Dislocation creep behavior of CoCrFeMnNi high entropy alloy at intermediate temperatures

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ABSTRACT
Dislocation creep behaviors of CoCrFeMnNi were investigated at intermediate temperatures. Shape of creep curves, stress exponents and the activation energies at high stresses (> 40 MPa) were distinctly different from those at low stresses, suggesting the transition of creep mechanism from climb-controlled creep to viscous glide creep. Lattice strain energy of dislocations plays an important role on the distribution of atoms over the configurational entropy in the vicinity of dislocation. The excellent agreement between the experimental transition stress and the theoretical stress using the data of Cr suggests that Cr is the most influential element to the viscous glide at high stresses.

INTRODUCTION
In multi-element high entropy alloys (HEAs), high configurational entropy stabilizes the single solid solution phase over the phase separation or intermetallic compound formation [1–3]. Structurally simple solid solution HEAs exhibit the excellent mechanical properties associated with the severe lattice distortion [4] and sluggish lattice diffusion [5]. Solution strengthened HEA also demonstrated the extensive strain hardening accompanied with the remarkable plasticity [6]. The unique mechanical and physical properties associated with the complex composition have attracted intensive interest of many investigators [1–3,6–8]. Recently, high temperature superplasticity was reported in fine-grained [9] CoCrFeMnNi. Chockshi [9] also observed the power-law creep behaviors at high temperature (> 850°C) and at high stresses.

Solution strengthening alloys exhibit excellent creep resistance at intermediate temperatures [10–12]. The interaction between dislocation and constituent atom would have a great influence on the creep of HEAs [7,8]. Creep resistance is expected to be improved by the severe lattice distortion and sluggish lattice diffusion in HEAs. It would be interesting to study the roles of constituent elements in creep resistance and performance of HEAs at intermediate temperatures. In this study, creep performance of CoCrFeMnNi were studied between 535°C and 650°C to investigate the creep deformation mechanisms at intermediate temperatures.

EXPERIMENTAL
Equiatomic CoCrFeMnNi alloy ingot (19.0 wt.%Co-21.5 wt.%Cr-20.0 wt.%Fe-20.4 wt.%Mn-19.1 wt.%Ni) produced by arc melting [13] were homogenized, rolled into 1.0 mm thick plates and annealed at 900°C. For more experimental details, the readers are directed to Ref. [13]. The grain shape of the annealed CoCrFeMnNi
was characterized using an electron backscatter diffraction system (Oxford Instruments, UK). Tensile creep specimens with a gauge length of 9 mm were machined by electrical discharge machining. Creep tests were carried out at intermediate temperatures (535 ∼ 650°C) in a constant stress creep tester with the specially designed Andrade-Chalmers lever arm [14]. The creep extension of the specimen was measured by Schaevitz model HR 1000LVDT with an accuracy of 0.5 × 10^{-5} m.

Results

The grain size of the annealed CoCrFeMnNi was 21.7 μm excluding twin boundaries [13]. Chokshi [9] reported that CoCrFeMnNi exhibited superplasticity for samples with initial grain sizes of 1.4 μm [9,15] whereas coarser grained HEA (∼12 μm) exhibited power-law creep at 850°C. The grain size of the specimens in the present study is therefore large enough to induce the dislocation creep [9,10–12].

Figure 1. Creep curves of CoCrFeMnNi HEA at temperatures between 535°C and 650°C. (a) lower stresses and (b) high stresses.
Creep curves of CoCrFeMnNi at temperatures between 535°C and 650°C are exhibited in Figure 1. The representative creep curves at lower stress (<40 MPa) and at high stress are exhibited in Figure 1(a,b), respectively. At low stresses, the creep rate was initially high and decreased during the primary creep, exhibiting the normal transient creep curves [10]. At high stresses, the creep curves exhibited the inverted transient curves in which the initially low creep rate increased gradually to reach the steady-state [10] (Figure 1(b)). Creep rate varied considerably with stress at high stresses, curves at high stresses are shown in the expanded view along the time axis. The shape of creep curves is closely related to the creep mechanism in alloys [10,11]. The inverted transient is indicative of initially stable substructure caused by viscous glide of dislocations [10–12]. The shape change of primary creep curves in Figure 1 supports the transition of creep mechanism [11,12].

In Figure 2, the stress dependences of the steady state creep rate of CoCrFeMnNi at three temperatures are presented. The slope of the creep rate vs. stress apparently changed as the stress increased from low stresses to higher stress region. The stress exponent (=n) decreased from ~6 to ~3 as the stress increased. The transition of the stress exponent from 5–7 to ~3 was suggested to be due to the creep mechanism transition from the climb-to glide-controlled creep [10–12]. The creep strain rates are predicted by the typical power-law creep equations [16]. For example, the creep rates in the climb-controlled region in Figure 2 is comparable to those predicted by the lattice diffusion controlled creep of iron and stainless steel [16]. The creep rate in the viscous glide creep region of CoCrFeMnNi is expected to be slower because of the low stress dependence of creep rates at higher stresses (>40 MPa).

He et al. [17] reported the increase of stress exponent for high temperature steady state deformation (750 ~850°C) in tensile testing, in contrast to decrease of the stress exponent with increasing stress. It is noted that the transition of stress exponent observed by He et al. [17] occurred at much higher strain rates (10−5–10−4/s) than the transition strain rate of the present study (10−8/s ~10−6/s). Oikawa et al. [18] reported the decrease of the creep stress exponent from ~5 to ~3 at the creep rates of 10−7–10−6/s and the increase to ~5 again as the creep rate increased above 10−5/s. Hong [12] proposed that the increase of stress exponent again to ~5 at strain rates above 10−5/s is due to the diminishing effect of solute dragging with further increase of stresses.

In Figure 3, the steady state creep rates of CoCrFeMnNi are plotted against the reciprocal of temperature. Creep activation energies were determined using the data at three temperatures. The creep activation energy in the low stress region (305–320 kJ/mol) is close to the average of the lattice diffusion activation energy of five elements in CoCrFeMnNi reported by Vaidya et al. (294 KJ/mol) [19,20] and Tsai et al. (303 kJ/mol) [6]. The creep activation energies (235–250kJ/mol) in the high stress region (>40 MPa) was noticeably smaller than the average activation energy of five elements (294–303 kJ/mol) [5,19,20] in CoCrFeMnNi.

**Discussion**

Viscous glide of dislocations in HEA may arise from the operation of one or more of following viscous drag processes as in conventional alloys [11]: (a) segregation of atoms to moving dislocations, (b) short range orders (SROs), (c) chemical interaction of atoms with stacking faults. Recently, Hong et al. [7] and Moon et al. [6] suggested that the interaction between dislocations and the
nanoscale inhomogeneity such as coclusters and/or SROs is the rate controlling deformation of CoCrFeMnNi at low temperatures. However, effects of SROs and stress-induced ordering diminish with increase of temperature because of homogenization effects of entropy at high temperatures. Since the stacking fault energy of CoCrFeMnNi increases with temperature [21,22], chemical effect of atoms on stacking faults is not likely to dominate at high temperatures. Toda-Caraballo et al. [23] suggested elastic misfit is prominent in solution strengthening of HEA.

At high temperatures, obstacles associated with the lattice distortion regardless of whether they be due to single constituent atom or the local arrangement of atoms cannot be treated as fixed obstacles [24,25] because of the high mobility of atoms. In order to take the effect of dislocation into consideration on the distribution of constituent atoms, the Gibbs free energy change $\Delta G$ of the particular volume with a dislocation is expressed as:

$$\Delta G = \Delta H_{\text{mix}} + \Delta E_d - T \Delta S_{\text{mix}}$$

where $\Delta E_d$ is the strain energy associated with a dislocation, $\Delta H_{\text{mix}}$ is the enthalpy of mixing, and $\Delta S_{\text{mix}}$ is the entropy of mixing. Influence of configurational entropy on the promotion of ideally homogeneously distribution of atoms diminishes in the small volume containing a dislocation because of its high strain energy. Atoms of the larger size misfit against the matrix of the average atomic size can be readily attracted to the dislocations to relieve the line energy at elevated temperatures, inducing the segregation of atoms.

In Figure 4(a,b), the possible the interaction of atoms of the same constituent element with a stationary dislocation (a) and a moving dislocation (b) are schematically shown. The free energy of the resting dislocation in Figure 4(a) can be lowered by the segregation of constituent atoms. The reduction of internal strain energy is far greater than the reduction of entropy, favoring the segregation of atoms at dislocations. Since the reduction of dislocation line energy due to segregation would increase with the increase of atomic size misfit [26–28], atoms with a larger size misfit are more likely to segregate at dislocations. As dislocations are forced to move by the external stress, the increase of internal strain energy associated with the liberation of dislocation from segregated atoms would cause the dragging stress on dislocations.

Chaudhury and Mohamed [11,27] suggested that the atomic size misfit plays an important role in inducing the transition from climb-controlled to glide-controlled creep. Viscous dislocation glide operates in the concentrated binary solid solution alloys [29] despite the rather small atomic size misfit [28,29]. The atomic size misfits of the constituent atoms of CoCrFeMnNi with the matrix were calculated assuming that the atomic radius of HEA matrix is the average of the constituent atoms [30] (Table 1). As summarized in Table 1. The atomic size misfit of Cr ($e_{\text{Cr}} = 0.0267$) is far greater than those of Co ($e_{\text{Co}} = 0.0138$), Fe ($e_{\text{Fe}} = 0.0138$) I Mn ($e_{\text{Mn}} = 0.0008$) and Ni ($e_{\text{Ni}} = 0.0024$). The element with the largest atomic size misfit in CoCrFeMnNi is Cr as shown in Table 1.

Chaudhury and Mohamed [11] suggested the following criterion for climb-glide transition of binary

![Figure 4. Hypothetical representations of interaction of atoms of the same constituent element with a stationary dislocation (a) and a moving dislocation (b).](image-url)
solid-solution alloys;

\[
\left( \frac{kT}{\varepsilon c^{1/2}Gb^3} \right)^2 = B\left( \frac{\gamma}{Gb} \right)^3 \frac{D_c}{D_g} \left( \frac{\tau}{G} \right)^2 \tag{2}
\]

where \( k \) is Boltzmann’s constant, \( T \) is creep temperature (K), \( \varepsilon \) is the atomic size misfit, \( c \) is the concentration of element, \( b \) is the Burgers vector (0.25 nm) [30], \( B \) is a dimensionless constant \( (4 \times 10^{13}) \) [10,11], \( \gamma \) is the stacking fault energy at intermediate temperatures \( (34–50 \text{mJ/m}^2) \) [22,30], \( G \) is the shear modulus [31], \( D_c \) is the diffusion coefficient related with the climb process and \( D_g \) is the diffusion coefficient related with the glide process [10–12]. The stacking fault energy used in this study \((45 \text{ mJ/m}^2 \text{ at 850–950 K}) \) is larger than the theoretically calculated stacking fault energy \((34 \text{ mJ/m}^2 \text{ at 850 K}) \) [22] of CoCrFeMnNi since the experimentally determined stacking fault energy of CoCrFeMnNi at 77 K [30] was reported to be 30 mJ/m² and the stacking fault energy increases with temperature [21].

The quantification of the critical stress for viscous glide creep by solute dragging in HEA is difficult because of the indistinguishable nature of solute and solvent. The greater interaction between dislocations and a specific element with a larger atomic size misfit [25–29] is expected to promote preferential segregation at dislocations (Figure 4). If the diffusivity of segregated atoms is comparable to the velocity of dislocations so that they cannot exert the larger dragging stress [22], the creep is controlled by viscous glide of dislocations [11,12,24–26]. Two important criteria to induce the drag stress for viscous glide in HEA would be the large atomic size misfit and the appropriate diffusivity [10–12]. Climb of dislocations is controlled by the lattice diffusivity [11] and \( D_c \) for climb controlled creep was calculated by averaging the inter-diffusion coefficient of constituent atoms \( (D_c = \sum_{n=1}^{5} X_n D_n) \), where \( X_n \) is the composition of the constituent element \( (=0.2) \) and \( D_n \) is the tracer diffusion coefficient [11] of the each constituent element. Activation energies \( (Q_n \text{ (kJ/mol)}) \) and the pre-exponential constants \( (D_0 \text{ (m}^2/\text{s})) \) for tracer diffusion in CoCrFeMnNi were \( Q_n = 276 \text{ and } D_0 = 4.52 \times 10^{-5} \) for Co, \( Q_n = 312 \text{ and } D_0 = 2.46 \times 10^{-3} \) for Cr, \( Q_n = 255 \text{ and } D_0 = 1.05 \times 10^{-5} \) for Fe, \( Q_n = 267 \text{ and } D_0 = 1.25 \times 10^{-4} \) for Mn, \( Q_n = 304 \text{ and } D_0 = 6.24 \times 10^{-4} \) for Ni, respectively [19,20]. Since viscous glide is controlled by the diffusivity of segregated atoms [12], tracer diffusion coefficient of segregated element was used for \( D_g \) of glide controlled creep [19,20].

The comparison of the calculated transition stress using the tracer diffusion coefficient of each element as \( D_g \) of glide-controlled creep with the experimental transition stress would reveal which element is most responsible for the transition from the climb- to glide-controlled creep. In Figure 5(a,b), \( \left( \frac{kT}{\varepsilon c^{1/2}Gb^3} \right)^2 \) is plotted against \( B\left( \frac{\gamma}{Gb} \right)^3 \frac{D_c}{D_g} \left( \frac{\tau}{G} \right)^2 \) on a logarithmic scale at 600°C and 650°C (b) along with the experimental data of CoCrFeMnNi marked on the Co, Cr, Fe, Mn and Ni horizontal lines.

![Figure 5](image-url)
suggests that Cr is the most influential element to the viscous glide behavior in CoCrFeMnNi. The influential role of Cr in the viscous glide creep at intermediate temperatures is associated with the large atomic size misfit to relieve the dislocation line energy and the appropriate diffusivity comparable to the dislocation velocity.

The creep activation energies (305–320 kJ/mol) at low stresses are close to the average of the lattice diffusion activation energy [21,22]. Chaudhury and Mohamed [11] noted that the creep activation energy (151 KJ/mol) of Al-Cu solid solution in the glide-controlled creep region is slightly smaller than that (155 KJ/mol) observed in the climb-controlled creep region. Chaudhury and Mohamed [11] associated the larger creep activation energy in the climb-controlled creep to that of self-diffusion in Al and the smaller creep activation energy for viscous glide creep to that for diffusion of solute atom (Cu) in Al. The apparent creep activation energies (235–250 kJ/mol) for the glide-controlled creep at higher stresses is smaller than those of lattice tracer diffusion of elements in HEA matrix. Hong [32] suggested that the low creep activation energies in Al-Mg at intermediate temperatures resulted from dynamic solute-dislocation interaction. The variation of interactions between dislocations and various constituent atoms at different temperatures may modify the dragging of dislocations as well as the creep activation energies in the viscous glide creep region.

**Conclusions**

The present study demonstrated the transition of creep mechanism from climb- to glide-controlled creep at intermediate temperatures (535–650°C) in CoCrFeMnNi. Influence of configurational entropy on the homogeneous distribution of atoms diminishes adjacent to a dislocation because of its high strain energy. The reduction of dislocation line energy by segregation of atoms with larger atomic size misfit is greater than the reduction of entropy, favoring the segregation of constituent atoms. The climb to glide creep transition criterion was used to predict the transition from the climb- to the glide-controlled creep. The excellent agreement between the experimental transition point of CoCrFeMnNi and the theoretical transition point using the data of Cr suggests that Cr is the most influential element to viscous glide behavior at high stresses. The influential role of Cr in the viscous glide creep at intermediate temperatures is attributed to the large atomic size misfit of Cr to relieve the dislocation line energy and the appropriate diffusivity comparable to the dislocation velocity in the glide-controlled creep.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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**References**

[1] Tsai MH, Yeh JW. High-entropy alloys: a critical review. Mater Res Lett. 2014;2:107–123.

[2] Zhang Y, Zuo TT, Tang Z, et al. Microstructures and properties of HEAs. Prog Mater Sci. 2014;61:1–93.

[3] Miracle DB, Senkov ON. A critical review of HEAs and related concepts. Acta Mater. 2017;122:448–511.

[4] Song H, Tian F, Hu Q-M, et al. Local lattice distortion in HEAs. Phys Rev Mater. 2017;1:023404.

[5] Tsai KY, Tsai MH, Yeh JW. Sluggish diffusion in Co-Cr-Fe-Mn-Ni. Acta Mater. 2013b:4887–4897.

[6] Moon J, Hong SI, Bae JW, et al. On the strain rate-dependent deformation mechanism of CoCrFeMnNi at liquid nitrogen temperature. Mater Res Lett. 2017;5:472–477.

[7] Hong SI, Moon J, Hong SK, et al. Thermally activated deformation and the rate controlling mechanism in CoCrFeMnNi. Mater Sci Eng A. 2017;682:569–576.

[8] Diao HY, Feng R, Dahmen KA, et al. Fundamental deformation behavior in HEAs: an overview. Curr Opin Solid Stat Mater Sci. 2017;21:252–266.

[9] Chokshi AH. High temperature deformation in fine grained HEAs. Mater Chem Phys. 2018;210:152–161.

[10] Murty KL, Mohamed FA, Dorn JE. Viscous glide, dislocation climb and Newtonian viscous deformation of high temperature creep in Al-3Mg. Acta Metall. 1972;20:1009–1018.

[11] Chaudhury PK, Mohamed FA. Creep and ductility in an Al-Cu Solid-Solution Alloy. Metall Trans A. 1987;18:2105–2114.

[12] Hong SI. Influence of DSA on the transition of creep characteristics of a solid solution alloy. Mater Sci Eng. 1989;110:125–130.

[13] Ko JY, Hong SI. Microstructural evolution and mechanical performance of carbon-containing CoCrFeMnNi-C. J Alloy Compd. 2018;743:115–125.

[14] Jeong GB, Kim IW, Hong SI. Influence of microstructure modification on the circumferential creep of Zr-Nb-Sn-Fe. J Nucl Mater. 2016;468:171–177.

[15] Reddy SR, Bapari S, Bhattacharjee PP, et al. Superplastic-like flow in a fine-grained equiatomic CoCrFeMnNi. Mater Res Lett. 2017;5:408–414.

[16] Ruano OA, Miller AK, Sherby OD. The influence of pipe diffusion on the creep of fine-grained materials. Mater Sci Eng. 1981;51:9–16.

[17] He JY, Zhu C, Zhou DQ, et al. Steady state flow of the FeCoNiCrMn HEA at elevated temperatures. Intermetallics. 2014;55:9–14.
[18] Oikawa H, Hinda K, Ito S. Experimental study on the stress range of class I behavior in the creep of Al-Mg. Mater Sci Eng. 1984;64:237–245.

[19] Vaidya M, Pradeep KG, Murty BS, et al. Bulk tracer diffusion in CoCrFeNi and CoCrFeMnNi. Acta Mater. 2018;146:211–224.

[20] Vaidya M, Trubel S, Murty BS, et al. Ni tracer diffusion in CoCrFeNi and CoCrFeMnNi. J Alloy Compd. 2016;688:994–1001.

[21] Lecroisey F, Thomas B. On the variation of the intrinsic stacking fault energy with temperature in Fe-18 Cr-12 Ni alloys. Phys Stat Sol A. 1970;2:K217–K220.

[22] Huang S, Li W, Lu S, et al. Temperature dependent stacking fault energy of FeCrCoNiMn. Scr Mater. 2015;108:44–47.

[23] Toda-Caraballo I, Rivera-Díaz-del-Castillo PEJ. Modelling solid solution hardening in HEAs. Acta Mater. 2015;85:14–23.

[24] Kocks UF. Kinetics of solution hardening. Metall Mater Trans A. 1985;16:2109–2129.

[25] Hong SI. Influence of dynamic strain aging on the dislocation substructure. Mater Sci Eng. 1986;79:1–7.

[26] Hong SI. Criteria for predicting twin-induced plasticity in solid solution copper alloys. Mater Sci Eng A. 2018;711:492–497.

[27] Chaudhury PK, Modamed FA. Creep characteristics of an Al-2wt.%Cu alloy in the solid solution range. Mater Sci Eng A. 1988;101:13–23.

[28] King HW. Quantitative size-factors for metallic solid solutions. J Mater Sci. 1966;1:79–90.

[29] Farid ZM, Mahmouda A, Ali AR, et al. On the transition in creep behaviour during primary creep of Cu-Zn. Phys Status Sol A. 1990;117:437–446.

[30] Okamoto NL, Fujimoto S, Kambara Y, et al. Size effect, critical resolved shear stress, stacking fault energy, and solid solution strengthening in the CrMnFeCoNi. Sci Rep. 2016;6:35863–(10pp.).

[31] Laplanche G, Gadaud P, Horst O, et al. Temperature dependencies of the elastic moduli and thermal expansion coefficient of an equiatomic, single-phase CoCrFeMnNi. J Alloy Compd. 2015;623:348–353.

[32] Hong SI. On the creep activation energies of alloys. Mater Sci Eng. 2016;86(1987):211–218.