In Situ HRTEM Observation of Electron-Irradiation-Induced Amorphization and Dissolution of the E ($\text{Al}_{18}\text{Cr}_2\text{Mg}_3$) Phase in 7475 Al Alloy

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Abstract Electron irradiation effects on phase stability of the E ($\text{Al}_{18}\text{Cr}_2\text{Mg}_3$) phase have been investigated by high-angle annular dark-field scanning transmission electron microscopy and high-resolution transmission electron microscopy (HRTEM). The in situ HRTEM observations show that the $\text{Al}_{18}\text{Cr}_2\text{Mg}_3$ particles with different thickness undergo amorphization and dissolution under 300 keV electron irradiation at 25 °C. The results indicate that the intermetallic compound $\text{Al}_{18}\text{Cr}_2\text{Mg}_3$ is unstable under electron irradiation, and structural changes mainly depend on the thickness of particles. Amorphization in the thick particles is caused by a combination of chemical disordering and an increase in point defect concentration. Dissolution after amorphization in the thin particles is attributed to the diffusion of point defect towards the Al matrix.

KEY WORDS: Intermetallic compound; $\text{Al}_{18}\text{Cr}_2\text{Mg}_3$; Irradiation effects; Amorphization; Dissolution

1 Introduction

7475 Al alloys have many advantages such as their high strength, low density, high fracture toughness, excellent workability and weldability. The alloys are mainly used in aircraft and rockets on complex structure and high strength requirement parts. During the process of serving in space, the parts will undergo space irradiation such as electron, ion, γ -ray, etc.

When solid materials are subjected to electron irradiation, their atomic structures may be altered. Crystal-to-amorphous

(C–A) transition was reported in various materials, such as $\text{Fe}_{17}\text{Nd}_2$ [1], Zr_3Fe [2], $\text{Nd}_2\text{Fe}_{14}\text{B}$ [3], B_2 phase in Ti–Ni–Fe alloys [4], and SiC [5]. Amorphous-to-crystalline (A–C) transition was observed by Jencic et al. [6] in amorphous Si, Ge, GaP and GaAs. Nagase et al. investigated crystal-to-amorphous-to-crystal (C–A–C) transition in Zr-based alloys [7, 8], and quasicrystal-to-amorphous-to-crystal (Q–A–C) transition in $\text{Zr}_{66.7}\text{Pd}_{33.3}$ metallic glass [9]. Migration and coalescence of Xe nanoprecipitates was found in Al matrix [10]. A variety of structural changes in carbon nanostructures were observed [11].

It was reported that irradiation can accelerate G.P. zones formation in 7 series Al alloys [12]. However, few studies have focused on the effects of electron irradiation on the stability of the E ($\text{Al}_{18}\text{Cr}_2\text{Mg}_3$) dispersoids in 7475 Al alloy. The E dispersoids can effectively inhibit recrystallization and control grain growth. Under electron irradiation, the atomic structures of E phase may change [13]. In this paper, therefore, the stability of E phase with different thickness under electron irradiation was investigated by in situ high-resolution transmission electron microscopy (HRTEM). Moreover, the mechanisms concerning the evolution of atomic structure were discussed.

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Fig. 1 HAADF-STEM micrograph of $\text{Al}_{18}\text{Cr}_2\text{Mg}_3$ particles in the 7475 Al alloy sample after solid solution treatment

2 Experimental

The 7475 Al alloy was chosen for investigation and the nominal chemical composition of the alloy is: Al–6.2Zn–2.6Mg–1.9Cu–0.25Cr (in wt%) with a small amount of Mn, Si and Fe. The cast ingot was first homogenised at 460 °C for 16 h, and then hot-rolled to a 20 mm thin sheet, followed by solution treatment at 475 °C for 1 h. The specimen for electron irradiation and TEM observation was prepared by twin-jet electro-polishing in a solution of 30% nitric acid and 70% methanol under –25 °C at 15 V. The electron irradiation was performed using a Tecnai F30G² TEM operating at an acceleration voltage of 300 kV. This acceleration voltage is believed to be higher than the threshold acceleration voltage required for initiating an electron knock-on effect in Al [14, 15]. Electron irradiation was carried out at 25 °C. The applied dose rate was selected as 2.3×10^{25} electron/(m²s) [5]. The beam heating was less than 10 °C. The vacuum in the microscope was better than 8×10^{-5} Pa during the irradiations. The changes in atomic structures of ten $\text{Al}_{18}\text{Cr}_2\text{Mg}_3$ particles with different thickness have been examined by in situ HRTEM observations.

3 Results

$\text{Al}_{18}\text{Cr}_2\text{Mg}_3$ is a face-centred cubic structure with 184 atoms per unit cell, whose space group is $\text{Fd}\bar{3}m$ (No. 227)

and lattice parameter a is 1.4526 nm [16]. Figure 1 shows a HAADF-STEM micrograph of the E phase with various morphologies and different thickness in the 7475 Al alloy after solid solution treatment. Due to Rutherford elastic scattering, HAADF-STEM image intensity is typically dominated by atomic number [Z^n ($1.5 < n < 2.0$)] [17]. So, the more white the particles, the more thick (see Fig. 1). The size of these particles normally ranges from 50 to 200 nm.

3.1 Electron-Irradiation-Induced Amorphization

Figure 2 show an in situ HRTEM observation of the electron-irradiation-induced C–A transition occurred in the E phase. Figure 2a shows the initial crystalline state of the E phase with $d(\bar{1}\bar{1}\bar{1})_{\text{E}} = 0.839$ nm and $d(351)_{\text{E}} = 0.246$ nm before electron irradiation. Although the HRTEM micrograph of the matrix is from $[\bar{1}\bar{1}2]_{\text{Al}}$ reflection (not shown here), the spots in the corresponding fast Fourier transform (FFT) spectrum are only from $[314]_{\text{E}}$. This indicates that the particle is relatively thick. In Fig. 2b, lattices begin to be chopped, or partly disturbed after 10 s irradiation. Specifically, the periodic arrangement of atoms along $[\bar{3}51]_{\text{E}}$ is partly disturbed, while that along $[\bar{1}\bar{1}\bar{1}]_{\text{E}}$ is still maintained (indicated by the parallel arrows). The FFT spectrum shows the spots from $\{351\}_{\text{E}}$ begin to weaken, while that from $\{111\}_{\text{E}}$ are still sharp.

With increasing dose of electron irradiation, the destruction extent of the E phase atomic structure increases. Figure 2c shows an HRTEM image of the E phase after 20 s irradiation. The periodic arrangement of the atoms along $[\bar{1}\bar{1}\bar{1}]_{\text{E}}$ becomes more and more weak (also indicated by parallel arrows). The spots from $\{351\}_{\text{E}}$ disappear completely, while that from $\{111\}_{\text{E}}$ is still maintained (see the corresponding FFT spectrum).

Figure 2d shows the full amorphous state of E phase after 30 s electron irradiation. The periodic arrangement of the atoms along $[\bar{3}51]_{\text{E}}$ and $[\bar{1}\bar{1}\bar{1}]_{\text{E}}$ are completely destroyed. The FFT spectrum shows a diffuse diffraction halo. In order to verify the stability of the final amorphous state of the E phase after electron-irradiation-induced amorphization, we have prolonged the irradiation time to 1 h, and the corresponding HETEM results (not shown here) are very similar to Fig. 2d.

3.2 Electron-Irradiation-Induced Dissolution

Figure 3a shows a HRTEM micrograph before electron irradiation. The spots in the FFT spectrum of the white rectangular region are from both the $[\bar{1}\bar{1}2]_{\text{E}}$ and the $[\bar{1}\bar{1}2]_{\text{Al}}$ projections, indicating the particle is relatively thin. Images shown in Fig. 3b–f are the magnifications of the white

Fig. 2 HRTEM micrographs sequence showing C–A transition in the thick $\text{Al}_{18}\text{Cr}_2\text{Mg}_3$ particle by 300 keV electron irradiation (insets are the corresponding FFT spectra): **a** Before irradiation; **b** After 10 s irradiation; **c** After 20 s irradiation; **d** After 30 s irradiation

Fig. 3 HRTEM micrographs sequence showing dissolution in the thin $\text{Al}_{18}\text{Cr}_2\text{Mg}_3$ particle by 300 keV electrons irradiation (insets are the corresponding FFT spectra): **a** before irradiation at low magnification; **b** magnifications of the white rectangular region in Fig. 3a before irradiation; **c** the same region of Fig. 3b after 10 s irradiation; **d** the same region of Fig. 3b after 20 s irradiation; **e** the same region of Fig. 3b after 30 s irradiation; **f** the same region of Fig. 3b after 50 s irradiation

rectangular region in Fig. 3a, show in situ observations of the amorphization and dissolution process occurred in the thin $\text{Al}_{18}\text{Cr}_2\text{Mg}_3$ particle during 300 keV electron irradiation. The thin $\text{Al}_{18}\text{Cr}_2\text{Mg}_3$ particle transformed into amorphous structure at first, and then dissolved in Al matrix. Figure 3b is the initial crystalline state, in which

the perfect lattice image can be observed along the $[\bar{1}12]_E$ direction, with $d(\bar{1}\bar{1}\bar{1})_E = 0.839$ nm and $d(\bar{2}20)_E = 0.514$ nm.

After 10 s irradiation, the lattice structure begins to be disturbed. In particular, the periodic arrangement of atoms along $[220]_E$ is seriously disturbed as shown in Fig. 3c,

Table 1 C–A transition in a variety of intermetallic compounds under electron irradiation [1–4]

Al ₇ Cr	Al ₅ Cr	Al ₄ Cr				
Al ₉ Co ₂	BCo ₂	BCo ₃	Co ₂ Ti			
Al ₁₀ V	Al ₄₅ V ₇	Al ₂₃ V ₄				
Al ₆ Mn	Al ₄ Mn	Mn ₂ TiFe ₄				
NiTi	NiTi ₂	BNi ₂	B ₃ Ni ₄ (o)	MoNi	Nb ₇ Ni ₆	ZrAlNi
Cu ₃ Ti ₂	Cu ₄ Ti ₃	CuTi	CuTi ₂	Cu ₁₀ Zr ₇	CuZr	CuZr ₂
Al ₂ Zr	Al ₃ Zr ₂	AlZr	Al ₄ Zr ₅	Al ₃ Zr ₄	Al ₂ Zr ₃	AlZr ₂
Ni ₃ Zr	NiZr	NiZr ₂	PdZr ₂	Pt ₃ Zr ₅	FeZr ₂	FeZr ₃ Cr ₂ Zr
Al ₃ Fe	BFe ₃	Fe ₂ Ti	Fe ₁₇ Nd ₂	Fe ₂₃ Nd ₂ B ₃	Fe ₁₄ Nd ₂ B	Fe ₈₁ Zr ₉ B ₁₀

whereas that along $[\bar{1}\bar{1}\bar{1}]_E$ was still maintained (indicated by parallel arrows). Meanwhile, the periodic arrangement of atoms along $[\bar{1}\bar{1}\bar{1}]_{Al}$ (indicated by a double-arrow) is able to be observed in Fig. 3c. The value of $d(\bar{1}\bar{1}\bar{1})_{Al}$ approximates to 0.234 nm. With increasing total dose of electron irradiation, the characteristics of the periodic arrangement of atoms along $[\bar{1}\bar{1}\bar{1}]_{Al}$ become more and more clear, while that along $[\bar{1}\bar{1}\bar{1}]_E$ become more and more weak, as shown in Fig. 3d. In Fig. 3e, the characteristics of the periodic arrangement of atoms along $[\bar{1}\bar{1}\bar{1}]_E$ are completely destroyed, while that along $[\bar{1}\bar{1}\bar{1}]_{Al}$ become more and more clear. At last, the Al₁₈Cr₂Mg₃ particle is entirely dissolved in Al matrix. The value of $d(\bar{1}\bar{1}\bar{1})_{Al}$ approximates to 0.236 nm, and changes little (compare Fig. 3c with Fig. 3f). The corresponding FFT spectra show that with increasing irradiation dose the crystalline diffraction spots from $[\bar{1}\bar{1}\bar{2}]_E$ gradually diminish, then are replaced by the diffused ring pattern, and finally transform to the crystalline diffraction spots from $[\bar{1}\bar{1}\bar{2}]_{Al}$.

4 Discussion

During 300 keV electron irradiation, the thick Al₁₈Cr₂Mg₃ particles undergo the C–A transition, as shown in Fig. 2. The Al₁₈Cr₂Mg₃ particle transforms into amorphous structure at first, and then dissolved in Al matrix, as shown in Fig. 3. The mechanisms of atomic structure in the intermetallic compound Al₁₈Cr₂Mg₃ can be considered from the following aspects.

A large number of intermetallic compounds (listed in Table 1) can undergo amorphization under electron irradiation, which contain early transition or refractory elements with unpaired d-electrons (e.g., Ti, Zr, V, Cr, Mo) and late transition or noble metals with nearly filled d-shells (e.g., Fe, Co, Ni, Cu) [13]. In the present study, external electron shell arrangement of Cr element is 3d⁵4s¹ with unpaired d-electrons, so the intermetallic compounds

Al₁₈Cr₂Mg₃ is prone to amorphization under electron irradiation.

According to Refs. [14, 15], the threshold energy of Al atomic displacement is about 16–17 eV, which corresponds to the threshold value of incident energy 170–180 keV. So, the acceleration voltage of 300 kV is enough to stimulate the atomic displacement of Al elements in the specimen under the irradiation. Motta et al. [2, 18, 19] proposed that electron-irradiation-induced amorphization of intermetallic compounds is caused by a combination of chemical disordering and an increase in point defect concentration, and result in increase of free energy. Electron irradiation can introduce a vacancy-interstitial pair due to single atom displacement in metallic crystal. With the accumulation of lattice defects in the E phase, a critical defect concentration can be reached to induce amorphization.

According to the modified free-energy criterion [2, 18, 19], the amorphization condition is:

$$\Delta G_{irr} \geq \Delta G_{ac}, \quad (1)$$

where ΔG_{irr} is the difference in free energy between the irradiated and unirradiated crystals, and ΔG_{ac} is the difference in free energy between the amorphous and unirradiated crystalline states.

The irradiation-induced free energy change ΔG_{irr} is generally subdivided into two parts:

$$\begin{aligned} \Delta G_{irr} &= \Delta G_{def} + \Delta G_{dis} \\ &= \sum_h [C_h E_h - T \Delta S_h] + \Delta C_p N \Omega - T \Delta S_{dis}, \end{aligned} \quad (2)$$

where ΔG_{def} and ΔG_{dis} are the increase in free energy due to the increase of the point defect concentration and chemical disordering, C_h is the concentration of defect h , E_h is its formation energy, ΔS_h is the configurational entropy change from introducing point defects, ΔC_p is the change in the number of atom pairs per Mole, N is the number of lattice sites per mol, Ω is the ordering energy, and ΔS_{dis} is the configurational

entropy change due to the introduction of antisite defects.

Following the rate theory [20], the concentration of defects is given by the two equations:

$$\begin{aligned}\frac{\partial C_v}{\partial t} &= D_v \nabla^2 C_v + G - K_{iv} C_i C_v - \sum_j K_{jv} C_j C_v \\ \frac{\partial C_i}{\partial t} &= D_i \nabla^2 C_i + G - K_{iv} C_i C_v - \sum_j K_{ji} C_j C_i\end{aligned}\quad (3)$$

where C_v and C_i are the vacancy and interstitial concentrations, respectively, D_v and D_i are their diffusion coefficients, G is the displacement rate, K_{iv} is the recombination rate, K_{jv} and K_{ji} are their respective annihilation rates at sink j , and C_j is the concentration of sink j .

According to Eq. (3), the concentration of point defect decreases with the defect sink concentration C_j . Therefore, the atomic structural change is related to the defect sink concentration C_j . Motta *et al.* [21] proposed that the dominant defect sink in thin foils is the foil surface under electron irradiation. Since the defect sink concentration C_j in thick particles is lower than that in thin particles, the defect concentration (C_v and C_i) is higher in thick particles than that in thin particles. Consequently, due to the high defect concentration in thick particles, it is difficult for a large number of defects to diffuse completely towards Al matrix. While in thin particles it is easy for a small amount of defects to diffuse completely towards Al matrix. Therefore, the thick $\text{Al}_{18}\text{Cr}_2\text{Mg}_3$ particles undergo amorphization under electron irradiation, and the thin $\text{Al}_{18}\text{Cr}_2\text{Mg}_3$ particles transformed into amorphous structure at first, and then dissolved in Al matrix.

5 Conclusions

- (1) The thick $\text{Al}_{18}\text{Cr}_2\text{Mg}_3$ particles undergo the C–A transition under electron irradiation, which is caused not only by chemical disordering but also by an increase in point defect concentration. Moreover, the amorphous phase is stable under further irradiation.
- (2) The thin $\text{Al}_{18}\text{Cr}_2\text{Mg}_3$ particles undergo dissolution under electron irradiation. $\text{Al}_{18}\text{Cr}_2\text{Mg}_3$ particles

transformed into amorphous structure at first, and then dissolved due to the diffusion of point defect towards Al matrix.

- (3) Amorphization or dissolution depends on the thickness of $\text{Al}_{18}\text{Cr}_2\text{Mg}_3$ particles, and the difference in the irradiation-induced structural change is related to the defect sink concentration.

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