Methods for Designing Concurrently Strengthened Severely Deformed Age-Hardenable Aluminum Alloys by Ultrafine-Grained and Precipitation Hardenings

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The age-hardenings behavior and precipitate microstructures with high dislocation density and/or ultrafine grains have been studied for 6022Al-Mg-Si and 2091Al-Li-Cu alloys. The high-pressure torsion (HPT) specimen of the former alloy exhibited either suppressed age hardenings or even age softening, unlike in the cases of the undeformed and cold-rolled specimens, at room temperature (RT) to 443 K (170 °C). On the other hand, the HPT specimen of the latter alloy successfully increased the hardness up to >HV290 at 373 K (100 °C), suggesting that concurrent strengthening by ultrafine-grained and precipitation hardenings can be activated if both alloy system and aging temperature are optimally selected. The corresponding transmission electron microscopy (TEM) microstructures attributed such a high level of hardness to the transgranular precipitation of the nanometer-scale particles within ultrafine grains. From the results of in situ small-angle X-ray scattering (SAXS) measurements, methods to maximize the effect of the combined processing of severe plastic deformation (SPD) and the age-hardenings technique are proposed based on the underlying phase transformation mechanisms.

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I. INTRODUCTION

IN general, strengthening mechanisms of aluminum alloys include strain hardenings, hardenings by grain refinement, solid-solution hardenings, and/or precipitation hardenings because no allotropic or martensitic transformation is available. Severe plastic deformation (SPD) such as equal-channel angular pressing (ECAP), accumulative roll bonding (ARB), and high-pressure torsion (HPT) has been successfully utilized as a method for improving the strength of metallic materials based on the first two strengthening mechanisms.^[1] However, the combined processing of SPD and age-hardenings treatment does not necessarily result in a further increase in strength of heat-treatable aluminum alloys, unlike in the case of non-heat-treatable aluminum alloys where solid-solution hardenings is almost additive to strain hardenings or ultrafine-grained hardenings (*i.e.*, hardenings by grain refinement to the submicrometer or nanometer level).^[2] This is because if the microstructure of age-hardenable aluminum alloys is controlled for strain hardenings and/or ultrafine-grained hardenings,

the subsequent precipitation hardenings is often limited due to the competitive precipitation among dislocations, grain boundaries, and the matrix. Table I summarizes previously reported experimental results on concurrent strengthening by SPD and the age-hardenings technique for a number of age-hardenable aluminum alloys.^[3–20] Although the specimens under no SPD condition (*i.e.*, equivalent strain less than 4) possess relatively good age-hardenability, most of the severely deformed and then artificially aged specimens exhibit either suppressed age hardenings or age softening as denoted by smaller Δ or large ∇ . The following are the main features extracted from Table I, where attained values of hardness/strength, the degree of age hardenings/softening, and the corresponding microstructures are reviewed according to the alloy system, equivalent strain, and aging temperature.

- (i) The higher the aging temperature applied, the lower the attained hardness/strength and the degree of age hardenings. This is of course not unusual regardless of the application of SPD, but the degree appears to be significant (Indeed, in some cases, only age softening occurs). This can be explained not only by the more predominant recovery of dislocations and growth of ultrafine grains but also by coarsened precipitation of stable phases at dislocations and grain boundaries, resulting in suppressed transgranular precipitation of refined metastable particles (*i.e.*, competitive precipitation).
- (ii) The larger the equivalent strain introduced by SPD, the lower the degree of age hardenings at a fixed aging temperature. This is also due to the

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Table I. Reported Experimental Results on Concurrent Strengthening of Age-Hardenable Aluminum Alloys by Severe Plastic Deformation (SPD) and Age-Hardenings Technique^[3-20]

Alloy	Solution Treatment	SPD Condition (Equivalent Strain)	Aging Treatment	Attained and Increment/ Decrement in HV or UTS	Microstructures	Ref.	
Al-2 pct Cu	823 K (550 °C), 1.8 ks, W.Q.	ARB, RT, 5 cycles (4.0)	463 K (190 °C), 1080 ks	HV45, ▼HV70	Lamellar boundary structure with mean boundary interval of ~67 nm after AR-Bed. Coarsened θ phase at grain boundaries	[3]	
	773 K (500 °C), 43.2 ks, W.Q.	ECAP, 433 K (160 °C), 1 pass (1.0)	373 K (100 °C), 72 ks	HV205, ΔHV17, UTS 715 MPa, Δ55 MPa	Small needle-shaped precipitates on or near dislocations. S phase at subgrain boundaries.	[4]	
2024Al-Cu-Mg	766 K to 813 K (493 °C to 540 °C), 3.6 to 36 ks, W.Q.	Cryo-rolling, <123 K (<-150 °C), 50 pct (0.80)	448 K (175 °C), 7.2 ks	HV205, ΔHV15	Mean grain size is 0.8 to 1.5 μ m. Homogeneous precipitation of S' phase with sizes 10 to 15 nm	[5]	
			373 K (100 °C), 108 to 144 ks	HV195, ΔHV15			
			373 K (100 °C), 360 ks	HV190, ΔHV10, UTS 620 MPa, Δ90 MPa			
			433 K (160 °C), 43.2 to 46.8 ks	HV195, ΔHV20 UTS 580 MPa, Δ50 MPa			
6061Al-Mg-Si	803 K (530 °C), 14.4 ks, W.Q.	ECAP, 398 K (125 °C), 1 pass (1.0)	373 K (100 °C), 173 ks	HV146, ΔHV23, UTS 394 MPa, Δ27 MPa	Mean subgrain size after ECAPed is 300 to 400 nm. Homogeneous distribution of globular and spherical particles with sizes 20 to 40 nm	[6]	
			413 K (140 °C), 43.2 ks	HV146, ΔHV23			
		ECAP, 398 K (125 °C), 4 passes (4.1)	448 K (175 °C), 3.6 ks	HV142, ΔHV19	Mean subgrain size after ECAPed is 300 to 400 nm. Homogeneous distribution of globular and spherical particles with sizes 20 to 40 nm	[7]	
			373 K (100 °C), 173 ks	HV161, ΔHV14, UTS 451 MPa, Δ26 MPa			
			413 K (140 °C), 14.4 ks	HV151, ΔHV4			
			373 K (100 °C), 173 ks	HV145, ΔHV10, UTS 438 MPa, Δ27 MPa			
		ECAP, 423 K (150 °C), 6 passes (4.0)	373 K (100 °C), 173 ks	HV134, ΔHV11, UTS 378 MPa, ▼3 MPa	Mean grain size is 280 nm (<i>cf.</i> ~240 nm after ARBed). Globular or spherical Mg ₂ Si precipitates with sizes 40 to 90 nm. Si-rich precipitates also formed	[8]	
			423 K (150 °C), 14.4 ks	HV135, ΔHV12			
		803 K (530 °C), 5.4 ks, W.Q.	ARB, RT, 5 cycles (4.0)	448 K (175 °C), 86.4 ks	HV116, ▼HV6	Mean grain size is 380 nm. Both Si-rich and Mg ₂ Si precipitates formed	[9]
				373 K (100 °C), 173 ks	HV131, ΔHV18, UTS 450 MPa, Δ95 MPa		
803 K (530 °C), 14.4 ks, W.Q.	ARB, RT, 6 cycles (4.8) HPT, RT, 5 revolutions (>100)	433 K (160 °C), 18 ks	HV115, ΔHV2, UTS 360 MPa, Δ5 MPa	Mean grain size is 380 nm. Both Si-rich and Mg ₂ Si precipitates formed	[9]		
		373 K (100 °C), 605 ks	HV140, ΔHV13				
		373 K (100 °C), 720 ks	HV165, ΔHV3				

Table I. continued

Alloy	Solution Treatment	SPD Condition (Equivalent Strain)	Aging Treatment	Attained and Increment/Decrement in HV or UTS	Microstructures	Ref.
6022Al-Mg-Si	823 K (550 °C), 0.06 ks, W.Q.	ARB, RT, 3 cycles (2.4)	343 K (70 °C), 1210 ks	HV128, ΔHV8	Coarsened β' phase with mean length of 52 nm on dislocations.	[9]
	823 K (550 °C), 0.06 ks, W.Q.	Rolling, RT, 30 pct (0.41)	443 K (170 °C), 0.6 ks	HV125, ΔHV5		
			298 K (25 °C), 864 ks	HV94, ΔHV14		
			343 K (70 °C), 173 ks	HV92, ΔHV12		
			373 K (100 °C), 173 ks	HV120, ΔHV40		
6082Al-Mg-Si			443 K (170 °C), 7.2 ks	HV120, ΔHV40	Mean grain size is ~280 nm (<i>cf.</i> ~170 nm after HPTed). Coarsened β phase with mean size of 116 nm at grain boundaries.	[12]
			443 K (170 °C), 86.4 ks	HV105, ΔHV25		
		HPT, RT, 5 revolutions (>100)	298 K (25 °C), 173 ks	HV160, ΔHV0		
			343 K (70 °C), 7.2 ks	HV170, ΔHV10		
			373 K (100 °C), 864 ks	HV120, ▼HV40		
Al-1.0 pct Si-2.2 pct Ge			443 K (170 °C), 86.4 ks	HV95, ▼HV65	Mean grain size is ~400 nm. Homogeneous distribution of fine particles	[13]
	803 K (530 °C), 10.8 ks, W.Q.	ECAP, RT, 1 pass (1.2)	373 K (100 °C), 21.6 to 108 ks	HV133, ΔHV10		
			398 K (125 °C), 25.2 to 54 ks	HV133, ΔHV10		
			423 K (150 °C), ~18 ks	HV130, ΔHV7		
			448 K (175 °C), 108 ks	HV98, ▼HV25		
Al-0.5 pct Si-0.5 pct Ge			473 K (200 °C), 108 ks	HV83, ▼HV40	Refined distribution of needle- and granular-shaped particles of Si-Ge precipitates	[14]
	823 K (550 °C), 3.6 ks, Iced-W.Q.	ECAP, RT, 8 passes (8.4)	373 K (100 °C), 360 ks	HV93, ▼HV5		
			423 K (150 °C), 360 ks	HV78, ▼HV20		
		ARB, 6 cycles (4.8)	373 K (100 °C), 120 ks	HV100, ΔHV20		
		Cryo-rolling, 77 K (−196 °C), 80 pct (1.9)	323 K (50 °C), 18 ks + 353 K (80 °C), 32.4 ks	UTS 680 MPa, Δ 90 MPa		
7075Al-Zn-Mg					Mean grain size is ~100 nm. Transgranular precipitation of spherical GP zones, plate-like η' and equiaxed η phase with sizes 4 to 10 nm	[15]
	773 K (500 °C), 18 ks, Quenched to 77 K (−196 °C)	HPT, RT, 3 revolutions (>20)	373 K (100 °C), 108 ks	HV240, ΔHV5, UTS 930 MPa, Δ90 MPa		
	763 K (490 °C), 18 ks, Iced-W.Q.					
Al-10.8 pct Ag					Mean grain size is ~1 μm. Transgranular precipitation of spherical η zones and plate-like γ' phase with sizes <50 nm. γ phase with sizes 200 to 300 nm at grain boundaries	[13, 17, 18]
	823 K (550 °C), 3.6 ks, Iced-W.Q.	Rolling, RT, 70 pct (1.4)	373 K (100 °C), 360 ks	HV78, ΔHV4		
		ECAP, RT, 8 passes (8.4)	373 K (100 °C), 360 ks	HV90, ΔHV11, UTS 270 MPa, ▼5 MPa		
					Mean grain size is ~1 μm. Transgranular precipitation of plate-like γ' phase. γ phase with sizes 100 to 200 nm forms both within the matrix and at grain boundaries	

Table I. continued

Alloy	Solution Treatment	SPD Condition (Equivalent Strain)	Aging Treatment	Attained and Increment/ Decrement in HV or UTS	Microstructures	Ref.
2091Al-Li-Cu	778 K (505 °C), 1.8 ks, W.Q.	Rolling, RT, 50 pct (0.80) HPT, RT, 5 revolu- tions (>100)	473 K (200 °C), 360 ks	HV52, ▼HV27	Mean grain size is >1 μ m. Precipitation of γ phase with mean size of 500 nm, resulting in the significant reduction in the density of plate-like γ' phase	[19]
			373 K (100 °C), 839 ks	HV170, Δ HV45	Mean grain size is ~140 nm. Transgranular precipitation of δ' phase	
			423 K (150 °C), 839 ks	HV156, Δ HV31		
			463 K (190 °C), 12 ks	HV150, Δ HV25		
			373 K (100 °C), 839 ks	HV270, Δ HV45		
	778 K (505 °C), 1.8 ks, W.Q.	Rolling, RT, 10 pct (0.12) HPT, RT, 5 revolu- tions (>100)	423 K (150 °C), 202 ks	HV270, Δ HV45	Mean grain size is ~160 nm. Transgranular precipitation of δ' phase.	[20, this study]
			463 K (190 °C), 47 ks	HV170, ▼HV55	Mean grain size is ~180 nm	
			373 K (100 °C), 2419 ks	HV160, Δ HV50	Mean grain size is ~206 nm (<i>cf.</i> ~194 nm after HPTed). Transgranular precipita- tion of refined δ' phase	
			463 K (190 °C), 36 ks	HV158, Δ HV48		
			373 K (100 °C), 2419 ks	HV290, Δ HV40		
				463 K (190 °C), 36 ks	HV195, ▼HV55	Coarsened precipitation of δ phase at grain boundaries

Δ and ▼ indicate the numerical values of increment or decrement, respectively, in Vickers hardness (HV) and ultimate tensile strength (UTS) during aging. The data under no SPD condition (*i.e.*, equivalent strain less than 4) are also included for reference.

Table II. Chemical Compositions of the Alloys Utilized in this Study (Mass Pct)

Alloy	Mg	Si	Cu	Li	Zr	Fe	Ti	Al
6022	0.57	1.02	—	—	—	0.17	—	bal.
2091	1.55	0.03	1.99	2.09	0.12	0.05	0.03	bal.

competitive precipitation in which dislocations and grain boundaries serve as heterogeneous nucleation sites for stable phases, restricting transgranular precipitation of strengthening phases. Unfortunately, we have to say at present that the best age-hardenability can be obtained in the undeformed specimens with no equivalent strain.

- (iii) When comparing alloy systems, all of commercial 2000 (Al-Cu-Mg), 6000 (Al-Mg-Si), and 7000 (Al-Zn-Mg) series aluminum alloys, as well as model alloys of Al-Si-Ge and Al-Ag, exhibit suppressed age hardenings as high as ΔHV_{30} under SPD conditions. This suggests again that concurrent strengthening by ultrafine-grained and precipitation hardenings is hardly activated. However, the authors reported recently that the HPT specimen of 2091Al-Li-Cu can increase the hardness up to HV270-290 by taking advantage of both initial hardenings by grain refinement (*i.e.*, 225-250HV after HPTed) and subsequent age hardenings of ΔHV_{40} to 45.^[19,20] This attained hardness is almost the highest among conventional wrought aluminum alloys and is certainly attributed to transgranular precipitation of nanometer-scale particles within ultrafine grains. Therefore, the combined processing of SPD and the age-hardenings technique still appears to leave open the possibility to fabricate novel aluminum alloys concurrently strengthened by ultrafine-grained and precipitation hardenings.

In this study, the age-hardenings behavior and precipitate microstructures of two age-hardenable aluminum alloys of 6022Al-Mg-Si and 2091Al-Li-Cu were investigated under the cold-rolled and severely deformed conditions. Although our preliminary studies^[10,11,19,20] classified the former into the alloy with limited effect of concurrent strengthening and the latter into the alloy with noteworthy effect, no comprehensive and comparative studies had been conducted, especially concerning the reason why such a difference in age-hardenability arises depending on alloy system and aging temperature. Our proposed method for designing concurrently strengthened severely deformed age-hardenable aluminum alloys^[20] will be also verified based on the underlying phase transformation mechanisms, *i.e.*, the nucleation and growth or spinodal decomposition (following after congruent ordering), detected by in situ small-angle X-ray scattering (SAXS) measurement.

II. EXPERIMENTAL PROCEDURE

Commercial 6022 and 2091 alloy cold-rolled sheets with a thickness of 1.0 mm (for 6022) or 1.6 mm (for

2091) were utilized in this study. The chemical compositions of the two alloys are listed in Table II. 10-mm squares and 10-mm ϕ disks were cut from the sheets and solution-treated in a salt bath at 823 K (550 °C) for 60 seconds (for 6022) or at 778 K (505 °C) for 1.8 ks (for 2091), followed by water quenching. Cold rolling and HPT were performed at room temperature [RT, ~298 K (25 °C)] within 3.6 ks after quenching, with rolling reduction of 30 pct (for 6022) or 10 pct (for 2091), and under a pressure of 6 GPa for 5 revolutions with a rotation speed of 1 rpm (for 6022 and 2091; the details of the HPT facility and operating procedures were reported in^[21]). The corresponding equivalent strain is 0.41, 0.12, and >100 (in the regions more than 1 mm away from the center of the HPTed disks^[19]).

Square pieces of the undeformed and cold-rolled specimens as well as disks of the HPT specimen were subsequently subjected to aging treatment in oil baths at 343 K to 463 K (70 °C to 190 °C) for various times. The surface of each heat-treated specimen was mechanically polished to eliminate Mg and/or Li loss layers induced by solution treatment. The age-hardenings behavior of the three specimens was investigated by a microhardness tester (Matsuzawa MMT-X1) with a load of 500 g for a dwelling time of 15 seconds. The hardness of each specimen was determined as an average value of five tested points out of seven ones with an accuracy of $\pm HV_2$. For the HPTed disks, the indenter was carefully pressed into the regions more than 3 mm away from the center to avoid unsaturated levels of hardness being measured.^[19]

The foils for transmission electron microscopy (TEM) observation were punched out in a form of 3-mm ϕ disks and thinned by the electrolytic twin-jet polishing technique in 20 vol pct nitric acid with 80 vol pct methanol at ~253 K (−20 °C). TEM microstructures and the corresponding selected-area electron diffraction (SAED) patterns were observed using a JEM-2100F microscope at an accelerating voltage of 200 kV. Special attention was paid again to the preparation of TEM foils for the HPT specimen; *i.e.*, 3-mm ϕ disks were punched out from regions far away from the center of the original 10-mm ϕ disk.^[19]

The wafers for small-angle X-ray scattering (SAXS) measurement were prepared as thin square pieces of ~200 μm thickness for the undeformed specimen of 2091Al-Li-Cu under the as-quenched condition. The thickness was preliminarily determined to achieve ideal transmission coefficient, *e.g.*, ~0.1, for CuK α radiation generated from an 18-kW rotating anode X-ray source. SAXS measurement was performed using a Bruker NanoSTAR SAXS system with a sample-to-detector distance of 1.06 m, by which a measurable range of scattering vectors $q = 4\pi\sin\theta/\lambda$ is defined as 0.06 to

7.5 nm^{-1} . Here, 2θ is the scattering angle and λ is the wavelength of $\text{CuK}\alpha$ (0.154 nm). The scattering intensity I from an area of $\sim 1 \text{ mm}^2$ within the wafer specimen (*i.e.*, point focus geometry) was recorded on a two-dimensional PSPC detector in an in situ manner at 373 K and 463 K (100 °C and 190 °C). The temperature of the wafer mounted on a miniature hot stage was controlled to an accuracy of $\pm 0.7 \text{ K}$ ($\pm 0.7 \text{ }^\circ\text{C}$), and the counting time per measurement lasted for 300 to 600 seconds to obtain acceptable counting statistics. Measurements at prolonged aging times, *i.e.*, 432 and 2419 ks at 373 K (100 °C), were conducted in an *ex situ* manner using the same wafer as that for in situ measurements at earlier aging times. Correction was applied for background noise, but no calibration was done for the normalization of I to absolute scattering intensities.

III. EXPERIMENTAL RESULTS

A. Concurrent Strengthening of 6022Al-Mg-Si Alloy

Figure 1 shows the Vickers hardness change of the undeformed, cold-rolled, and HPT specimens of 6022Al-Mg-Si during aging at RT–443 K (170 °C). It is confirmed from the initial hardness that the two deformation processes, *i.e.*, cold rolling by 30 pct and HPT for 5 revolutions, increased the hardness of the undeformed specimen from $\sim \text{HV}45$ to $\sim \text{HV}80$ or $\sim \text{HV}160$, depending on the equivalent strain introduced. This strengthening can be explained by the correspond-

ing TEM microstructures, *i.e.*, strain hardenings by a high dislocation density in the cold-rolled specimen (Figure 2(b)) and ultrafine-grained hardenings by sub-micrometer-scale grains in the HPT specimen (Figure 2(c)). Note that many of these grains were separated by high-angle grain boundaries^[19] and, therefore, retained a relatively low dislocation density as a result of absorption of dislocations at the high-angle grain boundaries.^[22]

In the subsequent stage of aging, however, the two deformation processes either suppressed the age-hardening of this alloy system or even induced age softening. For example, the hardness of the cold-rolled and HPT specimens changed by $>\Delta \text{HV}12$ and $\Delta \text{HV}10$ at 343 K (70 °C), or by $\Delta \text{HV}40$ and $\nabla \text{HV}65$ at 443 K (170 °C) (see Figures 1(b) and (d) or Table I), supporting the above-mentioned features (i) and (ii); *i.e.*, the higher the aging temperature applied or the larger the equivalent strain introduced, the lower the degree of age hardenings. These changes are much lower than those of the undeformed specimen, *i.e.*, $>\Delta \text{HV}40$ at 343 K (70 °C) and $\Delta \text{HV}75$ at 443 K (170 °C), and are therefore suggesting that the combined processing of SPD and age-hardening treatment unfavorably decreases the potential age-hardening of 6022Al-Mg-Si. Figure 2(d) through (f) shows typical TEM microstructures of the three specimens aged at 443 K (170 °C) for 86.4 ks. The transgranular precipitation of the refined β'' phase with a mean length of $\sim 35 \text{ nm}$ was predominant in the undeformed specimen (Figure 2(d)), whereas larger precipitates of the β'' needles were

Fig. 1—Vickers hardness change of the undeformed, cold-rolled, and HPT specimens of 6022Al-Mg-Si during aging at RT (a) 298 K (25 °C), (b) 343 K (70 °C), (c) 373 K (100 °C), and (d) 443 K (170 °C).

Fig. 2—Bright-field TEM images and the corresponding SAED patterns of the undeformed (*a, d*), cold-rolled (*b, e*), and HPT (*c, f*) specimens of 6022Al-Mg-Si before aging (*a* through *c*) and after aging at 443 K (170 °C) for 86.4 ks (*d* through *f*).

heterogeneously formed on dislocations in the cold-rolled specimen (as arrowed in Figure 2(e)). In the HPT specimen, on the other hand, the coarsened β -Mg₂Si phase with sizes of a few hundred nanometers was precipitated at grain boundaries (as arrowed in Figure 2(f)), resulting in the complete suppression of transgranular precipitation of refined β'' . Such competitive precipitation among dislocations, grain boundaries, and the matrix is obviously attributed to the reduced age-hardenability or significant age softening of the cold-rolled and HPT specimens in Figure 1. Recovery of dislocations and growth of ultrafine grains will be also the origin of such unfavorable decrease in age-hardenability with more pronounced tendencies at higher aging temperatures or at larger equivalent strain.

B. Concurrent Strengthening of 2091Al-Li-Cu Alloy

Figure 3 shows the Vickers hardness change of the undeformed, cold-rolled, and HPT specimens of 2091Al-Li-Cu during aging at 373 K and 463 K (100 °C and 190 °C). The initial hardness before aging at ~HV85, ~HV110, and ~HV250 suggests again that strain hardenings and ultrafine-grained hardenings are activated by means of cold rolling by 10 pct and HPT for 5 revolutions. This can be verified by the corresponding TEM microstructures in Figure 4(b) and (c), which demonstrates either a higher dislocation density or finer grains with high-angle grain boundaries for the cold-rolled and HPT specimens than those in the undeformed specimen (Figure 4(a)).

In contrast, unlike in the case of 6022Al-Mg-Si, concurrent strengthening by SPD and the age-hardenings technique was successfully activated in the investigated 2091Al-Li-Cu alloy. For example, the hardness of

Fig. 3—Vickers hardness change of the undeformed, cold-rolled, and HPT specimens of 2091Al-Li-Cu during aging at (*a*) 373 K (100 °C) and (*b*) 463 K (190 °C).

the HPT specimen changed by $>\Delta\text{HV}40$ at 373 K (100 °C) and reached almost the highest level of $>\text{HV}290$ among conventional wrought aluminum alloys (see Figure 3(a) or Table I). This suggests that the combination of HPT and age-hardenings treatment

Fig. 4—Bright-field (*a* through *c*) and dark-field (*d* through *i*) TEM images and the corresponding SAED patterns of the undeformed (*a*, *d*, *g*), cold-rolled (*b*, *e*, *h*), and HPT (*c*, *f*, *i*) specimens of 2091Al-Li-Cu before aging (*a* through *c*), after aging at 373 K (100 °C) for 2419 ks (*d* through *f*), and after aging at 463 K (190 °C) for 36 ks (*g* through *i*).

enables 2091Al-Li-Cu to be strengthened without diminishing extensively the excellent age-hardenability of the undeformed specimen, *i.e.*, $>\Delta\text{HV}75$. Figure 4(*d*) through (*f*) shows TEM microstructures of the three specimens aged at 373 K (100 °C) for 2419 ks. The dark-field image of the HPT specimen reveals that quite refined δ' -Al₃Li particles precipitate within the ultrafine grains of ~206 nm size (Figure 4(*f*)), as with the cases of the undeformed and cold-rolled specimens (Figure 4(*d*) and (*e*)). Note that no notable amount of coarsened precipitates was formed at grain boundaries, and the growth of ultrafine grains during aging was less pronounced, *i.e.*, ~194 to ~206 nm, at this temperature.

If the applied aging temperature is raised, however, the reduced age-hardenability and significant age softening were observed even in this alloy system. Figure 3(*b*) shows the age-hardenings/softening curves of the same three specimens, *i.e.*, undeformed, cold-rolled, and HPT specimens of 2091Al-Li-Cu, during aging at 463 K (190 °C). Although a slightly higher peak hardness of the cold-rolled specimen indicates that T8 treatment (cold work + artificial aging) exerts a positive effect on the mechanical strength of the undeformed

specimen, the HPT specimen with much larger equivalent strain only exhibited monotonous decrease in hardness, failing to take advantage of the initial hardness of ~250 HV. Figure 4(*g*) through (*i*) shows TEM microstructures of the three specimens aged at 463 K (190 °C) for 36 ks. While spherical particles of the metastable δ' phase homogeneously precipitate within the matrix of the undeformed and cold-rolled specimens (Figure 4(*g*) and (*h*)), only the coarsened δ -AlLi phase was found to form sparsely at grain boundaries in the HPT specimen (Figure 4(*i*)). This suggests that the fabrication of novel aluminum alloys concurrently strengthened by ultrafine-grained and precipitation hardenings depends not only on the selection of the alloy system but also on the optimization of aging temperature. Note that in this study, the main strengthening phase of this alloy system was regarded as δ' -Al₃Li, rather than Cu and Mg containing GPB zones or S' -Al₂CuMg phase, because no clear evidence of such precipitation was obtained for the cold-rolled and HPT specimens, unlike in the case of the undeformed specimen where lath-shaped precipitates of the S' phase are sparsely formed.

C. Phase Transformation Mechanisms of 2091Al-Li-Cu Alloy

Figure 5 illustrates the metastable two-phase field involving disordered α -Al and ordered δ' -Al₃Li in Al-Li proposed by Khachaturyan *et al.*^[23] The two-phase field computed based on a mean field model is subdivided into four distinct regions, each of which is expected to follow a characteristic phase transformation path after rapid quenching of a supersaturated solid solution. If it is assumed that the boundaries do not shift so much even for the present multicomponent 2091Al-Li-Cu, the aging temperatures applied in this study are located in region B for 373 K (100 °C) and in region D for 463 K (190 °C) because Li concentration of the alloy is ~ 7.9 at. pct. Therefore, since phase transformations occurring in the two regions are recognized as either spinodal decomposition following after congruent ordering or nucleation and growth of the δ' phase, a convincing explanation of the different precipitate microstructures, and thus different age-hardenabilities, between 373K and 463 K (100 °C and 190 °C) (Figures 3 and 4) appears to be drawn from their theoretic prediction on the underlying phase transformation mechanisms.^[23] In this study, experimental detection of such difference in phase transformation mechanisms was also conducted by in situ SAXS measurement.

Figure 6 shows in situ (*ex situ*) SAXS spectra for the undeformed specimen of 2091Al-Li-Cu aged at 373 K and 463 K (100 °C and 190 °C). The spectra were obtained by radially averaging isotropic scattering intensities on the recorded SAXS images and then expressing it as a function of q , *i.e.*, $I(q)$ vs q plot. For the as-quenched condition, a strong scattering was observed below $q = 0.2 \text{ nm}^{-1}$, followed by a nearly flat background above it (see spectrum at 0 ks in Figure 6(a); the similar spectrum was obtained at 0 ks in 463 K (190 °C) aging, but no data below $q = 0.2 \text{ nm}^{-1}$ are illustrated in Figure 6(b) for better

Fig. 5—Calculated metastable two-phase field of α -Al + δ' -Al₃Li in Al-Li.^[23] Li concentration of the utilized 2091Al-Li-Cu and aging temperatures applied to the alloy are additionally plotted.

visibility). This strong low- q scattering is generally believed due to the existence of lattice defects (*e.g.*, dislocations and grain boundaries), coarsened unsolved inclusions, and/or free specimen surfaces. With increasing aging time, however, the scattering intensity I monotonously increased with/without an interparticle interference peak at intermediate q . At 373 K (100 °C), the interference peak grew in amplitude at a constant q_m and then shifted to a lower q value (Figure 6(a); here, q_m was defined as the scattering vector showing the maximum intensity), whereas no interference peak was resolved during the evolution of I at 463 K (190 °C) (Figure 6(b)). In this study, interparticle distance L and Guinier radius r_G of precipitate particles were estimated as structural mean invariance through $L = 2\pi/q_m$ for 373 K (100 °C) and through $\ln I(q) \sim \ln I(0) - r_G^2 q^2/3$ (*i.e.*, Guinier approximation) for 463 K (190 °C), because such evolution of I reflects the temporal change in volume fraction V_f of nanometer-scale inhomogeneities such as precipitate particles, ordered domains, and modulated structure. Here, the radius of gyration r_g was deduced from the profile of $\ln I(q)$ in the very low- q region (*e.g.*, $q < 2/r_G$) of the Guinier plot, *i.e.*, $I(q)$ vs q^2 plot, and converted to r_G through $r_G = \sqrt{(5/3)r_g}$ because those microstructural inhomogeneities are basically of a spherical shape in this alloy system. Figure 7 summarizes the variation of r_G , L , V_f , and N (number density) of precipitate particles in 2091Al-Li-Cu during aging at 373 K and 463 K (100 °C and 190 °C). V_f was evaluated from integrated intensities $Q = \int 4\pi q^2 I(q) dq$ underneath the profile of $q^2 I(q)$ in Kratky plot, *i.e.*,

Fig. 6—In situ SAXS spectra for the undeformed specimen of 2091Al-Li-Cu aged at (a) 373 K (100 °C) and (b) 463 K (190 °C). Only spectra at 373 K (100 °C) for 432 and 2419 ks were obtained in an *ex situ* manner.

represented in Figure 8, where equivalent strain dependence of attained hardness and increment/decrement in hardness during aging is illustrated for a number of aluminum alloys in Table I. It is undoubtedly recognized that the HPT specimen of 2091Al-Li-Cu aged at 373 K (100 °C) (as arrowed) possesses not only a remarkable level of attained hardness, *i.e.*, >HV290 (Figure 8(a)), but also the good age-hardenability, *i.e.*, > Δ HV40 (Figure 8(b)), even at quite large equivalent strain of >100. Remember that this uniqueness was the basis of the authors' classification of 2091Al-Li-Cu into the alloy with a noteworthy effect of concurrent strengthening, but the others into the alloys with a limited effect.

B. Alloy Designing for the Alloys that Decompose via the Nucleation and Growth

As mentioned previously, concurrent strengthening by ultrafine-grained and precipitation hardenings has been hardly activated in most of the age-hardenable aluminum alloys. The results of 6022Al-Mg-Si in Section III-A are a typical example of the alloys that decompose *via* the nucleation and growth, *i.e.*, reduced age hardenings and significant age softening, either of which occurs depending on the aging temperature applied (Figure 1). The problem is that the excellent age-hardenability of this alloy system is diminished to a great extent, resulting in the lower degree of concurrent strengthening, K . Here, K is defined as a relative ratio of age-hardenabilities between the undeformed and cold-rolled/HPT specimens at a given aging temperature.

Fig. 8—Equivalent strain dependence of (a) attained Vickers hardness and (b) increment/decrement in Vickers hardness during aging of various aluminum alloys in Table I. Open and solid symbols indicate the results at aging temperatures lower than or equal to 373 K (100 °C), and higher than 373 K (100 °C), respectively.

Under this definition, $K = 1$ means that the addition law of strengthening mechanisms is validated. For the cold-rolled specimen with only equivalent strain of 0.41 (*i.e.*, no SPD condition) for example, relatively high values of $K = 0.3$ ($\approx \Delta$ HV12/ $>\Delta$ HV40) and 0.53 ($= \Delta$ HV40/ Δ HV75) were estimated at 343 K and 443 K (70 °C and 170 °C), respectively. On the other hand, lower values of $K = < 0.25$ ($= \Delta$ HV10/ $>\Delta$ HV40) and -0.87 ($= \nabla$ HV65/ Δ HV75) for the HPT specimen do represent the limited effect of concurrent strengthening by ultrafine-grained and precipitation hardenings in this temperature range. Most of the severely deformed and then artificially aged aluminum alloys in Table I (except 2091Al-Li-Cu) are expected to possess such lower values of K , although lower aging temperatures disallow the precise determination of K to be made due to their quite sluggish and unfinished increase in hardness/strength within the investigated aging time (For example, $K = < 0.25$ was estimated from undetermined age-hardenability of $>\Delta$ HV40).

To maximize such limited effect of concurrent strengthening, the authors^[10,11] modeled competitive precipitation behavior among dislocations, grain boundaries, and the matrix based on a classical heterogeneous nucleation theory. The developed numerical model predicted the dislocation density and grain size dependence of simultaneous precipitation at different nucleation sites in good qualitative agreement with observed TEM microstructures in the undeformed, cold-rolled, and HPT specimens of 6022Al-Mg-Si (*e.g.*, Figure 2). The model successfully showed that the larger the dislocation density or the smaller the grain size, the smaller the volume fraction of transgranular precipitates as is emphasized in previously mentioned feature (ii). Therefore, a method for designing can be drawn for the alloys that decompose *via* the nucleation and growth; *i.e.*, the largest dislocation density and the smallest grain size should be preliminarily given without diminishing the amount of transgranular precipitates, for example, by half of the total precipitates.^[10,11] Lowering of aging temperature is another method to increase the volume fraction of transgranular precipitates, but the effect will be limited as suggested by the fact that the increment of hardness during aging is only as high as Δ HV30 for a number of severely deformed age-hardenable aluminum alloys in Table I (except 2091Al-Li-Cu). Remember that the too severe plastic deformation plays a detrimental role in concurrent strengthening of the alloys that decompose *via* the nucleation and growth.

C. Alloy Designing for the Alloys that Decompose via Spinodal Decomposition

One of the most significant achievements in this study was to fabricate novel aluminum alloys with almost the highest level of hardness among conventional wrought aluminum alloys by means of concurrent strengthening by ultrafine-grained and precipitation hardenings. The results of 2091Al-Li-Cu in Section III-B verified that aging treatment at a lower temperature of 373 K (100 °C) increases the hardness of the HPT specimen up to >HV290 because of the refined precipitation of the

δ' phase within ultrafine grains (Figures 3(a) and 4(f)). The corresponding degree of concurrent strengthening amounts to $K = 0.53 (= \Delta HV40 / \Delta HV75)$, suggesting that high strength aluminum alloys can be fabricated if the combined processing of SPD and age-hardening technique is applied to 2091Al-Li-Cu. However, a higher aging temperature of 463 K (190 °C) only induced significant age softening with a value of $K = -0.85 (= \nabla HV55 / \Delta HV65)$. Figure 3(b) and, therefore, the optimization of aging temperature also becomes important even for 2091Al-Li-Cu with noteworthy effect of concurrent strengthening.

From the obtained SAXS results for 2091Al-Li-Cu aged at 373 K (100 °C) (Figures 6(a) and 7), methods for designing can be drawn for the alloys that decompose via spinodal decomposition (following after congruent ordering); i.e., aging treatment should be performed at temperatures below spinodal boundaries to maximize the effect of concurrent strengthening by ultrafine-grained and precipitation hardenings. If the conventional aging temperatures cannot be changed, higher solute-concentrated alloys should be utilized, even if those alloy compositions are far from the ones currently in use for wrought aluminum alloys because SPD, especially HPT, could achieve the supersaturated solid solutions of excess amount of alloying elements.^[27] These criteria appear to be applicable to any alloy systems, and in fact the authors^[28] recently found that the HPT specimen of Al-13.4 mass pct Mg alloy with equivalent strain of >100 possesses not only a remarkable level of attained hardness, i.e., HV296, but also the good age-hardenability, i.e., $\Delta HV31$, after aging at 343 K (70 °C) for 2226 ks. The age-hardenability was almost comparable to that in the undeformed specimen, i.e., $\Delta HV34$, leading to a quite high value of $K = 0.91 (= \Delta HV31 / \Delta HV34)$ and was certainly attributed to modulated structures corresponding to spinodal decomposition. Further investigation is in progress, especially to clarify the effects of (congruent) ordering during spinodal decomposition on concurrent strengthening of severely deformed age-hardenable aluminum alloys.

V. CONCLUSIONS

In this study, comprehensive and comparative studies on the age-hardening behavior and precipitate microstructures of severely deformed and then artificially aged 6022Al-Mg-Si and 2091Al-Li-Cu alloys had been conducted to clarify whether or not concurrent strengthening by ultrafine-grained and precipitation hardenings is activated in a given alloy system and aging temperature. The obtained experimental results and our proposed methods for alloy designing are summarized below.

- (i) The cold-rolled and high-pressure torsion (HPT) specimens of 6022Al-Mg-Si exhibited reduced age hardenings or significant age softening, depending on the aging temperature applied, failing to take advantage of the excellent age-hardenability of the undeformed specimen. This was because heterogeneous nucleation of coarsened precipitates becomes

predominant at dislocations and grain boundaries in place of transgranular precipitates of the strengthening β'' phase (i.e., competitive precipitation). For the alloys that decompose via the nucleation and growth, therefore, the fabrication of optimal microstructures without diminishing the amount of subsequent transgranular precipitation becomes important as well as lowering of aging temperatures.

- (ii) In contrast, the combined processing of severe plastic deformation (SPD) and aging treatment successfully activated concurrent strengthening of 2091Al-Li-Cu by ultrafine-grained and precipitation hardenings. Not just was the hardness of the HPT specimen (i.e., >HV290 at 373 K (100 °C)) attained, but the higher degree of age hardenings (i.e., > $\Delta HV40$) was also achieved by refined precipitation of the δ' -Al₃Li phase within ultrafine grains. From the obtained small-angle X-ray scattering (SAXS) results, methods for designing can be drawn for the alloys that decompose via spinodal decomposition; i.e., aging treatment should be performed at temperatures below spinodal boundaries, and if the conventional aging temperatures cannot be changed, higher solute-concentrated alloys should be utilized to maximize the effect of concurrent strengthening by ultrafine-grained and precipitation hardenings.

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