Corrosion of Ultrafine Grained Materials by Severe Plastic Deformation, an Overview

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Corrosion of ultrafine grain (UFG) materials by severe plastic deformation (SPD) is reviewed in light of the existing literature and microstructural change. Fortunately, by holistic survey of the literature, it seems likely that grain refinement by SPD, while enhancing mechanical properties, does not compromise the overall corrosion resistance, and in many case, improve it in comparison with coarse-grained counterparts, although there are some contradictory results within the same materials and same environment. The degree of impact of UFG formation on corrosion is highest in stainless steels followed by aluminum and magnesium alloys whereas it is relatively marginal in pure copper and titanium. The effect of UFG formation by SPD on corrosion is imparted by not only grain refinement, but also other microstructural change occurring commonly in SPD in general and unique to each specific SPD method. In this review, an attention is paid specifically to the former case, and this includes shuffling or redistribution of chemical inhomogeneity into a finer scale, deformation-induced grain boundaries and high internal stress stemming from these grain boundaries. The literature on stress corrosion cracking (SCC) of UFG materials are definitely insufficient to find the general trends, more studies are waited. [doi:10.2320/matertrans.M2015452]

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1. Introduction

Grain refinement of metallic materials to sub-micron or nano-scale by severe plastic deformation (SPD) has been well-recognized by the community of materials scientists. The advent of SPD have broken the wall of the minimum grain size achievable by the conventional thermomechanical processing, and realized the fabrication of materials with the so-called ultrafine grain (UFG) structure in a bulk form for load-carrying structural components. A vast number of papers on microstructures, mechanical, and other physical properties of ultrafine grained (UFG) or nanostructured materials by SPD represented by equal-channel angular pressing (ECAP), high-pressure torsion (HPT), and accumulative roll bonding (ARB) has been published for more than past two decades. Several comprehensive review papers on the principle of SPD processing and properties of UFG materials by SPD were published.¹⁻⁵⁾ The obvious advantage of SPD is to fabricate UFG materials in a bulk form of varying scales with no specific requirement of alloy elements, and applicable to a wide range of materials from pure metals to multi-phase materials except for very hard and brittle materials. This is especially important for biomaterials application where biocompatibility restricts applicable chemical compositions.⁶⁻⁸⁾

UFG structures by SPD are mostly composed of deformation-induced grain boundaries, and these grain boundaries are regarded as none-equilibrium boundaries.⁹⁻¹¹⁾ In deformation-induced grain boundaries, external grain boundary dislocation, or alternatively called extrinsic grain boundary dislocation, are comprised in grain boundaries lending grain boundaries energy higher than those at equilibrium state. This is evidenced by internal dislocations near the grain boundaries observed by transmission electron microscopy (TEM).¹²⁻¹⁵⁾ Indeed, several unique phenomena were reported, which seems to be attributed to high fraction of non-equilibrium grain boundaries, such as ultra-fast diffusion,¹⁶⁻²¹⁾

room temperature grain boundary sliding in aluminum.²²⁾ Strength and ductility are primary characteristics dependent on the microstructure of a material, and spectacular achievement of braking the trade-off between two has been reported in SPD-UFG materials.²³⁻²⁶⁾ Superplasticity,²⁷⁾ creep,²⁸⁾ viscous deformation,^{29,30)} fatigue strength^{31,32)} are also important “secondary” properties, which are more or less impacted by deformation-induced UFG structures.

Another property of great interest for structural materials is corrosion resistance. Corrosion in polycrystalline materials is affected by grain size, and one would expect to understand the corrosion behavior of UFG materials based primarily on grain size dependency, which is hopefully expressed by Hall-Petch type universal law.³³⁾ This is really challenging task, and has been tried with a wide range of grain size that is systematically changed.³³⁻⁵²⁾ Di Schino *et al.*⁴¹⁻⁴³⁾ investigated the effect of grain size on corrosion of several austenitic stainless steels, claiming that the rate of uniform corrosion increase by grain size reduction whereas the rate of intergranular corrosion is opposite. Table 1 lists the selected papers which investigated effect of grain size that spans for conventional range controlled by thermomechanical processing. Generally speaking, the rate of corrosion in a local mode such as pitting, intergranular corrosions decrease with decreasing grain size whereas it is opposite in general corrosion. Ralston⁴⁴⁾ reviewed the literature and clarified the general trends for grain size effect on corrosion by classifying them into three modes of corrosion with regards to dynamic polarization curves; (i) active, (ii) passive, (iii) active/passive types of corrosions. In the active type, corrosion currents are accelerated in finer grain size while an opposite trends are found in the passive type (Fig. 1).⁴⁴⁾ In the active/passive type, corrosion current show the mixed pattern of the previous two types, namely it is higher in the active region and lower in the passive region. Question arise if these trends hold for submicron- or nano-scale grain size. Corrosion resistance of nanocrystalline metals was first reported by Rofagha *et al.* on nanocrystalline nickel⁵³⁾ and Ni-P⁵⁴⁾ synthesized by elec-

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Table 1 Effect of grain size reduction on corrosion.

Materials	Grain size (μm)	Corrosion	Mode of Corrosion	Solution	Ref
Al (99.9999%)	120–1600	Better	PD	0.1 M NaCl	35)
Al	120–1600	Better	PD	—	33)
AA6063	2.4–2500	Worse	PD	1 M HCl	33)
High N SS	2.5–40	Worse	GC	boil.5% H_2SO_4	41)
High N SS	2.5–40	Better	IGC	Streicher	41)
Low Ni SS	2.5–50	Worse	GC	boil.5% H_2SO_4	42)
Low Ni SS	2.5–50	Better	IGC	Streicher	42)
AISI304	1.1–50	Worse	GC	boil.5% H_2SO_4	43)
AISI304	1.1–50	Better	IGC	Streicher	43)
AISI304	1.1–50	Better	Pitting	10% FeCl_3	43)
AISI304	1.1–50	Better	Pitting	3.5%NaCl	43)
316L	46–220	Worse	IGC(PD)	1.0 M H_2SO_4 +0.003 M $\text{Na}_2\text{S}_4\text{O}_6$	215)

Better=Corrosion resistance increases with grain size reduction, Worse=Vise versa.
 PD=Potentio-dynamic test, GC=General corrosion, IGC=Intergranular corrosion.

Fig. 1 Effect of grain size on polarization behavior of (a) active, (b) passive and (c) active/passive reactions. Reconstructed with some modification from the figure by Ralston.⁴⁴⁾

trodeposition. According to them, coarse-grained Ni and Ni-P exhibit passivation behavior while little passivation behavior was observed for the nanocrystalline counterparts, and this result does not follow Ralston's rule. Gupta and Birbilis's review⁵⁵⁾ on corrosion of nanocrystalline stainless steel fabricated by various methods such as magnetron sputtering, sand-blasting, high-energy ball milling, etc supports Ralston's rule, reporting that the resistance to corrosion, especially pitting is improved through higher passivation ability. Koch⁵⁶⁾ concluded that, as a general trend, in severe corrosive environments in low pH, nanocrystalline metals show lower corrosion resistance whereas in the passive state, pitting or selective corrosion tend to be suppressed. Similarly, nanocrystalline Co exhibit higher corrosion resistance in the passive state in NaOH solution whereas lower in the active state in HCl solutions.⁵⁷⁾

Grain refinement by SPD processing accompanies other microstructural changes in a complicated way. These change includes phase transformation,^{58,59)} redistribution of impurity and solute elements,^{60,61)} the morphology change of precipitation by partial dissolution and physical fragmentation,^{62–65)} residual dislocation density,^{66,67)} texture,^{68–71)} etc. Effect of these changes is superimposed on grain size effect on corrosion, and this may cloud the underlying law dominating grain-size-dependency, if any, generic to SPD.

In this paper, the corrosion properties of UFG materials fabricated by SPD are reviewed by a holistic examination of the existing literature, for presenting a possible rationale of corrosion behavior of UFG materials, based primarily on grain size dependency, but other metallurgical and structural changes occurring commonly during SPD are taken into account. Most of UFG materials in the list are pressed by ECAP, HPT, ARB as the core of SPD technology, but the recent emerging SPD for surface modification such as surface mechanical attrition treatment (SMAT),^{21,72–74)} cryorolling,^{75,76)} high-power shotblast,^{77–81)} burnishing,^{82–84)} friction stir processing (FSP)^{85,86)} are included. However, nanocrystalline metals, which are fabricated by the so-called bottom-up approaches such as magnetron and DC sputtering, powder consolidation by high-energy ball milling are excluded in this

review because these approach impart significant change in other metallurgical parameters which influence corrosion behavior.

2. Microstructural Change during SPD

2.1 Types of UFG materials processed by SPD

In addition to grain refinement, SPD processing modifies the microstructures in a complicated manner involving phase transformation, distribution of impurity and solute elements, segregation, the morphology of precipitation, dislocation density, texture, etc. Some of them are generic to SPD regardless of processing and some are specific to processing among SPD technology and deformation routes. In reviewing the existing literature on corrosion of UFG materials by SPD, microstructural changes are modeled and classified simply into four types according to the selected metallurgical variables as shown in Fig. 2. These four typified changes are supposed to occur commonly during SPD in general regardless of specific SPD procedures and deformation routes. Although they might occur concurrently in most alloy systems, they are classified by one according to the major microstructural change focused in the papers.

2.2 Pure metals with high and commercial purity (Type A)

As the most simple structure, a various kind of pure metals of high and commercial purity such as aluminum,^{87–94)} copper,^{6,37,95–106)} iron,^{76,107)} titanium,^{108–114)} magnesium,^{34,72,115–117)} have been processed by SPD for corrosion studies. In this simple system, grain size or grain boundary density impacts the corrosion resistance as a primary metallurgical variable with very few other metallurgical changes involved. Thus, hopefully, grain size dependency tends to appear and follow a simple law. In general, the minimum grain size achieved by SPD is somewhat larger than its aluminum alloy.¹¹⁸⁾ In many polycrystalline materials, grain boundaries

are preferentially attacked during corrosion because of (i) their enhanced energy compared to the perfect crystal, (ii) the less perfect atomic structure, and (iii) their susceptibility to segregation of impurities.¹¹⁹⁾ On the other hand, however, it may promote the formation of passive film and suppress the dissolution in the passive state because the grain boundaries become the nucleation site of passivation film.³³⁾ Higher charge-transfer resistance of passive film are interpreted as higher stability of passivation in UFG materials using electron impedance spectroscopy (EIS) in aluminum,^{88,90,92,120,121)} copper,⁹⁵⁾ magnesium,^{83,122,123)} steel,^{76,107)} stainless steels,^{73,124)} Mechanical adhesion of oxide film can be stronger in UFG materials than in coarse-grain materials by, for example, pegging mechanism.¹⁰⁶⁾ Purity of the metals also may influence the effect of grain size on corrosion properties because it affects the degree of impurity atoms residing at grain boundaries. During SPD these segregated atoms may be shuffled and redistributed, and hopefully diluted with increasing volume fraction of grain boundaries,¹²⁵⁾ although this is not necessarily true.^{60,61)}

2.3 Solid solutions under solution limit (Type B)

Second class of materials is solid solutions such as Fe-Cr, Cu-Zn, Al-Mg, Al-Cu, Mg-Al system with solute elements under the solution limit. Thermodynamically, some solute elements enhance the dissolution potential of the matrix such as Cr in Fe, Mn and Cu in Al and Al in Mg, or drop it such as Fe and Zn in Al, etc. Even in a complete solid solution, solute atoms may stay with some inhomogeneity due to an interaction with heterogeneous structure of crystal defects such as dislocations, grain boundaries, surface, etc. to reduce total free energy. Inhomogeneous distribution of these solute atoms may cause galvanic cells between the regions of high and low concentration, and degrade corrosion performance. The surface concentration of some solute elements often differs from inner bulk in some solid-solution, and the degree of it depends on grain size. If these are passivation former such as

Fig. 2 Four typical microstructural changes during SPD. A; Pure metals of high purity or commercial purity with impurity segregation according to its purity, B: Solid solution with solute elements under the solution limit at room temperature, C: Solid solution with solute elements over solution limit. It is supersaturated prior to SPD, the precipitation may occur during SPD, or post-SPD annealing, D: Two-phase or multi-phase materials, whose second phase may be fragmented physically, or dissolved partially or completely.

Cr in Fe and Al in Mg, then the degree of inhomogeneity impact corrosion resistance. It was reported that Cr concentration at the surface was higher in UFG Fe-Cr alloy than that in coarse grain counterparts as evidenced by secondary ion mass spectrometry (SIMS) or X-ray photoelectron spectroscopy (XPS),^{126–131} and this Cr enrichment of at the surface may result in the higher passivity and resistance to pitting corrosion.^{126–130} In corrosive media, selective dissolution of solute elements or solvent may also cause concentration gradient near the surface,^{126,132,133} and UFG structures may promote this tendency, resulting in higher corrosion resistance.¹²⁶⁾

2.4 Solid solutions over solution limit (Type C)

The supersaturated alloy systems with solute elements over solution limit were also processed by SPD in mostly Al,^{134–138} Mg,^{139,140} and Cu alloys.^{141–144} In this class of materials, the billets were annealed by solution treatment prior to SPD, and subsequently subjected to aging during SPD, or in the post-SPD final aging treatment. The temperature of SPD impacts the precipitation kinetics and resultant morphology such as shape, density and size of precipitates. When dissolution potential of the second phase and the matrix is different, the morphology of precipitation may impact corrosion behavior. No phase transformation occur in the aluminum alloys during their processing at cryogenic temperatures due to suppressed diffusion.^{1,144} However, complex phase transformation take place during SPD at room and elevated temperatures such as nucleation of second phase precipitates, their growth, fragmentation, or dissolution.¹⁾ High density of grain boundaries of equilibrium or non-equilibrium structures, along with dislocations and high density of vacancy result in increased diffusion coefficient and accelerated precipitation kinetic.^{145–149} According to Sha *et al.*,¹⁴⁸ evolution of second phase precipitates during ECAP processing of AA7136 at 200°C was found to be 50 times faster than during conventional aging treatments of coarse grained counter materials at the same temperature. It was also reported that the precipitation evolution bypass the metastable stage of strengthening phase, and proceeds directly in the growth stage.^{148,149} Thus, in some processing of aluminum alloys, SPD and aging treatments degrade the mechanical properties. Nevertheless, strengthening by both the grain refinement and precipitation can be compatible in UFG aluminum alloy by elaborate designing for alloys and processing as evidenced by further hardening by precipitation during the post-SPD aging treatment in UFG structure.^{137,144} Achieving it for magnesium alloy is technically more difficult and challenging, and to the best of my knowledge, its successful result is still waited. With decreasing diffusion path between grain boundaries, solute-depleted zone which inevitably accompany intergranular precipitation in conventional grain size can be eliminated or alleviated. Indeed, Cu-depleted zone in the vicinity of grain boundaries become much smaller⁸⁷⁾ or disappeared in UFG Al-Cu alloys,¹⁵⁰⁾ and this may lead to higher resistance to intergranular corrosion of Cu-Al alloy systems.^{75,150)} In passivated materials such as aluminum alloy, the passive film may be different in its stability¹⁵¹⁾ or even absent¹⁵²⁾ on second phase. Therefore, the distribution of the precipitation strongly affect the resistance to pitting corrosion, and in some cases, its im-

pact is stronger than grain size.

2.5 Two-phase, multi-phase materials (Type D)

Processing materials with second phase such as eutectic Al-Si,^{151,153} and two-phase ($\alpha+\beta$) AZ91,¹⁵⁴⁾ ($\alpha+\beta$) Ti-13Nb-13Zr alloy¹⁵⁵⁾ by SPD may impact the corrosion behavior because the dissolution potential between the two phases are generally different such as high-potential Al rich β -phase in AZ91 and Si-phase in Al. Most of commercially pure aluminum have also impurity precipitation, and can be regarded as this type. Aged materials with fine precipitation have also been processed by SPD, and in this case, structural change is very complicated. Mechanical fragmentation of the dispersions and precipitation during SPD was demonstrated, which results in finer size.^{62–65} Dissolution of the second phase into the matrix were also reported in Al alloys^{64,156)} and Mg alloy.¹⁵⁷⁾ These dissolved elements may precipitate again after SPD, thus Type C and D may occur concurrently and is hard to be clearly separated. When the second phase is nobler than the matrix by large potential difference as in the case of Al₂Cu intermetallics in aluminum and Al₃Fe in magnesium alloys, the change of size and distribution of the second phase may impact on the corrosion behavior or stability of passivity. Indeed, fine fragmentation of Al₂Cu, FeAl in aluminum alloys^{87,120,158)} and Al-Si alloy¹⁵¹⁾ raise passivity breakdown potential.

3. Corrosion of UFG Materials by SPD

3.1 General description

Corrosion behavior has been investigated on UFG materials fabricated mainly by processing of SPD such as ECAP, ARB, HPT for aluminum and its alloy,^{87–93,120,121,143,150–153,156,158–171)} magnesium and its alloy,^{34,72,115–117,122,123,154,157,172–179)} copper and its alloy,^{6,96–99,101,102,105,180)} stainless steels,^{124,181,182)} iron and steel,^{107,183)} titanium and its alloys.^{108–110,112,127,155,184–186)} Recently, other SPD processing emerged such as hydraulic extrusion (HE),¹¹¹⁾ severe- or cryo-cold rolling.^{45,75,76)} These SPD processing generates UFG metals in bulk form, but in other processing, UFG or nanocrystallization can be achieved in the surface layer using high power shot blast,⁷⁸⁾ ultrasonic peening,^{77,79,80)} surface mechanical attrition treatment (SMAT),^{72–74)} burnishing/brushing,^{82–84)} and friction stir processing (FSP).^{85,86)} Table 2 lists the papers reporting on the corrosion behavior of UFG materials by specifically SPD. Materials are divided into four types (Type A to D) according to the microstructural change described in the previous section. Although the actual metallurgical features are more complicated, this classification is simplified extracting the most influential metallurgical variables on corrosion. For example, in many age-hardenable aluminum alloys, type B, C and D may occur concurrently. The table is meant to provide a general overlook for embossing the common trend, if any, for the impact of UFG formation, and by no means were intended or capable of conveying many detailed conditions and results within the literature. In addition to these microstructural changes accompanied by UFG formation, there are also another ones such as dislocation density, phase transformation, residual stress and texture. Some of these factors are dis-

Table 2 Summary of corrosion experiments of UFG materials by SPD.

Materials	Material Type ¹⁾	Environment ²⁾	Grain size	Corrosion Tendency ³⁾	SPD	Ref.
Aluminum						
Al (99.99%)	A	0.3 M H ₃ PO ₃ +0.002 M NaCl+0.075 M Na ₂ B ₄ O ₇	-	Mar. worse	ECAP	87,158)
Al (99.99%)	A	0.1 M Na ₂ SO ₄ +8.46 mM NaCl	0.5–1.0 μ m	Better	ECAP	89)
Al (99.1%)	D	0.5 M NaCl	86 nm	-	ECAP	159)
Al (99.1%)	D	0.62 M NaCl	192 nm	Worse	ECAP	162)
Al (99.8%)	D	0.01 M NaCl	300–500 nm	Better	ECAP	171)
Al (99.5%)	D	0.5 M NaCl	380 nm	Worse	ARB	93)
Al 1050	D	0.1 M Na ₂ SO ₄ +100 ppmCl ⁻	-	Better	ECAP	88)
Al 1050	(D)	Sea water (0.6 M NaCl)	-	Better	ECAP	90)
Al 1050	(D)	Sea water (0.6 M NaCl)	-	4pass is best	ECAP	91)
Al 1100 (99.0%)	D	0.1 M Na ₂ SO ₄ +8.46 mM NaCl (300 ppmCl ⁻)	0.5–1.0 μ m	Better	ECAP	92)
Al 1100	D	0.2 M AlCl ₃	0.5–1.0 μ m	Better	ECAP	167)
Al-1.6%Mn	D	0.62 M NaCl	0.3 μ m	Mar. better	ARB	156)
Al-max.2%Mg	B	0.1 M NaCl, 0.05 M NaCl (0.5, 1, 2%Mg)	120 nm 200 nm (0.5 Mg)	Mar. worse	ECAP	161)
Al-3.0%Mg	B	0.2 M AlCl ₃	0.2–0.5 μ m	Worse	ECAP	169)
Al-1.6, 2.3%Li	D	0.1 M Na ₂ SO ₄ +100 ppmCl ⁻	0.32–1.5 μ m	Better (2.3Li) Equal (1.6Li)	ECAP+	165)
Al-5.0%Cu	D	0.62 M NaCl	0.3–0.5 μ m	Better	ECAP	121)
Al-5.0%Cu	D	0.075 M Na ₂ B ₄ O ₇ +0.3 M H ₃ BO ₃	-	Better	ECAP	87)
Al-5.4%Ni	D	0.075 M Na ₂ B ₄ O ₇ +0.3 M H ₃ BO ₃	-	Better	ECAP	87)
Al-5.4%Ni	D	0.075 M Na ₂ B ₄ O ₇ +0.3 M H ₃ BO ₃	-	Better	ECAP	158)
Al-Fe	D	0.1 M Na ₂ SO ₄ +8.46 mM NaCl (300 ppmCl ⁻)	-	Better (0.5–2.0%Fe) Mar. better (5.0%Fe)	HPT	120)
Al-26%Si	D	0.62 M NaCl	-	Mar. Better	ECAP	153)
Al-11%Si	D	0.6 M NaCl (pH6.7)	200–400 nm	Better	ECAP	151)
Al 2024	C	0.5 M NaCl	200 nm	Better	ECAP	150)
Al 2024	D	0.1 M NaCl	0.062 μ m (ECAP) 1.59 μ m (CrR)	Mar. better	ECAP, CrR	45)
Al 2024	D	0.2 M AlCl ₃	0.3–0.5 μ m	Better	ECAP	152)
Al 5052	D	0.62 M NaCl	100–300 nm	Worse	ARB	160)
Al 5052	D	0.1 M Na ₂ SO ₄ +8.46 mM NaCl (300 ppmCl ⁻)	0.2–0.5 μ m	Better	ECAP	92)
Al 5052	D	0.2 M AlCl ₃	0.2–0.5 μ m	Worse	ECAP	167)
Al 5083(4.5%Mg)	D	0.5 N NaCl, 0.5 M Na ₂ SO ₄ +0.1 N NaCl 0.5 M Na ₂ SO ₄ +0.05 N NaCl	100–300 nm	Better for	CrM	163)
Al-4Zn-2Mg	C	0.62 M NaCl	98 nm	Better	CrR	75)
Al 6082	C	0.1 M NaCl	100–300 nm	Better	ECAP	143)
Al 7150	B	0.62 M NaCl	120 nm	Equal	HPT	166)
Magnesium						
Mg (>99.9%)	A	0.1 M NaCl	1 μ m	Better	ECAP	115)
Mg (99.9%)	A	0.1 M NaCl	16.9 μ m	Better	ECAP,	72)
Mg (99.9%)	A	0.1 M NaCl	2.35 μ m	Equal	SMAT	72)
Mg (99.9%)	A	0.62 M NaCl	50–100 μ m	Worse	ECAP	116)
Mg (99.99%)	A	HCl+NaOH (pH = 1–13.2)	8.1 μ m	Better	ECAP	34)
Mg (99.99%)	A	Hanks sol.	9 μ m	Better	ECAP	117)
AZ31	D	0.62 M NaCl	3–60 μ m	Better	DDE	189)
AZ31	D	0.1 M NaCl	1 μ m	Depends	ECAP	175)
AZ31	D	0.62 M NaCl	10 μ m	Worse	ECAP	176)
AZ31	D	Hanks sol.	8.5 μ m	Better	ECAP	177)
AZ31	D	Hanks sol.	2.5 μ m	Better	ECAP	178)
AZ31	D	0.1 M NaCl	7 μ m	Better	ECAP	179)
AZ31B	D	0.91 M NaCl	260 nm	Better	BU	82)

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AZ31B	D	0.91 M NaCl	523 nm	Better	BU	83)
AZ61	D	0.1 M NaCl	1.1–1.5 μm	Mar. better	HRDSR	202)
AZ91D	D	0.62 M NaCl	1–2 μm	Worse	ECAP	154)
AZ91D	D	0.62 M NaCl	8–11 nm	Depends	SMAT	74)
ZE41A	D	Hanks sol.	2.5 μm	Better	ECAP	123)
ZE41A	D	0.6–2.5 M NaCl	2.5 μm	Better (0.6 M) Worse (2.5)	ECAP	173)
ZK60	D	0.1, 3.5 M NaCl	4.2 μm	Better (0.1 M),	ECAP	157)
AE42	D	0.1 M NaCl	3–4 μm	Better	ECAP	122)
AE21	D	0.1 M NaCl	2–3 μm	Better (AE42)	ECAP	174)
AE42	D	0.1 M NaCl	2–3 μm	Worse (AE21)	ECAP	174)
Mg-Zn-Ca	D	Hank's	1.2 μm	Better	HPT	172)
Mg-Y-Nd	B	0.62 M NaCl	0.7–70 μm	Better	FSP	46)
Copper						
Cu (99.96%)	A	0.5 M HCl	80–200 nm	Better	MA	95)
Cu (99.95%)	A	1 M H ₂ SO ₄	200 nm	Equal	ECAP	96)
Cu (99.99%)	A	0.62 M NaCl	300 nm	Worse	ECAP	97)
Cu (99.97%)	A	Hanks sol.	380 nm	Equal	ECAP	6)
Cu (99.96%)	A	Modified Livingston	300 nm	Mar. better	ECAP	98)
CP (99.95%)	A	1 M H ₂ SO ₄ , 0.5 M NaCl	200–300 nm	Equal	ECAP	101)
Cu (99.96%)	A	Modified Livingston	200 nm	Better	ECAP	102)
Cu (99.96%)	A	Modified Livingston	200 nm	Equal	ECAP	104)
Cu (99.96%)	A	0.01 M borax sol.	-	Mar. better	ARB	105)
Cu-10Ni	B	Na ₂ SO ₄ +10 ³ ppm	21 nm	Worse	PM	180)
Stainless Steels						
Fe-20%Cr	B	0.62 M NaCl	200 nm	Better	ECAP	181)
Fe-10, 20%Cr	B	0.5 M H ₂ SO ₄ , pH = 0.6	15 nm	Better	PM	126)
Fe-20%Cr	B	0.05 M H ₂ SO ₄	15 nm	Better	PM	130)
"	B	0.05 M H ₂ SO ₄ +0.5 M NaCl				
AISI409	B	0.6 M NaCl	55 nm	Depends	SMAT	73)
AISI 303	B	0.1 M NaCl	10–20 nm	Worse	HE	185)
AISI 304	B	0.5 M H ₂ SO ₄	80–120 nm	Better	ECAP	124)
AISI 304	B	0.62 M NaCl	20 nm	Better	SB	78)
AISI 304	B	0.53 M H ₂ SO ₄	-	Better	ECAP	182)
AISI316	B	HNO ₃ +NaF	20 nm	Equal	HE	184)
AISI316	B	Borate+0.1 M NaCl	20–70 nm	Better	.HE	127)
"	B	0.15 M NaCl	20–70 nm	Worse	HE	
AISI321	B	0.62 M NaCl	15 nm	Equal	UP	77)
Steels						
Pure Iron	A	0.5 M H ₂ SO ₄	350 nm	Better	ECAP	107)
Pure Iron	A	0.5 M H ₂ SO ₄ +0.25 M Na ₂ SO ₄	-	Better	SR	76)
Mild steels	B	0.5 M H ₂ SO ₄	250 nm	Better	ECAP	107)
IF-Steels	B	0.01, 0.1, 1.0 M NaCl	200–300 nm	Equal	ECAP	183)
	B	0.9 M NaOH+Cl ⁻ (5%)		Better		
IF-Steels	B	0.62 M NaCl, 0.1 M H ₂ SO ₄ ,	-	Better	WB	47)
"	B	0.44 M NaCl+0.05 M H ₂ SO ₄ ,		Better		
"	B	0.44 M NaCl+0.075 M H ₂ SO ₄ ,		Better		
"	B	0.62 M NaCl+0.1 M H ₂ SO ₄ ,		Better		
Titanium						
Ti(>99.36%)	A	1–3 M HCl, 1–3 M H ₂ SO ₄	300 nm.	Mar. better	ECAP	108)
CP-Ti	A	Hanks sol.	300–500 nm	Mar. better	ECAP	109)
CP-Ti (grade 2)	A	0.16 M NaCl	260 nm	Mar. better	ECAP	110)

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CP-Ti (grade 2)	A	0.15 M NaCl	90 nm+disl.	Worse	HE	111)
CP-Ti (grade 2)	A	0.62 M NaCl	110 nm	Equal	HPT	112)
CP-Ti (grade 2)	A	0.5 M H ₂ SO ₄	200–500 nm	Better	HRDSR	113)
CP-Ti (grade 2)	A	1 M H ₂ SO ₄ , 1 M HCl	200–500 nm	Better	HRDSR	114)
Ti-Zr-Ta-Nb	C	Ringer's sol.	-	Better	ARB	186)
Ti-13Nb-13Zr	D	Hank's sol.	644 nm (α) 590 nm (β)	Better	ECAP	155)

Zirconium

Zr-2.5Nb	B	0.62 M NaCl	150–200 nm	Mar. better	UP	79)
Zr-1Nb	B	0.62 M NaCl	100–200 nm	Mar. better	UP	80)

SPD; ECAP=equal channel angular pressing, ARB=Accumulative roll bonding, HE=Hydraulic extrusion,

HPT=High pressure torsion, CrR=Cryo rolling, CrM=Cryo milling, SMAT=Surface mechanical attrition treatment,

DDE=Dual directional extrusion, BU=Burnishing, HRDSR=High ratio differential rolling,

UP=Ultrasonic peening, SR=Severe rolling, WB=Wire brushing, SB=Sand blast, MA=Machining

"Better" means that UFG shows higher corrosion resistance than the coarse grain counterpart, and "Worse" is vice versa.

"Depends" means that superiority depends on conditions of SPD processing or corrosion tests.

Hanks solution; 0.185 g/L CaCl₂, 0.4 g/L KCl, 0.06 g/L KH₂PO₄, 0.1 g/L MgCl₂·6H₂O, 0.1 g/L MgSO₄·7H₂O, 8.0 g/L NaCl, 0.35 g/L NaHCO₃, 0.48 Na₂HPO₄, 1.0 g/L D-glucose, pH = 7.4

Ringer's solution; 0.20 g/L CaCl₂, 0.4 g/L KCl, 0.2 g/L MgSO₄·7H₂O, 6.8 g/L NaCl, 1.0 g/L NaHCO₃, 0.14 Na₂HPO₄, 1.0 g/L D-glucose, pH = 6.9

Livingston' etchant; 30 mL HCL, 10 mL CH₃COOH, 410 mL H₂O (0.48 M HCl, 0.40 M CH₃COOH)

1) Type C and D are also belong to B in alloys, therefore B is omitted.

2) All the units of concentration in the literature are unified and expressed by M (=mol/L) for comparison although many papers express the concentration of NaCl by mass%.

3) Change in corrosion resistance as grain size decreases by SPD

cussed later.

3.2 Aluminum and aluminum alloys

Aluminum and its alloy are readily passivated and become stable in neutral solution, but dissolve in acidic and alkali solution. Pitting tends to occur in neutral solution with chloride ion. Majority of papers report that the UFG materials in passive media exhibit higher corrosion resistance following the Ralston's rule⁴⁴⁾, its superiority manifests itself by breakdown potential rather than passive current. However, there is some inconsistency among the literature, even for pure aluminum, reporting favorable effect of UFG,^{89,92,171)} marginal change,¹⁵⁸⁾ unfavorable effect.^{87,93,158,162)} The favorable effect is attributed to the readily formation of oxide film because atoms at grain boundaries site are reactive to chemical species in the environment.^{89,92,171)} One possible explanation for this contradictory results is the purity; lower purity may results in the degradation of corrosion properties by SPD. Eizadjouet *et al.*⁹³⁾ attributed lower corrosion resistance to refinement of Al₃Fe, Al₆Fe intermetallics and related defective passive films. Pitting corrosion resistance of aluminum alloys with precipitation or the second phase (type D) is mostly improved by SPD,^{45,75,87,92,120,121,143,150–153,156,158,167)} and this improvement is mainly due to physical breakup of the second phase or precipitation which differs in dissolution potential from the matrix and causes defective structure of passive film. For example, pitting occurs at the interface between the matrix and nobler second phase.^{88,150–152,160)} When the precipitation is smaller than critical size, it does not work as a nucleation site of pitting. Effect of refinement of the second phase on corrosion is more evident in eutectic¹⁵³⁾ and hypereutectic Al-Si alloys¹⁵¹⁾ where nobler hard Si-phase was finely redistributed

during SPD, resulting in the more uniform corrosion. The physical breakup of the second phase also involve refinement or homogenization of solute-depleted zones, which results in improvement in corrosion resistance.^{87,156)}

Combined effect of UFG and precipitation on strengthening can be expected by an appropriate processing comprising SPD and post-SPD artificial or natural aging in order to achieve higher strength due to very fine precipitation in UFG microstructures.^{137,144)} The formation of finer θ -phase precipitation in UFG Al-Cu materials at the post-SPD aging treatment lead to smaller or disappearance of Cu-depleted zone.^{75,87,150)} Indeed, Jilani,¹⁵⁹⁾ Kus¹⁶³⁾ and Brunner¹⁵⁰⁾ reported transition from intergranular corrosion to pitting corrosion with decreasing grain size into a submicron scale. There are also some few opposing studies reporting unfavorable effect of SPD on corrosion of aluminum alloys.^{160,162,167,169)} Son *et al.* attribute its effect to internal stress induced by SPD, which break the oxide film and induce the pitting at defects of the oxide films. Korchef *et al.*¹⁶²⁾ explained the decrease of pitting corrosion resistance by the physical breakup of precipitation and increasing number of metal/precipitation interface where pitting starts to form. In summary, the physical fragmentation of precipitates by SPD appears to be double-edge swords for corrosion in aluminum alloys, and contradicting reports are concentrated in type D materials.

3.3 Magnesium and magnesium alloys

More papers are reporting the favorable effect of SPD on corrosion properties than those opposing. Those reporting unfavorable effect are many in type D, but the role of precipitation appears to be not important in magnesium alloys. Effect

for magnesium alloys is rather complex for several reasons; (i) unstable passive film, (ii) heterogeneous structures as a result of dynamic recrystallization, and (iii) strong texture dependency. Firstly, magnesium forms oxide or hydroxide film in neutral or alkali solutions, and they are unstable and time-dependent. EIS reveals that time-dependency of stability and anomalous change of permeability, either progressing^{122,123)} or regressing¹⁵⁴⁾ or both¹⁷⁵⁾ with immersion time for UFG materials. Therefore, evaluation of corrosion dependence either by polarization or immersion tests must be careful. Secondly, magnesium is the close-packed hexagonal structure, and is hard to deform at room temperature. Therefore, they are generally deformed by SPD at relatively high temperatures ranging from 200 to 300°C. As shown in Table 2, the final grain size of SPD magnesium alloys is rather large ranging from 1 to several micron meters as compared with other UFG metals. Processing at relatively higher homologous temperature cause dynamic recrystallization during SPD processing,^{27,177,187–189)} and this may render the microstructure inhomogeneous mixed with recrystallized and severely deformed microstructures.^{27,187)} The degree of mixture depends on the pressing temperature and starting grain size.^{27,187)} It seems that contradicting studies reporting inferior corrosion resistance after SPD of pure magnesium,¹¹⁶⁾ AZ31,^{176,189)} (type B) may be attributed to the inhomogeneous microstructures related with dynamic recrystallization. Finally, crystallographic orientation dependency of corrosion is very high in magnesium alloys,^{83,190–198)} and it seems to have higher impact than grain size. The high atomic coordination of basal plane make the electron working function higher, and has the highest resistance to dissolution. Texture is dependent on deformation routes, SPD technique, thus, it is hard to draw general conclusion on corrosion resistance.

3.4 Copper and copper alloys

Copper is a noble metal and exhibits passivity in neutral solutions, and it can be dissolve in acidic and alkali solutions with high oxidizing power. Effect of UFG formation on corrosion have mostly been investigated on copper of commercial purity, and is overall very small in all electrolytes tested.^{6,95–98,101,102,104,105,180)} Pure copper is the best suitable metal for studies using dislocation etchant,^{199–201)} which attack only crystal defects such as edge dislocations and grain boundaries and leaves other parts intact. Hinted by this, UFG pure copper by ECAP was immersed in modified Livingston etchant in an effort to extract the effect of grain size on dissolution in the active state.⁹⁸⁾ Therefore the initial expectation is that UFG copper with high grain boundaries density corrode faster than the coarse grain counterpart following the Ralston's rule. Surprisingly the result is opposite and against Ralston's rule, and the corrosion current is lower in as-ECAPed UFG copper than that in the coarse-grain counter materials because of suppressed cathode current and unchanged anode current (Fig. 3). This result can be explained by micro local-cells between grain boundaries and the grain interior. When grain size become smaller in submicron scale, areas for cathode sites are not enough as compared with coarse grained copper. Detailed mechanism is discussed later. Annealing ECAPed copper for very short time of 90 s at 200°C with little grain size change increased corrosion rate. The corroded surface of

Fig. 3 Dynamic polarization curves of as-ECAPed UFG and post-ECAP annealed copper by 200°C for 40–120 seconds.⁹⁸⁾

as-ECAPed copper was relatively smoother than those of annealed and coarse-grained ones, and it suggests transition from uniform to intergranular mode of corrosion.

3.5 Pure iron and steels

In this class of materials, all the literature without exception, though not so many, follow the Ralston's rule. Zhang *et al.*¹⁰⁷⁾ investigated anodic polarization behavior of UFG mild steels (C; 0.10–0.13 wt%) and pure iron produced by ECAP, and found that both have better passivity than as-cast counterparts. Similarly to aluminum, the densely populated crystalline defects in the UFG structures become the nucleation sites of the passive film, which improved passivity properties. Additionally, the refinement of iron carbide particles during ECAP processing contributes to the formation of continuous dense passive film in UFG mild steels.¹⁰⁷⁾ The more protective passive layer are also reported in UFG IF steels,¹⁸³⁾ as evidenced by higher pitting potential in 0.9NaOH+Cl⁻ solutions and in pure iron by EIS.⁷⁶⁾ Dehghani *et al.*⁴⁷⁾ reported polarization behavior of IF steels in the active region in a wide range of pH which was controlled by mixing 3.5%NaCl and 0.1 M H₂SO₄. Nanograined IF steels exhibited smaller corrosion current in a wide range of pH as a result of more protective surface layer.⁴⁷⁾

3.6 Stainless steels

To the best of my knowledge, stainless steels are the most benefitted materials by SPD. Essentially all the literature with few exception^{127,185)} reported the higher corrosion resistance of UFG stainless steels regardless of SPD processing. Mostly, UFG materials follow the Ralston's rule⁴⁴⁾ exhibiting lower passive current and higher breakdown potential in Cl⁻ containing solutions. As for the corrosion of nanocrystalline stainless steels, please refer to an excellent review by Gupta.⁵⁵⁾ This higher stability of passivation is attributed to higher Cr concentration (high Cr/Fe) in the surface of nanocrystalline structure^{126,130,131)}, and high Cr enrichment in nanocrystalline structure is speculated to be caused by higher fraction of grain boundaries which provide faster diffusion path for Cr¹³¹⁾, although other view is presented by Gupta that Cr enrichment is caused by selective dissolution of Fe.¹²⁶⁾ The only opposing report¹⁸⁵⁾ attributed the inferior corrosion resistance

Fig. 4 Relation between pitting potential and grain size in high purity UFG Fe-20%Cr alloys fabricated by ECAP. Grain size are controlled by post-ECAP annealing.¹⁸¹⁾

to high amount of MnS inclusions, which are physically broken up into finer size during ECAP and provide more nucleation size for pitting. Rifai *et al.*¹⁸¹⁾ investigated corrosion behavior of UFG Fe-20%Cr steels by ECAP, and effect of grain size controlled by post-ECAP annealing on pitting potential. It was found that pitting potential of as-ECAP was highest and decreased with increasing temperature of the post-ECAP annealing. The pitting potential of a series of the annealed materials decreased with increasing grain size and followed the so-called Hall-Petch type relationship, but the pitting potential of as-ECAPed was higher than that of annealed materials in spite of the comparable grain size as shown in Fig. 4. Higher corrosion resistance of as-ECAPed UFG than “recovered” UFG with the same grain size is noteworthy results, and is not clarified yet. As pointed out by Pan,¹³¹⁾ fast diffusion of Cr through non-equilibrium grain boundaries and resultant Cr enrichment are speculated to be the reason for higher corrosion resistance. Alternatively selective dissolution of Fe due to high density of non-equilibrium grain boundaries may be accelerated, which result in higher Cr concentration and passivity. Oppositely, favorable effect of such short-time recovering treatment on corrosion resistance is reported in pure titanium¹¹³⁾ and in magnesium alloy.²⁰²⁾

3.7 Titanium alloy

Titanium alloy is the most corrosion-resistant alloy among the structural materials with the very high stable passive film formation. In this class of materials, mostly pure titanium of commercial purity has been pressed by SPD for UFG formation for biomedical applications.^{108–114)} Pure titanium have good affinity with human bodies, and the strength can be boosted by SPD without sacrificing the affinity and corrosion resistance. On the other hand, titanium alloys are mostly very hard and have high strength, thus studies on these have been very limited.^{155,186)} The literature^{108–114,155,186)} on corrosion resistance of UFG pure titanium unanimously shows a little higher corrosion resistance than coarse-grained counterparts except for one paper¹¹¹⁾ which report inferior corrosion prop-

erty of UFG titanium processed by hydraulic extrusion. The corrosion properties were mostly investigated by potentiodynamic polarization or weight loss experiment by immersion tests. The passivity of UFG titanium follows the Ralson's rule⁴⁴⁾ and is more stable as evidenced by lower passive current with marginal difference in dynamic polarization, but superiority is more explicit in weight loss experiment.^{108,113,114)} As is described in magnesium alloy, the effect of texture on corrosion is strong because of the basal plane being most resistant to corrosion,^{109,110)} thus letting UFG effect be more dependent on specific SPD and processing route.

4. Effect of Grain Size

From the thermodynamic principle of electrochemistry, UFG materials have lower dissolution potential and therefore higher tendency to dissolution in aggressive media than coarse-grained counterparts because the former has high density of grain boundaries and higher internal energy. However, kinetics of corrosion is related with the mode of corrosion such as general or uniform corrosion, intergranular and pitting corrosion, and detailed micromechanism of electrochemical reaction is related with microstructure including inhomogeneity of impurity, solute elements and precipitation as well as grain size.

Let us consider a simple pure metal composed of grain boundaries and grain interior with different dissolution potentials, and it is under an active state in an acidic media. When the acidic media is aggressive, and the oxidizing power, i.e. the half-cell electrode potential of oxidizing agent, is higher than the dissolution potential of both grain boundaries and grain interior, then dissolution proceed in a uniform manner with little localization. However, oxidizing power is weaker, and its equilibrium electrode potential is ideally lower than dissolution potential of grain interior, and higher than that of grain boundaries, then dissolution proceed in a local manner, by forming local cell between grain boundaries and grain interior. In the former case, corrosion rate may increase with decreasing grain size and thus increasing grain boundary area because of high energy state of the atoms at the defective structures. On the other hand, in the latter case, corrosion rate may start to decrease with decreasing grain size when grain size become smaller than a certain critical size as shown in Fig. 5. Under the critical grain size, cathode area cannot counter the increasing grain boundary area as the anode site, resulting in the suppression of the cathode reaction. This grain size dependency become pronounced when corrosion kinetics is controlled by cathodic reaction such as diffusion of dissolved oxygen. This may be the reason why the corrosion of UFG pure copper in Livingston's dislocation etchant is slower than that of coarse grain copper as described in the previous section.⁹⁸⁾ An extreme case may be the low rate of intergranular corrosion of austenitic stainless steel.^{41–43)} Whether grain size dependency of corrosion rate become positive or negative is decided by the degree of locality of corrosion regardless of active or passive state.

5. Effect of Internal Stress

Another important factor which may impact corrosion re-

Fig. 5 Schematic diagram showing change in area distribution of cathode area (shadow area) and corrosion current with decreasing grain size under active dissolution. With decreasing grain size, the cathode area decrease while anode area increases, and the former do not counter the latter under the critical grain size, which leads to reduction of corrosion current.

sistance and may occur commonly in SPD is residual stress (generally macroscopic) and internal stress (microscopic). Those two notions are similar and frequently seem to be confused in the literature.⁴⁴⁾ For example, Ralston⁴⁴⁾ discussed the effect of residual stress on corrosion, and this “residual stress” seems to include both. In the former case in a common sense, tensile and compressive stress fields are distributed in macroscopic scale between, i.e., the surface and interior of components. The residual stress is more familiar than the latter for materials engineers, and arises from inhomogeneous thermal history and plastic strain that occurs in a common form of thermomechanical processing. On the other hand, the notion of internal stress is rather new, and considered to arise from deformation-induced microstructures, and its tensile and compressive stress fields are microscopic and distributed in grain-size scale.^{9,203–205)} The existence of high internal stress was evidenced by X-ray diffraction,^{203–205)} fringe contour visible in bright-field images by TEM.^{11,13,204,206–208)} These contour appears as a result of curvature of foil strained by high internal stress. The high internal stress has often attributed to the so-called non-equilibrium grain boundaries^{9,11–15,205,206,208,209)} although there are other views.^{203,204)} Grain boundaries generated by plastic deformation are at high-energy state with excessive grain boundaries dislocations, or alternatively called extrinsic grain boundary dislocations that extend long-range stress field into the grain interior.²⁰⁸⁾ The notion of the non-equilibrium grain boundaries was originally proposed by Grabski,¹⁰⁾ and was later demonstrated in UFG structure by TEM.^{12–15)} The high energy non-equilibrium grain boundaries cause fast diffusion,^{16–21,210)} and resultant room temperature grain boundary sliding in pure aluminum as evidenced by topographical observation by atomic force microscopy.^{22,32)} Under the high internal stress, atoms at the surface are at a high free energy state with low

electron work function of the surface. This facilitates either anodic dissolution or the formation of passive film.^{44,211)} The high internal stress can be relieved by annealing for the short time and at low temperature with little grain size change,^{9,203–206)} possibly accompanying transition from the non-equilibrium to an equilibrium state by dissipating extrinsic grain boundary dislocations.^{16,209,212–214)} The time required for grain boundary equilibration in pure nickel is estimated to be 40 s at 250°C in low segregation level while 1200 to 5000 s at 250°C in high segregation, and the time depends on the degree of segregation and grain boundary character.²¹⁴⁾ This is in contrast with the classic residual stress that requires heat treatment of several hours to be relieved. There are several experimental results that corrosion rate increased by the post-SPD short annealing aiming to relieve internal stress,^{98,104,181)} and these suggests that high internal stress, or non-equilibrium grain boundaries, or both concurrently, improve corrosion resistance. Miyamoto *et al.* examined the corrosion behavior of UFG copper by ECAP in a modified Livingston's dislocation etchant, and it is surprising that corrosion current increase by the post-ECAP annealing of the temperature of 200°C for 90 seconds with little grain size change.⁹⁸⁾ It is interesting to note that the corroded surface of UFG copper is rather uniform while that in annealed one is rougher, suggesting transition from uniform to intergranular mode of corrosion. This mode change can be interpreted in terms of the local-cells between grain boundaries and grain interior and energy difference between two. Namely, the annealing relieves the internal stress and decreases the free energy of grain interiors, which increases the energy difference between two, resulting in intergranular mode of corrosion. It is unlikely that macroscopic residual stress caused by plastic strain can be relieved by this short time annealing.

However, internal stress and possibly residual stress in a

Table 3 Summary of SCC experiments of UFG materials by SPD.

Materials	Environment	Grain size	Type of test	Susceptibility ¹⁾	SPD	Ref.
Al-Mg	3% NaCl	-	SSRT	Better	ECAP	164)
Al-Mg-Sc	3.5% NaCl	0.39 μm	SSRT	Worse	FSP	86)
Cu(99.99%)	3.5% NaCl		SSRT	Worse	ECAP	97)
CP Cu	1 M NaNO ₂	0.3 μm	SSRT	Better	ECAP	102)
CP Cu	1 M NaNO ₂	200 nm	SSRT	Better	ECAP	103)
Cu-10%Zn	Ammonia	200 nm	CLT	Worse	ECAP	216)
AZ31	3.5% NaCl	0.63 μm	SSRT	Worse	FSP	85)
SUS304	Boiled MgCl ₂		FPBT	?	SG	84)

Type of test: SSRT=slow strain rate technique, FPBS=Four points bending test, CLT=Constant load test

SPD; ECAP=equal-channel angular pressing, FSP=friction stir processing, SG=surface grinding,

1) Change as grain size decrease.

more common sense may play dual-edge roles as described in the previous section, i.e. acts as an enhancer by facilitating the passive film formation, or a degrader by introducing crack or defective film.^{44,169)} As the internal stress have dual-edge roles, so does the annealing intended for stress relief. Indeed, Kim *et al.* reported improvement of corrosion resistance in pure titanium¹¹³⁾ and AZ61²⁰²⁾ by annealing.

6. Stress Corrosion Cracking (SCC) of UFG Materials

SCC sensitivity of UFG materials by SPD has far less been studied as compared to corrosion property. One reason for this limited SCC studies of UFG materials is that structural materials which exhibit SCC are generally high alloys having high strength such as austenitic stainless steel and Cu-Zn alloys, and hard to be processed by SPD. The other reason may be that observation of crack path and fracture surface by scanning electron microscopy is difficult because grain size is very small, making it difficult to identify SCC mechanism. Table 3 summarize the published papers list of SCC studies of UFG materials. As shown in Table 3, SCC of UFG materials have been investigated by mostly slow-strain-rate-test (SSRT), and sensitivity to SCC is evaluated by the ratio of elongation to fracture in air and solution. As differing from corrosion, there are no systematic study reporting on effect of grain size on SCC sensitivity using a wide range of grain size. The existing literature are divided into two groups reporting favorable and unfavorable effect of UFG formation on SCC sensitivity. It should be pointed out that time-dependent deformation of UFG become higher by fast diffusion at grain boundaries as evidenced by room-temperature grain boundary sliding²²⁾, discrepancy of SCC sensitivity become larger in accelerated SSRT test and the constant-load tests for UFG materials as compared with counter materials. More studies are being waited to find the trend of impact of UFG formation on SCC.

7. Conclusions

In general, strengthening through grain refinement by SPD does not sacrifice the corrosion resistance. Indeed, UFG Fe-Cr alloys exhibit superior corrosion resistance than coarse-grain counterparts without exceptions while UFG copper and titanium are relatively comparable with coarse-grained mate-

rials. SPD enhance the corrosion resistance through grain size reduction and homogenization of chemical inhomogeneity by the “shuffling” of severe plastic strain, and corrosion tends to change from local to uniform mode, i.e., intergranular to general corrosion, large pitting to smaller or shallower ones. On the other hand, aluminum and magnesium alloys, although majority papers report favorable effect of UFG formation, there are contradictory reports in similar materials and similar environment. The morphology of nobler precipitates such as size and distribution has impact on micro-scale electrochemical polarization, which results in better or inferior corrosion performance. Additionally, magnesium alloys are more sensitive to microstructural change specific to SPD processing. Nevertheless, change to more structural homogeneity accompanied with grain size reduction have high potential for higher corrosion performance.

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