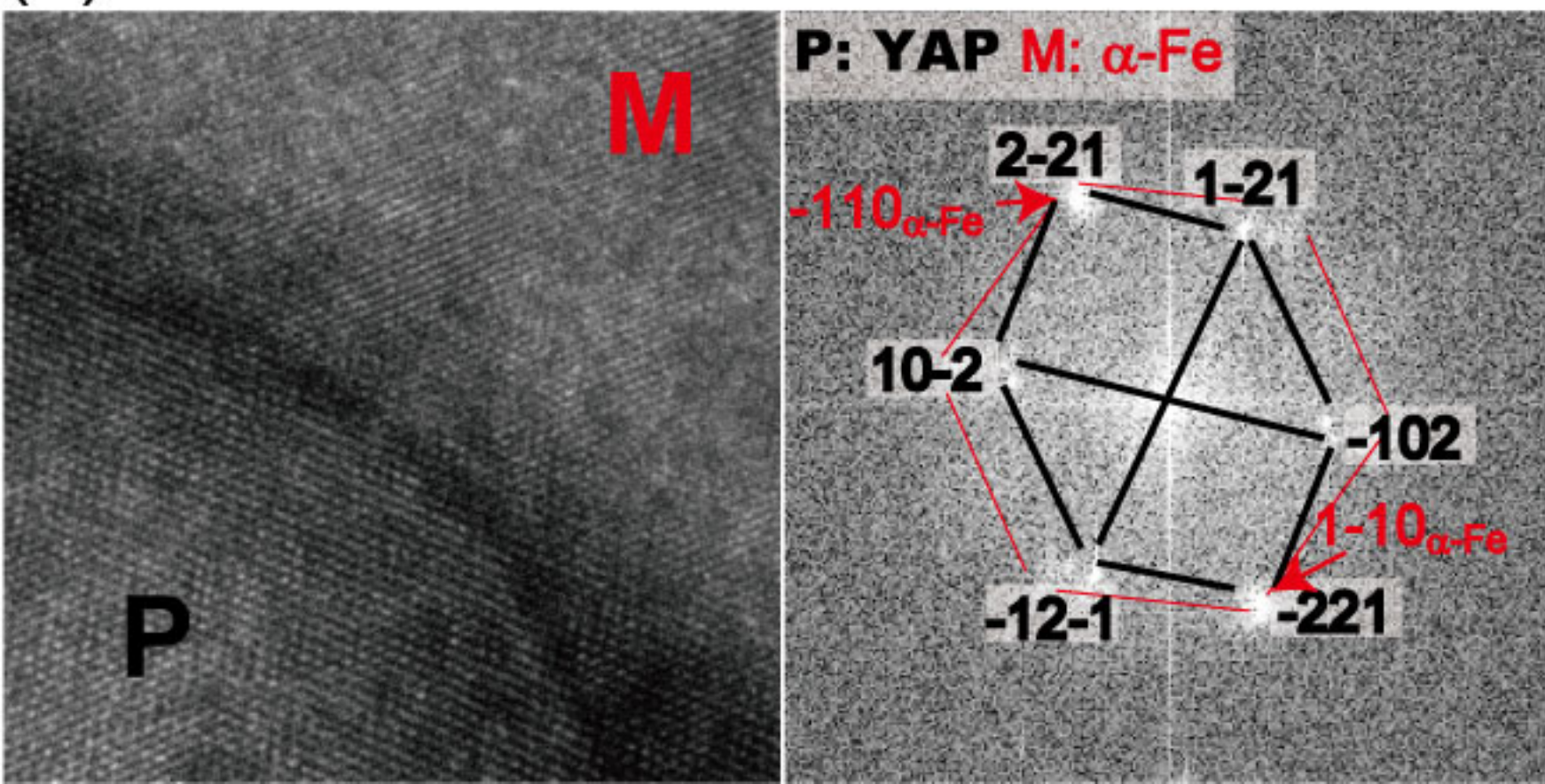
(a)



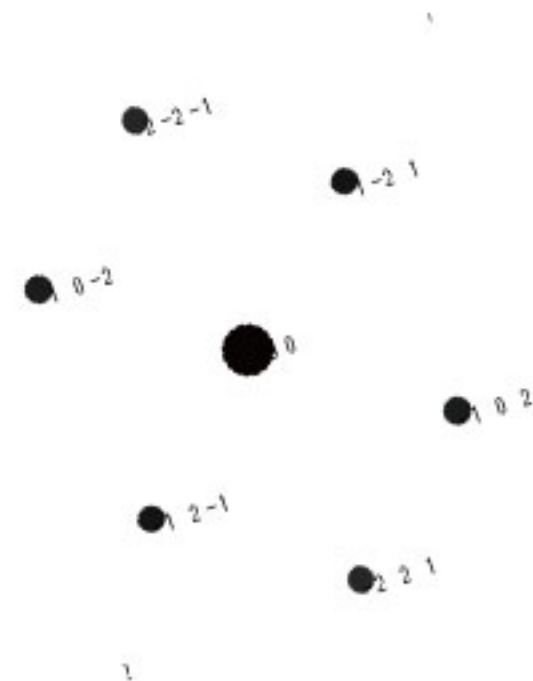
Simulation



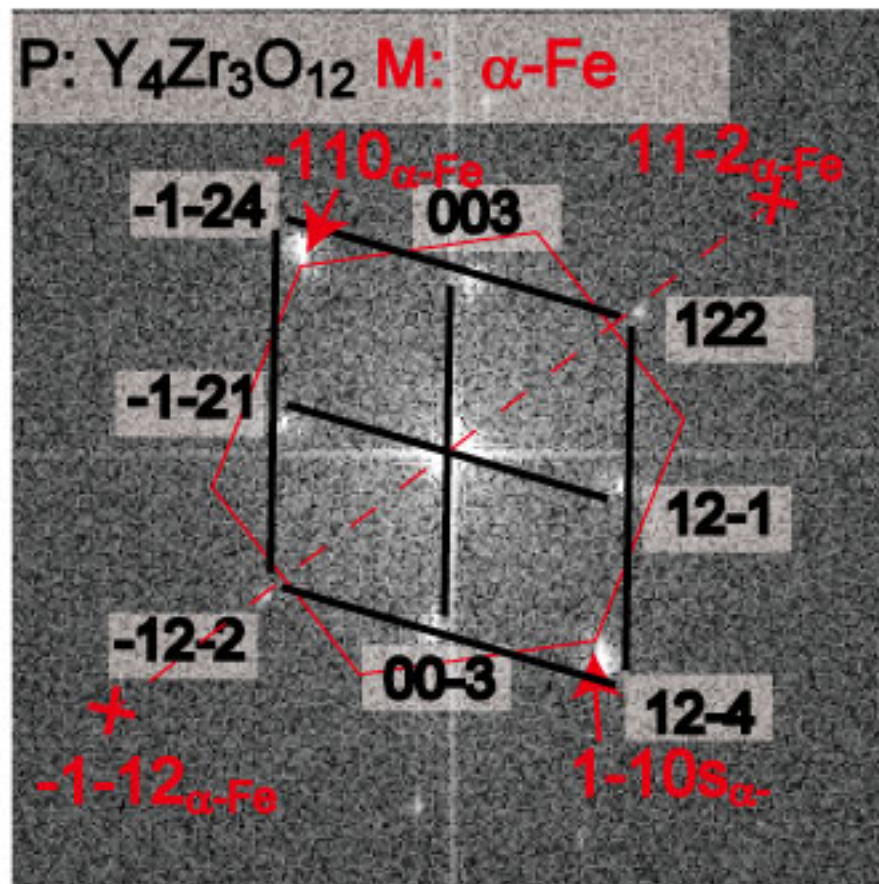
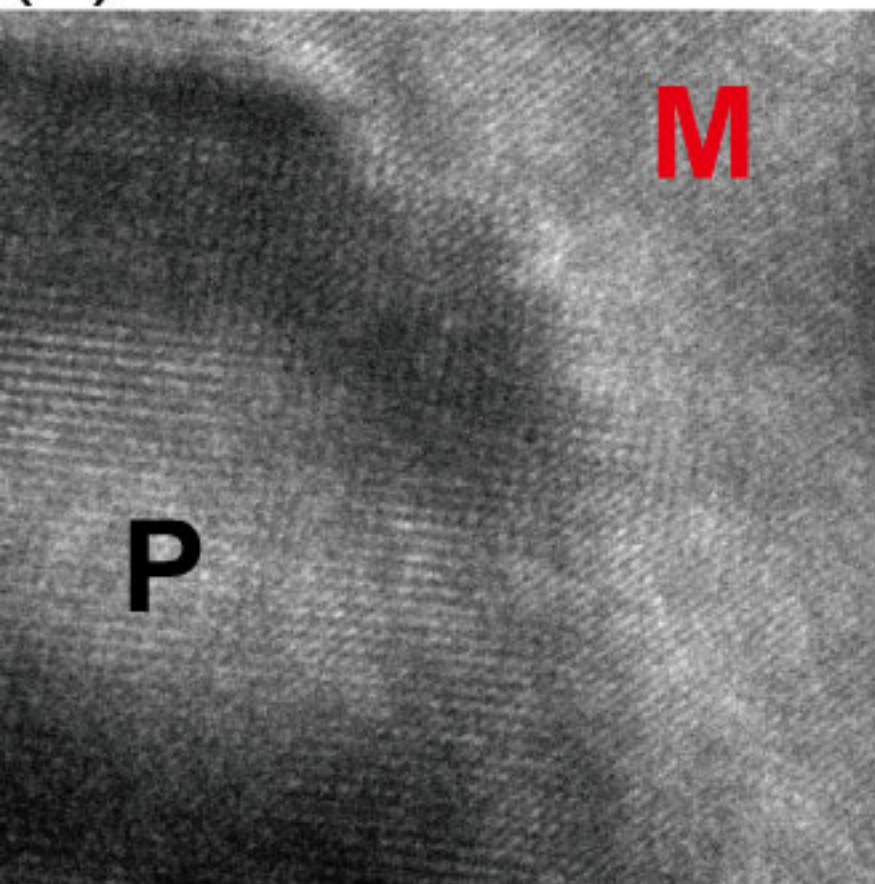
(b)



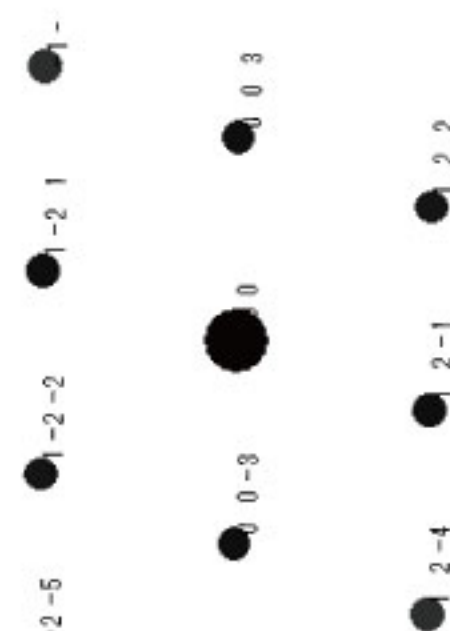
Simulation



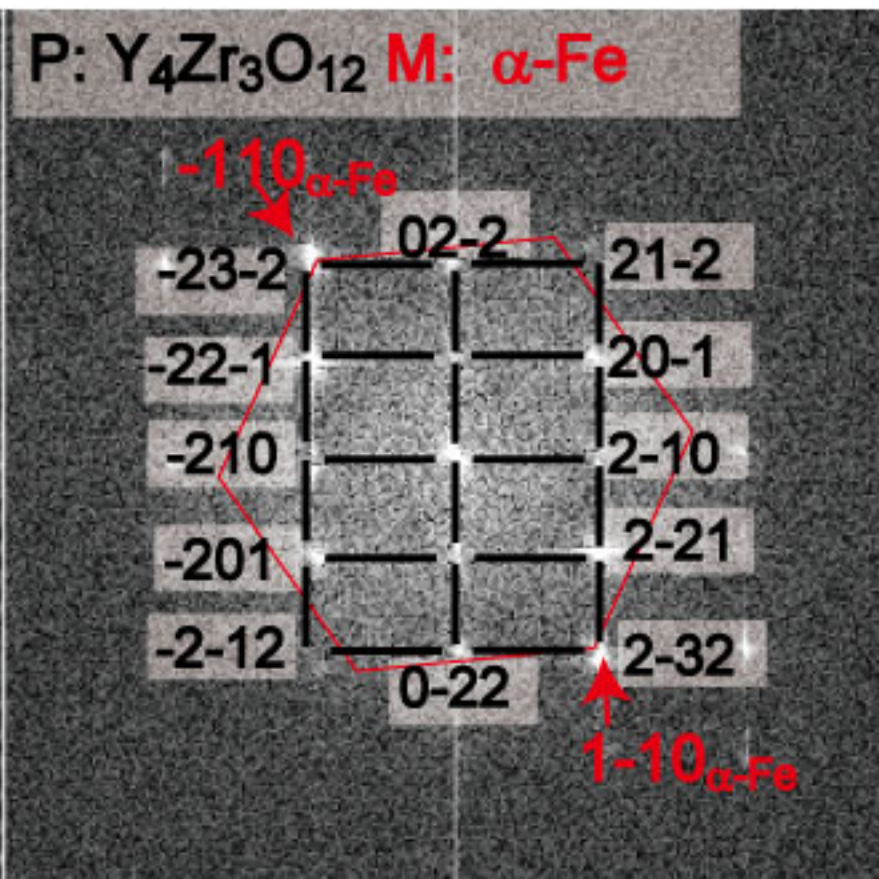
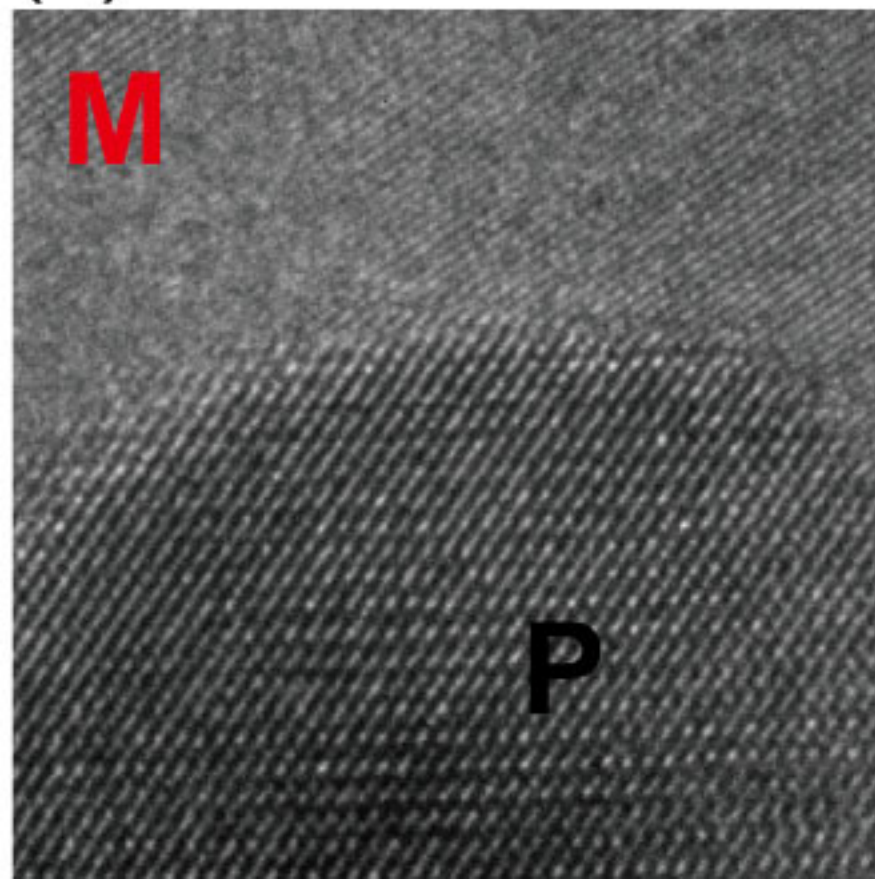
(a)



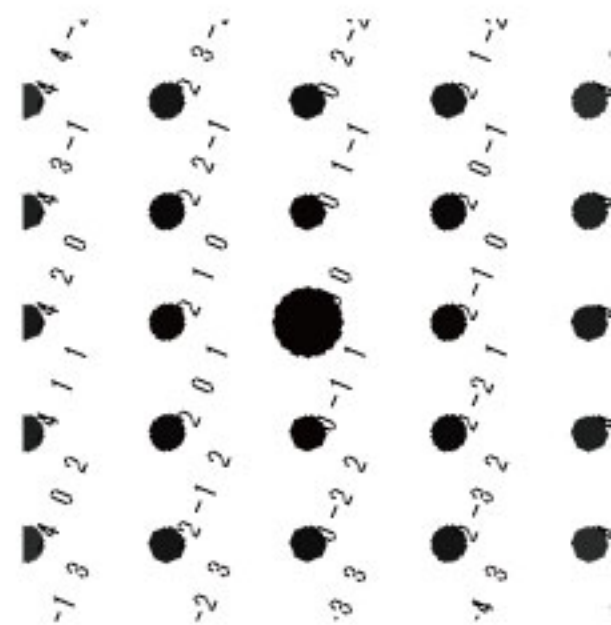
Simulation



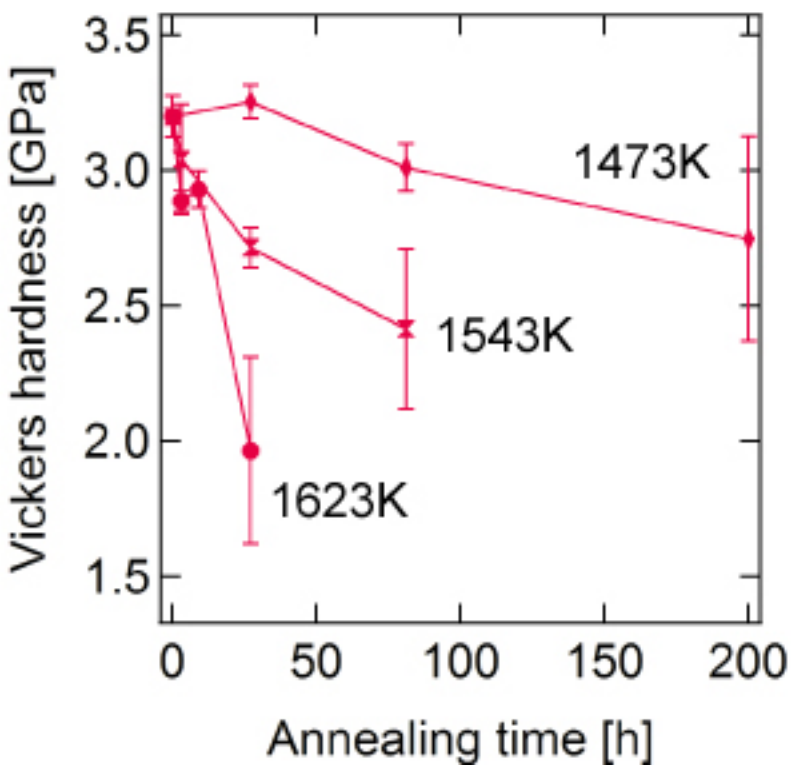
(b)



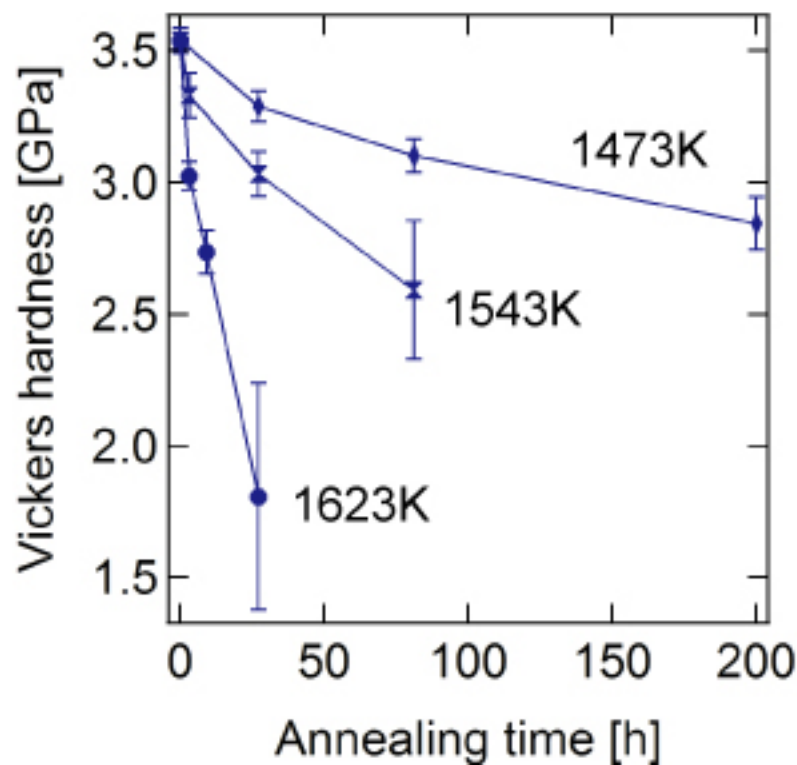
Simulation



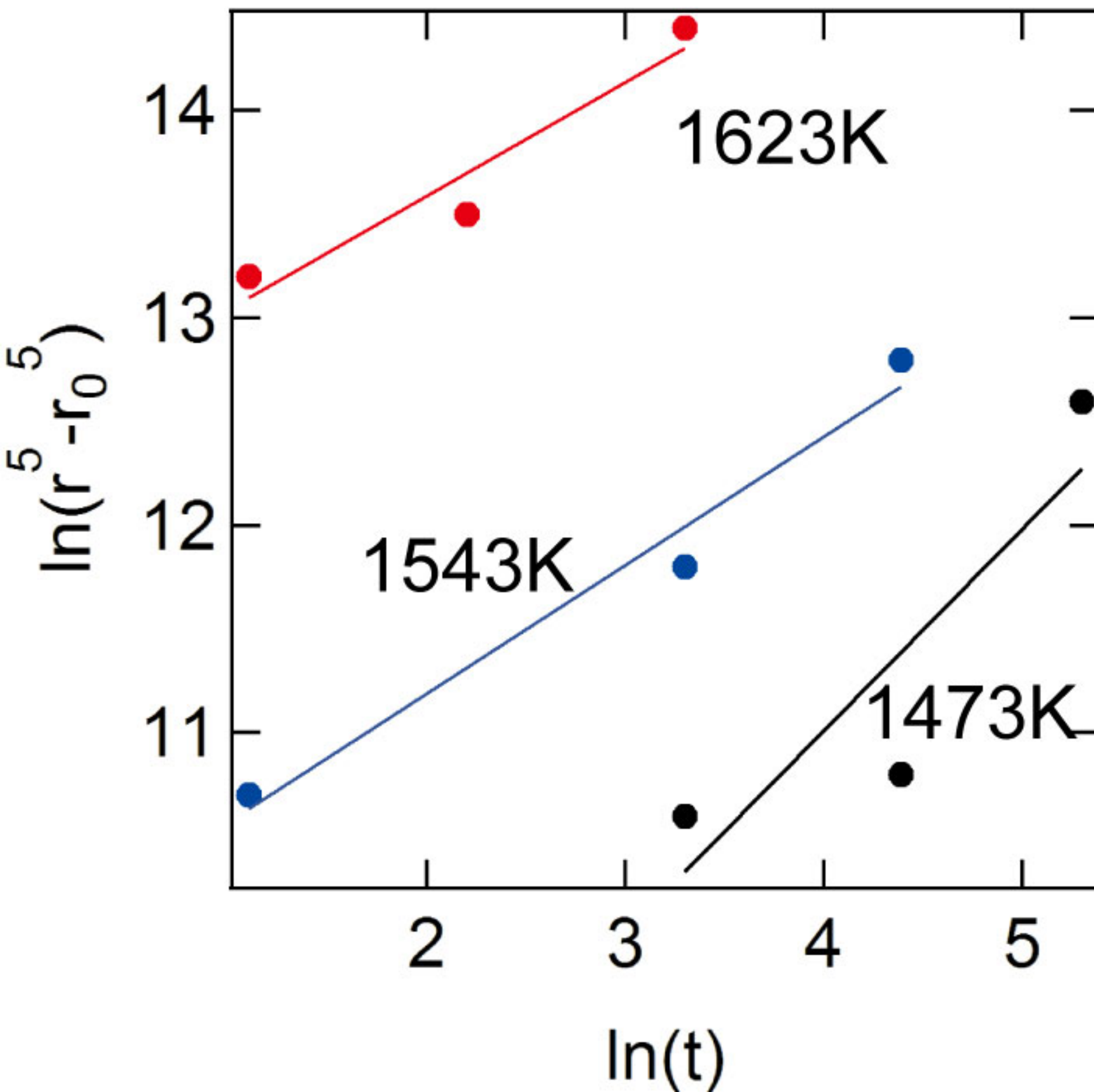
15Cr-7Al



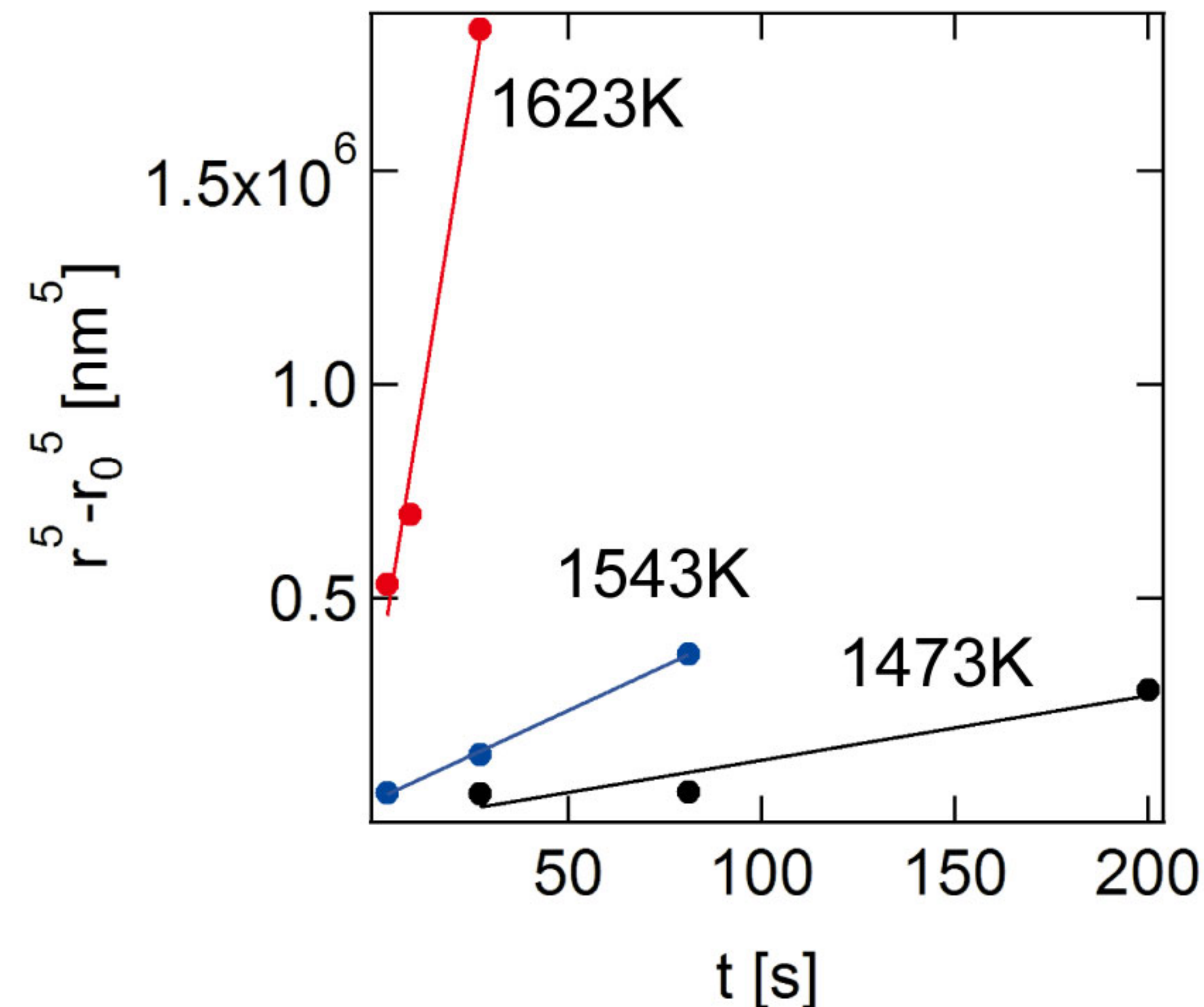
15Cr-7Al-0.4Zr



(a)



(b)



(c)

