



Effects of cobalt content on the decolorization properties of Fe-Si-B amorphous alloys

Changqin Zhang^{a,*}, Zhengwang Zhu^b, Haifeng Zhang^b, Qilei Sun^a, Kegao Liu^a

^a School of Materials Science and Engineering, Shandong Jianzhu University, Jinan 250101, China

^b Shenyang National Laboratory for Materials Science, Chinese Academy of Sciences, Shenyang 110016, China

ARTICLE INFO

Article history:

Received 19 January 2018

Received in revised form 20 February 2018

Accepted 21 February 2018

Available online 24 February 2018

Keywords:

Fe-based amorphous alloys

Cobalt content

Decolorization properties

Azo dyes

ABSTRACT

This research attempts to study the effects of Co addition on the decolorization properties of Fe-Si-B amorphous alloys. It was found that Fe-Co-Si-B glassy ribbons (GRs) with different cobalt contents could all decolorize acid orange II (AO) solution through adsorption or reductive degradation no matter at lower or higher temperatures. When Co content was low (10 at.%), Fe-Co-Si-B GRs showed similar decolorization properties to those of Fe-Si-B GRs. With the increase of Co content, reductive degradation of AO by the GRs was not detected basically at lower temperature, and Fe-Co-Si-B GRs could decolorize AO solution only through adsorption; at higher temperature, reductive degradation contributed a lot to the decolorization of AO solution, but adsorption effects still played an important role in the decolorization process. The higher the Co content in the glassy ribbons, the more prominent the adsorption effects, and the more time required to activate reductive degradation of dye molecules. The effects of Co addition on the decolorization properties of Fe-Si-B amorphous alloys are considered to be attributed to the compound effects of zero-valent iron atoms and zero-valent cobalt atoms in the GRs.

© 2018 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Introduction

In the past few years, Fe-based amorphous alloys have been widely investigated as a kind of environmental-friendly materials for wastewater treatment due to their great advantages in degrading azo dyes and other organic pollutants [1–10]. It is generally recognized that the efficient decolorization of azo dyes can be attributed to the amorphous nature, the unique electronic structure of zero-valent iron and the incompact surface structure of amorphous alloys [1–3,11]. It is well known that the addition of alloying elements in parent amorphous alloys has remarkable influences on their various properties. In our previous work [5], it was found that the observed activation energy of the decolorization process by Fe₆₈Co₁₀Si₈B₁₄ glassy ribbons (GRs) in the temperature range of 25 °C–50 °C (18.4 kJ/mol) was lower than that by Fe₇₈Si₈B₁₄ GRs (27.9 kJ/mol). That is to say, from the perspective of thermodynamics, appropriate Co addition is beneficial to the decolorization reaction. Moreover, Co-based (Fe-free) amorphous alloys were also reported to have desirable effects on decolorizing acid orange II (AO) solution [12]. In this paper, four kinds of Fe-Co-Si-B GRs with different Co contents were prepared by

melt-spinning technique, and their decolorization properties were investigated at lower and higher temperatures. On this basis, the differences of their decolorization properties were compared and the decolorization mechanism of these alloys was discussed briefly.

Experimental

Alloy ingots with nominal atomic compositions of Fe₆₈Co₁₀Si₈B₁₄ (Co₁₀), Fe₆₃Co₁₅Si₈B₁₄ (Co₁₅), Fe₅₈Co₂₀Si₈B₁₄ (Co₂₀) and Fe₅₃Co₂₅Si₈B₁₄ (Co₂₅) were produced respectively by arc-melting the raw materials under a Ti-gettered Ar-atmosphere. The purities of Fe, Co, Si and B were all higher than 99.9%. GRs with a width of ~2 mm and a thickness of 30–40 μm were then prepared by roller spinning melts under an Ar-atmosphere. The ribbons were cut into pieces of 2 × 10 mm² for subsequent decolorization. The structure of the ribbons was examined by X-ray Diffraction (XRD) with a Cu-Kα radiation. AO powder (wt.% ≥ 99.9%) was dissolved in distilled water to get aqueous solution of 100 mg/L. Ribbons with nominal surface area of 15,000 mm² were added in a beaker containing 180 mL solution, to ensure the same surface area concentration (8.3 × 10⁻² m² L⁻¹) for the decolorization process by different GRs. The beaker was placed in a constant temperature water-bath trough at scheduled temperatures, and mechanical agitation of

* Corresponding author.

E-mail address: zhangcq@alum.imr.ac.cn (C. Zhang).

200 r/min was executed in the beaker during reaction process. About 5 mL solution was taken from the beaker at scheduled intervals, and the UV-vis spectrum scanning from 200 to 600 nm was recorded using a UV-vis spectrophotometer after filtered through 0.45 μm membrane filter.

Results

Fig. 1 shows the XRD patterns of $\text{Fe}_{78-x}\text{Co}_x\text{Si}_8\text{B}_{14}$ ($x = 10, 15, 20, 25$) ribbons. As can be seen, the XRD patterns of these ribbons all show a single diffuse peak without any diffraction peaks, which means that the amorphous structure of $\text{Fe}_{78}\text{Si}_8\text{B}_{14}$ alloy is well retained after Co addition.

Fig. 2 (a) and (b) present the UV-vis spectra of AO solution reacting with $\text{Fe}_{78-x}\text{Co}_x\text{Si}_8\text{B}_{14}$ ($x = 10, 15, 20, 25$) ribbons for different times at 25 °C and 50 °C. The strong absorbance peak at $\lambda_{\text{max}} = 484$ nm in the visible region originates from a conjugated structure formed by azo bonds, the intensity of which denotes the dye concentration in the solution [13]. It can be seen that, at both temperatures, the bands at λ_{max} become weaker with the reaction time, revealing the concentration decrease of AO in the solution.

At 25 °C, in the primary stage (the first five minutes) of the decolorization process by these four kinds of GRs, all absorbance peaks become weaker, but no new peaks appear in the UV-vis spectra. This demonstrates that no new products come into the solution. However, with the proceeding of the decolorization process, the appearance of the absorbance peak at ~ 246 nm, corresponding to the $-\text{NH}_2$ groups [13], can be observed in the UV-vis spectrum after reacting for 30 min by Co_{10} ribbons, whereas no noticeable peaks are detected even after reacting for 60 min by Co_{15} , Co_{20} and Co_{25} ribbons. These results demonstrate that reductive degradation of AO in the solution can be readily induced at lower temperature when the Co content is lower (10 at.%), but cannot be activated even after reacting for 60 min when the Co content is higher.

For the decolorization reaction at 50 °C, an obvious absorbance peak appears at ~ 246 nm after reacting for 5 min by Co_{10} and Co_{15} ribbons, indicating that reductive degradation of AO occurs after primary adsorption; after reacting for 15 min by Co_{10} and Co_{15} ribbons, the intensity of the absorbance peak at ~ 246 nm becomes very strong and the absorbance peak at $\lambda_{\text{max}} = 484$ nm cannot be detected, which indicates that most dye molecules adsorbed by the ribbons can be degraded to form aniline compounds. With the increase of Co content, for the decolorization pro-

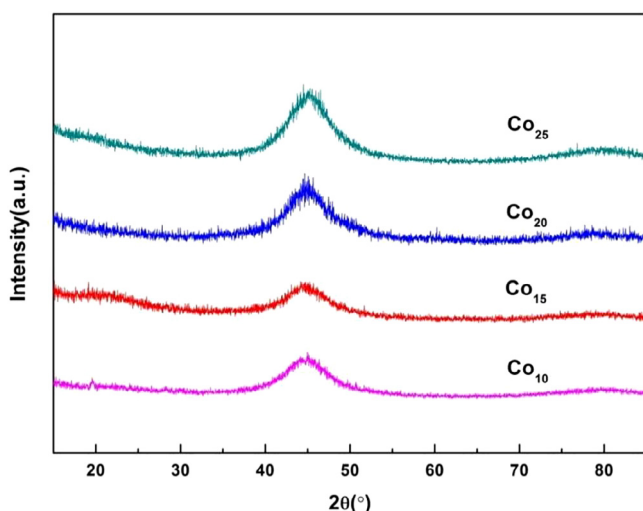


Fig. 1. XRD patterns of $\text{Fe}_{78-x}\text{Co}_x\text{Si}_8\text{B}_{14}$ ($x = 10, 15, 20, 25$) ribbons.

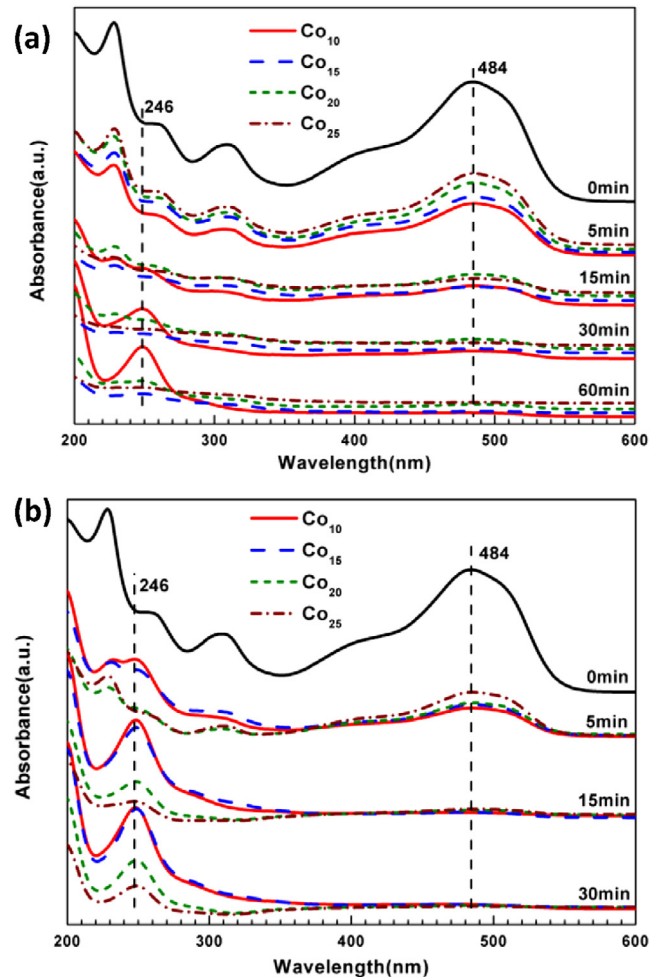


Fig. 2. UV-vis spectra of AO solution reacting with $\text{Fe}_{78-x}\text{Co}_x\text{Si}_8\text{B}_{14}$ ($x = 10, 15, 20, 25$) ribbons for different times at (a) 25 °C and (b) 50 °C.

cess by Co_{20} and Co_{25} ribbons, although the absorbance peak at $\lambda_{\text{max}} = 484$ nm has disappeared after reacting for 15 min, the absorbance peak at ~ 246 nm can just be detected and the peak intensity is relatively weak. On the whole, the decolorization process by the ribbons with higher Co content lags behind that by the ribbons with lower Co content. These results indicate that reductive degradation of AO by Co_{20} and Co_{25} ribbons can be induced after reacting for appropriate time at higher temperatures.

To sum up, lower Co content and higher reaction temperature can promote reductive degradation of AO molecules. With the increase of Co content, it becomes more difficult to activate the reductive degradation of AO molecules, and adsorption effects play a more important role in decolorizing AO solution.

Discussion

Co addition has significant influences on the decolorization properties of Fe-Si-B amorphous alloys. After Co addition, the amorphous nature of the alloys is retained. Co_{10} GRs show good decolorization effects (including adsorption effects and reductive degradation) on the dye solution at both low (25 °C) and high (50 °C) temperatures, but the decolorization process lags behind that by $\text{Fe}_{78}\text{Si}_8\text{B}_{14}$ GRs under the same reaction conditions [5]. With the increase of Co content, Fe-Co-Si-B GRs gradually lose the ability of degrading dye molecules, but just adsorb dye molecules at low temperature; at high temperature, although the

Fe-Co-Si-B GRs can decolorize the dye solution through both adsorption and reductive degradation, the decolorization process by Fe-Co-Si-B GRs with higher Co content significantly lags behind that by Fe-Co-Si-B GRs with lower Co content. In the decolorization process of azo dyes, Fe-based amorphous alloys have two roles. Firstly, the zero-valent iron is used as a reaction participant to promote the production of hydrogen from water for degrading the azo bonds [1,2,14,15]. Secondly, the amorphous structure can activate the formed hydrogen and catalytically promote the reductive hydrogenation of oxidative pollutants [1–3,7,16]. Thus, the decolorization ability decay can be partially attributed to the relatively lower Fe content in Fe-Co-Si-B GRs with the increase of Co content, since Co fails to donate electrons for the degradation reaction. At lower temperature (25 °C), the diffusion of reactants controls the decolorization process and the reactive sites (adsorption sites) provided by Co₁₀ and Co₁₅ ribbons are enough for the decolorization reaction, so that the decolorization rates by Co₁₀ and Co₁₅ ribbons are close to those by Fe₇₈Si₈B₁₄ ribbons, although Co₁₀ and Co₁₅ ribbons have lower Fe content. However, with the increase of Co content, the reactive sites provided by Co₂₀ and Co₂₅ ribbons are not enough for the decolorization reaction, so that the decolorization process lags behind the decolorization process by Fe₇₈Si₈B₁₄, Co₁₀ and Co₁₅ ribbons. At higher temperature (50 °C), since chemical reactions are very sensitive to temperature, lower Fe content in Fe-Co-Si-B GRs means fewer reactive sites for the decolorization reaction. Consequently, the decolorization rates by Co₁₀ GRs are significantly lower than those by Fe₇₈Si₈B₁₄ glassy ribbons [15], and the decolorization process by Fe-Co-Si-B GRs with higher Co content lags behind those with lower Co content.

In this study, Fe-Co-Si-B GRs with different Co contents are used for the decolorization of the same dye solution under the same conditions, so the influences of diffusion or mass transfer on the decolorization mechanism can be ignored. In terms of the alloy constituent, Fe and Co both belong to transition metals and have almost-full or just-filled 3*d* band; Si and B both belongs to metalloid elements and can be viewed as solute constituents of the alloys, and they have the same atomic percentages in these three alloys. Hence, the differences in their decolorization properties can reasonably be attributed to the relative contents of Fe and Co. That is to say, the different characteristics of Fe and Co determine the different decolorization properties of Fe-Co-Si-B GRs with different Co contents.

During the adsorption of decolorization process, the adsorbate in the solution is the same for the four kinds of GRs, so the adsorption of dye molecules mainly depends on the electronic structure of the GRs [17,18]. Considering the similar physical properties of these GRs, van der Waals forces, coulombic effect and exchange forces between the alloys and dye molecules are similar. Hence, the discussion in this study mainly focuses on the localized bonding or covalent bonding. According to the energy band theory [19,20], valence electrons of metallic atoms are shared by all atoms to form an electron cloud that is in a highly shared state. As for Fe and Co, their valence electron configurations are 3*d*⁶4*s*² and 3*d*⁷4*s*² respectively. Magnetic data showed that there were averagely 2.2 and 1.7 holes in *d* band for per Fe atom and Co atom respectively [17,20]. The more the *d* band holes, the more the unpaired electrons. The unpaired electrons can form localized adsorption bond with the adsorbate molecules, so that more unpaired electrons mean stronger adsorption ability. In Fe-Co-Si-B GRs, since Si and B cannot provide *d* electrons or *d* holes, their influences on the adsorption of the alloys can be ignored or can be considered to be similar for the four alloys due to their same atomic percentages in the alloys. Hence, Co₁₀ ribbons show the highest adsorption rate in the first five minutes of the decolorization reaction due to the more *d* band holes per unit of atom, while Co₂₅ ribbons show the lowest adsorption rate. On the other hand, the standard oxidation

potential of Fe/Fe²⁺ (−0.44 V) is more negative than that of H⁺/H₂ while that of Co/Co²⁺ is higher than −0.34 V, so the electron transfer between Co and H⁺ is impossible under our experimental conditions from the perspective of thermodynamics [5]. Hence, the reductive degradation of AO mainly depends on the Fe content in the Fe-Co-Si-B ribbons. When Co content is higher, fewer reductive sites can be provided. At low temperature, the reductive degradation of AO cannot be activated, so Co₁₅, Co₂₀ and Co₂₅ ribbons only have adsorption effects on dye molecules. At high temperature, more reductive sites can be activated to induce the reductive degradation of AO molecules. As a result, Co₁₀, Co₁₅, Co₂₀ and Co₂₅ ribbons all have reductive effects on AO molecules, but the reductive degradation of AO molecules needs more time to be activated with the increase of Co content.

Conclusions

In summary, the effects of Co addition on the decolorization properties of Fe-Si-B amorphous alloys were studied in this paper. Co addition could retain the amorphous nature of the alloys, but different Co contents in Fe-Co-Si-B GRs led to different decolorization properties of the alloys. Co₁₀ GRs show similar decolorization properties as those of Fe₇₈Si₈B₁₄ GRs. When Co content is higher, Fe-Co-Si-B GRs can decolorize AO solution only through adsorption at lower temperature, whereas reductive degradation still contributes a lot to the decolorization of AO solution at higher temperature. With the increase of Co content, adsorption effects become more prominent, while reductive degradation of AO molecules needs more time to be activated. It is considered that the effects of Co addition on the decolorization properties of Fe-Si-B amorphous alloys can be attributed to the compound effects of zero-valent iron atoms and zero-valent cobalt atoms in Fe-Co-Si-B GRs.

Acknowledgements

The authors gratefully acknowledge the financial support from the Doctor Fund of Shandong Jianzhu University (Grant No. XNBS1429).

References

- [1] Zhang C, Zhang H, Lv M, Hu Z. Decolorization of azo dye solution by Fe–Mo–Si–B amorphous alloy. *J Non-Crystalline Solids* 2010;356:1703–6.
- [2] Wang J-Q, Liu Y-H, Chen M-W, Xie G-Q, Louzguine-Luzgin DV, Inoue A, Perepezko JH. Rapid degradation of Azo Dye by Fe-based metallic glass powder. *Adv Funct Mater* 2012;22:2567–70.
- [3] Tang Y, Shao Y, Chen N, Liu X, Chen SQ, Yao KF. Insight into the high reactivity of commercial Fe-Si-B amorphous zero-valent iron in degrading azo dye solutions. *Rsc Adv* 2015;5:34032–9.
- [4] Jia Z, Zhang WC, Wang WM, Habibi D, Zhang LC. Amorphous Fe₇₈Si₉B₁₃ alloy: An efficient and reusable photo-enhanced Fenton-like catalyst in degradation of cibacron brilliant red 3B-A dye under UV-vis light. *Appl Catal B-Environ* 2016;192:46–56.
- [5] Zhang C, Zhu Z, Zhang H. Effects of the addition of Co, Ni or Cr on the decolorization properties of Fe-Si-B amorphous alloys. *J Phys Chem Solids* 2017;110:152–60.
- [6] Zhang C, Sun Q. Annealing-induced different decolorization performances of Fe–Mo–Si–B amorphous alloys. *J Non-Cryst Solids* 2017;470:93–8.
- [7] Liu P, Zhang JL, Zha MQ, Shek CH. Synthesis of an Fe rich amorphous structure with a catalytic effect to rapidly decolorize Azo Dye at room temperature. *ACS Appl Mater Interfaces* 2014;6:5500–5.
- [8] Liang SX, Jia Z, Zhang WC, Li XF, Wang WM, Lin HC, Zhang LC. Ultrafast activation efficiency of three peroxides by Fe₇₈Si₉B₁₃ metallic glass under photo-enhanced catalytic oxidation: a comparative study. *Appl Catal B-Environ* 2018;221:108–18.
- [9] Jia Z, Kang J, Zhang WC, Wang WM, Yang C, Sun H, Habibi D, Zhang LC. Surface aging behaviour of Fe-based amorphous alloys as catalysts during heterogeneous photo Fenton-like process for water treatment. *Appl Catal B-Environ* 2017;204:537–47.
- [10] Jia Z, Duan X, Qin P, Zhang WC, Wang WM, Zhang LC. Disordered atomic packing structure of metallic glass: Toward ultrafast hydroxyl radicals production rate and strong electron transfer ability in catalytic performance. *Adv Funct Mater* 2017;27:1702258.

- [11] Tang Y, Shao Y, Chen N, Yao K-F. Rapid decomposition of Direct Blue 6 in neutral solution by Fe-B amorphous alloys. *Rsc Adv* 2015;5:6215–21.
- [12] Qin XD, Zhu ZW, Liu G, Fu HM, Zhang HW, Wang AM, Li H, Zhang HF. Ultrafast degradation of azo dyes catalyzed by cobalt-based metallic glass. *Sci Rep* 2015;5.
- [13] Cao J, Wei L, Huang Q, Wang L, Han S. Reducing degradation of azo dye by zero-valent iron in aqueous solution. *Chemosphere* 1999;38:565–71.
- [14] Nam S, Tratnyek PG. Reduction of azo dyes with zero-valent iron. *Water Res* 2000;34:1837–45.
- [15] Zhang C, Zhu Z, Zhang H, Hu Z. Rapid decolorization of Acid Orange II aqueous solution by amorphous zero-valent iron. *J Environ Sci* 2012;24:1021–6.
- [16] Liu Y, Choi H, Dionysiou D, Lowry GV. Trichloroethene hydrodechlorination in water by highly disordered monometallic nanoiron. *Chem Mater* 2005;17:5315–22.
- [17] Dowden DA. Heterogeneous catalysis. Part I. Theoretical basis. *Journal of the Chemical Society (Resumed)* 1950:242–65.
- [18] Brewster JH. Mechanisms of reductions at metal surfaces. I. A general working hypothesis. *J Am Chem Soc* 1954;76:6361–3.
- [19] Pauling L. The nature of the interatomic forces in metals. *Phys Rev* 1938;54:899–904.
- [20] Pauling L. A resonating-valence-bond theory of metals and intermetallic compounds. *Proc R Soc London Ser A Math Phys Sci* 1949;196:343–62.