JMEPEG (1999) 8:424-428

Corrosion-Fatigue Behavior of an Annealed AISI 1045 Carbon Steel Coated with Electroless Nickel-Phosphorus

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(Submitted 21 December 1998; in revised form 4 February 1999)

The influence of an industrial electroless nickel-phosphorus deposit on the corrosion-fatigue properties of an annealed AISI 1045 steel has been investigated. For this purpose, three corrosive media were selected: distilled water and two NaCl solutions of different concentration (3 and 5%) in distilled water. Corrosion-fatigue tests were conducted at alternating stress levels ranging between 219 and 329 MPa at a frequency of 50 Hz. The corrosion-fatigue properties of the coated and uncoated substrates are very similar when testing is conducted in salty water. However, for testing in distilled water the corrosion-fatigue properties of coated substrates were diminished in relation to the uncoated material. The fractographic analysis of the fracture surfaces revealed the presence of fatigue marks within the electroless nickel-phosphorus deposit, which indicate that the fracture mechanism of the coating is associated to the cyclic loading of the material.

Keywords AISI 1045, corrosion-fatigue, electroless nickel, steel

1. Introduction

The growing need of information required to fill the existing gap between mechanical design and the material behavior in service have given rise to a number of research studies aimed at understanding the role of corrosion on the fatigue properties of engineering materials, particularly on the nucleation and propagation of fatigue cracks, when cyclic loading occurs under the action of an aggressive medium. In order to decrease the deleterious effect of the environment on the fatigue properties of metals and alloys a number of methods have been developed including the deposition of coatings that could enhance the corrosion resistance of such materials. In order to explain the role of the environment on the nucleation of fatigue cracks, different mechanisms have been proposed (Ref 1, 2), including the rupture of protective layers and the electrochemical attack of the material at the rupture sites, formation of corrosion pits and the subsequent generation of stress risers, strain enhanced dissolution of slip steps, and finally the decrease in the surface energy of the material due to the effect of a specific environment. All the mechanisms proposed involve the systematic contribution of chemical and mechanical effects.

In mechanisms that involve the rupture of protective layers, the nucleation of fatigue cracks is intensified due to the mechanical damage to which the protective layer is subjected. Once the protective layer has fractured the substrate is exposed to the corrosive environment, and this results in the formation of preferential zones for the corrosive attack. Conversely, in relation to the mechanisms that involve the formation of corrosion pits, in some cases corrosion produces a deep and localized attack at some sites. In this sense, McAdam and Geil (Ref 3) conducted a number of research studies regarding the effect of notches produced either by machining or chemical attack on the fatigue properties of steels. It has been determined that chemical notches have a similar effect to those produced by machining.

The fatigue strength of metals and alloys can be severely reduced if corrosion effects occur concurrently with cyclic loading of the material. For example, it is well documented in literature that the corrosive damage induced by tap water can give rise to a reduction of up to 110 MPa in the fatigue strength of most steels, including those of high strength. However, in the presence of salty water, the fatigue strength of such materials hardly reaches 50 MPa. Bogar and Crooker (Ref 4) have conducted a number of tests with steels, aluminum alloys, and chromium alloys employing natural sea water, artificial sea water (ASTM), and a solution of 3% NaCl in distilled water. It has been determined that the chemical composition of the solutions used very rarely have any influence on the corrosion-fatigue behavior of such materials. Most corrosion-fatigue experiments have been conducted at frequencies of 30 to 60 Hz, and in general it has been found that the corrosive effects of the environment are more marked as the frequency decreases because the exposure time of the material to the corrosive medium increases.

The electroless nickel-phosphorus deposits are considered to be more noble from the electrochemical point of view than steels, which gives these coatings good corrosion resistance both in tap water and marine environments. This general behavior has been well documented in the literature (Ref 5-8). However, very little research has been conducted to investigate the corrosion-fatigue resistance of such deposits. Electroless nickel-phosphorus coatings have been reported to be resistant to alkaline solutions, organic acids, and oil environments. However, they could be affected by strongly oxygenated acids. The corrosion resistance of such coatings is attributed to their

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amorphous state and the formation of a passive film on the surface (Ref 9). Broziet et al. (Ref 6) investigated the corrosion-fatigue behavior of a 52-type steel plated with an electroless nickel-boron alloy, which has similar properties to electroless nickel-phosphorus deposits. The corrosive medium used was a 3% NaCl solution, and the coating was subjected to different post-plating heat treatments (PPHT). The results indicated that the corrosion-fatigue behavior of the material increased in the as-plated condition but decreased after a PPHT at 673 K for 60 min and also for 12 h. However, the best results were obtained for the longest PPHT.

Chitty et al. (Ref 7) have also conducted corrosion-fatigue experiments with an AISI 1045 steel employing a solution similar to that used by Broziet et al. (Ref 6). In this study it was determined that the corrosion-fatigue life of the material increases in the as-plated condition and that such an increment is more marked as the stress amplitude decreases. In this investigation the electroless nickel-phosphorus deposit was also subjected to a PPHT at 473 K for 4 h. It was observed that such a treatment gave rise to a reduction in the corrosion-fatigue life of the material.

Chitty et al. (Ref 8) have also conducted an investigation of the corrosion-fatigue behavior of the same material (AISI 1045 steel) coated with a commercial electroless nickel-phosphorus deposit, where the initial mechanical strength of the substrate was increased in relation to the annealed condition by quenching and subsequent tempering. This study involved the use of both notched and unnotched samples and employed a solution of 3% NaCl as the corrosive medium. From this investigation it was concluded that the corrosive environment gives rise to a significant reduction of the fatigue life of the steel in the quenched and tempered condition, which only, at a stress amplitude of 550 MPa, can reach up to approximately 73%. Also, it has been found that the electroless nickel-phosphorus deposit has a slight influence on the corrosion-fatigue behavior of the material (20% increase at 481 MPa) when testing is conducted in this medium, whereas the corrosion-fatigue life of the notched samples was not affected by the deposition at least in the stress interval of interest.

Thus, the present investigation has been conducted in order to explore in more detail the corrosion-fatigue behavior of an AISI 1045 plain carbon steel in different corrosive media, when this material is plated with a commercial electroless nickel-phosphorus deposit without any PPHT.

2. Experimental Techniques

The material used in the present investigation was an AISI 1045 steel with 0.43 C, 0.65 Mn, 0.30 Si, 0.013 S, and <0.02 P. The material was supplied in bars approximately 12.5 mm in diameter. Specimens for both tensile and fatigue tests were machined to the following dimensions: 100 mm total length, 10 mm external diameter, 24 mm gage length, 6.24 mm gage diameter, and 30 mm fillet radius. All the samples were ground with emery paper, 80 to 600 grit, applied consecutively. Subsequently, they were annealed at 1113 K for 20 min in an argon atmosphere. The samples were electroless nickel-phosphorus plated with a commercial bath containing 30 g/L nickel sulfate, 30 g/L sodium hypophophite, 35 g/L malic acid, 1.5 ppm lead sulfate, 10 g/L succinic acid, and a stabilizer. The bath was kept at a pH of 4.6 to 4.8 and a temperature of 358 to 361 K. The deposition rate was maintained at 12 to 15 μm/h. Prior to the electroless nickel-phosphorus plating, the samples were degreased for 1 h, submerged in a solution of 5% HCl for 7 min, submerged in a solution of 100 g/L of sodium bicarbonate, and water cleansed.

The monotonic mechanical properties were evaluated in tension (Instron 8502, Instron, Canton, MA), and the corrosion-fatigue tests were conducted under rotating bending conditions (Fatigue Dynamics Ltd., Walled Lake, MI). The experiments were carried out at alternating stresses ranging between 219 and 329 MPa at a frequency of 50 Hz. Three corrosive media were employed in the study: a solution of 3% NaCl in distilled water, a solution of 5% NaCl in distilled water, and distilled water alone. Fractographic analyses were conducted by means of a scanning electron microscope (Hitachi S-2400, Hitachi Ltd., Tokyo, Japan) with electronic dispersive spectroscopy (EDS) capabilities.

3. Results and Discussion

3.1 Fractographic Analysis

Figure 1 shows a general view of the transverse section of an uncoated fatigue sample. Thus, it is possible to observe a fracture surface with multiple steps, which indicates the nucleation of a number of cracks all over the surface of the specimen, possibly generated at corrosion pits. These fracture steps are typi-

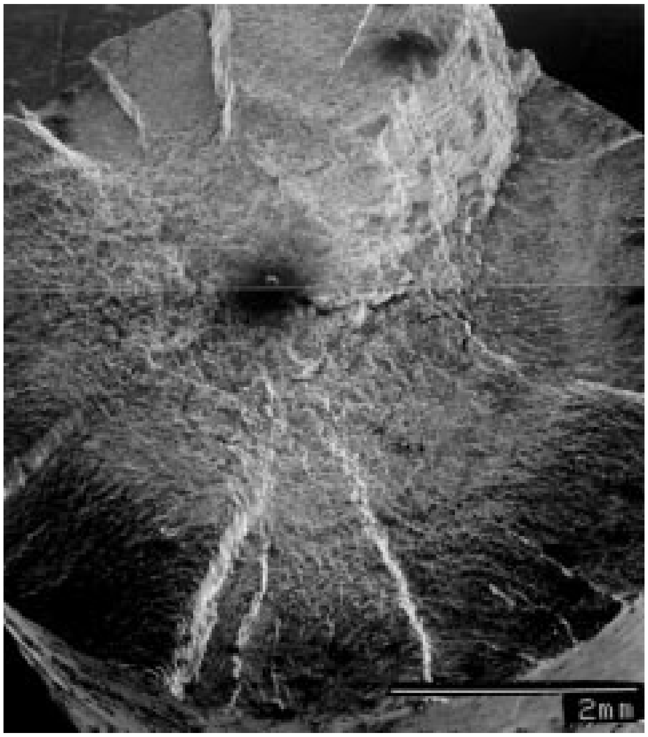

Fig. 1 Scanning electron micrograph of the fatigue fracture surface corresponding to a sample of unplated substrate tested in a solution of 3% NaCl

cal of corrosion-fatigue phenomena, and they were observed less frequently in coated samples. Therefore, it is suggested that the electroless nickel-phosphorus deposit increases the corrosion resistance of the substrate until the fatigue fracture of the coating occurs.

The micrograph in Fig. 2 shows a general view in which the deposit detachment from the substrate can be clearly observed. A possible crack initiation site is also pointed out, noting that the detachment of the coating has not occurred as a consequence of the cyclic loading to which the sample has been subjected but due to the bad adherence of the deposit to the substrate. Therefore, it would not be expected that such a deposit would provide either a residual stress pattern capable of enhancing the fatigue behavior of the substrate, as suggested by Puchi et al. (Ref 10), or even an appropriate protection against corrosion during cyclic loading, which are essential requirements to increase the corrosion-fatigue properties of the material.

The micrograph shown in Fig. 3 illustrates a possible site for fatigue crack initiation and the adjacent section of the sample periphery where the deposit has been completely detached from the substrate, possibly as a consequence of the combined action of a bad adherence of the deposit and the cyclic loading applied during testing. It is believed that fatigue cracks are nucleated at the deposit-substrate interface, where the coating had previously cracked and detached. This is supported by the observation that fatigue cracks propagate in the substrate first, following an intercrystalline path and subsequently in a transgranular manner. As suggested by Sudarshan et al. (Ref 1), this behavior is typical of nucleation and propagation of cracks under corrosion-fatigue conditions.

The micrographs shown in Fig. 4 and 5 illustrate very clear evidence of fatigue markings in the deposit, although such marks do not follow the same orientation observed in the substrate. Therefore, it is suggested that the deposit fails by fatigue at an early stage, leaving the substrate exposed to the corrosive environment. The EDS analysis conducted in the area where the fatigue marks were observed indicated the presence of nickel (80%), iron (10%), and phosphorus (10%). The presence of iron is believed to be associated with corrosion products generated during testing.

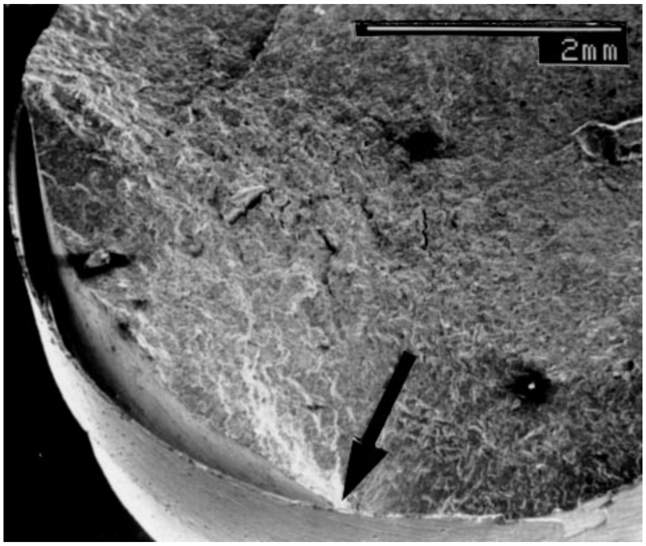

Fig. 2 Scanning electron micrograph showing the detachment of the electroless nickel-phosphorus deposit after testing in distilled water at 292 MPa

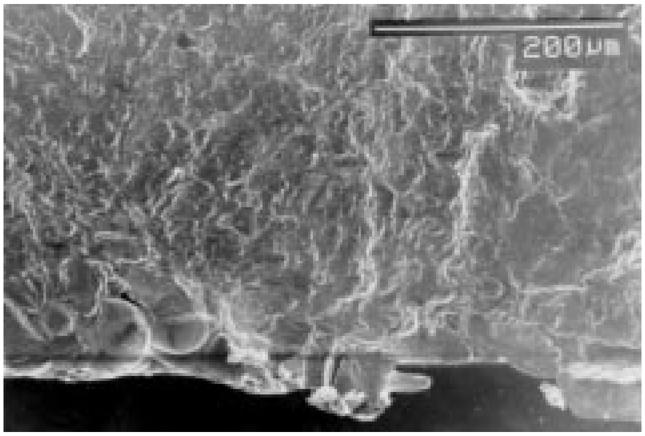

Fig. 3 Scanning electron micrograph illustrating the possible nucleation site of a fatigue crack in a plated sample tested in a solution of 3% NaCl at 266 MPa

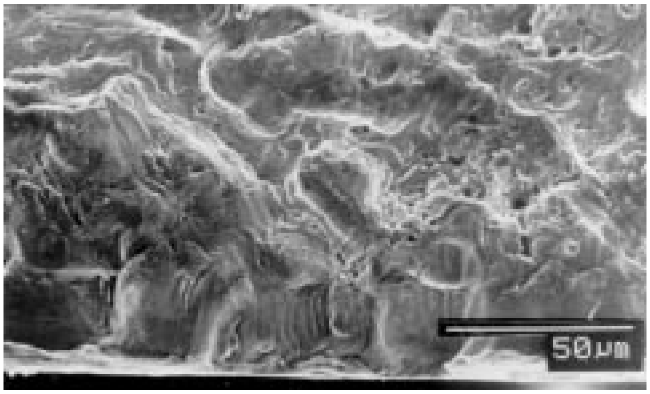

Fig. 4 Scanning electron micrograph illustrating fatigue markings both in the electroless nickel-phosphate deposit and the substrate. The sample was tested in distilled water at 219 MPa.

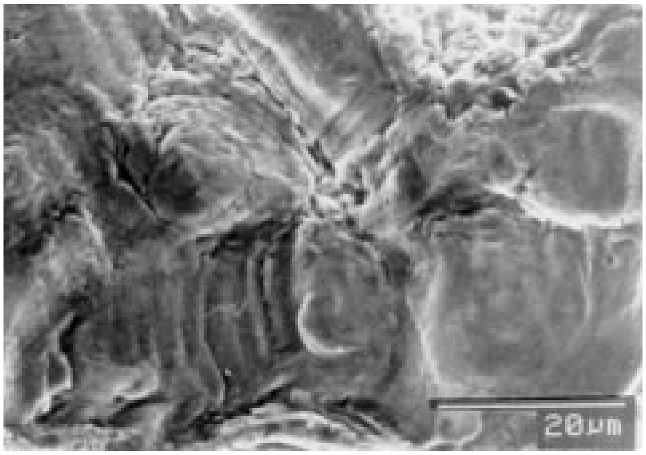

Fig. 5 Scanning electron micrograph illustrating a magnified detail of Fig. 4. Fatigue markings in the electroless nickel-phosphate deposit are clearly visible.

3.2 Corrosion Fatigue

Figure 6 illustrates the results of the corrosion-fatigue tests in terms of the number of cycles to failure versus alternating stress, corresponding to the substrate without any coating. The experimental data, reported in Table 1, are plotted in a double logarithmic scale. They can be described adequately by means of straight lines within the stress interval investigated, which suggests the validity of the equation earlier proposed by Basquin (Ref 11):

$$S = A N_{\mathrm{f}}^{-m} \qquad \text{(Eq 1)}$$

where both A and m are constants that depend on the material properties and testing conditions. Therefore, it would seem that in the stress interval of interest to the present work, no change in the fatigue mechanism occurs.

Table 2 summarizes the results of the linear least square analysis conducted with the experimental data in order to determine the constants involved in Eq 1. In Fig. 6 it can be seen that for the three corrosive media, the corrosion-fatigue life of the material decreases significantly in comparison with the behavior displayed in air. This reduction can achieve up to approximately 20%, which confirms the results reported in literature (Ref 1) in the sense that aqueous media are much more aggressive in comparison with air. It can also be observed that the corrosion-fatigue life of the substrate tested in distilled water is somewhat higher than the life of this material when it is tested in salty water, which again indicates that NaCl solutions are also more aggressive than distilled water. From this figure it can also be seen that an apparent increase in the corrosion-fatigue life exists when the tests are conducted in a 3% NaCl solution in comparison with the 5% NaCl solution. However, taking into consideration that the data collected in the corrosion-fatigue tests follow a normal distribution, all the values corresponding to the number of cycles to failure determined at low stresses are within the standard deviation of the mean for both conditions.

Conversely, Fig. 7 illustrates the results of the corrosion-fatigue tests corresponding to the substrate when it has been plated with an electroless nickel-phosphorus deposit as described previously. As in Fig. 6, the experimental data, also reported in Table 1, are represented in a double logarithmic scale in Fig. 7 and can be described by means of straight lines. Table 2 summarizes the results of the evaluation of the constants involved in Eq 1 when it is employed to describe such data.

An interesting feature shown in Fig. 7 is that even for the substrate plated with the electroless nickel-phosphorus deposit, the aqueous media are also much more aggressive than air in relation to the corrosion-fatigue behavior of the material. The behavior displayed for the 3% and 5% NaCl solutions is very similar, and it can be appreciated that testing in distilled

Table 1 Number of cycles to failure as a function of the alternating stress, determined experimentally both for the unplated and plated substrate tested in different media

	Number of cycles to failure						
Alternating stress, MPa	**Unplated substrate in air**	**Unplated substrate in 3% NaCl**	**Unplated substrate in 5% NaCl**	**Unplated substrate in distilled water**	**Plated substrate in 3% NaCl**	**Plated substrate in 5% NaCl**	**Plated substrate in distilled water**
329	93,600	53,900	81,300	84,780	50,090	63,920	59,600
310	224,560	…	…	…	…	…	…
292	443,475	165,913	138,117	247,840	181,100	155,317	163,150
274	1,219,780	…	…	…	…	…	…
266	…	344,713	280,467	528,720	355,975	296,000	391,250
219	…	971,360	892,080	1,610,040	1,097,880	1,038,250	1,281,480

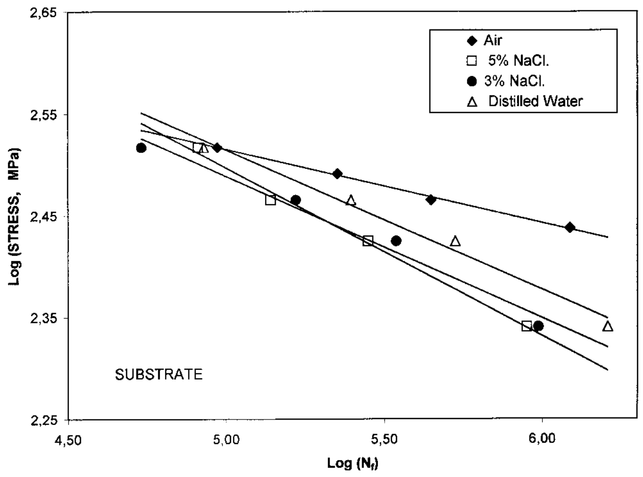

Fig. 6 Alternating stress versus number of cycles to failure for the unplated substrate samples tested in different media

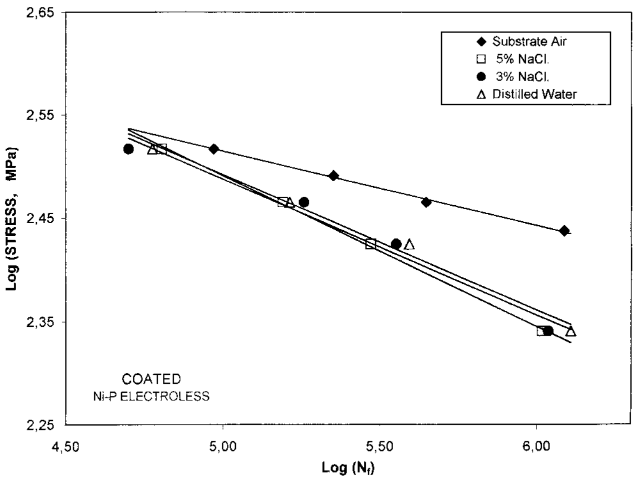

Fig. 7 Alternating stress versus number of cycles to failure for the plated substrate samples tested in different media

Table 2 Parameters in the Basquin equation determined for the unplated and plated substrate tested in different media

Testing media	Unplated substrate		Plated substrate	
Corrosive	*A*, MPa	*m*	*A*, MPa	*m*
Solution 5% NaCl	2108	–0.17	1672	–0.15
Solution 3% NaCl	1535	–0.14	1400	–0.13
Distilled water	1591	–0.14	1406	–0.13
Air	753	–0.07	…	…

water does not improve notably the fatigue life in comparison with the chloride solutions. All these results seem to indicate that the industrial electroless nickel-phosphorus deposit evaluated in the present investigation does not give rise to a favorable residual stress pattern such that the corrosion-fatigue life of the substrate could be significantly improved. In fact, the micrograph given in Fig. 2 indicates that the behavior observed could be due to the lack of adhesion between the electroless deposit and the substrate.

Conversely, the micrographs shown in Fig. 4 and 5 indicate that the electroless nickel-phosphate deposit is susceptible to cracking due to cyclic loading because even fatigue markings within the deposit have been observed. The fatigue failure of the deposit at an early stage limits the protective action of the coating against the corrosive medium to just the first load cycles applied to the material. Thus, it is suggested that after the deposit failure, a galvanic cell is formed that enhances the generation of corrosion pits and the nucleation of fatigue cracks during testing in different aqueous media. Also, it is expected that if the substrate has not been plated, the corrosion pits appear on the surface of the material exposed to salty environments much earlier than it would occur in distilled water.

A comparison of Fig. 6 and 7 shows that the corrosion-fatigue life of the unplated substrate in distilled water is longer than that of the electroless nickel-phosphorus plated substrate in the same medium, which supports the previously suggested mechanism. In salty environments the electroless nickel-phosphorus plated substrate displays a somewhat better corrosion-fatigue performance than the unplated substrate, possibly due to the protective action of the coating during the first loading cycles. As was reported previously, Chitty et al. (Ref 7), reported a significant increase in the corrosion-fatigue life of the same substrate when plated with an electroless nickel-phosphate deposit at laboratory scale in which the adhesion properties of the deposit to the substrate were observed to be much better than those in the present work.

4. Conclusions

This study has shown that electroless nickel-phosphorus deposits undergo fatigue failure during corrosion-fatigue testing in aqueous media, which subsequently gives rise to the formation of corrosion pits that act as stress risers and nucleation sites for fatigue cracks that continue to propagate along the substrate. The corrosion-fatigue behavior in 3% and 5% NaCl solutions, respectively, is similar. As the corrosive medium is more aggressive, the electroless nickel-phosphorus plated substrate presents better fatigue properties. Adhesion properties of electroless nickel-phosphorus deposits are of fundamental importance regarding the potential capabilities of such coatings to improve corrosion fatigue properties of medium strength steels.

Acknowledgments

The present investigation has been conducted with the financial support of the National Council for Scientific and Technological Research (CONICIT) through the project LAB-97000644. The financial support of both the Scientific and Humanistic Development Council (CDCH-UCV) and the Postgraduate Studies Council of the Central University of Venezuela is also acknowledged.

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