Formation of Micro/Nano Pits with High Catalytic Activity
on Fe$_{80}$B$_{20}$ Amorphous Alloy

X.H. Zhang[1, 2], Yuqiao Zeng[1], L. Yin[1], J.Q. Jiang[1], Y. Pan[1], Rui Li[2],

L. Liu[3], T. Li[4], K. C. Chan [2*]

1) Jiangsu Key Laboratory of Advanced Metallic Materials, School of Materials Science and

    Engineering, Southeast University, Nanjing 211189, China,

2) Advanced Manufacturing Technology Research Centre, Department of Industrial and Systems

    Engineering, The Hong Kong Polytechnic University, Hong Kong

3) State Key Lab for Materials Processing and Die & Mould Technology, School of Materials

    Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074,

    China

4) School of Chemistry and Chemical Engineering, Huazhong University of Science and

    Technology, Wuhan 430074, China

* Corresponding author

Abstract

In this work, micro/nano size pits were introduced to the surface of Fe$_{80}$B$_{20}$ amorphous ribbons by electrochemical etching treatment with the aim of increasing the catalytic activity for the degradation of Azo dye. The results show that the size of the pits is more sensitive to the applied etching potential rather than the etching time while the pit homogeneity is time dependent. The etching treatment at -0.30 volt (vs saturated calomel electrode) for three hours in 1M HCl solution saturated by KCl leads to the formation of numerous pits with an average diameter of 222 nm on the surface of the Fe$_{80}$B$_{20}$ amorphous ribbons. The large amount of pits provides more sites for both catalytic reaction and the formation of H$_2$O$_2$ under ultrasound and thus results in higher degradation efficiency on Direct Blue 15 when compared with the as-spun amorphous alloy.

Keywords: Amorphous alloy; Direct Blue 15; Pitting; Porous; Catalytic activity;

1. Introduction

Amorphous alloys have attracted great attention in many fields due to their unique mechanical and chemical properties, such as low Young's modulus, high yield strength and good corrosion resistance [1-4]. Amorphous alloys are also good catalysts. For instance, the amorphous $Fe_{40}Ni_{40}P_{16}B_4$ alloy was found to be able to catalyze hydrogenation of CO as early as in 1980 [5]. More recently, Fe-based amorphous alloys were found to be an ideal choice for wastewater treatment at ambient temperature because of its high catalytic activity towards the degradation of organic chemicals. Wang *et al*. reported that when compared with conventional crystalline Fe powders, the $Fe_{73}Si_7 B_{17}Nb_3$ amorphous alloy was capable of decomposing the $C_{32}H_{20}N_6Na_4O_{14}S_4$ azo dye in aqueous solution 200 times faster [6]. In the study by Pan's Group, the $Fe_{78}Si_9B_{13}$ amorphous ribbon was adopted as a heterogeneous catalyst to degrade rhodamine B by a Fenton-like process. Complete degradation of rhodamine B with an initial concentration of 20 mg L^{-1} was achieved within 10 min by a small 0.5 g L^{-1} dosage of $Fe_{78}Si_9B_{13}$ amorphous catalyst [7]. Tang *el al* used a simpler $Fe_{84}B_{16}$ amorphous ribbon to degrade Direct Blue (DB) 6 and found that the surface area normalized reaction rate constant of the amorphous alloy was 1.8 times that of its crystalline alloy and 89 times that of 300 mesh Fe powders [8]. The high catalytic activity of the Fe-based amorphous alloys was attributed to their low activation energy for electron transfer [9].

Porous materials have high specific surfaces, which can provide more active sites for electron transfer, and thus usually exhibiting higher catalytic activity than corresponding bulk or even nanoparticle catalysts [10, 11]. Therefore, it is expected that a porous structure can further improve the catalytic activity of the Fe-based amorphous alloys. However, due to limited glass-forming ability, conventional fabrication methods for porous metals, such as foaming or powder firing can hardly be applied to Fe-based amorphous alloys. Recently, there have been several reports attempted to prepare porous Fe-based amorphous alloys by selective corrosion. For instance, Chan *et al*. chose an Nb-containing Fe-based alloy as a pre-alloy. Since Nb has more positive standard electrochemical potential and the remaining Fe-Si-B alloy has relatively high glass-forming ability, a porous amorphous Fe-based alloy was achieved by leaching Nb from the glassy alloy, and the leached alloy exhibited a much higher degration rate than the precursor amorphous alloy [12]. Dan *et al*. annealed a Cu-containing Fe-based amorphous alloy and achieved a composite alloy composed of nanocrystalline α-Fe particles and an amorphous

Fe-based matrix. They further applied dealloying on the composite precursor selectively leached the crystalline α-Fe phase from the more stable amorphous matrix, resulting in a porous amorphous structure [13]. Although porous surfaces can be obtained by the above methods, the precursor alloys require either a complex composition design or precise control of devitrification, besides tuning the corrosion process. Moreover, these methods can only be applied on quite limited Fe-based amorphous systems. For instance, the $Fe_{80}B_{20}$ alloy, which is a classical amorphous alloy, can hardly be transformed into a porous structure by the methods mentioned above. The glass-forming ability of the Fe-B system is quite limited. The complete selective dissolution of B will lead to crystallization. If the amorphous $Fe_{80}B_{20}$ alloy is annealed, α-Fe and Fe_3B will be precipitated simultaneously since its crystallization process is a eutectic reaction. Leaching crystalline α-Fe phase from stable amorphous matrix becomes impossible. In this work, we will show that even for the $Fe_{80}B_{20}$ amorphous alloy with simple chemical composition and low glass forming ability, porous surfaces can simply be obtained by tuning the pit morphology during pitting corrosion. Moreover, small pits can provide the amorphous alloys with higher catalytic activity.

Pitting is extremely localized corrosion which leads to the creation of small holes. Although the pioneering work of Naka *et al*. pointed out the superior corrosion resistance of several amorphous alloys compared with stainless steel [14], other studies regarding the corrosion behavior of amorphous alloys showed that pitting was still a common failure mode during corrosion, no matter in chemically simple Fe-B system [15] or more complex alloys such as ($Fe_{44.3}Cr_5Co_5Mo_{12.8}Mn_{11.2}$ $C_{15.8}B_{5.9})_{98.5}Y_{1.5}$ [16]. Even a single pit may lead to a serious engineering failure, so a considerable number of studies focused on the prevention of pit formation. For instance, elements like Cr, Mo Nb，Ni and P were introduced to amorphous alloys to improve the corrosion resistance [17-21]. There have also been some reports on the pitting formation process and mechanism in Fe-based amorphous alloys. The study of Gostin *et al*. [16] on the amorphous Fe-Cr-Co-Mo-Mn-C-B-Y alloy showed that during free corrosion in acid, the distribution of the pit size changes according to the corrosion duration. After 200 days exposure to a 0.5 M H_2SO_4 solution, pits with diameters ranging from about 200 nm to 12 um coexisted on the surface of the amorphous alloy. The wide distribution of the pit size was attributed to a progressive nucleation process. Ha *et al*. investigated the pit formation by TEM and found that during free corrosion, nano-sized Y-Mo-rich islands

preferentially dissolved and led to the formation of pores in Fe-Cr-Mo-C-B-Y amorphous alloys at an early corrosion stage [22]. However, not so much attention has been paid so far to control the pitting morphology, especially the pit size and pit homogeneity which might provide Fe-based alloys with higher catalytic activity. In this work, we used potentiostatic corrosion at different potentials for tuning the pit size. The applied potential far below the critical dealloying potential led to a dramatic decrease in the pit size from micrometers to 150-525 nanometers. The amorphous alloy with small pits exhibited higher catalytic activity towards the degradation of DB 15 solution than the as-prepared ribbons.

2. Experimental

The pre-alloy with a nominal atomic composition of $Fe_{80}B_{20}$ were prepared by induction melting a mixture of pure Fe and B in a highly purified argon atmosphere. The purity of the elements used in this study was higher than 99.9 at.%. Ribbon samples with a cross section of 0.02 mm x 2 mm were produced by single-roller melt spinning. The X-ray diffraction (XRD) analysis with Cu-K$_\alpha$ radiation confirmed the amorphous structure of the as-spun $Fe_{80}B_{20}$ alloys.

Amorphous ribbons with pits on the surface were prepared by electrochemical etching the as-spun samples in a standard three-electrode electrochemical cell in CHI 760D electrochemical workstation. The ribbons were used as the working electrode. The counter electrode was a Pt foil and the reference electrode was a saturated calomel electrode (SCE). All the potentials used in this work are referred to SCE. 1M HCl solution saturated by KCl was used as the etching electrolyte. The applied potential and duration were varied to tailor the porous structure. After etching, all samples were rinsed with distilled water and methyl alcohol to remove the electrolyte. The chemical compositions of the etched specimen were characterized by an energy dispersive X-ray spectrometer (EDS) and X-ray photoelectron spectroscopy (XPS). The microstructure was observed using scanning electron microscopy (SEM, FEI. Sirion 200).

The solutions for the degradation test were made by directly dissolving DB 15 solid reagent in deionized water, at a concentration of 200 mg/L. The well-washed and dried ribbon samples were immersed in the DB 15-containing solution as catalysts for the degradation and the dosage was kept at 0.222 m^2/L (about 12 g/L). About 5 mL of the solution was taken out at a time interval of 10 min during the degradation test, and UV-vis spectrum scanning with an excitation wavelength

of 598 nm was performed on these solutions. The DB 15 solution degradation rate (R) was calculated by $R=C_t/C_o$ (100%), where C_0 is the original DB 15 concentration and C_t is the DB 15 concentration at a given time, respectively.

3. Results and Discussion

3.1 Formation and characterization of the Fe$_{80}$B$_{20}$ amorphous alloy

The XRD patterns of the as-spun Fe$_{80}$B$_{20}$ ribbon specimen and the etched ribbons is shown in Figure.1. The ribbon exhibits a diffused halo peak centered at a 2θ of about 45 degrees. Sharp peaks corresponding to crystalline phases cannot be seen, demonstrating the formation of an amorphous structure in the as-spun Fe$_{80}$B$_{20}$ sample.

For a better understanding of the electrochemical properties of the Fe$_{80}$B$_{20}$ amorphous alloy, open potential measurement and a potentiodynamic polarization test were performed on the as-spun sample in a 1 M HCl solution saturated by KCl. The open potential was about -0.42 mV, similar to that of pure Fe (-0.43 mV) in the same electrolyte. The corrosion potential was determined to be 0.41 mV and the corresponding corrosion current density is 9.8×10^{-5} A/cm^{-2} (the inset of Figure.2). As can be seen in Figure 2, the active dissolution can be divided into two different regions. In the potential range of -0.42～-0.25 V, only a slight increase in the current density can be observed, i.e. from 0 to 5×10^{-4} A/cm^{-2}. Once the potential is higher than the critical dealloying potential [23] of -0.25 V, the current density rises rapidly without stable passivation, suggesting accelerated corrosion kinetics in this region.

3.2 Formation of micro/nano pits on Fe$_{80}$B$_{20}$ amorphous alloy

In the corrosion experiments, -0.10 V, -0.20 V, -0.25 V and -0.30 V were chosen as the applied etching potentials. The current density vs time curves of the potentiostatically etched Fe$_{80}$B$_{20}$ ribbons were recorded and are shown in Figure 3. The curves first experience a rapid rise within 5-30 s and then go into a steady state stage. The zoom-in view reveals that the currents in the steady stage are not smooth. Instead, they fluctuate and result in some transient features. As the etching potential shifts towards the negative side, the occurrence of the transient features becomes more frequent. Moreover, the characteristic parameters of the transient features vary according to the etching potential. For instance, the transient life time is about 160-200 s and the spike height is about 10^{-3}

A/cm^2 when the applied potential is -0.20 V. Once a more negative potential of -0.40 V is applied, the transient life time decreases down to 30-50 s and the spike height is only several 10^{-6} A/cm^2. The differences suggest the variation in pit numbers and sizes according to the applied etching potential. For the samples etched at -0.10 and -0.20 V, the ribbons become broken near the surface of the electrolyte after a period of corrosion, leading to a sudden drop in the current density. The broken samples are grey on the surface while the fracture plane has a metallic luster. For the samples etched at -0.25 V and -0.30 V, the ribbons remain intact in the electrolyte, even after 3600 s of corrosion, except that the surfaces turn black.

The detailed surface morphologies of the etched samples were observed using SEM and the images are shown in Figure 4. The specimen etched at -0.10 V exhibits a rough surface with thick deposits. The EDS analysis demonstrates a high O content. Beneath the oxides layer, there are some pit-like shallow pores. Most of the pores are about 1-2 um in diameter. There are also a few which have much smaller diameter of about 300-500 nm. The samples etched at -0.20 V and -0.25 V exhibit similar morphologies as that etched at -0.10 V except that the oxides layer in these two samples seems much thinner. When -0.35 V is applied, the sample becomes highly porous with numerous pits of diameters 150-850 nm dispersed on the surface. The dramatic decrease in pit size demonstrates different kinetics in pitting corrosion. It has been reported that in acid solutions, corrosion starts from the local depletion of B in the amorphous $Fe_{80}B_{20}$ system since B is higher in the activity series and has a much lower standard electrode potential compared to Fe (B/H_3BO_3: E = -1.15 V, Fe/Fe^{2+}: E= 0.72 V). B becomes oxidized by forming oxides hydrate at rates growing exponentially with the electrode potential, while in the acid solution with high Cl$^-$ concentration, Fe atoms are oxidized by forming Fe^{2+}. Thus, the following discussion may help to explain the dependence of pit size on etching potential. At a potential above -0.20 V, when B is preferentially dissolved by the solution, the Fe atoms nearby will also be rapidly attacked since the applied potential provides a sufficient overpotential. The dissolution of a large number of Fe atoms further improves the oxidation rate of the B atoms which lose their coordinating atoms. Therefore pits with large cap size can form at the initial stage of the corrosion. Due to the rapid oxidation rate of B, the local concentration of BO_3^{3-} along the solid-liquid interface is quite high and the dissolution speed of the newly formed boric acid hydrate is delayed. A thick B oxide layer will then cover the surface of the pits. In this case, the steady state dissolution rate will be determined by the flux of B

to the surface and the growth rate of the pits will be similarly slow. In the condition of etching at -0.30 V，although B can be depleted quickly, the overpotential for dissolving Fe is much lower. Only a few Fe atoms which lose their coordinating bonding might be attracted. Therefore much smaller pits are formed. Meanwhile, since the oxidation rate of B is far below that etched at -0.25--0.10 V, thick B oxides layer may not remain and cover the newly exposed surfaces and the steady state dissolution rate will be determined by the dissolution rate of Fe.

The O content of the samples etched at different potentials is measured by EDS. For the samples etched at -0.10 V, -0.20 V, -0.25 V and -0.30 V, the atomic concentrations of O (O/(O+Fe)) are 24%，23%, 11% and 8%, respectively. It can be seen that even though the corrosion time is much longer, the samples etched at more negative potentials have lower O content, agreeing with the supposed model described above.

3.3 Further tuning of the small pits on $Fe_{80}B_{20}$ amorphous alloy

In general, smaller pores and higher porosity benefit catalytic activity. Therefore, the amorphous $Fe_{80}B_{20}$ ribbon was etched at -0.30 V for different durations for further tuning of the pit size. Figure 5 (a) and (b) displays the SEM images of the samples etched for 1 h and 3 h. At first glance, there are no distinct morphology changes, and the surface contains a great number of nano pits and is highly porous. However, the histograms of the scaled probability density of the pit diameters (pit sizes) in Figure 5 (c) and (d) reveals some differences. In these figures, the pit diameters were determined by counting the diameters of the darker circles on the sample surface. For the sample etched for 1 h, the two-dimensional data set contains 1295 pits (supporting fig.1 (a)), and for the one etched for 3 h, it has 1633 pits (supporting fig.1 (b)). The pit size distribution in both samples is found to follow a Gaussian distribution. Apparently，the ribbon which experiences shorter etching time has a wider distribution range (125-875 nm) than that etched for longer time (125-525 nm). The average pit diameter was determined to be 250 nm for the ribbon etched for 1 h and 222 nm for that etched for 3 h, respectively. The differences in the pit size distribution and the average pit diameter may be related to the geometric and chemical inhomogeneity of the ribbon surface. The as-spun ribbons are not smooth on the surface, especially on the side in contact with the copper roller. There are lots of irregular humps and caves of different sizes. The edges of these areas can be more easily oxidized than in the even areas

during cooling or storage, resulting in chemical inhomogeneity on the ribbon surface before etching. Due to the varied size of the inhomogeneous chemical locations, the nucleation and growth rate of the pits will be uneven on the sample surface. A wide pit size distribution may thus be observed when a shorter etching time is applied. With the etching time extended, more internal places are exposed. These areas contain much fewer oxides, as shown in Figure 6(a). Since pure amorphous alloys always have a homogeneous composition and structure down to the subnanoscale, homogenous nucleation is the dominant nucleation pathway for pit formation when the corrosion extends to the inner sides of the ribbons. Further, the growth rate is more potential sensitive as compared to chemical inhomogeneity. Thus the newly formed pits should be more homogenous than those formed at the sample surface. Moreover, the continuous formation of the homogenous small pits between and on the walls of the already-formed pits will make some of big pits collapse. Therefore, it looks like that the big pits disappear as the etching time is extended and the porous structure is refined.

XPS analyses were performed on the as-corroded samples to determine the chemical composition of the porous structure and to estimate the corrosion depth. The as-spun ribbon is included for comparison. The peaks of the Fe, B and O elements were considered and the relative peak areas of these elements were measured during sputtering. The concentration-depth profiles obtained are shown in Figure 6 (a-c). For the as-spun samples, the O content is about 43 at% in the outmost layer and the Fe/B atomic ratio is about 8. When sputtered for 400 s, corresponding to a depth of approximately 12 nm, the sample has an O concentration lower than 2 at%, demonstrating that there are some oxides on the surface of the as-spun ribbon that are rich in Fe. For the sample etched for 1 h, the outmost layer contains about 40 at% of Fe, 9 at% of B and 51 at% of O. The O concentration becomes lower than 3% after 1000 s of sputtering, suggesting that the corrosion depth is about 30 nm. In the case of the ribbon etched for 3 h, the outmost layer has about 24 at% of Fe, 8 at% of B and 68 of O. The Fe/B atomic ratio (about 3) there is much lower than that (about 4) in the outmost layer of the sample etched for 1h, suggesting that dissolution of Fe element is the dominant reaction in the steady state. After sputtering for 1600 s, the sample still has an O content higher than 20 at%, demonstrating that the pits penetrate towards the inner side of the ribbon and the corroded depth is larger than 50 nm. The deeper pits might provide the sample with higher specific area and better catalytic performance.

As evidenced from the XPS results, the etched ribbons experienced severe corrosion. XRD measurements were performed on the sample etched at -0.30 V for 1h and 3 h. The results as shown in Figure illustrate that the etched samples exhibit similar diffraction patterns as the as-spun ribbon, a diffused halo peaks centering at 2 of about 45^0 without any sharp peaks corresponding to crystalline phases. It demonstrates that the etched samples are still amorphous.

3.4 Formation of micro/nano pits on other Fe-based amorphous alloys

It should be emphasized that the etching method presented here is easily applicable to other Fe-based amorphous alloys for fabricating highly porous surfaces. Figure 7 illustrates two more examples. Using the same three electrode setup, multicomponent Fe-Co-B and Fe-Si-B amorphous alloys were etched at -0.35 V. As a result, highly porous surfaces with a large number of micro/nano pits were obtained.

3.5 High Catalytic activity of the pits

The DB 15 degradation test was firstly done without an ultrasonic setup. The $Fe_{80}B_{20}$ ribbons etched at -0.30 V for one hour and three hours as well as the as-spun sample were used as the catalysts. The inset in Figure 8 (a) shows a typical UV-vis spectra development as a function of the degradation time, where the sample etched for three hours is used as the catalyst. The original DB 15 solution has a strong absorption peak at 599 nm and the intensity of the peak becomes weaker during the degradation treatment. The DB 15 solutions treated by other samples have similar UV-vis spectra development with degradation time. Based on the UV-vis results, the parameter C_t/C_o, where C_o is the original Direct Blue 15 concentration and C_t is the Direct Blue 15 concentration at a given time was calculated and is summarized in Figure 8 (a). The as-spun ribbon sample exhibits a relatively low catalytic activity towards the degradation of DB 15 when compared with that reported by Chen *et al*. The reasons may lie in the fact that a smaller dosage was used, and there were no agitated tank and filter in our set-up. After 50 min, the degradation rate (100%- $C_t/C_o \times 100\%$) was 24%. The solutions with the other two etched catalysts showed a higher degradation rate of 32% (etched for 1 h) and 34% (etched for 3 h), respectively. The slight improvement of degradation rate may be related to the larger surface area caused by the pits.

The DB15 degradation test was conducted in an ultrasonic setup. Figure 8 (b) shows the DB

degradation rate as a function of the degradation time. When compared with the degradation undertaken without using an ultrasonic setup, the degradation speed is improved in this experiment. Moreover, the difference in catalytic activity between the ribbons with and without pits is much more notable. After 50 mins of treatment, the degradation rate is only about 38% for the as-spun ribbon catalyst, but 54% for the catalyst etched at -0.3 V for one hour and 67 % for the catalyst etched at -0.30 V for three hours, respectively. The much higher degradation rate of the etched samples is attributed to the numerous micro/nano pits. These pits can provide more sites for both catalytic reaction and the formation of H_2O_2 in solution and thus result in a high efficiency towards the degradation of Direct Blue 15. However, more work is needed to fully understand the mechanisms of catalytic activity improvement related to the pits.

The reusability of the porous ribbon was also evaluated by a degradation-cycle test. In the test, the alloy etched at -0.30 V for 3 h was used as the catalyst under an ultrasound setup. Co and the catalyst dosage were kept the same as described in the degradation test shown above. In each cycle, the C_t/C_o parameter was recorded after 50 min of degradation. Figure 9 shows $C_{50\,min}/C_o$ as a function of the degradation cycles. It can be seen that although the $C_{50\,min}/C_o$ parameter fluctuates, the degradation rates of the porous sample are still far below than that of the as-spun ribbon. After the 10th cycle, the degradation rate of the porous sample (35%) is comparable with that of the 1th cycle (32 %). These results demonstrate that the porous sample is highly reusable. The reason for the fluctuation of $C_{50\,min}/C_o$ might be attributed to the change of the porous surface state. On one side, the degradation will cause the formation of complex oxides on the alloy surface, which reduces the catalytically active area. On the other side, the oxides might be stripped away by the ultrasound, and thus more active sites can be exposed. The changes of the catalyst surface morphology was found to be in agreement with the $C_{50\,min}/C_o$ fluctuation. Insert (a) of Figure 9 reveals the surface morphology of the porous catalyst used for degradation beforer the 2th cycle. It displays an irregular surface morphology, and loose island-like oxidation products cover part of the pits. Insert (b) of Figure 9 shows the surface morphology of the catalyst used before the 10th cycle. It is clear that more pores are exposed on the surface and the degradation rate is higher than that in the 2th cycle.

4 Conclusions

When the $Fe_{80}B_{20}$ amorphous ribbons are potentiostatically etched, the applied potential at or higher than the critical dealloying potential leads to the formation of inhomogeneous pits in micrometer level. When the alloy is etched at a potential far below the critical dealloying potential, a highly porous surface can be obtained by forming a large number of micro/nano pits with diameters ranging within 150-850 nm. The extending of the etching time from 1 to 3 h can further refine the porous structure. The $Fe_{80}B_{20}$ amorphous ribbons with a refined porous surface exhibit much higher catalytic activity towards the degradation of DB 15 when compared with the as-spun alloy.

5 Acknowledgements

References:

[1] A.L. Greer, Metallic glass, Science 267 (1995) 1947-1953.

[2] A. Inoue, Stabilization of metallic supercooled liquid and bulk amorphous alloys, Acta Mater. 48 (2000) 279-306.

[3] W.H. Wang, Bulk metallic glasses with functional physical properties, Adv. Mater. 21 (2009) 4524-4544.

[4] W.L. Johnson, Bulk glass-forming metallic alloys: Science and technology, Mrs. Bull. 24 (1999) 42-56.

[5] H. Komiyama, A. Yokoyama, H. Inoue, T. Masumoto and H. Kimura, Sci Rep. Res. Inst. Tohoku Uniu. Ser. A, 1980, 28, 217

[6] J. Wang, Y. Liu, M. Chen, G. Xie, D.V. Louzguine-Luzgin, A. Inoue, J.H. Perepezko, Rapid degradation of azo dye by Fe-Based metallic glass powder, Adv. Funct. Mater. 22 (2012) 2567-2570.

[7] X. Wang, Y. Pan, Z. Zhu, J. Wu, Efficient degradation of rhodamine B using Fe-based metallic glass catalyst by Fenton-like process, Chemosphere 117 (2014) 638-643.

[8] Y. Tang, Y. Shao, N. Chen, K. Yao, Rapid decomposition of Direct Blue 6 in neutral solution by

Fe-B amorphous alloys, Rsc. Adv. 5 (2015) 6215-6221.

[9] S. Das, V. Bandi, H.S. Arora, M. Veligatla, S. Garrison, F. D'Souza, S. Mukherjee, Synergistic catalytic effect of iron metallic glass particles in direct blue dye degradation, J. Mater. Res. 30 (2015) 1121-1127.

[10] T. Fujita, P. Guan, K. McKenna, X. Lang, A. Hirata, L. Zhang, T. Tokunaga, S. Arai, Y. Yamamoto, N. Tanaka, Y. Ishikawa, N. Asao, Y. Yamamoto, J. Erlebacher, M. Chen, Atomic origins of the high catalytic activity of nanoporous gold, Nat. Mater. 11 (2012) 775-780.

[11] Y. Zeng, S. Yang, H. Xiang, X. Dong, L. Chen, M. Chen, A. Inoue, X. Zhang, J. Jiang, Multicomponent nanoporous metals prepared by dealloying Pd80-xNixP20 metallic glasses, Intermetallics 61 (2015) 66-71.

[12] Z. Deng, X.H. Zhang, K.C. Chan, L. Liu, T. Li, Fe-based metallic glass catalyst with nanoporous surface for azo dye degradation, Cheosphere 174 (2017) 76-81.

[13] C. Fu, L. Xu, Z. Dan, A. Makino, N. Hara, F. Qin, H. Chang, Structural Inheritance and Redox Performance of Nanoporous Electrodes from Nanocrystalline $Fe_{85.2}B_{10-14}P_{0-4}Cu_{0.8}$ Alloys., Nanomaterials 7 (2017).

[14] M. Naka, K. Hashimoto, T. Masumoto, Corrosion resistivity of amorphous iron alloys containing chromium, J. Jpn. Inst. Metals. 38 (1974) 835-841.

[15] M. Wislawska, M. Janik-czachor, Effect of heat treatment on corrosion behaviour of Fe80B20 glassy alloys, British Corrosion Journal 20 (1985) 36-40.

[16] P.F. Gostin, S. Oswald, L. Schultz, A. Gebert, Acid corrosion process of Fe-based bulk metallic glass, Corros. Sci. 62 (2012) 112-121.

[17] C. Souza, M.F. de Oliveira, J.E. May, W.J. Botta, N.A. Mariano, S.E. Kuri, C.S. Kiminami, Corrosion resistance of amorphous and nanocrystalline Fe-M-B (M=Zr, Nb) alloys, J. Non-Cryst. Solids 273 (2000) 282-288.

[18] K. Hashimoto, 2002 W.R. Whitney Award Lecture: In pursuit of new corrosion-resistant alloys, Corrosion 58 (2002) 715-722.

[19] Z.L. Long, C.T. Chang, Y.H. Ding, Y. Shao, P. Zhang, B.L. Shen, A. Inoue, Corrosion behavior of Fe-based ferromagnetic (Fe, Ni)-B-Si-Nb bulk glassy alloys in aqueous electrolytes, J. Non-Cryst. Solids 354 (2008) 4609-4613.

[20] W.J. Botta, J.E. Berger, C.S. Kiminami, V. Roche, R.P. Nogueira, C. Bolfarini, Corrosion

resistance of Fe-based amorphous alloys, J. Alloy Compd. 5861 (2014) S105-S110.

[21] K. Asami, S.J. Pang, T. Zhang, A. Inoue, Preparation and corrosion resistance of Fe-Cr-Mo-C-B-P bulk glassy alloys, J. Electrochem Soc. 149 (2002) B366-B369.

[22] H.M. Ha, J.R. Miller, J.H. Payer, Devitrification of Fe-Based Amorphous Metal SAM 1651 and the Effect of Heat-Treatment on Corrosion Behavior, J. Electrochem Soc. 156 (2009) C246-C252.

[23] K. Sieradzki, N. Dimitrov, D. Movrin, C. McCall, N. Vasiljevic, J. Erlebacher, The dealloying critical potential, J. Electrochem Soc. 149 (2002) B370-B377.

Figure capitals:

Figure 1: XRD pattern of the as-spun $Fe_{80}B_{20}$ ribbon and the ribbons etched at -0.30 V for 1 h and 3 h .

Figure 2: Liner sweep voltammetry of the as-spun $Fe_{80}B_{20}$ ribbon in 1 M HCl solution saturated by KCl, 0.01 V/s. The inset is the Tafel curve of the same sample measured under the same condition as the liner sweep voltammetry curve.

Figure 3: The current density *vs* time curves of the potentiostatically etched $Fe_{80}B_{20}$ ribbons .

Figure 4: Surface SEM images of the $Fe_{80}B_{20}$ ribbon etched at -0.10 V(a), -0.20 V (b), -0.25 V (c) and -0.30 V (d).

Figure 5: Surface SEM images of the $Fe_{80}B_{20}$ ribbon etched at -0.30 V for 1 h (a) and 3 h(b); histograms of scaled probability density of the pit diameters of the $Fe_{80}B_{20}$ ribbon etched at -0.30 V for 1 h (c) and 3 h(d).

Figure 6: Concentration-depth profiles of the as-spun $Fe_{80}B_{20}$ ribbon (a) and $Fe_{80}B_{20}$ ribbons etched at -0.30 V for 1 h (b) and 3 h (c), measured by XPS.

Figure 7: Surface SEM images of the Fe-Co-B (a) and Fe-Si-B (b) ribbons etched at -0.35 V for 1h.

Figure 8: The degradation curves without (a) and with (b) ultrasonic setup. The inset in (a) is UV-vis absorption spectra of Direct Blue 15 degraded by the $Fe_{80}B_{20}$ ribbon etched at -0.30 V for 3 h.

Figure 9: Degradation-cycle curve for the Fe80B20 ribbon ribbon etched at -0.30 V for 3 h.   The inserts are the SEM images of the catalyst surface before the 2th cycle (a) and before the 10th cycle (b), respectively.