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The influence of ingot annealing on the corrosion resistance of a PrFeCoBNbP alloy

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Abstract

The influence of the annealing time on the corrosion resistance of a Pr–Fe–Co–B–Nb alloy with the addition of 0.1 wt% P was investigated here using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The cast ingot alloys were annealed at 1100 °C for 10, 15 and 20 h. The specimens were immersed for 30 days in naturally aerated 0.02 M Na_2HPO_4 solution at room temperature, during which period the evolution of the electrochemical behavior was assessed using EIS. The results indicated that the corrosion resistance of the $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}P_{0.25}$ alloy was related to the annealing time and, hence, to its microstructure. Annealing at 1100 °C for 10 h was insufficient to eliminate the Fe-α phase from the alloy microstructure, whereas annealing for 15 and 20 h removed an increasing amount of Fe-α phase, thereby increasing the alloy's corrosion resistance.

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Keywords: Pr–Fe–B magnet; Corrosion; Electrochemical technique

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1. Introduction

Bonded magnet powders prepared by the hydrogenation, disproportionation, desorption and recombination (HDDR) process are highly coercive materials, which can be obtained by exposing rare earth-based alloys to hydrogen at elevated temperatures [1–3]. Several alloying elements, such as Cu and Al, have been tested to improve the magnetic and corrosion properties of Pr-based magnets [4]. Additions of phosphorus of up to 0.02 wt% have also been tested and have proved to increase the remanence of bound Pr-based HDDR magnets. Recently, it was also shown that the corrosion resistance of annealed PrFeCoBNb alloy may be influenced by the addition of phosphorus [5]. The corrosion improvement due to phosphorus in ferrous alloys has been associated to the formation of a phosphate compound that acts as corrosion inhibitor of these alloys. Results obtained in our laboratory suggested that the microstructure of phosphorus containing PrFeCoBNb alloy is very complex and it must affect its corrosion resistance. This study aimed to evaluate the effect of annealing time on the microstructure and corrosion resistance of $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}P_{0.25}$ alloy in a Na_2HPO_4 solution.

2. Experimental

The commercial $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}P_{0.25}$ (5 kg cast ingot) alloy was cut into small rectangular samples, which were then annealed under a vacuum atmosphere (10^{-4} and 10^{-5} mbar) at 1100 °C for 10, 15 and 20 h. The annealed samples were then welded to copper wire and embedded in epoxy resin, leaving an area of 1.5 cm^2 exposed to the electrolyte and ground with SiC up to #1200. The corrosion performance was evaluated by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization. The test solution was a naturally aerated solution of 0.02 M Na_2HPO_4. The evolution of the electrochemical behavior was assessed by EIS during 30 days of immersion in the electrolyte. The experimental setup consisted of a three-electrode cell arrangement with a platinum wire as counter-electrode and a saturated calomel electrode as

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reference electrode. EIS plots were obtained using a Solartron 1255 spectrum analyzer coupled to a potentiostat/galvanostat (EG&G 273A) with an amplitude of 10 mV in the frequency range of 10 kHz–10 mHz. After 30 days, the samples were anodically polarized at $1\,\mathrm{mV\,s^{-1}}$. All the electrochemical tests were conducted at room temperature. The microstructure of the magnetic alloy after annealing was examined using scanning electron microscopy (SEM).

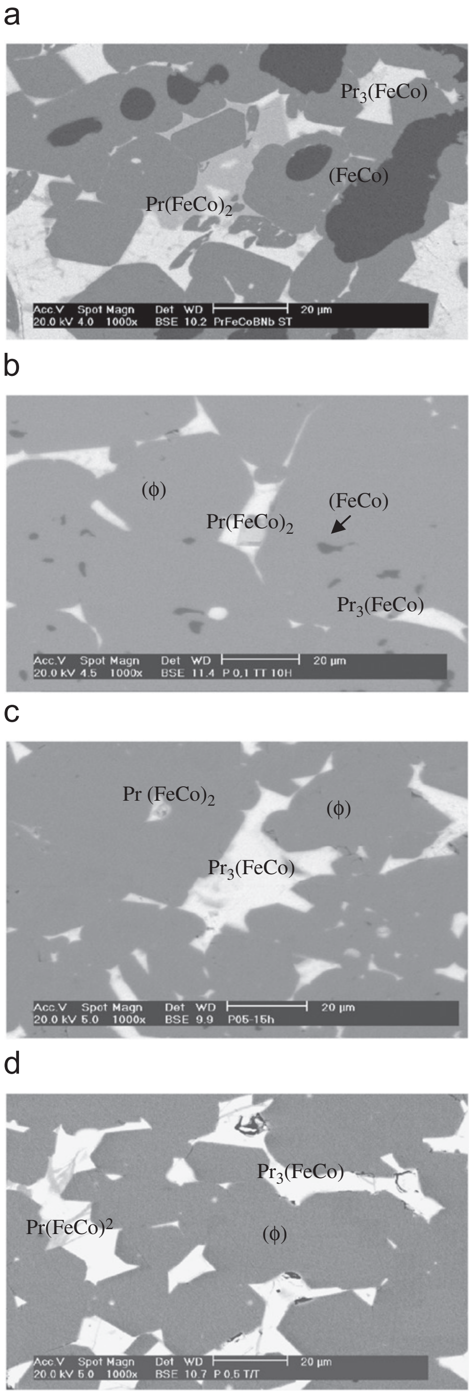

Fig. 1. SEM micrographs of $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}P_{0.25}$ alloy before (a) and after annealing at 1100 °C for (b) 10 h, (c) 15 h and (d) 20 h.

3. Results and discussion

SEM micrographs of the $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}P_{0.25}$ alloy before and after annealing for 10, 15 and 20 h are shown in Fig. 1a–d. The sample annealed for 10 h showed a higher amount of Fe-α (FeCo phase) than the samples annealed for longer periods. The other phases in the alloy's microstructure were Laves phase $Pr(FeCo)_2$ (gray phase) and Pr-rich phase $Pr_3(FeCo)$ (white phase).

Fig. 2 shows Nyquist and Bode (phase) diagrams for the $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}P_{0.25}$ alloy annealed for 10, 15 and 20 h. The results were obtained after 30 days of immersion in a naturally aerated solution of 0.02 M Na_2HPO_4 at room temperature. Note that some of the features are common to all the plots. The Nyquist plots present a single, well-defined flat capacitive loop. The Bode plots indicate a time constant, which is indicated by a peak in the low frequency range (0.1 Hz). This time constant is likely due to charge transfer reactions, mainly at the interface between the more active phases in the Pr-based alloy) and the electrolyte. The results revealed higher impedance values for the specimens annealed for 15 and 20 h periods than for those annealed

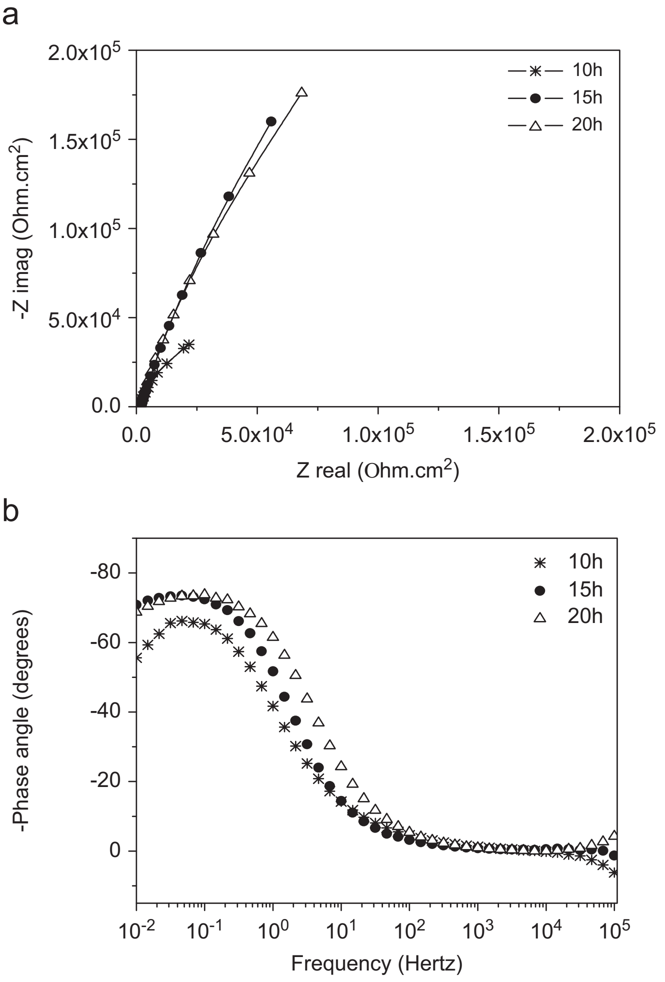

Fig. 2. EIS results obtained after 30 days in 0.02 M Na_2HPO_4 solution: (a) Nyquist, and (b) Bode (phase) of $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}P_{0.25}$ alloy annealed for 10, 15 and 20 h.

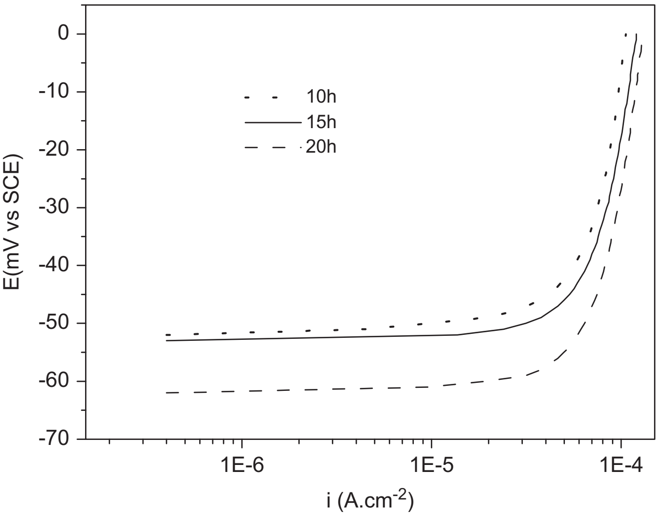

Fig. 3. Anodic polarization curves of $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}P_{0.25}$ alloy annealed for 10, 15 and 20 h. Results obtained after 30 days of immersion in 0.02 M Na_2HPO_4 solution.

for 10 h. This behavior denotes the lower corrosion resistance of the latter type of specimen, which seems to be related directly to its higher Fe-α content.

The results in Fig. 2 also show that there are no significant changes between the samples annealed for 15 and 20 h, suggesting that from the standpoint of corrosion, annealing treatments of more than 15 h are unnecessary. In fact, the results in Fig. 2b indicate that the phase angle peak associated with the sample annealed for 20 h occurred at higher frequencies than for 15 h, suggesting a slightly higher kinetics for the former type of sample.

Fig. 1 suggests that the area ratio related to the Pr-rich phase (white phase) in the annealed samples increased with annealing time, with the samples annealed for 20 h reaching the highest values. Note also that several boundary regions between this phase and the matrix phase were attacked during the surface preparation of the latter sample, suggesting that galvanic cells with high activity are easily established in these regions. This might explain the EIS results obtained for the samples annealed for longer periods.

Fig. 3 shows the anodic polarization curves obtained for the $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}P_{0.25}$ alloy annealed for 10, 15 and 20 h and immersed for 30 days in naturally aerated 0.02 M Na_2HPO_4 solution at room temperature. Much nobler corrosion potentials (around 0.5 V) were obtained for the specimens annealed for 15 and 20 h than for those annealed for 10 h. A comparison of the corrosion potentials (E_{corr}) of these two latter samples also indicated very similar values, although the E_{corr} value of the sample annealed for 20 h was approximately 0.05 V more negative than that annealed for 15 h. This finding corroborates the EIS results, indicating that the partial or total removal of Fe-α (FeCo phase) and the increasing proportion of Pr-rich phase in the alloy must have resulted from the heat treatment.

The i_{corr} values for the annealed specimens were estimated from the cathodic polarization curves (data not shown) and further corroborated the aforementioned results, indicating that the samples annealed for 15 and 20 h produced lower values than the sample annealed for 10 h.

4. Conclusions

The corrosion resistance of $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}P_{0.25}$ alloy depends on its microstructure. Electrochemical tests showed that annealing at 1100 °C is a key manufacturing parameter of this material's corrosion performance. Annealing for 10 h did not effectively remove the free iron phase from the alloy. Therefore, specimens subjected to this treatment showed a lower corrosion resistance than those heat-treated for 15 and 20 h. The increase in annealing time from 15 to 20 h caused a slight decrease in the corrosion resistance of the alloy, which was attributed to the increasing proportion of Pr-rich phase in the alloy as a function of the treatment time. In terms of corrosion, our results suggest that annealing for 15 h suffices to improve the corrosion resistance of $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}P_{0.25}$ alloy.

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