A Comparative Study of Hardness in Nanostructured Cu–Zn, Cu–Si and Cu–Ni Solid-Solution Alloys Processed by Severe Plastic Deformation^{*1}

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Although the maximal strength of Cu with a mean grain size of 10 nm has been reported as ~1000 MPa, the maximal strength of nanostructured Cu processed by severe plastic deformation (SPD) is ~450 MPa, owing to the saturation of accumulated strain caused by recovery or recrystallization during the SPD process. The strength of SPD-processed Cu can be increased by adding solid-solution atoms. A significant increase in the strength of nanostructured Cu after adding a small amount of Si solute atoms was reported in our previous study. In this study, various-composition Cu–Zn, Cu–Si, and Cu–Ni solid-solution alloys were subjected to high-pressure torsion (HPT) processing, which is one of the SPD processes. To reveal the role of solid-solution atoms on the deformation of Cu during the SPD process, the effects of Zn, Si, and Ni additions on hardness and microstructure of Cu after various HPT rotations were systematically investigated, up to the solubility limits of these atoms. It is well known that Zn and Si atoms decrease the stacking fault energy (SFE) of Cu. On the other hand, Ni atoms have the opposite effect to that of Zn and Si on the SFE of Cu. Experimental results were considered in terms of the atomic concentration of solute atoms c_a , electron-atom ratio e/a , and the SFE. The hardness of 140 HV of the nanostructured Cu significantly increased with increasing addition of Zn, Si, and Ni. The maximal hardness values of the nanostructured Cu–Zn, Cu–Si, and Cu–Ni alloys were 250 HV (29.4 at%Zn), 275 HV (4.5 at%Si), and 360 HV (81.4 at%Ni), respectively. In the case of the nanostructured Cu–Zn and Cu–Si alloys, the hardness increase correlated with the reduction in the SFE as a function of e/a . The decreased SFE by Zn and Si additions increased strain hardening during the SPD process. This strengthened the nanostructured Cu–Zn and Cu–Si alloys. On the other hand, hardening of the nanostructured Cu–Ni alloys is related not to the SFE changes, but to dislocation pinning or dragging by Ni solute atoms followed by suppression of recovery or recrystallization during the SPD process. [doi:10.2320/matertrans.MF201944]

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1. Introduction

The maximal strength of about ~1000 MPa has been demonstrated for pure Cu with a mean grain size of 10 nm, synthesized by pulsed electrodeposition.¹⁾ Severe plastic deformation (SPD) is one of the grain refinement techniques applicable to bulk samples. The SPD process changes coarse-grained materials to ultrafine-grained or nanocrystalline counterparts with deformation structure (so-called nanostructured materials) by generating a giant strain. Since dynamic recovery or recrystallization usually occurs during the SPD process after formation of nanostructured materials, these phenomena suppress further grain refinement, resulting in the saturation of grain size.²⁾ The mean grain size of pure Cu processed by the SPD process is 200–400 nm^{2,3)} with tensile strength of ~450 MPa.^{3,4)}

To obtain a finer mean grain size by the SPD process, addition of solute atoms³⁾ or dispersion of precipitate particles⁵⁾ have been demonstrated to effectively suppress the dynamic recovery or recrystallization during the SPD process. Consequently, stronger materials are obtained after the SPD process in solid-solution or precipitation-type alloys with finer grain structures.

An alternative way to obtain finer grain structures after the SPD process is to decrease the stacking fault energy (SFE) of Cu by adding alloying elements to suppress the cross-slip of screw dislocation. When the work-hardening capability

Fig. 1 Relationships between the stacking fault energy (SFE) and electron-atom ratio e/a , for the Cu alloys.⁹⁾

during the SPD process is increased by suppressing the dynamic recovery, finer grain structures are expected by enhanced accumulation of dislocations in materials. This approach is very effective for improving the strength of SPD-processed materials, as reported by many researchers.^{6–8)} Figure 1 shows the relationships between the SFE and electron-atom ratio e/a in Cu solid-solution alloys, for typical elements as solute additions as reported by Gallagher.⁹⁾ The electron-atom ratio e/a is based on the number of valence electrons per atom in an alloy, and is given as

$$e/a = Z_1 + c_a(Z_2 - Z_1), \quad (1)$$

where Z_1 and Z_2 are the number of valence electrons for the metal matrix and solute atoms, respectively, and c_a is the

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atomic concentration of solute atoms.⁹⁾ For Cu alloys, the electron-atom ratio e/a monotonically increases with increasing the atomic concentration of solute atoms c_a . Thus, it was demonstrated that the SFE monotonically decreases with increasing e/a , and attains a minimum at ~ 1.3 of e/a for all Cu solid-solution alloys of typical elements, as shown in Fig. 1. Since the maximal solubility of many elements in Cu and Ag alloys corresponds to the e/a ratio in the 1.35–1.4 range,¹⁰⁾ the SFE almost reaches a minimum near the solubility limit. In addition, some variation is observed around SFE minima values for different Cu solid-solution alloys in Fig. 1. For example, there is a difference of 7 mJ/m² between the SFE minima for Cu–Si and Cu–Zn alloys, as indicated by the solid lines in Fig. 1. If these factors are taken into account for strengthening of SPD-processed materials, higher strength after the SPD process can be expected, up to the solubility limit, for all Cu solid-solution alloys in Fig. 1.

Although the SFE can be controlled by controlling the amount of solute atoms, it is relatively difficult to compare the effects of different solid-solution elements on increasing the strength for the same atomic concentration of solute atoms c_a , because the maximal solubility limits for different elements in Cu are different, owing to the differences between atomic radii and electronegativity of solute atoms.¹¹⁾ Therefore, it should be appropriate to discuss the strengthening mechanisms of various SPD-processed Cu solid-solution alloys in terms of the e/a ratio, for understanding universal trends.

Meanwhile, for the Cu–Ni complete solid-solution alloy system, the SFE does not monotonically decrease as a function of the e/a ratio. It was reported that the SFE is almost constant, regardless of the e/a ratio (or atomic concentration of solute atoms c_a) and increases around the e/a ratio of 1.1 (61.9 at%Ni).^{12,13)} Thus, it should be possible to observe strengthening mechanisms of SPD-processed Cu solid-solution alloys from a viewpoint that is different from the above-mentioned SFE effect.

In the present study, changes in the hardness and microstructures of SPD-processed Cu solid-solution alloys were systematically investigated in terms of the atomic concentration of solute atoms c_a , the e/a ratio, and the SFE, by adding solute atoms of Zn, Si, and Ni, which differ in the number of their valence electrons Z_2 , up to near the solubility limits in Cu. This study attempts to understand the general effects of different solid-solution elements on the hardness of Cu after the SPD process.

2. Experimental Procedure

Cu–Zn, Cu–Si, and Cu–Ni alloys with various compositions were chosen as materials. The detailed compositions of the alloys are listed in Table 1. The number of the valence electrons Z_2 for Si and Zn were 4 and 2, respectively. In the case of Ni, Z_2 was 1.16, since the electron atom ratio e/a for Ni was reported as 1.16.¹⁴⁾ The atomic radii of Cu, Zn, Si, and Ni were 128, 137, 118, and 125 pm, respectively.¹⁵⁾ These Cu alloys were fully annealed and confirmed as solid-solution alloys by X-ray diffraction. After machining the alloys to 10-mm-diameter and 0.8-mm-thickness disc-shaped specimens using a wire-discharge machine, the specimens

Table 1 Compositions of the Cu–Zn, Cu–Si, and Cu–Ni alloys.

	Cu–Zn			Cu–Si			
C_w (wt.%)	10	20	30	0.18	0.73	2.04	4.19
C_a (at.%)	9.7	19.5	29.4	0.4	1.6	4.5	9.0
e/a	1.10	1.20	1.29	1.01	1.05	1.14	1.27

	Cu–Ni				
C_w (wt.%)	10	30	60	80	100
C_a (at.%)	10.7	31.7	61.9	81.4	100.0
e/a	1.02	1.05	1.10	1.13	1.16

were subjected to high-pressure torsion (HPT) processing, which is one of the SPD processes, up to the 10 rotations at 6 GPa and 0.2 rpm. Vickers microhardness tests were performed on the prepared specimens. Backscattered electron (BSE) images were obtained using a field emission scanning electron microscope (FE-SEM: JSM-7100F, JEOL, Tokyo, Japan), following which the mean grain size values d , of the samples were evaluated using the linear intercept method.

3. Results and Discussion

3.1 Effects of Zn, Si, and Ni solute additions on the hardness of the HPT-processed Cu

Figure 2 shows changes in the hardness as a function of the distance from the center, for disc-shaped specimens of a Cu–4.5 at%Si alloy, for various HPT rotation values. The hardness of the annealed specimen was ~ 70 HV and nearly saturated at 275 HV after five HPT rotations, at all tested points in the specimen. Although the saturated hardness was different for different alloys, the Cu–Zn, Cu–Si, and Cu–Ni alloys with different compositions became increasingly harder.

The effect of the Zn concentration on the hardness of Cu, for various HPT rotations, is shown in Fig. 3. Hardness was measured at 2.5 mm from the center of the disc-shaped specimens. The solid solubility limit of Zn in the Cu matrix is

Fig. 2 Vickers microhardness vs. the distance from the center for the HPT-processed disc-shaped specimens of Cu–4.5 at%Si, for various HPT rotations.

Fig. 3 Vickers microhardness vs. Zn concentration in HPT-processed disc-shaped specimens, for various HPT rotations.

Fig. 4 Vickers microhardness vs. Si concentration in HPT-processed disc-shaped specimens, for various HPT rotations.

~30 at.%. The HPT-processed specimen became significantly harder with increasing amount of added Zn, beyond the estimated values based on the solid-solution strengthening theory, then almost saturated at 19.5 at.%Zn, and reached 250 HV at 29.4 at.%Zn. Figure 4 shows the similar effect of Si concentration on the hardness of Cu, for various HPT rotation values. Although the solid solubility limit of Si in the Cu matrix is ~9 at.%, precipitates were detected using X-ray diffraction in a Cu–9.0 at.%Si alloy. The hardness data for the Cu–9.0 at.%Si alloy are shown in Fig. 4 for reference. The hardness of the HPT-processed specimen also significantly increased, and reached the saturation value of 275 HV at 4.5 at.%Si. The hardness of the HPT-processed Cu–9.0 at.%Si alloy with precipitates was relatively lower than that of the Cu–4.5 at.%Si alloy.

Figure 5 shows the effect of Ni concentration on the hardness of Cu, for various HPT rotation values. The Cu–Ni alloy system possesses complete solid solubility. The hardness has been reported to peak at 60 at.%Ni for coarse-grained Cu–Ni alloys.¹³⁾ This is owing to the fact that Ni-rich Cu–Ni solid solution alloys exhibit higher hardness than Cu-rich ones, for the same amount of solute additions, because Ni is harder than Cu. The HPT-processed Cu–Ni

Fig. 5 Vickers microhardness vs. Ni concentration in HPT-processed disc-shaped specimens, for various HPT rotations.

Fig. 6 Typical microstructure of Cu–4.5 at.%Si, for five HPT rotations.

became significantly harder with increasing Ni addition, reaching the maximum of 360 HV at 81.4 at.%Ni, compared with the estimates based on the usual solid-solution strengthening theory.

3.2 Effects of Zn, Si, and Ni solute additions on the microstructure of HPT-processed Cu

Figure 6 shows an SEM-BSE image of the Cu–4.5 at.%Si alloy, for five HPT rotations. The mean grain size was estimated as 60 nm, based on the nanostructures observed in the image. Since the specimen was processed by the SPD process, it also includes high density of dislocations as deformed microstructures.¹⁶⁾ The mean grain size values d for Cu, Cu–Zn, Cu–Si, and Cu–Ni alloys with five HPT rotations are summarized in Table 2. The mean grain size decreased with increasing the amount of the solute additions, for the Cu–Zn and Cu–Si alloys. The minimal mean grain size of 75 nm for the HPT-processed Cu–Si alloy was relatively smaller than that for the Cu–Zn alloy near the solid solubility limit. The mean grain size for the Cu–9.0 at.%Si alloy was 95 nm, which is larger than that for the Cu–4.5 at.%Si alloy. This is owing to the precipitates in the 0R specimen, as mentioned in the previous section. These results for the mean grain size are in a good agreement with the results for hardness.

Table 2 Mean grain sizes d for the Cu, Cu–Zn, Cu–Si, and Cu–Ni alloys with five HPT rotations.

	Cu	Cu–Zn			Cu–Si			
C_a (at.%)		9.7	19.5	29.4	0.4	1.6	4.5	9.0
d (nm)	175	105	90	75	140	110	60	95

	Cu–Ni				
C_a (at.%)	10.7	31.7	61.9	81.4	100.0
d (nm)	95	80	110	110	150

Fig. 7 Vickers microhardness and stacking fault energy (SFE)^{9,12} vs. the electron-atom ratio e/a , for HPT specimens processed with five HPT rotations, for Cu–Zn, Cu–Si, and Cu–Ni alloys.

For the Cu–Ni alloy, whereas the mean grain size monotonically decreased with increasing the amount of solute Ni up to 31.7 at%Ni, the mean grain sizes increased for Ni solute amounts above 31.7 at%Ni.

3.3 Effects of Zn, Si, and Ni solute additions on the hardness of HPT-processed Cu and their comparison

Figure 7 shows the relationship between the hardness and the electron-atom ratio e/a , for Cu–Zn, Cu–Si, and Cu–Ni alloys, for five HPT rotations. The SFE as a function of the electron-atom ratio e/a are also shown in Fig. 7 for the Cu–Zn, Cu–Si, and Cu–Ni alloys.^{9,12} As the SFE data were obtained from the Ref. 9) for the Cu–Zn and Cu–Si alloys and from the Ref. 12) for the Cu–Ni alloy, respectively, the differences between the SFE values for Cu can be attributed to the differences between the evaluation methods that were used in the Refs. 9 and 12). Here, it should be emphasized that the SFE monotonically decreases with increasing the e/a ratio for the Cu–Zn and Cu–Si alloys, while it increases for the Cu–Ni alloys. In the case of the Cu–Zn and Cu–Si alloys, it can be seen that the increase in the hardness followed by the saturation through the HPT processing strongly correlates with the reductions in the SFE and mean grain size. Because adding typical elements with more valence electrons Z_2 to Cu generally further decreases the SFE,¹² the saturated hardness of the Cu–Si alloy is relatively higher than that of the Cu–Zn alloy. These trends can be also seen in the experimental results of the addition of Ge ($Z_2 = 4$) or Al ($Z_2 = 3$) to

Cu.^{17,18} Therefore, adding solute atoms with more valence electrons Z_2 to Cu in general decreases the grain size, and increases saturation hardness following the SPD process. In terms of the size misfit between the solute atoms and the Cu matrix, Cu alloys with finer microstructure and higher strength after the SPD process can be obtained by adding solute atoms with larger size misfit, because Si is larger than Zn. In terms of the atomic concentration of solute atoms c_a , increased strengthening after the SPD process can be obtained by smaller amounts of solute atoms with larger size misfit in Cu alloys.

On the contrary, the Cu–Ni alloy became harder following the HPT processing, similar to the Cu–Zn and Cu–Si alloys, despite the constant SFE until 30 at%Ni. In addition, the size misfit of Ni in the Cu matrix was smaller than that of Si and Zn. Enhanced strength after the SPD process in the Cu–Ni alloys can be attributed to the suppression of dynamic recovery or recrystallization during the SPD process, owing to the dislocation pinning or dragging by Ni solute atoms. Actually, because the recrystallization temperature determined by the isochronal annealing of the Cu–31.7 at%Ni alloy with five HPT rotations was 723 K (which is higher than that for Cu with five HPT rotations, which is 403 K), it is expected to result from the enhanced strain-hardening capability caused by the increase of recovery and recrystallization temperatures. Since the recovery and recrystallization temperatures of Cu increase by adding solute atoms such as Zn,¹⁹ there should be dislocation pinning or dragging by solute atoms in the Cu–Zn and other Cu alloys as well. However, it is suggested that the SFE dominates the microstructure and strength in SPD-processed materials, as indicated by the results in Fig. 7.

As described in section 3.1, the maximal hardness was obtained at 61.9 at%Ni for the coarse-grained Cu–Ni alloy (0R), while for the Cu–Ni alloy with five HPT rotation the maximal hardness was obtained at 81.4 at%Ni. As the SFE monotonically decreased with increasing the amount of Cu in the Ni-rich region, finer microstructures were obtained after the SPD process by adding more Cu, as shown in Table 2. However, Ni is harder than Cu in the coarse-grained material. In addition, since the difference of hardness between Ni and Cu after the SPD process increased further, it can be said that the composition of the maximal hardness of the Cu–Ni alloys after the SPD process shifted toward the higher Ni concentration: 81.4 at%Ni.

4. Conclusion

Changes in the SFE and recrystallization temperature caused by solute atoms significantly affect the maximal hardness of Cu solid-solution alloys after the SPD process. In the case of adding solute atoms of typical elements such as Si or Zn, the maximal hardness after the SPD process is primarily dominated by the SFE, and increases with increasing the number of valence electrons and size misfit of solute atoms. In the case of adding solute atoms that do not significantly affect the SFE, such as Ni, it can be said that increasing the recovery and recrystallization temperatures by adding solute atoms affects the evolution of the microstructure during the SPD process.

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REFERENCES

- 1) K. Lu, L. Lu and S. Suresh: *Science* **324** (2009) 349–352.
- 2) N. Takata, K. Yamada, K. Ikeda, F. Yoshida, H. Nakashima and N. Tsuji: *Mater. Trans.* **48** (2007) 2043–2048.
- 3) T. Kunimine, T. Fujii, S. Onaka, N. Tsuji and M. Kato: *J. Mater. Sci.* **46** (2011) 4290–4295.
- 4) T. Kunimine, N. Takata, N. Tsuji, T. Fujii, M. Kato and S. Onaka: *Mater. Trans.* **50** (2009) 64–69.
- 5) M. Hibino, C. Watanabe, Y. Tsuji, R. Monzen, Y. Todaka and W. Sato: *Mater. Trans.* **58** (2017) 1346–1350.
- 6) K. Youssef, M. Sakaliyska, H. Bahmanpour, R. Scattergood and C. Koch: *Acta Mater.* **59** (2011) 5758–5764.
- 7) C.X. Huang, W. Hu, G. Yang, Z.F. Zhang, S.D. Wu, Q.Y. Wang and G. Gottstein: *Mater. Sci. Eng. A* **556** (2012) 638–647.
- 8) X.X. Wu, X.Y. San, Y.L. Gong, L.P. Chen, C.J. Li and X.K. Zhu: *Mater. Des.* **47** (2013) 295–299.
- 9) P.C.J. Gallagher: *Metall. Trans.* **1** (1970) 2429–2461.
- 10) W.F. Hosford: *Physical Metallurgy*, (CRC Press, Boca Raton, 2005) pp. 87–100.
- 11) W. Hume-Rothery: *Acta Metall.* **14** (1966) 17–20.
- 12) H. Suzuki: *Introduction to the Theory of Dislocations*, (AGNE, Tokyo, 1967) pp. 140–212.
- 13) J. Schell, P. Heilmann and D.A. Rigney: *Wear* **75** (1982) 205–220.
- 14) U. Mizutani, H. Sato, M. Inukai, Y. Nishino and E.S. Zijlstra: *Inorg. Chem.* **54** (2015) 930–946.
- 15) P. Atkins, T. Overton, J. Rourke, M. Weller and F. Armstrong: *Shriver & Atkins Inorganic Chemistry Fourth Edition*, (Oxford University Press, Oxford, 2006) pp. 3–34.
- 16) Y. Miyajima, H. Abe, T. Fujii, S. Onaka and M. Kato: *Acta Mater.* **61** (2013) 1537–1544.
- 17) Y.L. Gong, C.E. Wen, Y.C. Li, X.X. Wu, L.P. Cheng, X.C. Han and X.K. Zhu: *Mater. Sci. Eng. A* **569** (2013) 144–149.
- 18) K. Edalati, D. Akama, A. Nishio, S. Lee, Y. Yonenaga, J.M. Cubero-Sesin and Z. Horita: *Acta Mater.* **69** (2014) 68–77.
- 19) K. Maki, Y. Ito, H. Matsunaga and H. Mori: *Scr. Mater.* **68** (2013) 777–780.