

PASSIVITY BEHAVIOR OF A Fe-25at%Sn SUPERSATURATION SOLID SOLUTION IN 0.1M H₃PO₄

S.M. Seyedi-Nasab, M.H. Moayed, J. Vahdati-Khaki.
Materials and Metallurgical Engineering Department, Faculty of Engineering, Ferdowsi
University of Mashhad, Mashhad 91775-111, Iran
mhmoayed@um.ac.ir

ABSTRACT

A supersaturated solid solution of Fe-25at%Sn was produced by mechanical alloying of iron and tin powders for 24 hours using a planetary ball mill. Electrochemical measurements were performed on cold compacted specimens without sintering. XRD investigation on produced alloy showed the characteristics of a supersaturated solid solution. The passivity of solid solution alloy was investigated in 0.1M H₃PO₄ by employing potentiodynamic and potentiostatic polarization techniques. The passivity behavior of mechanically alloyed specimens was compared with anodic behavior of compacted iron specimens. A sharp decrease of diffusion controlled anodic current density of iron was observed due to establishment of quasi passivation as the result of Sn presence in mechanically alloying prepared specimen. The passivation behavior of anodically polarized Fe-25at%Sn supersaturated solid solution specimens was similar to passivity of binary Fe-Cr alloys.

Keywords: Passivity of Fe-Sn alloy, supersaturated Fe-Sn alloy, Mechanical alloying

INTRODUCTION

Iron is an example of metals which displays an active-passive transition when anodically polarized in many aqueous solutions. Passivity is generally ascribed to the presence of a thin oxide film 1-4 nm thickness which isolates the metal surface from the aqueous environment. The in situ study of passive film described it as 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 element on passivity of iron. The most important simple alloy of iron is probably Fe-Cr and this system has been investigated extensively for more than 50 years and the results clearly show addition of Cr to iron improves its passivity [4-7]. This improvement is most probably due to change in the nature of passive oxide because of the presence of chromium in the film. Although the majority of works have been concentrated on Fe-Cr system, the effect of various Ni content in binary Fe-Ni alloy has been investigated by Marcus and Olefjord [8]. They expressed alloy dissolution results in surface enrichment with nickel and leads to the formation of passive film composed of an inner layer of NiO and an outer layer of nickel and iron hydroxide. Thermodynamically Sn has no solubility in iron at ambient temperature, instead they make four intermetallic compounds namely Fe_5Sn_3 , Fe_3Sn_2 , FeSn with the ferromagnetic property and Fe_5Sn_3 , Fe_3Sn_2 which are not [9-10]. The present study deals with the effect of addition Sn to iron prepared from mechanically alloying of associated powders on anodic behavior of the prepared alloy in dilute phosphoric acid.

EXPERIMENTAL PROCEDURE

For production of Fe-25at.%Sn supersaturated solid solution, commercially pure Fe and Sn powders were mechanically alloyed in a planetary ball mill. Mechanical alloying was performed in air atmosphere. The vials and the balls were made of hardened SPK and ball-bearing steel successively. Twenty one balls with diameter of 12mm and 10gr of the powder mixture was used in a vial of 200 cm³ volume.

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 ball milling). These powders were cold compacted in disk shape without sintering. For each sample, 65kN compact force was applied by Zwick-250kN tensile machine. Gray density of Fe, Sn, mixed and supersaturated solid solution samples were 6.77, 6.96, 7.19 and 5.36 (gr/cm³) respectively.

The electrical contact was made by soldering copper wires to the samples, before mounting. The compacted samples were surrounded in polymer resin and obtained an exposed circular area of 0.785 cm². Before being used, the electrodes were polished successively with emery papers down to 1000 grads and then rinsed with distilled water. A platinum wire was used as a counter electrode. The potential was measured against a saturated calomel reference electrode (SCE). The solution was prepared using analytical grade chemicals and distilled water, and used freshly. All tests were carried out in 0.1M H₃PO₄ solution (pH≈1.0) at room temperature. The potentiodynamic and potentiostatic polarization techniques were employed by using a Potentiostat/Galvanostat (Gill AC) connected to a computer. The potentiodynamic polarization was carried out from the starting potential -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 the any polarization test on supersaturated solid solution samples, two preparation steps were carried out. First, the working electrode was held at the

potential of -1000mV for 900s to reduce any oxide/hydroxide layer on the surface, probably formed during ball milling and immersion in solution prior to running the tests. Secondly, 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.

RESULT AND DISCUSSION

Fig. 1 shows the XRD patterns of Fe-25at.%Sn powder mixtures before and after various mechanical alloying periods. At the bottom of the figure, the dash-patterns of some phases are shown. According to the figure, at the first stage of 0 to 6 h ball milling, reflections 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 [11]. Formation of $FeSn_2$ intermetallic compound could be related to the predominant diffusion of Fe into Sn. The low temperature diffusion coefficient of Fe into Sn is higher about four orders of magnitude than that of Sn into Fe. 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 the initial Sn content in the mixture, was the only phase observed in the X-ray patterns.

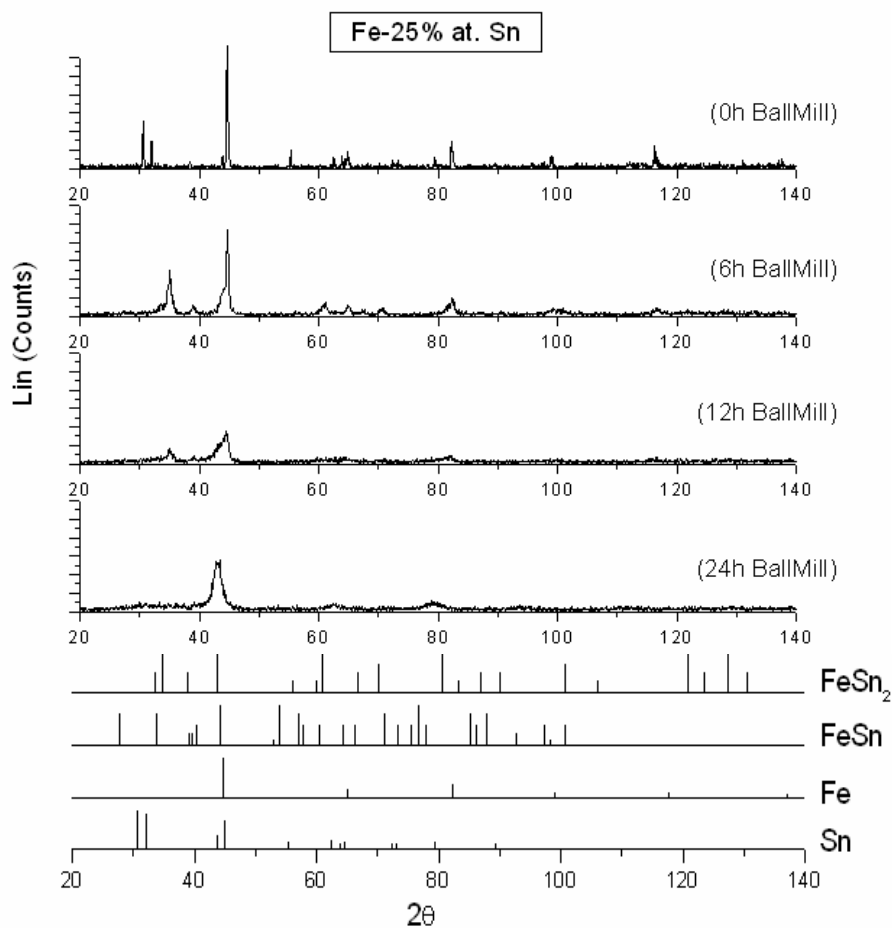
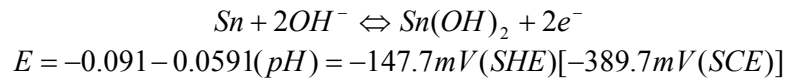
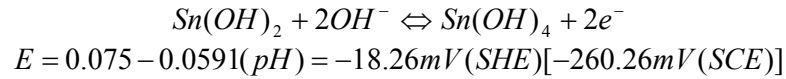


Figure 1. X-ray diffraction patterns of Fe-25 at.%Sn mixture after various mechanical alloying periods.

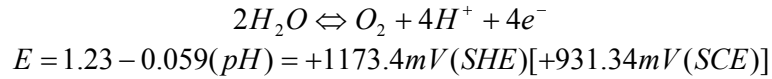
Potentiodynamic polarization technique permits the measurement of polarization behavior of investigated metal or alloy by continuously scanning the potential while monitoring the current response. Fig.2 shows typical potentiodynamic polarization curve of electrodes of compacted tin and iron powders and also as-wrought iron in 0.1M H₃PO₄. The rightwards shift of curve 2, as compared with curve 3, may be due to the higher porosity of the compacted powder sample rather than the wrought sample. The compacted iron sample has a density of 6.96gr/cm³; and so the fraction of porosities is around 11.43%. In the compacted sample, the porosities in the surface increase the effective surface area, and consecutively the associated current density in compared with the wrought sample. The anodic region in potentiodynamic polarization curve of tin involves two peaks (A₁ and A₂) prior to permanent passive region. These results are similar to those reported by Refaey for tin in borate solution [12]. The first anodic peak, A₁, at about -483 mV SCE (-274 mV SHE) is due to the formation of Sn(OH)₂ according to the following reaction:



The second anodic peak, A₂, at about -241 mV SCE (-32 mV SHE) corresponds to the formation of Sn(OH)₄ according to the following reaction:



When the surface is covered with the passive film, the dissolution current falls down severely, because of permanent passivation. With increasing potential, current density was increased due to water oxidation reaction at about +1650 mV SCE (+1408 mV SHE).



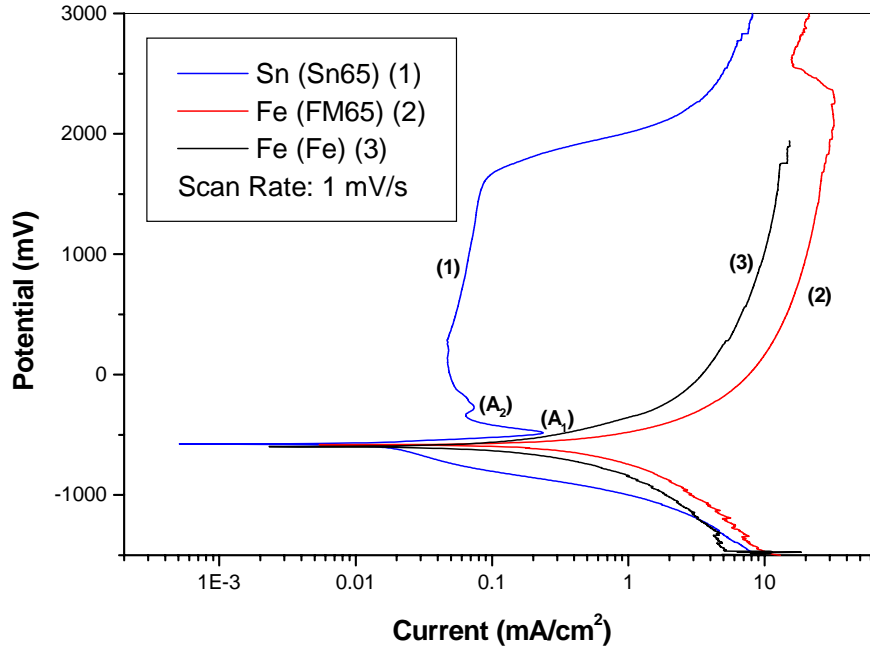


Figure 2. Potentiodynamic polarization curves of electrodes of compacted tin and iron powders and dense iron in 0.1M H₃PO₄ solution.

Fig.3 shows potentiodynamic polarization curves of compacted powders of tin, iron, mixed and supersaturated solid solution Fe-25at.%Sn in 0.1M H₃PO₄ solution. Clear difference was observed between passivation behavior of mixed and supersaturated solid solution samples. Fe-25at.%Sn supersaturated solid solution samples passivated at -4 mV, whereas mixed samples passivated at +1682 mV. This difference is due to the various passivation mechanisms for these samples.

Passivation mechanism of Fe-25at.%Sn supersaturated solid solution is similar to Fe-Cr alloys. The dissolution of base element (Fe) in both alloys enriches the amount of passivating element (Sn in this alloy and Cr in Fe-Cr alloys). When sufficient passivation atoms are available in the surface, a thin passive layer forms and prevents rapid dissolution of the base atoms, which causes the current density drop down to I_{pass} . Passivity range is about 1500 mV. Current density of mixed Fe-25at.%Sn in potentiodynamic polarization curve is summation of tin and iron current densities. Except in low and high anodic potentials, potentiodynamic polarization curve of mixed Fe-25at.%Sn 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 pick is due to the summation of the current densities associated with iron and tin that is visible in a small drop of current density at about 0.3 mA/cm². Since the amount of current density in both iron and tin samples are very small in this overpotential, summation of them is appeared in small drop at about 0.3 mA/cm².

In high anodic potential of about +1800 mV, dissolution of large amounts of iron particles at the surface leads to the increase of the incorporation of tin particles on the surface. A sudden decrease in current density about an order of magnitude may be related to the passivity of tin particles on the surface. Similar passivation also is visible for iron samples at quiet high

anodic potential of 2400 mV. This drop of current density is also related to the formation of iron oxide underneath of saturated iron phosphate. Eventually increase in current density that is appeared at about 2550 mV is due to water oxidation.

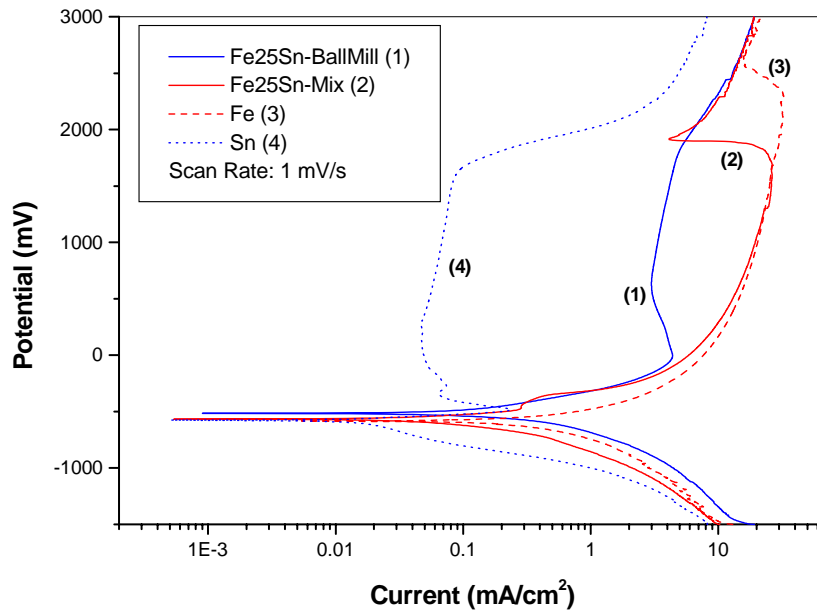


Figure 3. Potentiodynamic polarization curves of compacted powders of tin, iron, Fe-25at.%Sn mixed and Fe-25at.%Sn supersaturated solid solution in 0.1M H₃PO₄ solution.

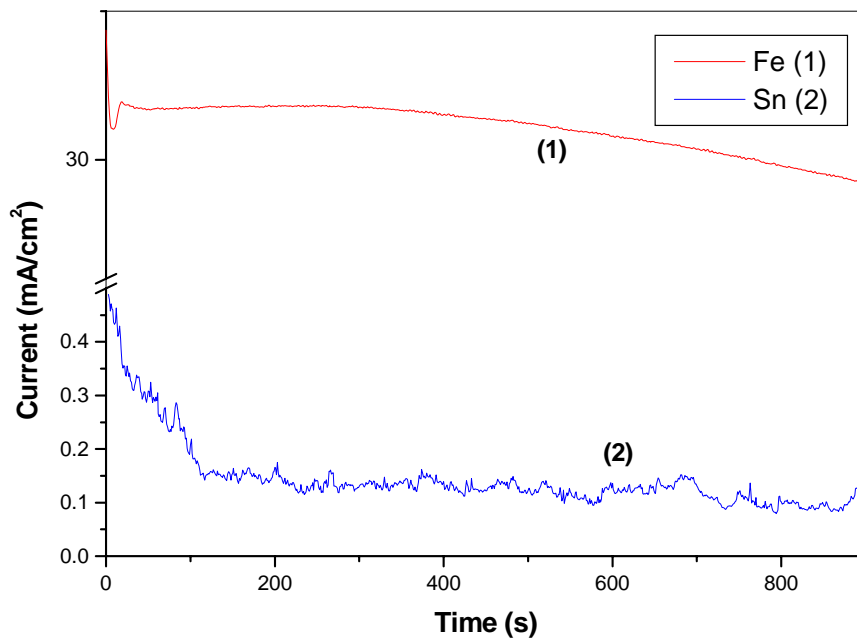


Figure 4. Potentiostatic polarization curves of compacted tin and iron powders polarized at +1000 mV in 0.1M H₃PO₄ solution.

In order to confirm the passivity 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 1000 mV at room temperature. Iron specimen shows an active behavior and dissolved very fast with a current density 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 passivity as a result of thin hydroxide on the surface and dissolved very slow in compared to iron. These behaviors are also expected from their appropriate potentiodynamic polarization curves.

Fig.5 shows SEM image of tin surface after applying +1000 mV on it, in 0.1M H_3PO_4 solution for 15 min. The morphology of corrosion products formed on tin surface is visible in this figure.

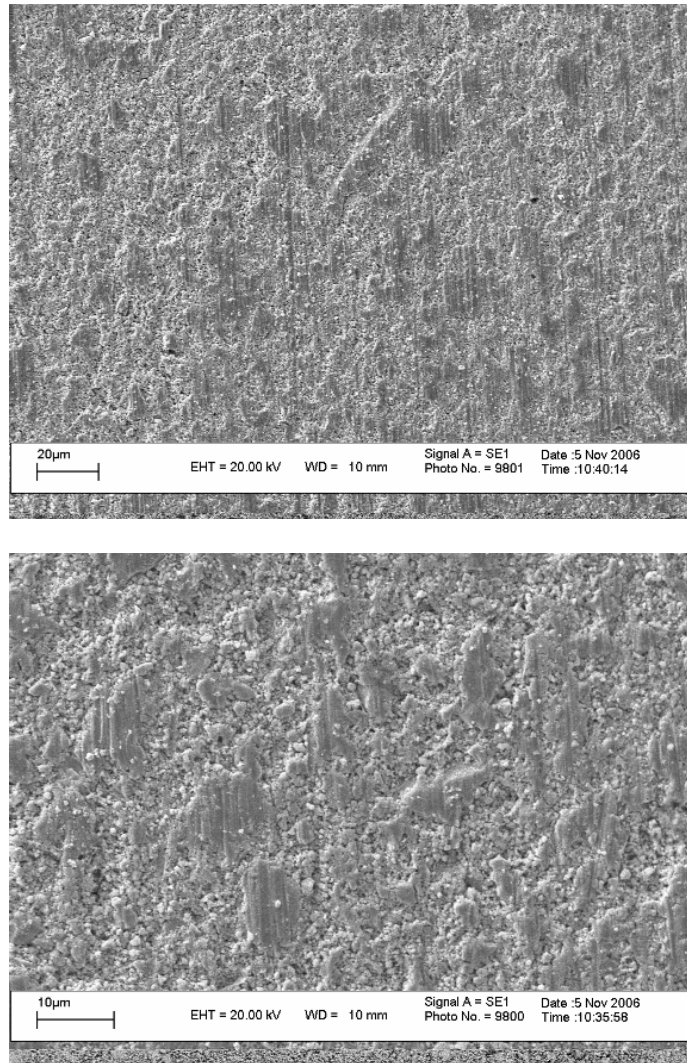


Figure 5. SEM image of morphology of Fe-25at.%Sn supersaturated solid solution surface after for 15 min at polarization at +1000 mV in 0.1M H_3PO_4 solution.

Fig.6 shows the result of anodic potentiostatic polarization of compacted powders of mixed Fe-25at.%Sn and supersaturated solid solution specimen of Fe-25at.%Sn in 0.1M H_3PO_4 solutions at applied potential of 1000 mV. A sharp decrease of current density for supersaturated solid solution specimen reveals conventional passivity similar to many alloys with passive behavior. Different behavior of current density decay is observed for specimen

prepared from compacting a mixture of Fe-25at.%Sn. The decrease of current density from 28 mA/cm² to 25 mA/cm² follows with fluctuations with the magnitude with the highest of 5mA/cm² just before sharp decrease due to passivation of the specimen. Although both specimen experience passivation but the time of formation passive layer on both samples is different.

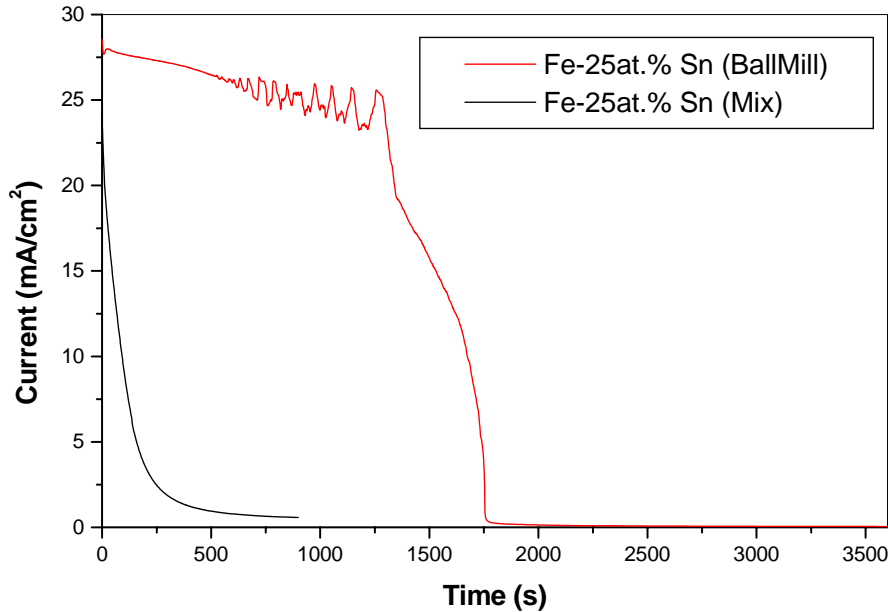


Figure 6. Potentiostatic polarization curves of compacted powders of Fe-25at.%Sn mixed and Fe-25at.%Sn supersaturated solid solution electrodes in 0.1M H₃PO₄ solutions for 60 and 15 minute at potential +1000 mV respectively.

Current density of Fe-25at.%Sn supersaturated solid solution sample decayed sharply from about 21 to 2 mA/cm² during 286 s. During this time, passive layer formed and grew and the thickness of passive layer was enough to cause in decrease of current density. But the behavior of current density associated with the Fe-25at.%Sn mixed specimen contains two steps. At first step, current density decreased slowly from about 28 to 19 mA/cm² during 1100 s. In this period, the fluctuation of current density is due to dissolution of iron particle leads to increase in effective area (result in an increase in current density). Any sharp decrease in this part is associated to the passivation of tin particles. At second step, current density decreased suddenly from about 19 to 2 (mAcm⁻²) in about 653 second due to establishment of continuous network of tin particle and formation of tin hydroxide that covers all the specimen surface area. In fact two distinguished passivation mechanisms were observed for these samples that are associated with surface enrichment by tin. The first mechanism based on enrichment of tin atoms as a result of iron atom dissolution on the surface in supersaturated Fe-25at.%Sn solid solution. The second mechanism based on increasing the volume fraction of tin particles as a result of iron particles dissolution followed by formation of tin hydroxide on the surface.

Topographical investigation of the specimen of mixed powder at the end of a course of potentiostatic polarization after establishment of passivity is illustrated in figure 7. A porous feature of the surface reveals the proposed mechanism for passivity. The porous structure is

created as a result of iron particle dissolution and formation of continuous network of tin particles.

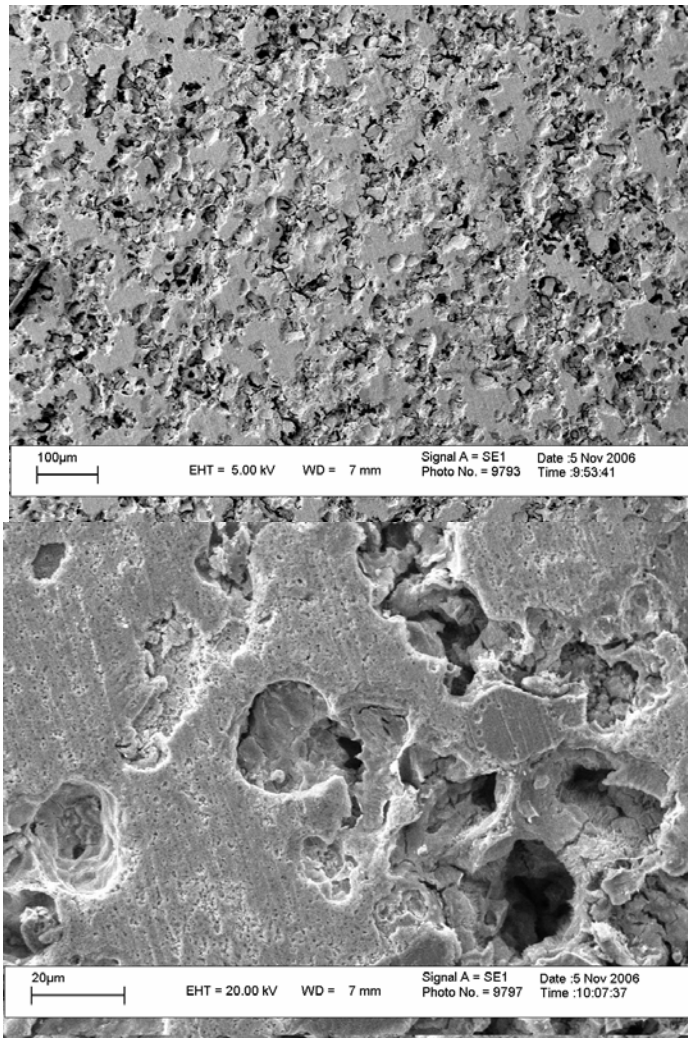


Figure 7. SEM image of morphology of compacted powders of Fe-25at.%Sn mixed after 15 min polarization at +1000 mV in 0.1M H₃PO₄ solution.

CONCLUSION

- 1) A supersaturated solid solution of Fe-25at.%Sn was produced by mechanical alloying of appropriate amount of iron and tin powders.
- 2) Potentiodynamic polarization of supersaturated alloy and specimen produced by physical mixture of iron and tin powders shows different behavior. The supersaturated alloy shows a passivation with distinguished critical current density, passivation potential and passive current density in compared the mixed powder specimen.
- 3) Anodic potentiostatic polarization of both specimen reveals different trend of passivity. A fast passivity by supersaturated alloy in compared to mixed powder specimen was attributed to enrichment of tin atoms on the surface while formation of passive layer on mixed powder specimen was related to the formation of continuous network of tin particles on the surface.

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