

NANO-STRUCTURE OF STAINLESS STEEL MATERIALS AND CORROSION

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ABSTRACT

The use of nanotechnology in the ground of corrosion protection of stainless steels attracts the attention of academics. Many of these claims involve good understanding of the corrosion behavior of the stainless steels as a gathering of microstructure. Important progress has been made in various aspects of combination of nano-scale materials. In adding, nanostructures encourage selective oxidation, forming a protecting oxide scale with higher adhesion to the substrate. Nano-structured stainless steels of 1–100 nm are known for their exceptional mechanical and physical properties due to their very reasonable grain size and high grain boundary volume fraction. They are important due to their unique properties that may lead to new and exciting applications.

Keywords: nanostructure, stainless steel, mechanical properties, corrosion.

Introduction

Nanocomposites of polymer coating can successfully combine the benefits of organic polymers, such as elasticity and water resistance to that of advanced inorganic materials, such as hardness and absorbency. The nano-structured silica coating showed comparable or better performance than hexavalent chrome passivation (Honggang, 2000). Such behavior of nano-structured materials, which relates to corrosion resistance, relies on materials micro-structure. In fact, most properties of solids are subject to the materials micro-structure. The micro-structure includes a number of parameters such as the chemical composition, the arrangement of the atomic structure and the size of a solid in one, two or three dimensions. Comparable differences have been noted if the atomic structure of a solid differs far from steadiness or if its size is reduced to a few inter-atomic spacing in one, two or three dimensions. Nano-porous metals made by dealloying characterize a class of functional materials with the unique structural properties of mechanical rigidity, electrical conductivity, and high corrosion resistance (Nalwa, 2000). It is stated that the prospect of using alloy corrosion as a means of making nano-materials for important studies and functional applications has led to a recovered interest in the process. The quite different mechanical properties of nano-porous metals are one of the focus points of this interest, as relevant studies probe the deformation behavior of crystals at the lower end of the size scale. Besides, the coupling of bulk stress and strain to the forces acting along the surface of nano-porous metals provide unique opportunities for controlling the mechanical behavior through external variables such as the electrical or chemical potentials. The relation between chemical architecture of thin (10 and 50 nm) chromium and tantalum oxide coatings grown by filtered cathodic curve deposition on carbon steel and their corrosion protection properties is reported (Scott, 2005). In statistic, the coatings of oxides improve sealing properties of the alloy but there is a beginning for the contained corrosion. This may be due to the imperfectness of the coats and unsuitable finishing for the alloy surface.

The corrosion performance in chloride media of chromium coatings obtained by direct current and pulse current was studied (Kekkonen, 1985). The obtained results show similar hardness values and a greater corrosion performance of pulse current coatings, which is related to their roughness, morphology, wett-ability and mainly, their crack absence. Silver or silicon oxide coreshell nano-particles about 60 nm were used in marine antimicrobial corrosion coatings. The results show that the nano-particles coat could improve long term corrosion protection in comparison with the copper biocides. This composite has a strong possible use in environmentally friendly antimicrobial coatings.

Properties of nanostructured materials and controlling procedures

Nano-structured materials can be produced by using different combination and processing methods. This will lead to difference of their grain sizes or phase dimensions in the nano-meter size system. The importance in these new ultrafine grained materials results mainly from the special nature of their various physical, chemical, and mechanical properties and the possibilities of controlling these properties during the combination and subsequent processing procedures (Gleiter, 2000). As it is now becoming more and more apparent that their properties can be engineered effectively during combination and processing, and that they can also be produced in quantity, nano-phase materials should have significant potential for technological development in a variety of applications. As the properties of solids depend on size, atomic structure and chemical composition, the nanostructured materials exhibit new properties due to one or several effects.

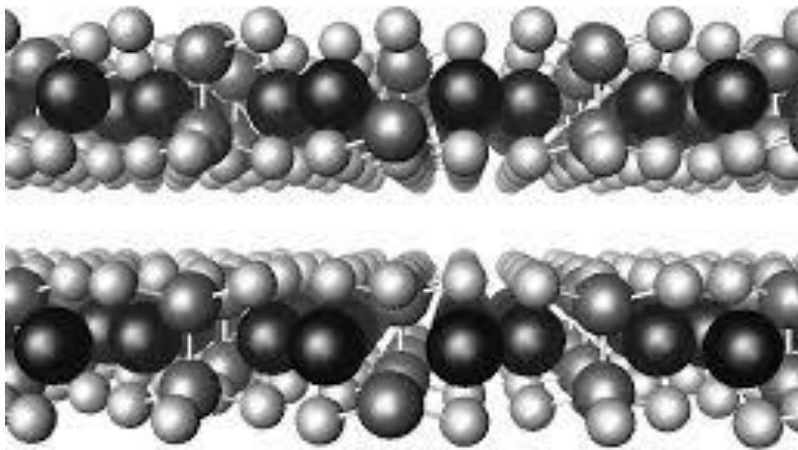
Effects Of Size

The effects of size result if the specific size of the building blocks of the micro-structure is reduced to the point where critical length scales of physical occurrences for example, the mean free paths of electrons or phonons, a coherency length, a screening length, become comparable with the specific size of the building blocks of the micro-structure (Saji, 2007).

Dimensionality Change

If nano-structured materials contain of thin needle shaped or flat, two dimensional crystallites, they become a two or one dimensional system with respect to this occurrence. For example, layered materials MPS3, where M is the transition metals, are ordered in layers with interspacing of 6.4 Å, as shown in Figure 1. These materials are crystalline and could be used for many applications, such as, a cathode for the rechargeable batteries, sensors, optical applications, and hydrogen storage. Processing map for hot working of hot extruded AZ31–1.5 vol% nanoalumina magnesium composite prepared by disintegrated metal deposition technique has been developed in the temperature range of 250 to 500°C and strain rate range of 0.0003 to 10 S⁻¹. The nanoalumina composite helps in decreasing the preferred placement in AZ31 alloy. This may growth its corrosion resistance (Jon, 2010).

Figure 1: Layered structure of MPS3.



Atomic Structure

A high concentration of incoherent interfaces or other lattice defects such as dislocations will change the atomic structure. The cores of lattice defects represent a constrained state of solid matter differing structurally from unconstrained crystals. As a result, a solid containing a high concentration of defect cores differs structurally from a defect-free solid with the same average chemical composition. The boundaries represent an example of this effect, the misfit between in line crystallites changes the atomic structure in the boundary areas relative to the perfect crystal (Yuriy, 2010). At high defect densities the volume fraction of defect cores becomes comparable with the volume fraction of the crystalline areas. In statistic, this is the case if the crystal diameter becomes comparable with the thickness of the interfaces, as example, for crystal sizes on the order of one or a few nano-meters as is the case in nano-structured materials.

Alloying Elements

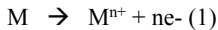
The alloying elements have great effect on the alloys structure and properties. For example, the addition of alloying elements less than iron increases the corrosion resistance in the active area improving the protective quality of the corrosion product film in which the cations of alloying elements are considerably concentrated. The impact of the alloying elements on the interface reactions of zinc coatings during the galvanization process was examined. These reactions affect the illustration and the structure and properties of the outer layer of the coatings. Depending on the type and concentration of the alloying additions in the galvanizing bath differences were induced in the crystallization process of the Fe Zn phases. It was found that both the concentration and the distribution of the alloying elements played an significant role in the growth of the phases. It has been found out for alloys with elements, which are capable of forming passive films, that the atoms of these elements can diffuse easily through the grain boundaries to the surface of the alloy to form the protective passive layer (Pardo, 2008).

The following cases of this type of immiscible components in nano-structured may be notable, solute atoms with little solubility in the lattice of the crystallites frequently isolate to the boundary cores. The second case of nano-structured alloys results if the crystallites of nano-structured materials have different chemical compositions. Even if the elements are immiscible in the crystalline or liquid state Fe and Ag, the formation of solid solutions in the boundary regions of the nano-structured has been noticed.

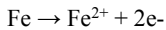
Materials' Corrosion

Corrosion is the chemical or electrochemical reaction between a material and its environment. It produces weakening of the material or of its properties. Also, corrosion has different forms of occurrence (Dennis, 1990). The basic corrosion theory is that the corrosion is an electro-chemical reaction composed of two half cell reactions, an anodic reaction and a cathodic reaction. The anodic reaction releases electrons as shown in equations, while the cathodic reaction consumes electrons. Each half cell reaction has an electrical potential, known as the half cell electrode potential. The anodic reaction potential E_a , plus the cathodic reaction potential E_c , adds up to E the cell potential. If the overall cell potential is positive, the reaction will proceed spontaneously. The corrosion reactions can be represented as follows:

Anodic reaction:

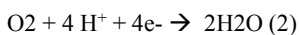


Where M stands for a metal and n stands for the number of electrons that an atom of the metal will easily release, an example for iron and steel:

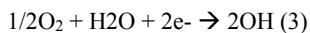


Cathodic reactions:

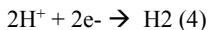
- Oxygen reduction in acidic solution



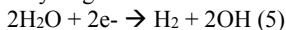
- Oxygen reduction in neutral or basic solution



- Hydrogen evolution from acidic solution



- Hydrogen evolution from neutral water



The chemical occurrence or dry corrosion occurs under dry conditions, such as high temperatures in gassy environments, liquid salts and liquid metals. Dry corrosion process is a direct reaction between a metal and the corrosive environment (Lai-Duien, 1998). Dry corrosion is of great importance in a number of petroleum refining processes. It includes the attack of hydrogen sulfide and other sulfur compounds on steel and several alloys at elevated temperatures. Solutions to this type of corrosion generally depend on metallurgical approaches, such as differences in composition, heat treatment of the selected metal or alloy. In fact, high temperature corrosion of metals and alloys always involves oxidation process. For example, a metal reacts with oxygen at high temperature by initial adsorption of oxygen, chemical reaction to form the surface oxide, oxide nucleation and later growth into a continuous film. Such film may protect the underlying metal. One of the well known oxidation is the iron oxidation in oxygen as pure metal or in carbon steel alloys at high temperature.

Wet corrosion is an electrochemical process in practice it limits to nearly 250 °C as an upper temperature. The electrochemical corrosion effects from reaction between a metal surface and an ion conducting environment. This process happens by metal contact with an electrolyte for transport of electric current. Most cases of electrochemical corrosion proceed in aqueous medium such as water, atmospheric moisture, rain, and wet soil. Furthermore, other environments increase the corrosion process for example, acids, petroleum products, cooling water, chemical solutions. For instance, water presents in refinery by different sources, such as the crude itself, through injection of water of steam to aid in the steam distillation of various petroleum fractions, water washing or solution contacting various intermediate and product streams in refining and petrochemical processes. In detail, metal surfaces have corrosion cells in contact with an electrolyte. Different areas on the metal surface could also have different potentials with deference to the electrolyte (Raymond, 1994). These differences could be due to a number of factors such as metallurgical behaviors, differences in their composition, micro-structure, fabrication, and field installations, and environmental factors. Carbon and low alloy steels are the most widely used material in different industries in corrosive environments and the metallurgical factors have great effect on the corrosion process.

Corrosion resistance of alloys

A number of ways have developed to increase the corrosion resistance of metals such as applying inhibitor, adding passive alloy element, putting protective coating and so on. The application of inhibitors has to follow some regulations such as environmental impact, low toxicity, and structure of inhibitor and alloys. Nano-structure inhibitor is very important in protection metals and alloys (Kumaraguru, 2006). Changing microstructure of materials will bring surprised results to promote the corrosion resistance of metals' alloys. This change happens by using new microstructures such as single crystalline, nano-crystalline or microcrystalline and amorphous to replace the traditional cast alloy. Nanostructured materials illustrate by their small grain sizes from 1 to 100 nm and high volume fraction of grain boundaries. These properties improve unique physical, chemical and mechanical properties compared with those of their cast counter-parts. The properties are mainly useful in corrosion protection applications.

Nano-Size And Effect On Corrosion Resistance

Electro-deposition is a useful technique for producing nano-structured materials. It is a technologically and economically workable production route to metals, alloys and metal matrix composites, both in bulk form and as coatings. Properties of nano-structured electrodeposits such as hardness, wear resistance and electrical resistivity are strongly grain size dependent. Corrosion behaviour of nano-structured alloys has been evaluated by several techniques in several environments. Studies shown an enhanced corrosion resistance of nano-structured Fe₃₂ - Ni₃₆ - Cr₁₄ than that of its unstructured counterpart. The research attributed this enhanced corrosion resistance to the observed greater Cr improvement of the electrochemical surface film via fast interphase boundary distribution.

Other report improved corrosion resistance with nano-structured Fe₇₂Si₁₀Cr₃ metallic glass wires. In that study, the valuable effects of nano-structured processing for corrosion resistance were not evident with a nonpassivating alloy composition. Some report, an enhanced corrosion resistance of nano-structured Fe 8 wt% Al in Na₂SO₄ solution. The research shows that defect density of grain boundaries encourages metal dissolution. As the diffusion of aluminum is fast enough in the grain boundaries, it is possible that the oxide film on nano-structured and crystalline FeAl₈ alloy provides better protection than on the same polycrystalline alloy. Weak acid and weak base ease passive film formation of nano-structured FeAl₈ where Al forms stable passive film. The recently developed Ti₆₀Cu₁₄Ni₁₂Sn₄Nb₁₀ nano-structured composite exhibits a particular micro-structure that discusses outstanding mechanical properties and improves corrosion resistance (Dennis, 1990). It has been reported that the presence of a yielding second phase can considerably improve the mechanical properties of nano-crystalline alloys. Lately developed Ti base bulk alloy dispersed in a nano-structured greatly improves the usual low ductility of similar nano-crystalline alloy. Separation tests of Ti₆₀ Cu₁₄ Ni₁₂ Sn₄ Nb₁₀ copper mould cast samples indicate good corrosion resistance in acidic, medium resistance in alkaline but the alloy experiences pitting in chloride media. The behaviour of the alloy in H₂SO₄ is similar as the typical behaviour of pure titanium and titanium alloys. It shows a wide anodic passive area between 90 mV and 1.5V, about, and passive current concentrations in the order of 10⁻³ mA due to the formation of highly protective surface films. The voltage range of passivation in NaOH electrolyte is shorter than in H₂SO₄. It finishes when the current increases to 470mV, nearly. In chloride medium, sharp increase in current concentration interferes the passivation during anodic separation. The interval occurs by a sudden passive film failure followed by an excessive pit growth and the subsequent dissolution of the surface of the alloy. The increase of NaCl concentration shifts pitting potentials to more negative values. This behavior differs from general findings on poly-crystalline pure titanium and diluted titanium alloys.

The pitting corrosion and limited occurrence on the alloys don't observe in marine environments (Salvago, 1992).

Corrosion resistance of stainless steel

Stainless steel uses as a structural material in many applications. Corrosion and wear limits its service life (Raymond, 1994). Effective measures are taken to improve its corrosion and wear resistance properties. A passive film precludes contact between corrosive environments and the metallic surface. However, weakness of the passive layer can cause corrosion. The use of inhibitive creates active corrosion protection to decrease corrosion strength.

The use of both strategies jointly could sufficiently protect the metallic substrate. The conversion coatings such as chromating and phosphating treatments have generally played important role in different industries. It provides corrosion protection to both ferrous and non ferrous metals. Besides in many cases the anti-corrosive property of zinc phosphate treatment is insufficient for outdoor exposure. Electroplated Ni and Cr are relatively expensive and Cr(VI) is environmentally unacceptable. As an alternative, siloxane based solgel coatings have been suggested as passive corrosion protection. It has the ability to form dense Si-O-Si network following to substrate through Me-O-Si bonds. The bonds form good corrosion slow down properties. Adding specific organic functional groups such as siloxane improve connections on alloys surface. Collections of metal oxides reinforces silica network during solgel combination from the particular metal alk-oxides. Moreover, solgel coatings do not need high process temperature and vacuum conditions are important in the case of many of thin layer coating techniques. Besides, solgel is relatively simple, low cost and applicable to materials having complex geometry. It is considered to have low negative environmental impact. However, defects or pores in the solgel coating let in the corrosive and start the corrosion processes. The defects indicate the need for additional active corrosion protection. Combination of inhibitive into inorganic fillers develops corrosion resistance. Many kinds of inhibitors could be used to protect many metallic materials, however very often this negatively affects the stability of the solgel matrix. Acetylenic alcohols are deliberated excellent inhibitors of corrosion. Nano-structure solgel saturated with propargyl alcohol can protect defects of solgel.

Anti-corrosive primers and coatings based on conducting polymers gain force Owing to the severe environmental regulations on the usage of toxic heavy metals in the formulation of corrosion protective coatings. The recent progresses in nano-technology have accelerated the development of high performance nano-structured coatings. They have a broad range of anti-corrosive activity under a wider range of aggressive environments. Inhibitor coatings based on conducting polymers are either chemically or electrochemically deposited on the metal substrate.

Figure 2: Variation of surface roughness as a function electropolishing time.

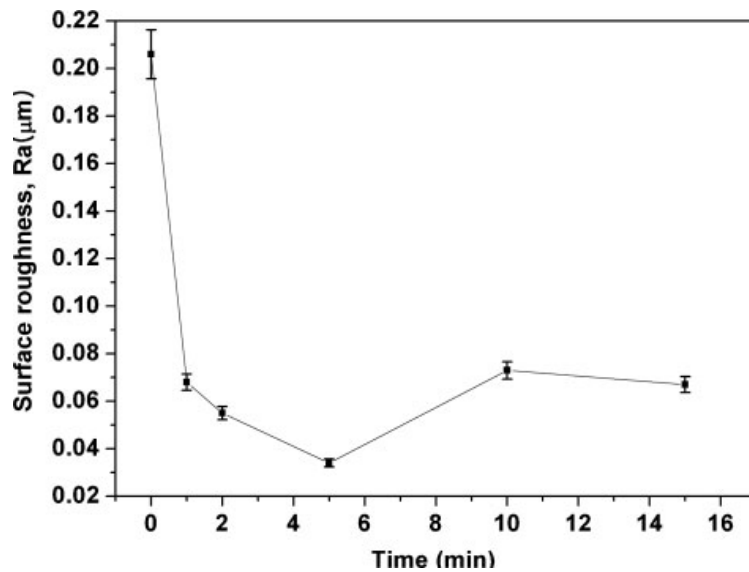
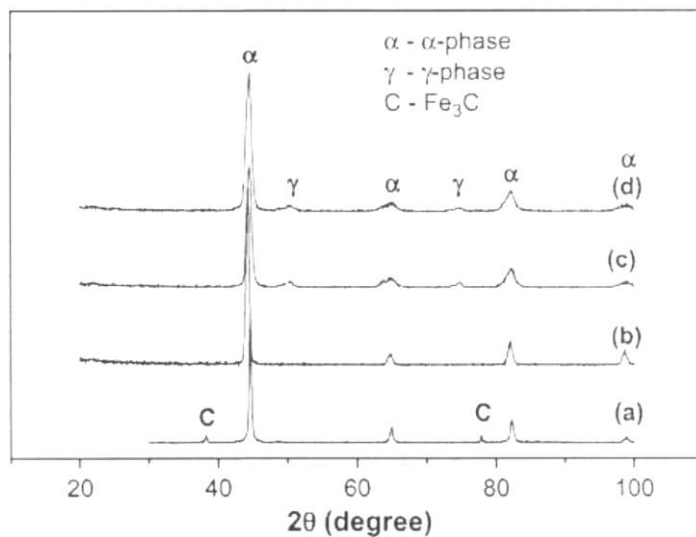


Figure 3: XRD patterns collected from the surface of the initial no. 20 steel (a), irradiated with 1 pulse (b), 5 pulses (c), and 10 pulses (d). The energy density of HCPM is 4 J cm².



Stainless Steel Corrosion And Nano-Structure

The family of stainless steels is large and varied, in fact there are more than 100 listed types. Each of these was originally designated for some specific use. For instance, SS316 is used for severe environments. Of course, there are many industrial processes that require a higher level of resistance to corrosion. Carburizing has been applied to austenitic stainless steel to promote increased corrosion resistance. Nano-metric sized carbide based crystallites have been created successfully through the pulsed nano-crystalline plasma electrolytic carburizing method on the surface of 316 austenitic stainless steel. It was found that the corrosion resistances of coated samples have a direct connection with the average size of complex carbide based nano-crystallites. The produced carbide based crystallites show average sizes at around 37 to 80 nm. The minimum average size of nano-crystals was found to be 37.7 nm in 600 V of peak of applied cathodic voltage, 10 kHz of frequency of pulsed current, 40 °C of temperature of electrolyte, 10 min of treatment time. Separation resistances of different samples found through the potentiodynamic corrosion tests performed after surface hardening treatment. The separation resistances due to corrosion in sample groups treated at different conditions varied between 153.4 kΩ/cm² and 635 kΩ/cm². The figure explains which specimen has maximum or minimum corrosion resistance. From the above results, it can easily be said that a high corrosion resistance has been obtained with higher applied voltages and treatment times of carburizing.

These results specify that the corrosion resistances of the obtained layers are a direct function of the average size of the nano-crystallites.

Enhancement in the surface layer properties by changing their structure remains actual due to the fact that the destruction of the materials, including fatigue failure and corrosion depends usually on the surface structural state. The surface nano-structure, which is formed in the surface layers with thickness of about of 30 to 50 nm, plays a main role in the improvement of properties. At the same time, only a few recent reports have given attention to the corrosion behavior of stainless steels with nano-grained surface structure. These reports have shown that the corrosion resistance can also be significantly improved, particularly by shot peening or sandblasting with subsequent low temperature toughening. For instance, a nano-crystalline surface layer was produced on an 321 stainless steel by severe plastic deformation via ultrasonic peening. The nano-structured surface layer formed after straining already contains mainly the martensite nano-grains characterized by an average size of about 10 nm. Grain size increased slowly up to 60 nm within the layer containing both austenite and martensite phases at a depth of about 30 nm from the treated surface. Both the micro-hardness behavior of the stainless steel surface and its corrosion performance in 3.5% NaCl solution (sea water) can be improved by the ultrasonic peening. They are shown to be in connection with, the grain improvement process and the increase in the volume fraction of strain induced martensite.

Nano-structure changes the thickness of passive film. XPS Cr spectra from the passive films in 3.5% NaCl solution on nano-structure coating and the cast alloy are shown in Figure 4. After 40 s testing using the same test parameters, the Cr³⁺ peak disappeared in the passive film on the nano-structure coating but was still present in the film on the cast alloy. This indicates that the passive film on the nano-structure coating was thinner than that on the cast alloy in normal NaCl solution. Nevertheless, nano-structure increased the thickness of passive film on the magnesium alloy with rare earth elements. It is well known that the passive film on the magnesium alloy is mostly the corrosion product layer on the sample, which blocks the dissolution of the material and inhibits the corrosion. As a result, nano-structure promotes the dissolution of alloy and forms more products on the sample.

To conclude, the film layer was much thicker than that of the cast alloy. Nano-structure also changes the compact property of the passive film. After cathodic reduction, the variation of current with time could be measured at a fixed potential. If the influence of the double layer charge is neglected, the initial drop of current concentration should be related to the growth of a protecting film on the electrode surface. The current decreases with time as follows:

$$I = I_0 - (A + kt)$$

where I represents current concentration, t is time, A is constant and k represents the slope of the double log plot for potentiostatic separation. k = -1 indicates the formation of a compact, highly protective passive film, while k = -0.5 indicates the presence of a absorbent film, growing as a result of a dissolution and precipitation process. A absorbent passive film presents on the 310 stainless steel and nano-structure improves formation of a compact film.

Conclusion

Properties of nano-structured electrodeposits such as resistance, electrical resistivity and hardness depend strongly on grain sizes of metals and alloys. Nano-crystallization decreases grain size and changes surface condition. The surface condition considerably influences the electrochemical corrosion behaviors of metals' alloys in liquid system. There are a number of advanced techniques have been developed to achieve the nano-structure. Many applications of the nano-materials made to improve the devices and industries. The application of nano-technology in the field of corrosion prevention of metals is very important. Nano-metric sized carbide based crystallites have been produced successfully through the pulsed nano-crystalline plasma electrolytic carburizing method on the surface of 316 austenitic stainless steel.

The corrosion resistance of coated samples has a direct connection with the average size of complex carbide based nano-crystallites. Important corrosion resistance achieved with higher voltages and treatment times of carburizing. These results show that the corrosion resistances of the obtained layers are a direct function of the average size of the nano-crystallites. In localized corrosion, nano-crystallization increases the unstable points on the surface of the materials, which increases the possibility of local corrosion. Yet, the exceptional ability of element diffusion helps to heal the localized corrosion points. These points inhibit the growth of the local corrosion. The research continues to develop nano-structure of alloys. This will decrease the corrosion of metals and alloys.

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