EFFECT OF GRAIN REFINEMENT ON CORROSION RESISTANCE

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Abstract - *Grain refinement is the driving factor for improved strengths and scratch resistances. Changes in grain refinement can change the surface as well as bulk properties leading to an impact on the electrochemical behaviour and resistance to corrosion. However, limited work exists towards establishing a clear relationship between the corrosion resistances and the grain size of an alloy. A survey of the past work on connection between grain size and corrosion obstruction for different metals will be introduced. Examining the current relationship will help identify the catalyst and the factors responsible such as environment, residual stress, post treatment and texture. An analytic establishment of a possible Hall-Petch relationship between the corrosion rate and grain size will be worked upon.*

KEY WORDS

Magnesium, Aluminium, SPD (severe plastic deformation), ECAP, steel, grain size, grain refinement.

1. INTRODUCTION

Grain boundaries can be affected depending upon the atomic coordination, diffusion rates and reactivity all corresponding to bulk material properties[1]. The number of atoms at inter crystalline decreases as the surface area decreases due to smaller grain size. Consequently, the surfaces with high grain boundary densities display a different electrochemical behaviour as compared to a similar material with low grain boundary density.

Hall-Petch relationship very well establishes the improvement in mechanical properties such as ductility, strength and wear all achieved through thermomechanical processing or cold working. Considering the relationship is very handful because of the trouble in separating the grain size impacts from other microstructural changes that are brought about by thermochemical handling to accomplish variety in grain size. This powerlessness to recognize the impacts has made the assurance of a precise relationship troublesome. Achievement of grain size can be accomplished with a number of processes including- rolling, extrusion, working, severe plastic deformation and various milling operations. With changes in grain size, corrosion resistance, internal stresses and alloy texture may also change. Furthermore, the post processing and the heat treatment processes lead to internal stresses and collection of impurity around grain boundary.

Previous papers have worked upon connecting the two sides of grain refinement and corrosion resistances, but an understanding how this works and a summed up relationship is yet to be introduced. The point of this paper is to give an audit of the corrosion opposition and grain size relationship for number of various alloys. The compilation of the works existing and a combined result with grey patches for future research areas will lead to better understanding of the critical factors and generalised behaviour for different alloys. This will also help eradicate some of the contradicting results published previously.

2. LITERATURE REVIEW

2.1 MAGNESIUM

Literature highlights the inverse relationship between grain size and corrosion resistance of magnesium, i.e., as the grain size decreases, the corrosion resistance increases. The study being observed in alkaline(NaCl) and neutral medium [2]. Further improvement in corrosion resistance was observed with decreased cathodic kinetics, corrosion current and rate, and weight loss. [3]

This superior corrosion resistance for magnesium was credited to the formation of a better passive film which was proved through the experiment of repassivation and lower corrosion in NaCl electrolytes.[4] Be that as it may, passive film alone won't influence corrosion. Op't Hoog and co-creators state that huge remaining stresses after grain refinement lead to expanded cathodic kinetics. [5][6]. Hamu and co-authors presented that residual stresses proves fatal for corrosion resistance of Mg. They experimented by SPD through ECAP and determined the samples were 3.5% more corrosion prone in NaCl electroytes [7]. These results directly contradicted the results of Op't Hoog et al. This indicated that internal stresses do not necessarily lead to an increase in increased corrosion susceptibility.

2.2 ALUMINIUM

The literature available denotes that as the corrosion susceptibility falls with decreasing grain size [8][9][10][11].

However, contradictions exist due to the inability to generalize the effects of grain refinement under a reference line [20][21]. For example, in sodium chloride and sodium sulphate electrolytes, grain refinement may lead to lowered cathodic kinetic reactions. Fine grained aluminium is associated with better resistance to stress corrosion cracking. This is due to the fact that ECAP breaks down the intermediate particles up-to critical size and disables them to act as localised attack initiation site [8].

The contradicting results were also presented on the topic by Mahmoud, FSP (friction stir processing) was used and the smaller grains thus produced on AA 6063-T6, were more prone to corrosion [12]. In NaCl electrolytes aluminium with coarse grains showed better resistance to corrosion due to fewer initiation sites.

Little mention of segregation and residual stress can be found in the literature online. Although some literatures attributed the presence of residual compressive stress with improved corrosion [14]. The literatures bring up that the grain refinement process itself changes the chemical microstructure and thus grain refinement is no longer just a structural change.

Table -1: Observations

MATERIAL	ENVIRONMENT	GRAIN SIZE RANGE	Corrosion susceptibility towards decreasing grain size	Process Method	References
Magnesium					
Mg(AZ31B)	3.6% NaCl	7 to 18	Lowered	HT, SPD, FSW	28
Mg-Y-RE_Zr	3.6% NaCl + Mg(OH)2	26	Lowered	HT	27
Mg (99.9%)	0.15M NaCl	3 to 874	Lowered	SPD, HT	6
Mg (99.9%)	0.15M NaCl	2 to 875	Lowered	HT, SPD	5
Mg (AZ91D)	1N NaCl (ph 11)	11 to101	Decreases	C	29
Mg(AZ31)	3.6% NaCl+Mg(OH)2	4 to 34	Processing Dependent	SPD	7
Mg(WE43)	1.5% NaCl	0.6 to 16	Raised	SPD	2
ALUMINIUM					
AA 6063 T6	1M HCl	4 to 31	Raised	SPD	12
Al 99.99%	3.5% NaCl	651 to 2751	Raised	C	13
Al 5083	0.51 N NaCl, 0.51 M Na2So4+ NaCl, HNO3	101 to coarse	Lowered	CM, HIP, E	8
FE alloy					
Fe	1M HCl DA	39 to 51	Lowered	SPD	15
304SS	3.51% NaCl	21 to Coarse	Both/Depending upon surface stress	Sb and A	17
FeAl8	0.15M Na2SO4 at pH 6 DA without 0.15 M NaCl	41 to 301	Environment Dependent	MS	18

2.3 IRON/STEEL

There is not much literature available for ferrous alloys on a similar electrolyte, but general outcome suggests that the direct relationship between the grain size and corrosion susceptibility [15][16]. Ferrous alloy's grains directly influence the corrosion rate under the influence of electrolyte pH and surface stress [17][18].

Better resistivity leads to improved passive film stability which in turn is the result of increased diffusion rates in fine grained structures. It has been practically shown by Wang and Li that finer grains form a stable passive film than course grained iron [17][19]. Nonetheless, almost all the results of higher rate of general corrosion as grain size decreases, were attributed to passive film destabilisation [21][22] .

3. EFFECT OF ENVIRONMENT

How the grain refinement acts out, depends very highly upon the environment it is being treated in. Most of the studies are performed in a limited number of electrolyes and represent a limited environment cases. However, some of the literatures do highlight the dependencies of the environment on the grain size and hence corrosion. If the coarse grained structure is active towards the electrolyte, the corrosion rate increases but if the course grained structure is inactive towards the electrolyte the, it will result in a stable passive film.

Yu and co-authors demonstrate this on FeAl8 in pH1 and pH6 Na2SO4 solutions. The pH1 solution demonstrated finer grains and higher rates of corrosion while on the other hand, pH6 solution solution showed more aggressive passive film [18].

Wang and co-authors establish a link between the corrosion, grain size and environment for work performed on Cobalt [23]. NaOH, NaCl, HCl and H2SO4 were used as electrolytes. It was observed that NaOH and NaCl (passivating electrolytes) reduced corrosion while HCl and H2SO4 (non-passivating electrodes) enhanced corrosion rates.

4. EFFECT ON OTHER FACTORS

There are many other factors that affect the relationship of grain size and corrosion resistance just like the environment. Some of them are discussed below.

Texture- Crystallographic texture has effects on corrosion resistance. These factors inclusion with packing density directly affect the passive film formation. Regarding this, Schultze and co-authors said that if iron grains are oriented in a close packed direction, then the atoms would be difficult to remove and the corrosion resistance would increase [24]. Lee and White, through surface atom number density of various crystal orientations, determined the change in effect of corrosion on the metal [25]. Suggesting that the number of atoms impacts reaction kinetics. The exact effect of texture on corrosion cannot be determined, but it is clear that the texture does affect the electrochemical properties of the surface. This knowledge comes in handy while considering the processes like ECAP, where grain boundary characteristics can change with the number of passes.

5. RESIDUAL STRESS

Grain structure refinement imparts stresses, strains changes the dislocation density which impacts the corrosion rates. The anount of residual stress alters the surface energy of the material and thus the reactivity of the surface. Although, decreased surface energy and increased rates of diffusion can promote the formation of passive layer. The stresses and strains can also induce defects such as cracks and dislocations. However, grain refinement due to heat treatment to reduce the internal stresses may lead to segregation, leading to new dependencies.

Impurity Segregation- Segregation of impurity can have huge impacts on corrosion resistance of an alloy. A number of literatures have cited that removing impurities from the melt can make the alloy more prone to localised intergranular attack. Also, presence of impurities can hinder with the formation of a protective coating. It is argued that grain refinement has a set of advantages too, like the compositional difference between the grain and grain boundary is decreased, which helps lower the effect of impurity segregation. [26]

6. CONCLUSIONS

Since there could be no general theory derived through the literatures, the statements will be made on general concept only. It is clear that the same bulk material, when modified can lead to changes in corrosion rate that is significant enough. This observation is used professionally to alter the corrosion rates in a given environment.

Also, surface processes or grain refinement that changes the surface properties, will impact the corrosion rate of the metal.

Grain refinement decreases the corrosion rate for magnesium, this can increase or decrease too, depending upon the processing environment.

Grain refined material can have an improved corrosion resistance depending upon the passive film formation.

Residual stresses also affect the corrosion resistance or oxide formation. Unlike texture, it cannot be generalised for different metal surfaces.

7. FUTURE SCOPE

It would be very fascinating to see a generalised relationship being drawn for corrosion resistance and grain size. Also, a Hall petch like graph relationship would be very helpful for the future development in this field.

REFERENCES

[1]K.D.Ralston, D.Fabijanic, N.Birbilis, Electrochimica Acta 56 (2011) 1729-1736

[2] K.V.Kutniy, I.I.Papirov, M.A. Tikhonovsky, A.I. Pikalov, S.V. Sivtzov, L.A. Pirozhenko, V.S.Shokurov, V.A.

Shkuropatenko, Materialwiss. Werkstofftech. 40, 4 (2009): p. 242-246

[3] Y.H.Jang, S.S. Kim, C.D. Yim, C.G. Lee, S.J. Kim, Corros.Eng., Sci. Technol. 42, 2 (2007): p. 119-122

[4] R. Ambat, N.N.Aung, W.Zhou, Corros. Sci. 42 (2000): p. 14331455

[5] C. Op't Hoog, N. Birbilis, Y. Estrin, Adv. Eng. Mater. 10, 6 (2008): p. 579-582.

[6] C. Op't Hoog, N. Birbilis, M.-X. Zhang, Y. Estrin, Key Eng. Mater. 384 (2008): p. 229-240.

[7] G.B.Hamu, D.Eliezer, L.Wagner, J. Alloys Comp. 468 (2009): p. 222-229

[8] E.Kus, Z.Lee, S.Nutt, F.Mansfeld, Corrosion 62, 2 (2006): p. 152-161.

[9] M.-K.Chung, Y.-S.Choi, J.-G. Kim, Y.-M. Kim, J.-C.Lee, Mater. Sci. Eng. A 366, (2004): p. 282-291.

[10] E.Sikora, X.J.Wei, B.A.Shaw, Corrosion 60, 4 (2004): p. 387398.

[11] D.Song, A.B.Ma, J.-H.Jiang, P.H.Lin, D.H.Yang,Trans.Nonferrous Met. Soc. China 19 (2009): p. 1065-1070

[12] T.S.Mahmoud, J.Mech.Eng. Sci. 222 (2008): p. 1117-1123.

[13] W.R.Osorio, C.M.Freire, A.Garcia, Mater. Sci. Eng. A 402 (2005): p. 22-32.

[14] X. Liu,G.S.Frankel, Corros. Sci. 48 (2006): p. 3309-3329.

[15] S.G.Wang, C.B.Shen, K.Long, H.Y.Yang, F.H.Wang, Z.D.Zhang, J.Phys. Chem. B 109 (2005): p. 2499-2503.

[16] V.Afshari, C. Dehghanian, Corros. Sci. 51 (2009): p. 1844-1849.

[17] X.Y.Wang, D.Y.Li, Wear 255 (2003): p. 836-845

[18] W.Zeiger, M.Schneider, D. Scharnweber, H.Worch, Nanostruct. Mater. 6 (1995): p. 1013-1016

[19] X.Y.Wang, D.Y.Li, Electrochim, Acta 47(2002): p. 3939-3947

[21] A.D.Schino, J.M.Kenny, J.Mater. Sci. Lett. 21 (2002): p. 19691971

[22] A.D.Schino, M.Barteri, J.M.Kenny, J. Mater. Sci. 38 (2003): p. 3257-3262

[23] L.Wang, Y.Lin, Z.Zeng, W.Liu, Q.Xue, L.Hu, J. Zhang, Electrochim. Acta 52 (2007): p. 4342-4350

[24] J.W.Schultze, B.Davepon, F.Karman, C.Rosenkranz, A.Schreiber, O.Voigt, Corros. Eng., Sci. Technol. 39, 1 (2004): p. 4552.

[25] S.Lee, H.S.White, J.Electrochem. Soc. 151, 8 (2004): p. B479B483

[26] D.Cheng, V.L.Tellkamp, C.J.Lavernia, E.J.Lavernia, Ann. Biomed. Eng. 29 (2001): p. 803-809

[27] G.Ben-Hamu, D.Eliezer, K.S.Shin, S.Cohen, J.Alloys Compd. 431 (2007): p. 269-276

[28] Y.H.Jang, S.S.Kim, C.D.Yim, C.G.Lee, S.J.Kim, Corros. Eng., Sci. Technol. 42, 2 (2007): p. 119-122

[29] G.Song, A.Atrens, M.Dargusch, Corros. Sci. 41 (1999): p. 249273.