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Research Paper

Comparison of electroless Ni-P/ Ni-B on corrosion performance

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Abstract

This research work compares annealed and as-coated electroless Ni-P's resistance to corrosion and electroless Ni-B coating prepared on the mild steel substrate. The coatings' resistance to corrosion was estimated by Tafel electro chemical polarization method utilizing electrochemical analyser in 3.5wt % solution of Sodium Chloride. Both the coatings' annealing temperatures were maintained at normal intervals to consider their corrosion resistance performance. Further, the corrosion behaviour of both the coatings with their as-coated and various annealed temperature were discussed for the deliberation of deposits phases, crystallite sizes and micro strain.

Keywords: Electroless Nickel (EN); Corrosion Performance; The Coatings of Electroless Ni-P; Ni-B; XRD.

1. Introduction

Coatings like metallic play a vital role in the surface engineering field such as vehicle technology, aerospace and nautical science. The superiority of the surface coating depends on the process in which it was produced. Through electroless production process, good quality of surface metallic coating layer can be produced economically [1]. Electroless plating of Nickel is a well-known auto catalytic chemical technique, adopted for the metal deposition on the surface of substrate without external power source from solution [2]. Electroless coating is to produce coating of Nickel alloys and composites and metalloids of Phosphorous or Boron. If the metalloids of Boron or Phosphorous present in Nickel matrix have less solubility they will be as supersaturated solutions of either boron or Phosphorous in Nickel matrix [3].

The metallic coating produced using electroless technique could be used with several configurations such as crystalline, amorphous or combination of both the nature [4]. Record of the researchers [5-7] approved that the coating of electroless Ni-P annealed at temperatures beyond ambient may be carried out variations in their phases with the precipitation of Ni-P phases. If the second phase of nickel phosphides formed along with the first phase of Nickel and Phosphorus which enhanced the coating's hardness. However, the hardness of the coating tainted with the disproportionate annealing temperature is caused by the coarsening of Nickel and Nickel Phosphides [8-10].

Study on Electroless Ni-B deposition has increased due to its unique properties like uniform deposition, low cost, increased micro hardness, good wear resistance, excellent solderability and electrical properties [11]. The coating of as-coated electroless Ni-B has the combination of microcrystalline nickel phase and the amorphous Ni-B phase. Moreover, the increasing Boron content in the coating enhances the amorphous phase [12]. During deposition process, oxidation of Sodium Borohydride makes the Boron enter into the coating. Hence, the amount of boron in the coating depends on the kinetics of Borohydride oxidation. The kinetics of oxidation reaction will vary with the concentration of chemicals such as Sodium Borohydride, Ethylenediamine, Thallium acetate and the coating bath pH and temperature [13]. The coating bath is maintained at a high temperature range of 90 to 95ºC for Ni-B coating [14] and 80°C for Ni-P coatings [15 and 16].

The behaviour of Ni-B coating relies on the content of boron present in the coating [17]. The mechanical characteristics such as hardness and wear resistance of the Ni-B coating enhances by increasing boron content present in the coating matrix [18]. Most of the researchers have suggested that corrosion behaviour of Ni-P is better compared to that of Ni-B [19]. Ziyuan et. al., [20] contradictorily reported that the corrosion performance of as coated Ni-B is greater than that of as coated Ni-P coating. Due to the contradiction in corrosion performance of Ni-B coating, this work has concentrated on comparing the corrosion performance of Ni-P and Ni-B in as-coated as well as varying annealing temperatures.

2. Experimental methods

2.1. Production of electroless Ni-P / Ni-B coatings

For electroless Ni-B coating, a mild steel substrate with a diameter of 25 mm and 3 mm in thickness was used. The surfaces of the substrates were fine polished using various grades of emery sheets. The pickling treatment was done on the polished substrates with the use of 10% Hydrochloric acid. Thereafter, the substrates surfaces which were treated were cleansed using de-mineralized water and had subsequent cleaning by acetone. The electroless bath was then prepared for the Ni-P and Ni-B coating for the following compositions and operating conditions as indicated in Table 1 [21] & 2 respectively.

Table 1: Coating Bath Composition and Operating Condition of the Electroless Ni-P Coating

Chemical Composition	Quantity
Nickel Chloride ($NiCl_2.6H_2O$)	30g/l
Sodium Hypophosphite ($NaH_2PO_2H_2O$)	40g/l
Sodium Citrate ($Na_3C_6H_5O_72H_2O$)	30g/l
Ammonium Chloride (NH_4Cl)	50g/l
Operating Conditions	
Temperature	80°C
PH	9-10

Table 2: Coating Bath Composition and Operating Condition of the Electroless Ni-B Coating

Chemical Composition	Quantity
Nickel Chloride ($NiCl_2.6H_2O$)	30g/l
Sodium Borohydride ($NaBH_4$)	0.8g/l
Ethylenediamine ($C_2H_8N_2$)	100ml/l
Thallium Acetate (CH_3COOTl)	14mg/l
Sodium Hydroxide (NaOH)	90g/l
Operating Conditions	
Temperature	95ºC
PH	14

2.2. X-ray diffraction measurement (XRD)

The Siemens X-ray Diffractometer with monochromatic Cu-Kα radiation was used to measure XRD for the coated substrates. From the obtained XRD the phases of element present in the coating, grain size and micro strain of the elements were calculated. The range of scanning angle (2θ) between 10° and 90° with 0.02º step and 2 sec/step was used for the measurement. The phases of elements present in the coating obtained from the XRD were recognised by comparing them with the JCPDS files.

2.3. Corrosion test

The corrosion test was conducted using Electrochemical Analyser. The corrosion resistances of the coatings were observed through Tafel electrochemical technique. The test was conducted at room temperature in 3.5 wt % Sodium Chloride solution with a scan rate of 2mV/s. The three electrode cell configuration was used for this purpose. The three electrodes are calomel electrode, platinum electrode and the third electrode they are used as reference, counter and test specimen respectively.

3. Results and discussion

The Electrochemical corrosion measurement was carried out on the as-coated and various annealed samples using the electro chemical analyzer. Electro chemical test was performed on the coated surface using sodium chloride (NaCl) solution as the medium of corrosion. It could be significantly accelerated by the pitting corrosion and by replacing oxygen molecules in water to absorb on the coating surface and to create a soluble $NiCl_2$ ($Ni^{2+} + 2Cl_2 \longleftrightarrow NiCl_2$). Also the absorbed chlorine ions from the corrosion medium penetrate into the voids present in the coating surface enhancing the pitting corrosion. The electrochemical polarization curves for the coatings of Ni-P and Ni-B were depicted in Figure 1. The corrosion resistance was determined by the equation given below (1) [21].

$$\text{CR (mpy)} = \frac{0.13\ \text{Icorr}(\ \text{Eq.wt.})}{\text{d}} \qquad (1)$$

Where, Equation (1) wt is the equivalent weight, d is the density of the coating in g/cm^{3}and Icorr is the corrosion current in µA/cm^2.The base metal corrosion rate was high and has the value of 21.85mpy. The as-coated Ni-P and Ni-B samples corrosion rates were found to be 0.427mpy and 2.808mpy respectively. Both these values are very much less than that of the base metal value. When comparing both the coatings, the coating of Ni-P has lesser value than the Ni-B coating.

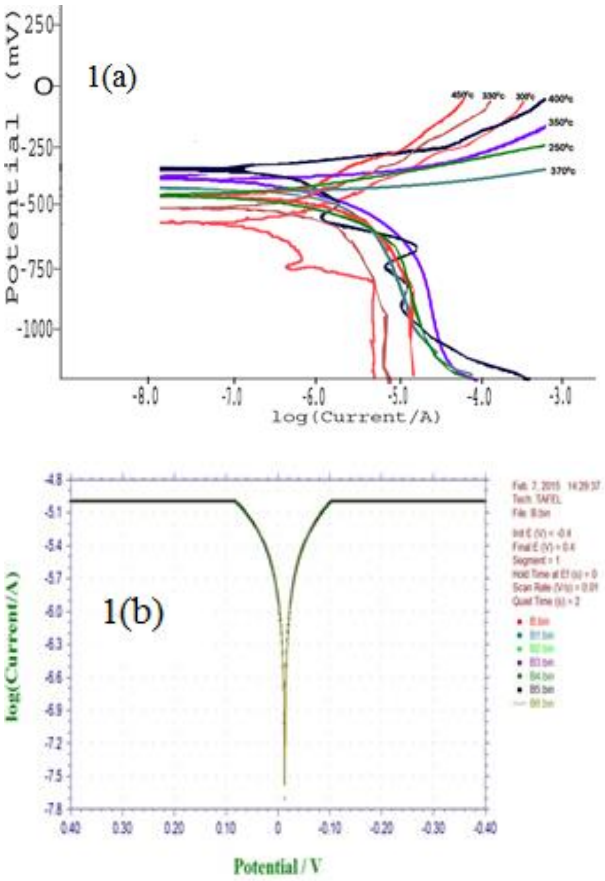
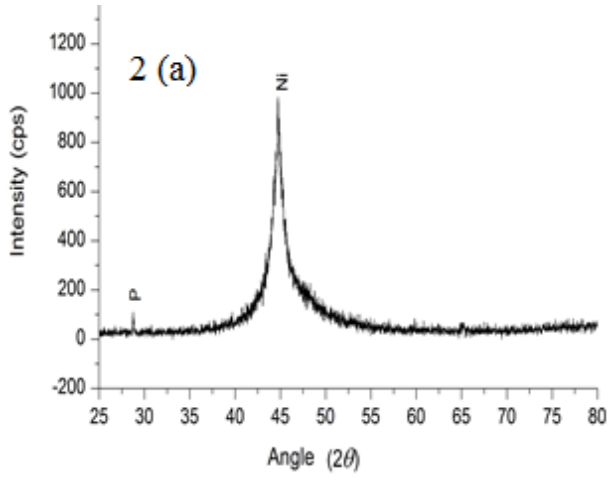


Fig. 1: Polarization Curves for (A) Ni-P Coatings (B) Ni-B Coatings.

XRD pattern of Electroless Ni-P's and Ni-B coating in it's as–coated state showed only a broad single peak around 2θ = 45° as shown in Figure 2. The broad peak showed that the coating was in amorphous nature. The amorphous deposits have higher corrosion resistance as compared with those of annealed deposits. In general, the corrosion medium attacks the coating through their grain boundaries. The as coated coating does not have grain boundaries therefore the corrosion resistance of as coated coating has higher resistance.



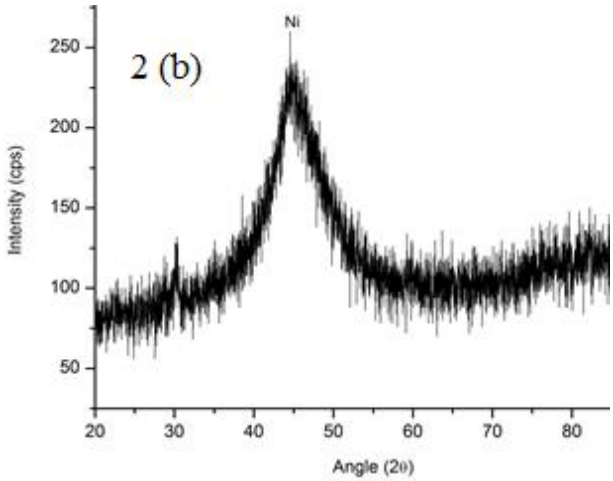


Fig. 2: XRD of As-Coated Electroless Coatings (A) Ni-P (B) Ni-B.

The corrosion rates of both the coatings are depicted in Figure 3. It is clear from the figure that the corrosion resistance of the annealed coatings was lower than that of as-coated coatings of Ni-P as well as Ni-B deposits which could be due to the changes in crystalline occurring from amorphous to crystalline. When comparing the corrosion rates, the coatings of Ni-P decreased initially but by elevating the temperature of the heat treatment it increased but for the Ni-B coatings it increased gradually.

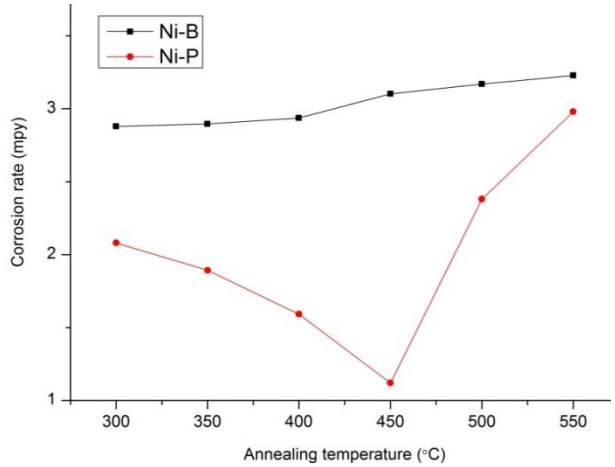


Fig. 3: Comparative Corrosion Rate of Ni-P and Ni-B Coatings.

The lowest corrosion rate of Ni-P coating was obtained at the annealed temperature 450°C. For temperatures above 450°C, corrosion rates were found to be increased. The reduction in phosphorus content is the prime reason for increasing corrosion rate. During lower annealing temperatures for the Ni-P coating, the contents of the phosphorus were augmented on the surface. This phosphorus had reacted with the NaCl solution to produce an adsorbed film of hypophosphite. This formed hypophosphite prevented the molecules of water from reacting further with the surface of the electrode in order to avoid the nickel's hydration [21]. For the Ni-B coating, the rate of increasing corrosion rate was lesser in lower annealing temperatures from 300°C to 400°C. During these temperatures, nucleation of grains occurred. Therefore, the corrosion rates of these temperatures are closer to the as-coated condition. In contrast, if the temperatures were above 400°C, the corrosion rates would also be higher than the as-coated condition. This could be due to the recrystallization of grains that are formed as various borides of Nickel. These Nickel borides increases the grain boundaries of the coating surface.

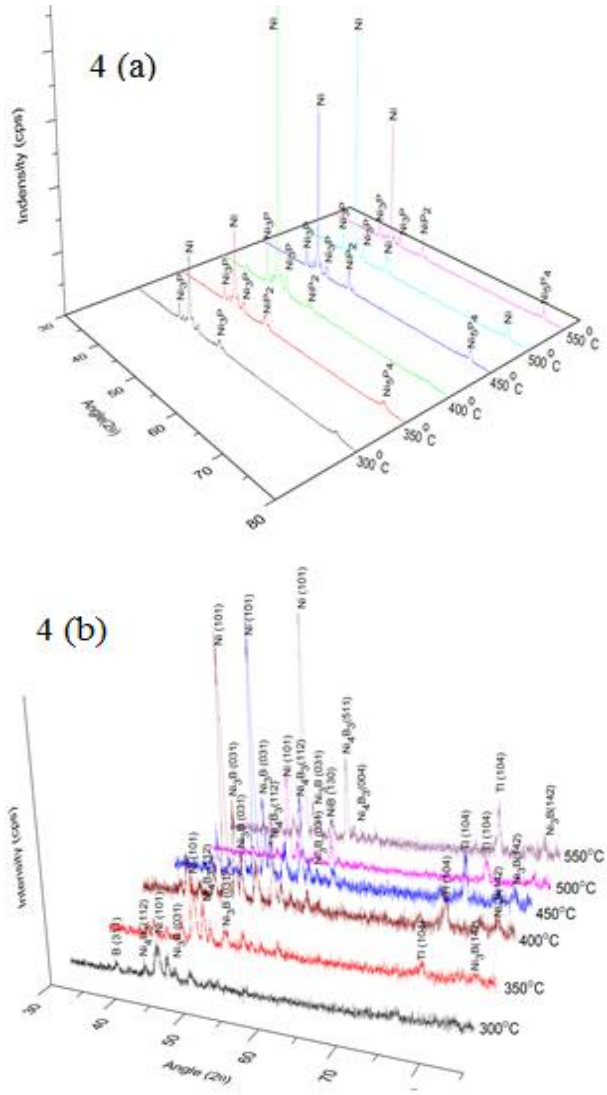


Fig. 4: XRD of Annealed Electroless Coatings (A) Ni-P (B) Ni-B.

When the annealing temperature was beyond 450°C for Ni-P coatings, the Ni_3P phase coarsened to diminish the available phosphorus content and create Ni and Ni_3P phases which are evident from XRD as shown in Figure 4(a). The formed Nickel and Nickel-Phosphide phases enhanced the surface heterogeneity. These phases increased the grain boundaries within the coating, enhancing the corrosion attack which decreases the corrosion resistance. The annealing temperature was beyond 450°C for Ni-B coating, nickel boride phases would be increased as shown in Figure 4(b). The increasing Boron phase contents, Nickel phase contents and the co-deposited thallium phases were made heterogeneity of the phases present in the coating surface. The increasing heterogeneity of the phases boosted the boundaries of the coating well within itself, the impact of which is intense chemical attack resulting in increased rate of corrosion.

The crystallization behaviour of the coating surface is clearly seen in Figure 5. A glossy like film is identified in the Figure 5 (A1 & B1) revealing that the coating was partially in an amorphous state or the mixture of amorphous and micro crystalline nature. The increasing annealing temperatures shot up the grain formation which is evident by vanished the glossy film as shown in the Figure 5 (A2 & B2). Also, pores (black dots) were existing on the coating surface. The corrosion medium moved to substrate surface through these pores causing pitting corrosion.

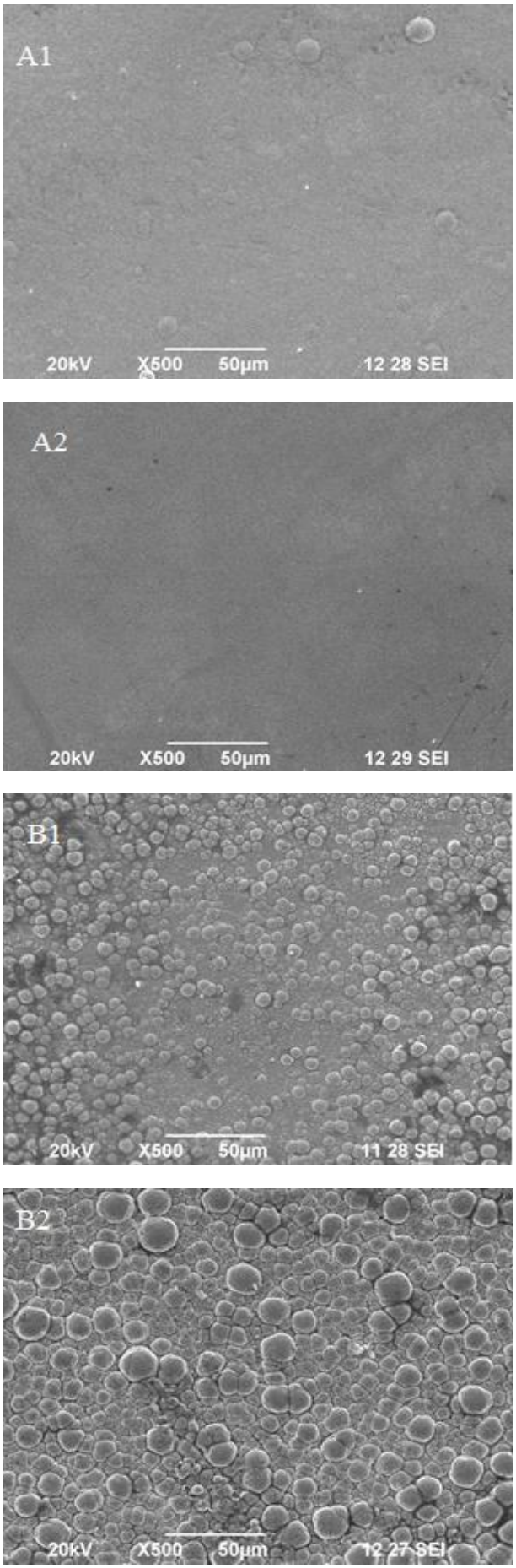


Fig. 5: SEM for Ni-P Coating ANNEALED at (A1) 300°C (A2) 500°C and Ni-B Coating Annealed at (B1) 300°C (B2) 500°C.

Figure 4 gives the results derived from the XRD which in turn are utilized to measure the size of the crystallite and micro strain for varied treatments of temperatures by using Stokes – Wilson expression and Debye-Scherrer Equation [16]. The calculated values of crystallite sizes and micro strain of the coatings' Ni-P and Ni-B are shown in the Figures 6 and 7. It is observed that the crystallite sizes of both the coatings were raised by raising the annealing temperature and the micro strain of the coatings decreased by increasing annealing temperature. On comparing, crystallite sizes of the Ni-P coating are greater than those of the Ni-B coating. Also, the micro strains of the Ni-P coating are lesser than those of the Ni-B coating. The higher in crystallite size and lower in micro strains are responsible for Ni-P coating's higher resistance to corrosion than the Ni-B coating.

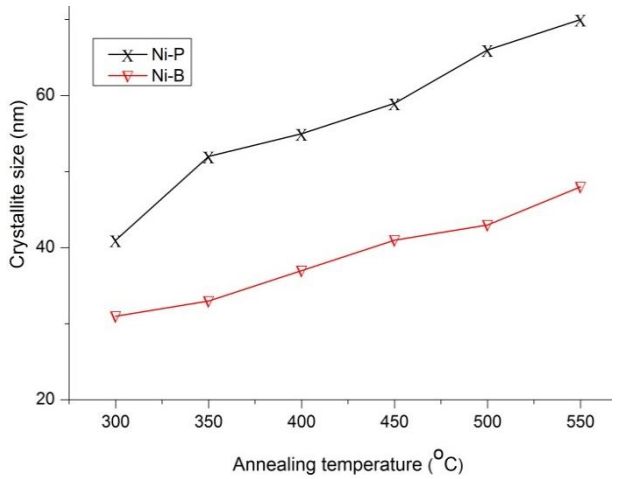


Fig. 6: Comparison of Crystallite Sizes of Ni-P and Ni-B Coatings.

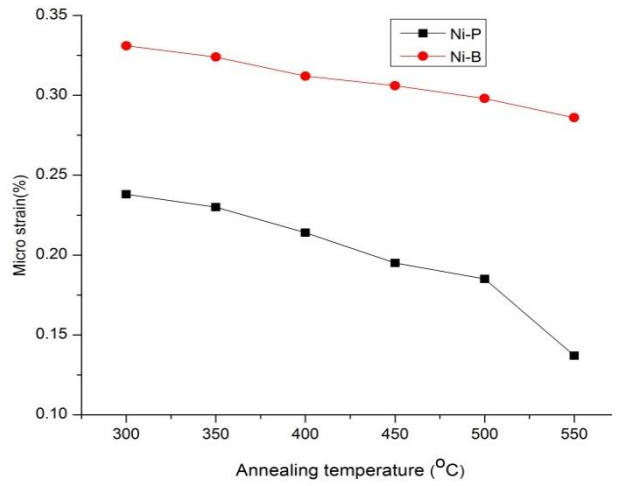


Fig. 7: Comparison of Micro Strains of Ni-P and Ni-B Coatings.

4. Conclusion

The electroless Ni-P as well as Ni-B coatings were successfully coated on the surface of mild Steel substrate. Both the coatings were of amorphous nature in their as-coated state. The as-coated deposits had higher corrosion resistance than the annealed deposits. This is because of the non-existence of grain boundaries which give conducive glossy film structure for corrosion resistance in the surfaces. The coatings of Ni-P have higher resistance to corrosion than those of the Ni-B coating in their as-coated and annealed state. Phosphorus content's presence in the coating of Ni-P is the prime cause for the higher resistance to corrosion than the Ni-B coatings. The higher crystallite sizes and lower micro strains of the coatings of Ni-P are another reason for Ni-P coatings to have higher resistance to corrosion.

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