Development of Corrosion Resistance of Structural Steel with Nano-silver Coatings

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Abstract

The aims of this study are to examine the effect of metallic coatings to reinforcement on the perspective of the durability properties of concrete structures. Also, considering the importance of laboratory production of cover while investigating how it can be applied to steel. In this research, in order to increase the corrosion resistance of the structural steel, the reinforcements were coated with thin films with a system called thermionic vacuum arc (TVA). As a result of recent studies, it has been observed that such thin films protect the reinforcement from corrosion. In this study, the effect of coated reinforcement on corrosion, which is one of the most important structural defects, was investigated.

The applied coatings are nano-sized and protect the structural steel against corrosion reactions occurring on the surface. Moreover, these coatings increase the adherence between concrete and reinforcement. Specifically, for this study, silver (Ag) was used as a coating component. After the coating process was completed, the reinforcements were placed in cylindrical concrete samples and their resistance to corrosion was measured with the help of accelerated corrosion technique. The results show that the rebars coated with the TVA system was prolonged the damage occurrence time (first crack) and diminished the corrosion reactions that occurred on the reinforcement surface.

Keywords: Concrete; Nanocoatings; Corrosion; Reinforcement; Silver alloys

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1. Introduction

Reinforcement in concrete, when the alkaline protective layer around the rebar was dissolved because of any reason (chloride attack, cracks, alkaline silica reactions), structural steel becomes vulnerable to corrosion reactions (Topcu and Boga 2010). Although this event can be largely prevented by increasing the concrete cover, under various and severe environmental conditions, this cover may eventually be damaged, it cannot protect the reinforced concrete structure sufficiently (Topcu *et al*. 2009). Therefore, researchers focus their studies on methods that will protect the reinforced concrete structure from the inside, such as reinforcement coating, instead of preventing corrosion from the surface (Topcu and Uzunomeroglu 2021, Topcu and Uzunomeroglu 2022).

The reasons for covering the structural rebar are:

- Prolong the service life of the structural element by preventing corrosion reactions that may occur on the rebar.
- Provide the necessary time for people to evacuate the structure by protecting the construction steel from high temperature in case of emergency such as fire.
- To increase the durability of the structure under the estimated design loads by providing an increased bond strength (adherence) between the reinforcement and the concrete.
- Reduce the crack width or deployment caused by volume expansion due to various factors of structural steel (Topcu and Uzunomeroglu 2022, Topcu and Atesin 2016).
- The coating element is more resistant to the aggressive environment than the base metal (Topcu *et al.* 2021).
- In some cases, the coating element preferentially dissolves and sacrifices itself to protect the base metal.

The coating to be applied generally depends on the aggressive environment to which the structural element is exposed, the type of cement, and the water/cement ratio of the concrete. The accurate implementation of the coating also has a great effect on controlling the cracks (Uzunomeroglu *et al.* 2022). Achieving this significantly extends the life of the structure by preventing premature deterioration. Most importantly, concrete that exhibits structural deterioration can pose a safety risk. Preventing the corrosion phenomenon before it starts will also prevent the dramatic amount of money spent on the precautions to be taken after the corrosion occurs (Cheng *et al.* 2021, Di *et al.* 2016, Mardare and Benea 2017, Afshar *et al.* 2020, Böhm 2014).

Recent studies around the world have shown that the application of coatings achieved in practice does not usually meet the expectations of the designer (El-Zahrani *et al.* 2002, Arukalam *et al.* 2018). The reason for this is that any problem that may arise during the production of the coating may result in an increase instead of reducing the corrosion. Therefore, the most important factors in the production of reinforcement coating; It is expected that the coating completely encloses the reinforcement, does not allow any gaps, works in with harmony the reinforcement with strong adhesion, and does not reduce the adherence forces, which are defined as the adhesion between the reinforcement and the concrete (Boga *et al.* 2020, Chen *et al.* 2020).

In this study, the corrosion resistance of structural rebar coated with silver (Ag) nanostructure composite coatings were investigated. The thermionic vacuum arc (TVA) system, which was previously implemented in the coating of industrial materials, has been used in the field of civil engineering. The method that we use is a novel and unique coating system. TVA generates a plasma that constitutes the nanocoatings that are also compact, durable, homogeneous, and nanostructured. SEM analysis was also examined in Ag coatings and the formation of thin-film was observed. Accelerated corrosion test was applied in order to determine the durability properties of reinforced concrete lollipop samples prepared with nanocoated rebars. Finally, with the help of the data obtained as a result of the accelerated corrosion test, the initial corrosion current and damage occurrence times were determined and evaluated. In the last part of this study, the experimental results of different types of coatings, which were executed by our research team in previous studies with using this method, were compared with the results in this article.

2. Experimental Study

The measurement of the stage of corrosion on the structure is generally difficult to access and inconvenient. Methods used on a structure already in service are restricted, expensive, or impractical. However, it is impossible to ideate an opinion about corrosion before it hardens after concrete pouring. Therefore, researchers predict the corrosion of the structure by simulating it on reinforced concrete samples with the help of laboratory experiments. In this study, the exposure of the reinforced concrete structure to the corrosion effect was illustrated with the help of laboratory experiments. The accelerated corrosion method was used, which is one of the most preferable and reliable methods for predicting corrosion.

2.1 Materials

CEM I Portland cement (CEM I 42.5 R), sand, aggregate and water were used in the experimental studies. The cement we used covers the standard of TS EN 197-1 (2012) and ASTM C150/C150M-21 (2021). In this study, the maximum size of aggregate was 22.4 mm and sand was 0-4 mm. Concrete mixing ratios are calculated for 1 m^3 of concrete and given in Table 1.

The sizes of aggregates are entitled No I and No II which refers to fine and coarse aggregates. The concrete quality used in this study will represent the concretes that are widely applied nowadays. So, the percentage of aggregate that was used was tried before and gave us sufficient mechanical properties according to our former experiences. Also in this study, deformed reinforcement was used with a diameter of 16 mm (Ø16) S420 and the length of the rebar was 20 cm for all the samples (ASTM A615/A615M-20 2020, TS 708 2016). Industrial sodium chloride salt was used in the accelerated corrosion tests.

Table 1. Concrete mixing ratios

CEM I Cement (kg)	**Water (kg)**	**Sand (kg)**	**Crushed Stone No. I (kg)**	**Crushed Stone No. II (kg)**	**Unit Weight (kg/m^3)**
400	200	825	310	600	2335

2.2 Sample Preparation

The water/cement ratio of the concrete produced in the study was 0.50 and the cement dosage was 400 kg/m^3. The mix proportion of concrete samples is shown in Table 1 and there is no addition of chemical or mineral admixtures in the mixes. For the accelerated corrosion tests in this research, 100 × 200 mm cylindrical samples were used which have 16 mm diameter rebar was placed center of it. Concrete samples were cured under laboratory conditions (Rh = 40, T = 25 °C). Samples were demolded after 24 hours, and they were put into the water pool for water-curing for 28 days.

3. Test Procedure

3.1 TVA Method

The Thermionic Vacuum Arc (TVA) system allows high high-quality nano-structure thin film coatings at very high adhesion. TVA principle generally works under high voltage between in anode and cathode. In the TVA chamber, the cathode is an electron gun with Wehnelt cylinder (containing a heated tungsten filament) and the anode involves material that is to be used as a thin-film coating (Pat *et al.* 2021). The appearance of the TVA system in operation and during the recording of the data simultaneously in the software system is as in Figure 1.

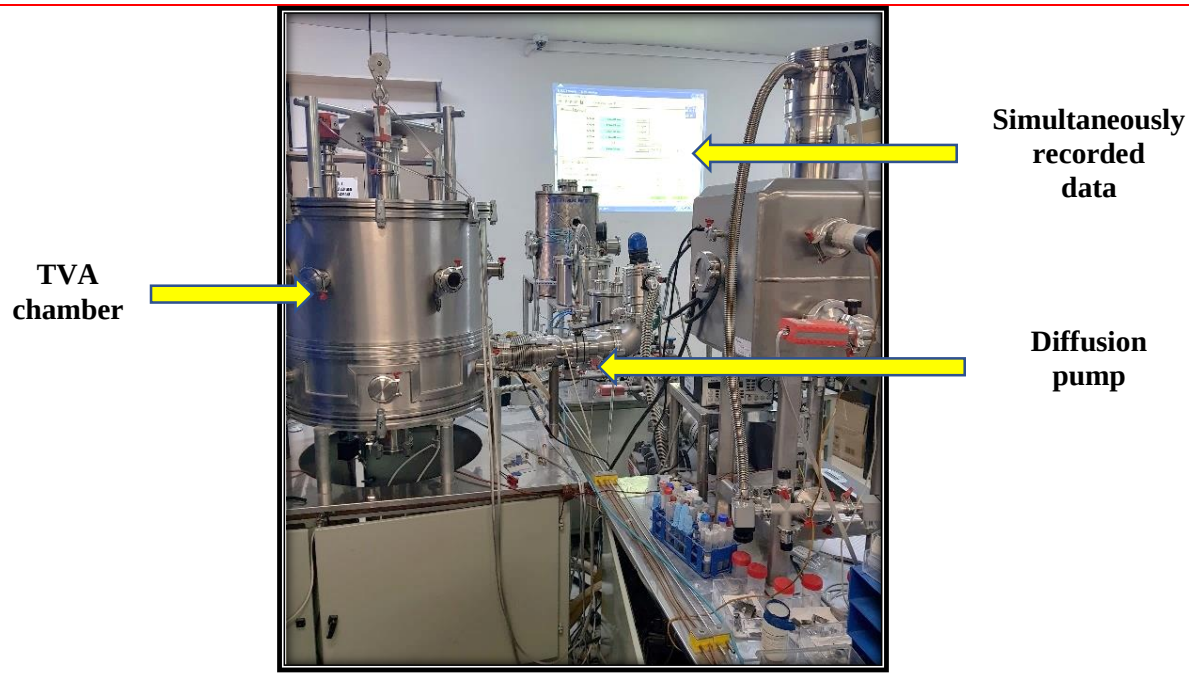
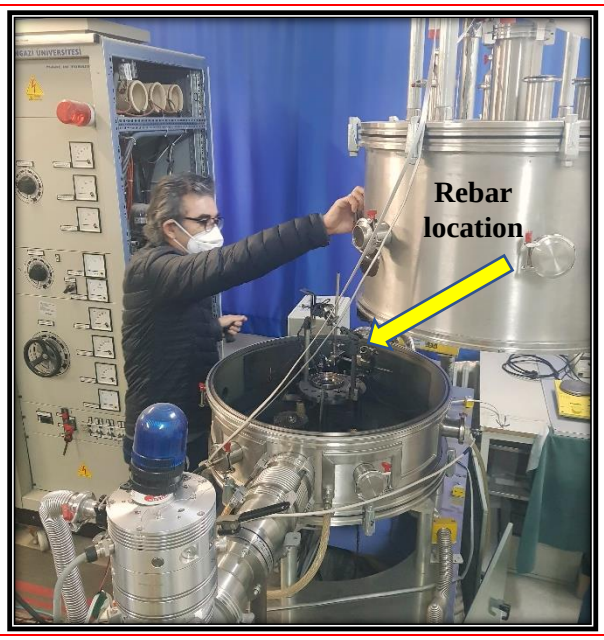
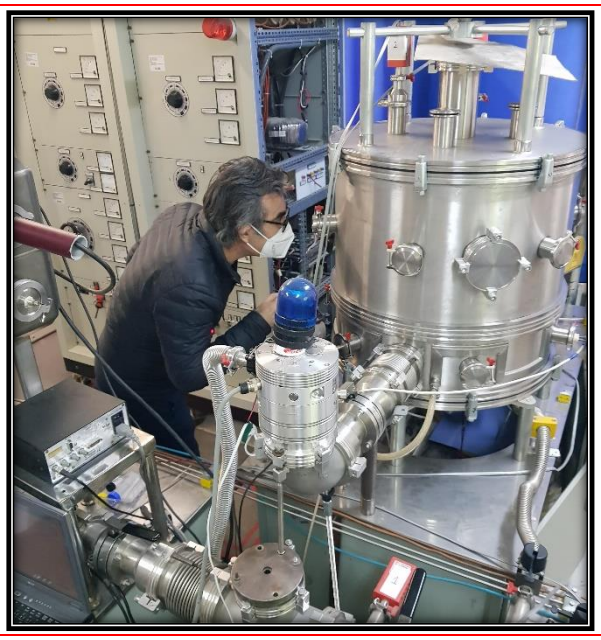


Fig. 1 General view of the TVA coating system and simultaneous monitoring of the data from the computer.



(a) Placing the samples in the TVA chamber



(b) Observing the rebars during the coating process

Fig. 2 Application and controlling of coating on reinforcement

Beginning of the test, accelerated electrons due to the high DC voltage reach the anode. Then because of the electron bombardment, the heat of the anode element increases rapidly and the material (which is used as a coating) starts to melt (Pat *et al.* 2022, Ozkan *et al.* 2022). Afterwards, with the help of high pressure in the vacuum chamber evaporated atoms of anode material (plasma) are coated on the substrate (rebar) as nano-structure thin films (Figure 2) (Pat *et al.* 2021, Pat *et al.* 2018, Korkmaz *et al.* 2012, Ozkan *et al.* 2012).

Table 2. Operating parameters of the TVA system during the coating process

	Unit	Ag
Deposition time	Minute	8
Accelerated voltage	Volt	750V → 0
Filament current	Ampere	18
Deposition Pressure	Torr	9 x10^{-5}
Bombarding current	Miliampere	0 → 500

Table 2 shows the operating parameters of the TVA system. These parameters vary according to the material to be coated (substrate material) and the element which transforms to plasma (Akkurt *et al.* 2020). Figure 3 shows the structural steel before and after coating. After the coating process, the steels were placed in the molds.



Fig. 3 Ag sample after coating in the TVA system

4. Experimental Results and Discussion

4.1 Examination of Surface Analysis

SEM analysis was used to visualize the reinforcements with Ag nano-coating. For this purpose, specific rebar samples were prepared (1 cm thickness) which their surfaces were polished. Figure 4 show the Ag element peaks in EDX analysis. The surface morphology of coated and uncoated reinforcement samples was shown in Figure 5.

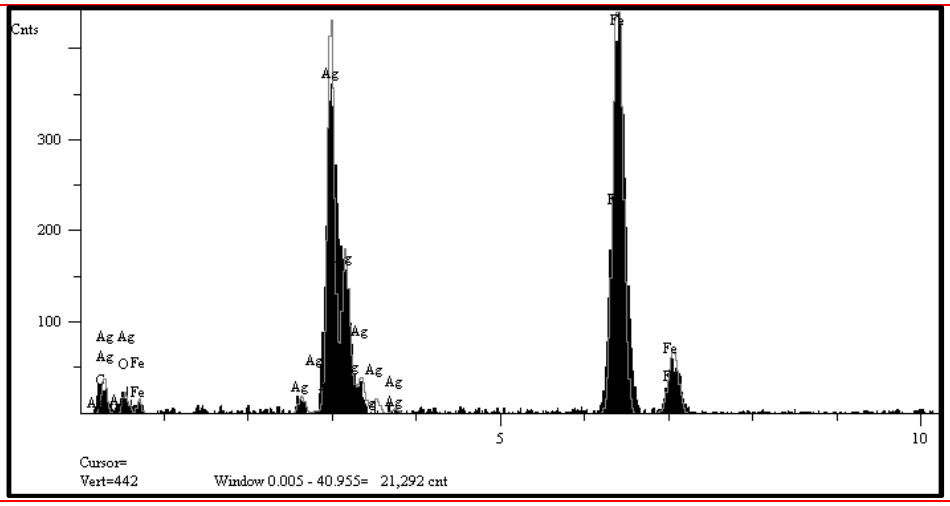
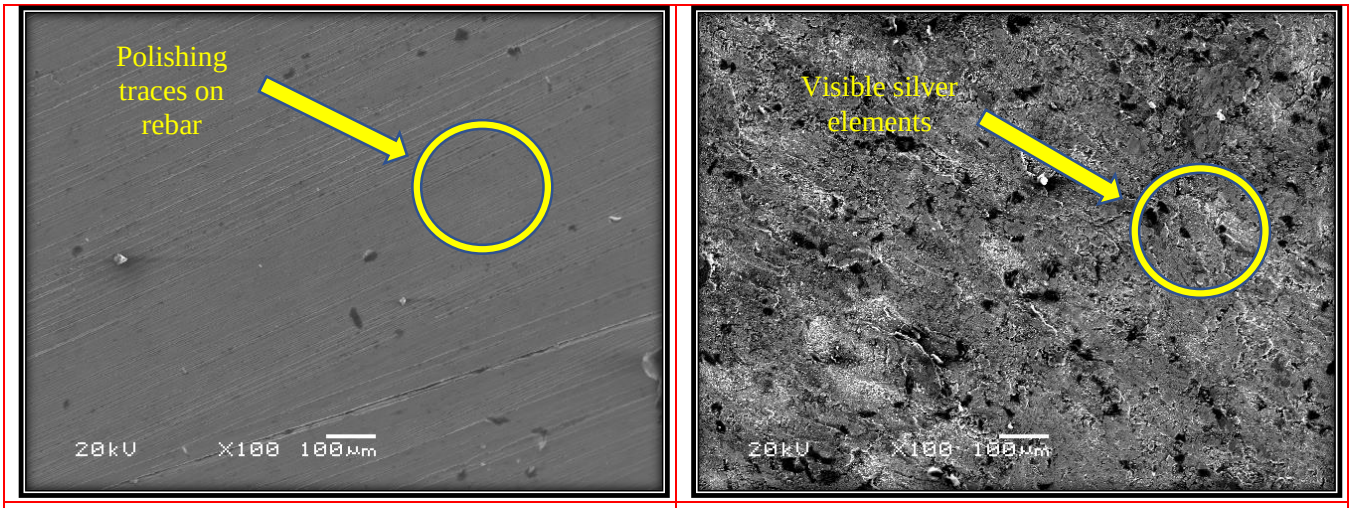


Fig. 4 EDX analysis of Ag coated sample

Table 3. Concentration of component in coatings

Component	Concentration	Units
Fe	46.682	wt.%
C	3.009	wt.%
O	0.804	wt.%
Ag	49.505	wt.%
Total	**100.000**	**wt.%**

In the EDX analysis, the peaks of the elements detected on the surface are shown. In Table 3, the percentage weights of the elements in the EDX analysis are indicated. The percentages of iron, carbon, oxygen and silver elements in a specific region of analysis are shown in Table 3. Ag element concentration on the surface was found to be 49.505%.



(a) Surface image of bare uncoated steel

(b) Surface image of Ag coated steel

Fig. 5 SEM surface analysis of uncoated and coated samples with TVA system

Both images were taken in the rate of the same magnification. In the first image, the polished surface of the uncoated sample was seen. The second image crystal structure of Ag coating can be observed. This structure which is visible in the images is proof that the coating has successfully adhered to the surface. In addition, this nano-coating, which is not very smooth, increases the adherence forces between concrete and the reinforcement. Since the thickness of the thin films is between 2-50 nm, they fill all invisible cracks and voids on the rebar.

4.2 Investigation of Accelerated Corrosion Test Results

The volume of the reinforcement in the concrete increases when it is corroded due to environmental reasons. This increase in volume creates an internal force in reinforced concrete elements from the inside to out. The rigid structure of the concrete does not allow the development of these forces and after a certain critical level is exceeded, the concrete cannot show further resistance and that results formations of cracks around the rebar. Cracks reach the surface by advancing along a certain line through micro-voids in the concrete. Figure 6 shows the concrete samples before and after accelerated corrosion tests.



(a) Before test | (b) After test

Fig. 6 The state of the prepared lollipop samples before and after the accelerated corrosion test

Figure 7 shows the final state of the coated and uncoated concrete samples, which were subjected to accelerated corrosion test in an aggressive environment for a certain period of time. It can be seen from the figure that Ag-coated reinforcement by using the TVA system has shown less corrosion damage than uncoated reinforcement in the same time interval.



(a) Ag coated sample | (b) Uncoated control sample

Fig. 7 The interior of samples subjected to accelerated corrosion testing for a specific period of time

Figure 8 below shows the time-dependent initial corrosion current and damage occurrence time graph. These data were obtained from the data logger device, which records data every 2 minutes from the beginning to the end of the experiment; illustrated on a graph with the help of specific software programs. The initial corrosion current can be defined as the initial resistance of the sample to the current after the current is delivered by the DC source. Corrosion reactions develop more rapidly in samples which have porous structure or have no coatings on rebar; therefore, if this current is high, more current will be applied by the system to that sample, and as a result, it means corrosion will occur in a shorter time.

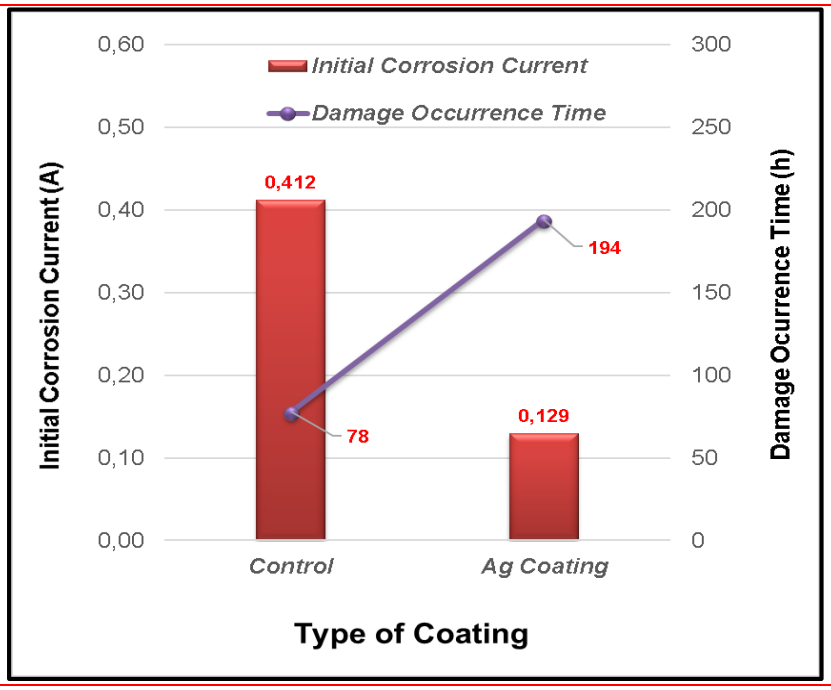


Fig. 8 Time-dependent graph of initial corrosion current and damage occurrence time

The obtained data confirm that the uncoated control sample reached a high initial corrosion current value compared to the Ag coated sample. In addition, the first crack was seen tardy in Ag coated samples and the damage occurrence time was longer compared to the uncoated control sample. As a result of the experimental studies, the thin nano-coated reinforcements with the TVA system decreased the initial corrosion current by 68.8% and expanded the damage occurrence time by 148.7% compared to the uncoated reinforced samples (Figure 8).

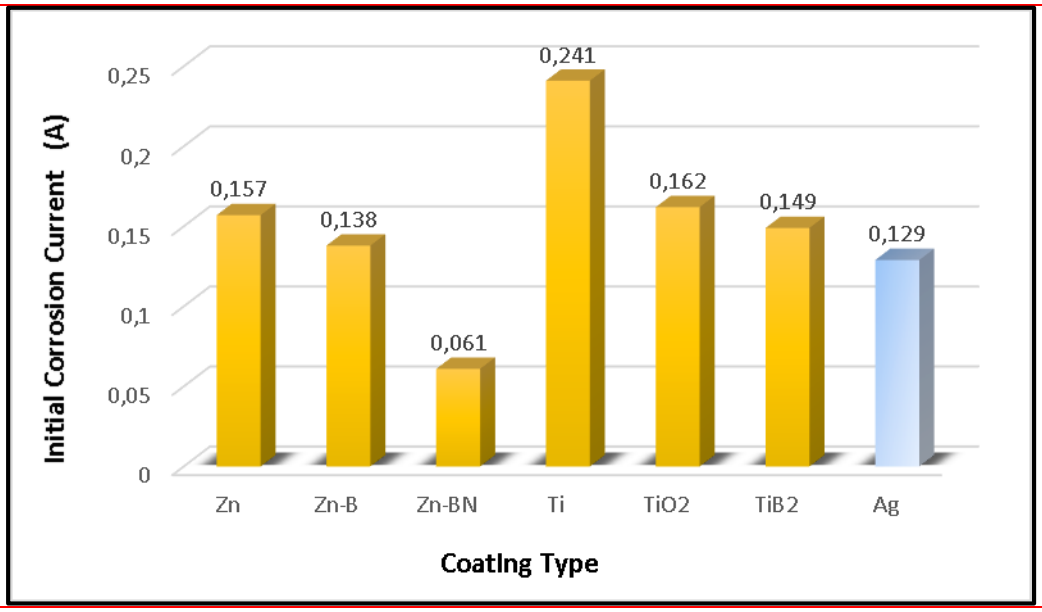


Fig. 9 Comparison of initial corrosion current with other studies

Uzunomeroglu *et al.* (2022) were applied Zinc (Zn), Zinc-Boron (Zn-B) and Zinc-Boron-Nitrogen (Zn-BN) nanocrystal coatings to reinforced concrete reinforcements with Thermionic Vacuum Arc (TVA) system. Then, the corrosion rates of coated and uncoated reinforcements were compared with accelerated corrosion tests. After these

tests, the real weight losses were determined by removing the reinforcements in the samples. The real weight loss that occurred after exposing the reinforcement to corrosion effect was compared with the theoretical weight loss calculated from the Faraday equation. Their experimental results showed that; compared to the uncoated reinforcements, the initial corrosion currents of the Zn, Zn-B, Zn-BN coated reinforcements decreased by 93.9%, 93.0 and 95.1%, respectively, and the real weight losses caused by corrosion decreased by 32.67%, 50.64% and 90.08% in Zn, Zn-B and Zn-BN nanocoatings, respectively (Figure 9).

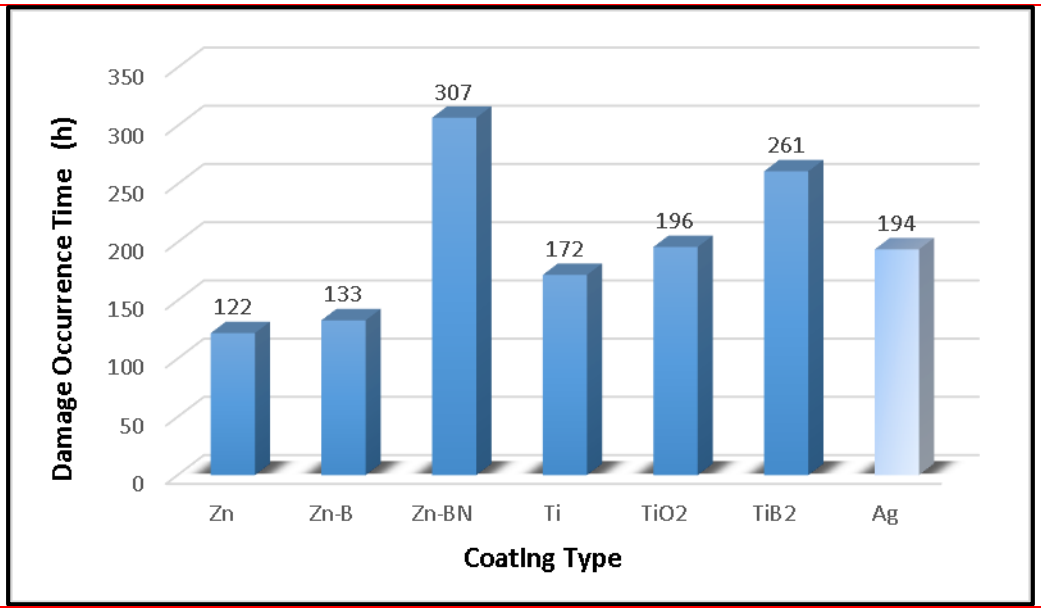


Fig. 10 Comparison of occurrence time with other studies

Topcu *et al.* (2022) used thermionic vacuum arc (TVA) system in order to apply nano-coatings on the structural rebar using titanium (Ti), titanium dioxide (TiO_2) and titanium diboride (TiB_2). After the implementation of these coatings on reinforced concrete samples, they used accelerated corrosion tests so that the effectiveness of coatings against corrosion can be examined. Their experiments showed that nano-coatings increased the corrosion resistance of the structural steels used in reinforced concrete structures. During the harmful effects that threaten the reinforced sample, the impact of coatings has emerged and reduced the corrosion of steel reinforcements. The best results of their experiments were obtained with TiB_2-coated sample with 48% lower corrosion current and this coating also expanded the damage occurrence time by 119% compared to uncoated rebar (Figure 10).

5. Conclusions

In this manuscript, structural steel was coated with Ag element by using a thermionic vacuum arc system. TVA is such a different technique that produces plasma the reinforcements gained significantly high corrosion resistance. In recent years, corrosion prevention methods of efforts gained momentum. In this study, nanotechnology which is used in different fields was applied as a reinforcement coating method within the scope of civil engineering. Our studies are proceeding on the developing corrosion resistance of steels applied by TVA system, with using different elements.

The nanocoating we produce is so durable that it acts as a proper and stable barrier around the rebar and prevents it from adverse effects. As a result of the experimental studies, the thin nano-coated reinforcements with the TVA system decreased the initial corrosion current by 68.8% and expanded the damage occurrence time by 148.7% compared to the uncoated reinforced samples.

This coating technology has been tested by our team on many different elements. Some of these are mentioned in the sections above. Silver coatings applied with this technique have shown sufficient resistance to corrosion and give one of the best results compared to other studies. The conversion of different elements or compounds to plasma as a coating material can change the structure and properties of the coating and it may also give different results against corrosion. Our research continues in order to obtain the least costly and most effective coating composition against reinforced concrete corrosion.

Also, one of the most important points to be mentioned is that corrosion is a worldwide issue and may occur anywhere iron and aggressive media are present. As a result of our research and laboratory experiments, the corrosion resistance of reinforced concrete reinforcement has been improved, but this will be beneficial not only in civil engineering but also in many engineering and industrial areas.

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