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Corrosion Behavior of a Fe-25at%Sn Supersaturated Solid Solution in H₃PO₄ Solution

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A R T I C L E   I N F O

A B S T R A C T

Corrosion resistance of iron can be drastically improved by addition of passivating alloying elements. A supersaturated solid solution of Fe-25at%Sn was produced by mechanical alloying of commercially pure iron and tin powders for 24 hours using a planetary ball mill. Electrochemical measurements were performed on cold compacted unsintered specimens.. XRD investigation on produced alloy showed the characteristics of a supersaturated solid solution. Corrosion behavior of the solid solution alloy was investigated in 0.1M H₃PO₄ employing potentiodynamic and potentiostatic polarization techniques. The anodic behavior of mechanically alloyed specimens was compared with specimens prepared from individually compacted iron, tin and appropriate admixture of tin/iron powders. Potentiodynamic polarization of supersaturated specimen featured a gradual decrease in anodic current density, indicating a feature of quasi passivation which was attributed to the tin surface enrichment as a result of preferential iron dissolution. Anodic current density from the result of potentiostatic polarization of the prepared alloy also showed a gradual decrease with time following $i \propto t^{-0.45}$ relationships indicating a characterization of passivity. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) examination of the specimen surface after potentiostatic anodic polarization test confirmed the presence of high tin content on the surface.

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1. INTRODUCTION

Iron is an example of metals which display an active-passive transition when anodically polarized in many aqueous solutions. Passivity is generally ascribed to the presence of a thin oxide film of 1-4 nm thickness which isolates the metal surface from the aqueous environment. In situ study of passive film described it as an amorphous and polymeric consisting of a chain of iron atoms bonded together by dioxy and dihydroxy bonds further linked by water to form a continuous film [1-3]. Numerous researches have been carried out to find out the effect of alloying elements on rate of dissolution of iron. The most important simple alloy of iron is probably Fe-Cr, and this system has been investigated extensively for over 50 years. The results clearly show that addition of Cr decreases iron dissolution drastically as a result of passivity [4-7]. This improvement is most probably due to the change in the nature of alloy surface composition because of the presence of chromium in the produced oxide film. Although the majority of works have been concentrated

on Fe-Cr system, the effect of different Ni contents in binary Fe-Ni alloy has also been investigated by Marcus and Olefjord [8]. They expressed alloy dissolution results in surface enrichment with nickel and leads to the formation of insoluble film composed of an inner layer of NiO and an outer layer of nickel and iron hydroxide. The effect of molybdenum on passivity of stainless steel has been widely investigated [9-11]. It is proposed that when molybdenum is included as an alloying element in a stainless steel, it is incorporated into the passive film, showing complex oxide chemistry with different states of oxidation [12]. Tungsten is another alloying element that its behavior in stainless steel is believed to be similar to those of molybdenum [13]. The surface properties of ferritic alloy containing Mo and/or W have been thoroughly investigated by Landolt et al. [14,15]. An important difference between tungsten and molybdenum lies in the different stability of their oxide films in acid solution.

Since, thermodynamically Sn has no solubility in iron at ambient temperature, no attempt has been made to investigate the effect of addition of tin on electrochemical behavior of iron. Tin and iron, instead of forming complete or partial solid solution, make four

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intermetallic compounds, namely Fe_5Sn_3, Fe_3Sn_2, $FeSn_2$ and FeSn. The last two compounds are thermodynamically stable at room temperature [16-17]. The present study deals with the corrosion behavior of supersaturated solid solution Fe-25%Sn prepared by mechanical alloying of associated powders, in dilute phosphoric acid.

2. EXPERIMENTAL PROCEDURE

For production of supersaturated solid solution of Fe-25at.%Sn, commercially pure Fe and Sn powders with a purity of greater than 99% and with the average particle size of 100 and 250µm respectively, were mechanically alloyed in a planetary ball mill (planetary ball mill model 2400) in nitrogen atmosphere. The vials and balls were made of hardened SPK and ball-bearing steel successively. Twenty one balls with diameter of 12 mm and 10 g of the powder mixture was used in a vial of 200 cm^3 volume. The mass ratio of ball to powder was 14.85. Particle size distribution of mechanical alloyed powder of Fe-25Sn was measured by particle size analyzer machine (Shimadzu/Sald 2101). The average size of 80% of powder was found to be less than 8µm and the remaining less than 20µm.

A three electrode assembly was used for electrochemical investigations. The working electrodes were made of powders of Fe, Sn, Fe-25at.%Sn supersaturated solid solution and Fe-25at.%Sn mixture (identical weight as supersaturated specimen but without applying ball milling). These powders were cold compacted in a disk shape mold under 65kN compaction force applied by a Zwick-250kN tensile machine. Green density of Fe, Sn, admixture and supersaturated solid solution samples were 6.96, 6.77, 7.19, 5.36 and g/cm^3, respectively. The measured porosity of Fe, Sn, admixture and supersaturated solid solution alloy samples were 11.43, 7.27, 5.77 and 29.75 percent respectively.

The electrical contact was made by connecting copper wire to the sample, before mounting. The compacted samples were embedded in polymer resin and obtained an exposed circular area of 0.785 cm^2. Before being used, the electrodes were polished successively with emery papers down to 1000 grade and then rinsed with distilled water. A platinum wire with a surface area of 2 cm^2 was used as a counter electrode. All potentials were measured against a saturated calomel reference electrode (SCE). Fresh solution was prepared from analytical grade of chemicals and distilled water. All tests were carried out in 0.1M H_3PO_4 solution with the pH value of 1.6 at room temperature. Potentiodynamic and potentiostatic polarization techniques were employed using a Potentiostat/Galvanostat (Gill AC) connected to a

computer. The potentiodynamic polarization was carried out from the starting potential of -1500mV (SCE), using scan rate of 1 mV/s. The potentiostatic transients were recorded for all electrodes at constant anodic potential of 1000mV. Before running any polarization test on supersaturated solid solution samples, the following two preparation steps were performed. First, the working electrode was held cathodic at the potential of 1000mV for 900s to reduce any oxide/hydroxide layer on the surface, possibly formed during ball milling and immersion in solution prior to running the tests. Second, the electrode was held in the electrolyte for 300s, so that the corrosion potential flattened. Prior to electrochemical examination, XRD investigation (using Cu K_α monochromatized radiation) was used to determine the formation of Fe-25at.%Sn supersaturated solid solution. After a course of potentiostatic measurement, the electrode surface was investigated by scanning electron microscopy (SEM) as well as an energy dispersive X-ray spectrometer (EDX) to investigate the qualitative analysis of the surface.

3. RESULT AND DISCUSSION

Fig. 1 shows the XRD patterns of Fe-25at.%Sn powder mixtures before and after different mechanical alloying periods.
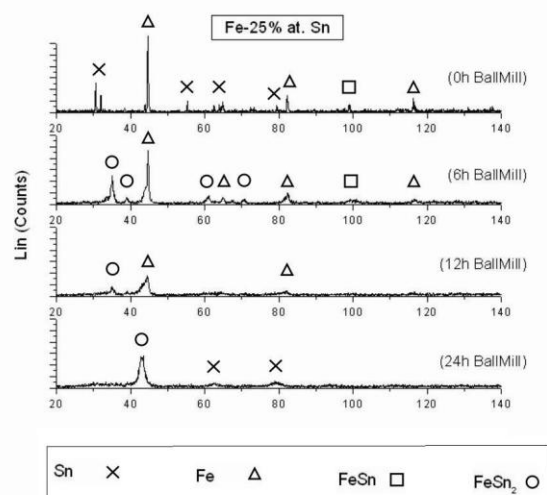

Figure 1. X-ray diffraction patterns of Fe-25 at% Sn admixture after different mechanical alloying periods.

According to this figure, at the first stage of ball milling (0 to 6 h), peaks of tetragonal $FeSn_2$ intermetallic compound appeared in the X-ray diffraction patterns. Similar results at this stage of mechanical alloying (MA) have been obtained by other researchers for closed composition of the initial mixture of 70Fe-30Sn

[18]. Formation of $FeSn_2$ intermetallic compound may be related to the predominant diffusion of Fe into Sn. By further ball milling, at the next stage of MA, solid solution of α-Fe(Sn) formed and the amounts of Fe and $FeSn_2$ phases decreased, and finally disappeared completely. After 24 h milling, α-Fe(Sn) supersaturated solid solution containing all the initial Sn content in the mixture, was the only phase observed in the X-ray patterns.

Potentiodynamic polarization technique permits the measurement of polarization behavior of investigated metal or alloy by continuously scanning the potential while monitoring the current response. Figure 2 shows typical potentiodynamic polarization curve of electrodes of compacted tin and iron powder samples and also as-wrought iron for comparison with the compacted iron specimen in 0.1M H_3PO_4. The polarization behavior shows a Tofel (activation control) up to about 200 mV and then gradually enters to mixed activation-diffusion control for about 300 mV. At higher overpotentials the fraction of diffusion control from the total polarization increases, indicating presumably the formation of iron phosphate salt at the electrode surface. The rightwards shift of Curve 2, as compared with Curve 3, can be due to the higher porosity of the compacted powder sample rather than the wrought sample. The compacted iron sample had a density of 6.96 g/cm^3; hence, the relative porosity was around 11.43%. In the compacted sample, the surface porosities increase the effective surface area, and consequently, the associated current density compared with the wrought sample. The anodic region in potentiodynamic polarization curve of tin involves two peaks (A_1 and A_2) prior to permanent passive region. These results are similar to those reported by Refaey for tin in borate solution [19].
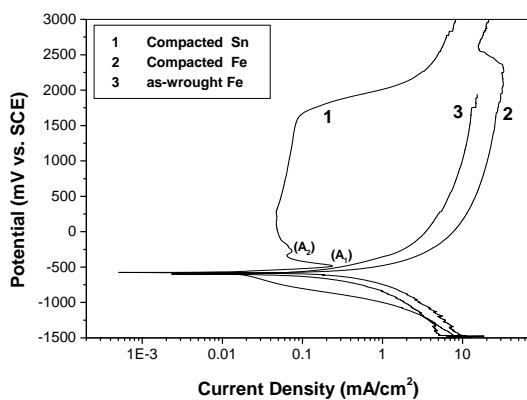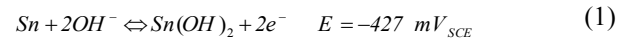

Figure 2. Potentiodynamic polarization curves of electrodes of compacted tin and iron powders compared with as-wrought iron in 0.1M H_3PO_4 solution.

Considering a pH value of 1.6 for the test solution; the first anodic peak, A_1, at about -483 mV_{SCE} (-241 mV_{SHE}) is related to the formation of $Sn(OH)_2$ according

to the following reaction:

$$Sn + 2OH^- \Leftrightarrow Sn(OH)_2 + 2e^- \qquad E = -427 \ mV_{SCE} \tag{1}$$

The second anodic peak, A_2, at about -241 mV_{SCE} (1 mV_{SHE}) corresponds to the formation of $Sn(OH)_4$ according to the following reaction:

$$Sn(OH)_2 + 2OH^- \Leftrightarrow Sn(OH)_4 + 2e^- \qquad E = -262 \ mV_{SCE} \tag{2}$$
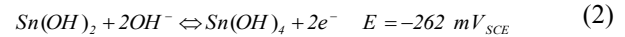
When the surface is covered with the anodic film, the dissolution current falls down severely, because of passivation. At quite high anodic potentials an increase in current density is attributed to the water oxidation reaction that occurs at about 1650 mV_{SCE} (1892 mV_{SHE}).

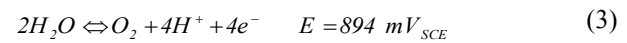$$2H_2O \Leftrightarrow O_2 + 4H^+ + 4e^- \qquad E = 894 \ mV_{SCE} \tag{3}$$

Figure 3 shows potentiodynamic polarization curves of compacted powders of tin, iron, admixture of iron and tin powder samples and a supersaturated solid solution Fe-25at.%Sn in 0.1M H_3PO_4 solution. Anodic current density associated to the solid solution specimen has similarity to the admixture specimen up to -4mV, then decreases several times . A gradual decrease in anodic current density at around 0 mV might be due to the formation of less soluble compound on the surface acting as barrier for continued dissolution. When sufficient tin atoms are available in the surface, a thin layer of mainly tin hydroxide or tin oxide forms and suppresses further dissolution of the base atoms. This causes the current density to drop down to almost constant value of 3 mA/cm^2 that lasts up to 1500 mV followed with gradual increase in current density as a result of water oxidation.
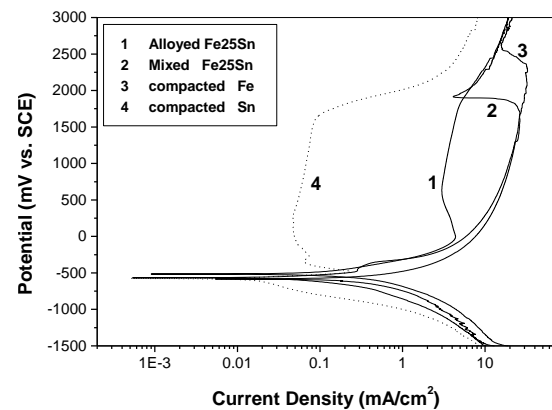

Figure 3. Potentiodynamic polarization curves of compacted powders of tin, iron, Fe-25at.% Sn admixture and Fe-25at.%Sn supersaturated solid solution   in 0.1M H_3PO_4 solution.

Current density of admixture of Fe-25at.%Sn in potentiodynamic polarization curve is expected to be the sum of the associated tin and iron current densities.

Except in low and high anodic potentials, potentiodynamic polarization curve of Fe-25at.%Sn admixture is similar to that of iron. In small anodic potentials (a little higher than corrosion potential), a small drop in anodic current density is visible. This noticeable change in anodic current density may be related to the beginning of the passivity of tin powders (see the polarization behavior associated with the compacted tin sample) that causes the total current density not to obey the same pattern as iron polarization behavior. In high anodic potential of about 1800 mV, a sudden decrease in current density of about one order of magnitude may be related to the domination of tin particles on the surface. As s result of larger dissolution of iron particles than tin powder from the surface, the fraction of tin powder gradually increases and this merges as sudden drop of current density at 1800 mV. Similar anodic behavior featuring a small drop in anodic current density is also visible for iron samples at quiet high anodic potential of 2400 mV. Eventually, increase in current density that appears at about 2550 mV is related to water oxidation.

In order to extend the investigation of anodic behavior of prepared solid solution alloy, potentiostatic polarization technique was employed. Figure 4 shows the result of anodic potentiostatic polarization of compacted specimens of tin and iron powders in 0.1M H_3PO_4 solution at quiet high anodic potential of 1000 mV at room temperature.
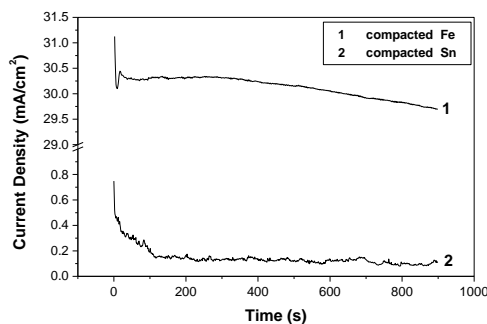

Figure 4. Potentiostatic polarization curves of compacted tin and iron powders polarized at anodic potential of 1000 mV in 0.1M H_3PO_4 solution.

Iron specimen showed active behavior and dissolved very fast with a current density of about 30 mA/cm^2. The current density shows a gradual decrease due to establishment of diffusion controlled anodic dissolution as a result of formation of saturated iron phosphate salt on the surface. Anodic behavior of tin shows much lower anodic current density due to stability of tin hydroxide on the surface which dissolves slower as compared to iron phosphate. This behavior is also evident on their associated anodic potentials from their potentiodynamic polarization curves. In their

potentiodynamic polarization, in all anodic potentials, the lower current density for tin samples compared to iron sample is obvious.

The feature of anodic current density of compacted powders of Fe-25at.%Sn admixture and supersaturated solid solution specimen of Fe-25at.%Sn in 0.1M H_3PO_4 solutions at applied anodic potential of 1000 mV is illustrated in Figure 5.
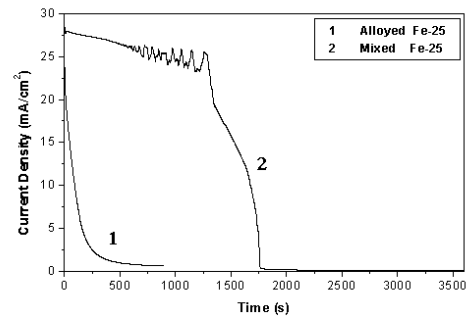

Figure 5. Potentiostatic polarization curves of compacted powders of Fe-25at.%Sn admixture and Fe-25at.%Sn supersaturated solid solution electrodes in 0.1M H_3PO_4 solutions at applied anodic potential of 1000 mV.

Current density of Fe-25at.%Sn supersaturated solid solution sample decreases sharply from about 21 to 2 mA/cm^2 286 seconds. The behavior of current density associated with the Fe-25at.%Sn admixture specimen contains two regions. In the first region, current density decreased slowly from about 28 to 19 mA/cm^2 in 1100 seconds. In this period, the fluctuation of current density may be attributed to the dissolution of iron particle causing to increase the effective area that leads to an increase of current density. Any sudden decrease in this part may be associated with the formation of less soluble tin compounds. In second region, current density decreased suddenly from about 19 to 2 (mA/cm^2) in about 653 second due to establishment of continuous network of tin particles and formation of tin compound, presumably tin hydroxide, that covers all the surface areaof the specimen. In fact, the two distinguished anodic behaviors observed for these samples may be associated with the ability of tin enrichment on the surface. When the result of anodic polarization of alloyed Fe-25Sn is observed, the current density drops from 23 mA/cm^2 to about 1 mA/cm^2 after 700 seconds. It is obvious the produced total anodic charges to bring down the current density to 1 mA/cm^2 are much less for alloyed samples. Therefore, different mechanisms can be proposed for such a different behavior between two samples. The first mechanism is proposed for supersaturated Fe-25at.%Sn solid solution alloy, based on atomic enrichment of tin as a result of iron atom dissolution from the alloy. The second mechanism is proposed for iron and tine admixture specimen based on increasing the volume fraction of tin

particles followed by formation of tin hydroxide as a result of higher extent of iron particles dissolution from the surface.

In order to clarify the difference between the two proposed mechanisms -for anodic behavior of solid solution and admixture prepared specimens- topographical investigation with the scanning electron microscope (SEM) in conjunction with the EDX analysis were used after anodic polarization potential of 1000 mV. SEM morphology of Fe-25at.%Sn supersaturated solid solution alloy reveals a partially smooth feature surrounded with the porous matrix which is formed during preparation (Fig. 6). The surface texture in porous parts remains uniform after polarization.
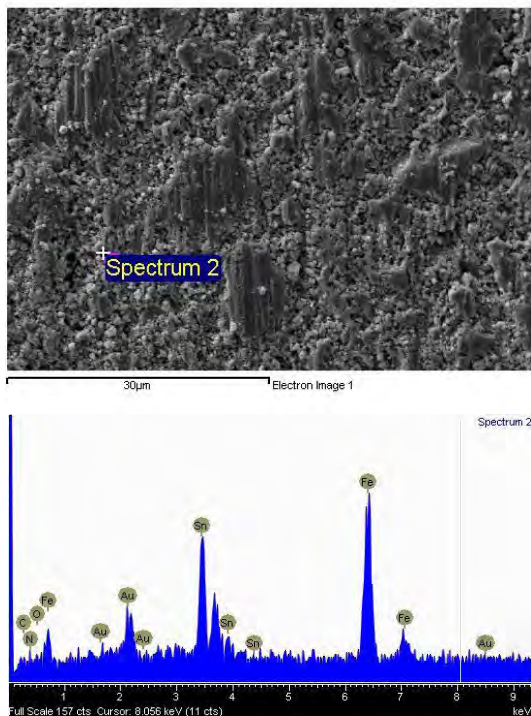

Figure 6. Scanning electron micrograph with corresponding EDX spectra for Fe-25at.%Sn supersaturated solid solution electrodes in 0.1M H_3PO_4 solution after polarization at applied anodic potential of 1000 mV.

EDX analysis of porous region of the surface shows pick spectrum associated with the presence of iron and tin showing larger pick for iron. Qualitatively, higher participation of iron as compared with tin in surface is evident. Since the samples have been already anodically polarized and achieved a sustained current density of less than 1mA/cm^2 prior to EDX analysis, the composition of the surface showed lower concentration of tin as compared to iron. This may be attributed to higher dissolution rate of iron atoms as compared to tin atoms. Similar effect of concentration of Fe and Cr

within the anodic surface layer on Fe-Cr alloy has been reported by Caliski and Strehblow [20]. They found that the outer region of the anodic film consists of a layer enriched in iron, a feature that has also been observed with the XPS sputter depth profile [21].

Topographical and analytical investigations of the polarized surface of the Fe-25at.%Sn admixture powders was carried out in two distinguished steps. The first one, after the sharp drop in anodic current density (after 2000 s of polarization), and the second one after 1000 s of anodic polarization (just before sharp drop in anodic current density). Figure 7 illustrates the SEM micrograph of the surface after 1000s anodic polarization and just before drop of the anodic current density. Porosity of the surface reveals the proposed mechanism for current density behavior. It seems that the porous morphology is created as a result of the dissolution of iron particles and formation of continuous network of tin particles on the surface. It is expected that EDX spectra of the selected part of the surface reveal the presence of elemental iron. Investigating the surface of the polarized specimen after polarization shows the trace of preferential dissolution of iron powder and replacement of iron by tin powder.
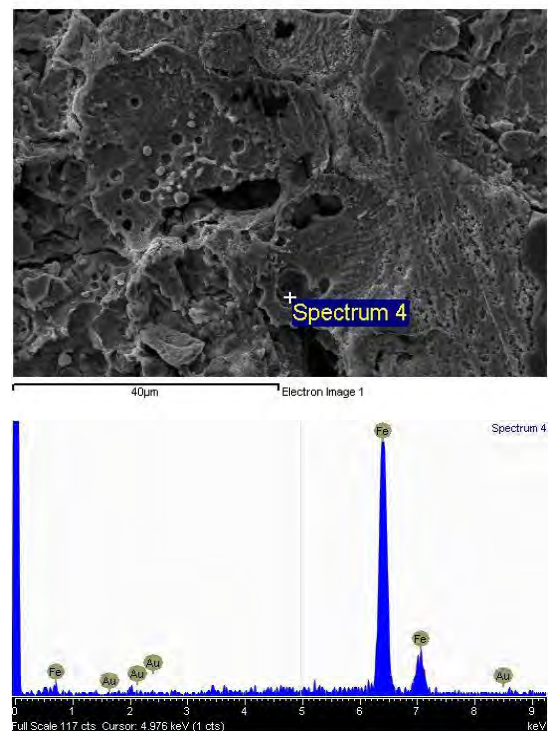

Figure 7. SEM photomicrograph and surface EDX analysis of Fe-25at.%Sn admixture electrode in 0.1M H_3PO_4 solutions prior to polarization at applied anodic potential of 1000 mV.

Figure 8 shows the SEM micrograph and EDX analysis of the selected part of the surface after applied

anodic potential of 1000 mV for 2000 s when the current density dropped to its lowest value. The surface cavities are associated with the iron particles that have been dissolved out from the surface and the holes have been closed by the presence of tin particles. EDX spectra of the cavity created by iron dissolution show the presence of chemical compositions of tin. In fact, a sudden decrease in anodic current density of the admixture powders specimen may be attributed to the preferential dissolution of iron particle rather than higher dissolution rate of iron atoms that was proposed for Fe-25at.%Sn supersaturated solid solution alloy.
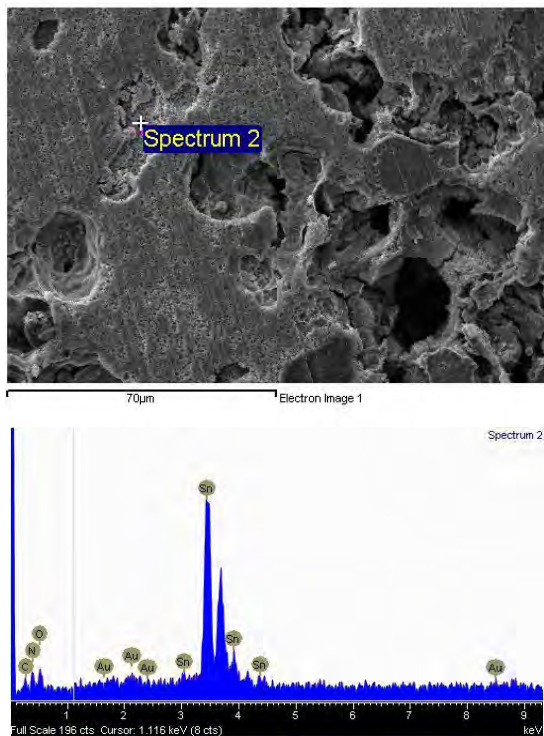

Figure 8. SEM photomicrograph and surface EDX analysis of Fe-25at.%Sn admixture electrode in 0.1M H_3PO_4 solutions after polarization at applied anodic potential of 1000 mV.

4. CONCLUSION

1) A supersaturated solid solution of Fe-25at.%Sn was produced by mechanical alloying of appropriate amounts of iron and tin powders.
2) Potentiodynamic polarization of supersaturated alloy and specimen produced by physical mixture of iron and tin powders showed different behaviors. The supersaturated alloy showed a passive-like behavior showing features of critical current density, passivation potential and passive current density as compared with the admixture powder specimen.
3) Anodic potentiostatic polarization of both specimens revealed different trends of passivity. A fast passivity by supersaturated alloy compared with admixture powder specimen was attributed to enrichment of tin atoms on the surface, while formation of passive layer on admixture powder specimen was related to the formation of continuous network of tin particles on the surface.

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Corrosion Behavior of a Fe-25at%Sn Supersaturated Solid Solution in H$_3$PO$_4$ Solution

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A R T I C L E   I N F O

چکیده

مقاومت به خوردگی آهن به طور چشمگیری با اضافه کردن عناصر آلیاژی پسیو کننده بهبود می باشد. محلول جامد فوق اشباع از آهن و ۲۵ درصد اتمی قلع با آلیاژ سازی مکانیکی به مدت ۲٤ ساعت از مخلوط پودرهای آهن و قلع در آسیاب سیاره ای تهیه شد. بررسی های الکتروشیمیایی بر روی نمونه های تهیه شده از این آلیاژ با فشردن سرد پودر بدست آمده بدون عملیات تف جوشی انجام شده است. انجام آزمون تفرق اشعه ایکس بر روی آلیاژ تهیه شده نشان داد که محلول جامد فوق اشباع تولید شده است. رفتار خوردگی آلیاژ تهیه شده در محلول ۰٫۱ مولار اسید فسفریک با بکار گیری تکنیکهای پلاریزاسیون با پتانسیل متغیر و ثابت انجام شده است. سپس بررسی پلاریزاسیون آلیاژ تهیه شده با نمونه های تهیه شده از پودر آهن، پودر قلع و مخلوط پودرهای آهن و قلع (بدون عملیات آسیاب کاری مکانیکی) پس از پرس سرد انجام شده است. رفتار شبه پسیویتی دیده شده در دیاگرام پلاریزاسیون آلیاژ فوق اشباع به غنی شدن اتمهای قلع در اثر انحلال ترجیحی اتمهای آهن نسبت داده می شود. بررسی رفتار پلاریزاسیون آندی شدت جریان پسیویتی آلیاژ فوق اشباع نشان دهنده رفتار کاهشی شدت جریان با گذشت زمان متناسب با i∞t$^{-0.45}$ را نشان می دهد که نشان دهنده رفتار پسیویتی آلیاژ تهیه شده می باشد. بررسیهای انجام شده با استفاده از تکنیک آنالیز کیفی (EDX) و میکروسکوپ الکترونی روبشی بر روی سطح آلیاژ در پایان پلاریزاسیون آندی نیز از وجود غلظت بالای قلع و توپوگرافی پسیویتی بر روی سطح را تایید می کند.

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