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Elaboration of Thin Foils in Copper and Zinc by Self-Induced Ion Plating

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The aim of this work was to determine the ability to produce thin metallic foils by self-induced ion plating. Foils of pure copper and pure zinc with a thickness of 35 μm have been successfully produced and their characteristics have been compared to foils obtained by conventional techniques (i. e. electroplating and rolling). Results show the following: (i) more or less compact microstructures can be obtained by self-induced ion plating depending on gas pressure and substrate temperature; (ii) microstructures obtained by self-induced ion plating are quite different from those obtained by electroplating and rolling; (iii) Young's modulus depends on foils roughness; (iv) hardness depends on grain size by exhibiting a Hall-Petch behavior in the case of copper foils and an "inverse" Hall-Petch behavior in the case of zinc foils.
Keywords: metallic foils, vacuum deposition, self-induced ion plating, nanoindentation tests.

1. INTRODUCTION

Because of the rapid development of modern technology, thin metallic foils are more and more used in various areas such as microelectro-mechanical systems (MEMS), integrated circuits, flexible solar cells, fuel cells, batteries, etc. Consequently, the techniques [1 – 5] employed to characterize their properties have been strongly developed during last decades since their response differs from that of bulk materials due to size effects [6]. On the other hand, the techniques employed for their elaboration have not known the same development.

Foils are indeed mainly produced by two different techniques: either by electroplating or by rolling. The first technique consists in moving metal ions contained in an acid solution thanks to an electric field in order to coat an electrode until the desired thickness. This technique is commonly employed in the case of conductive materials like copper [7]. The second one consists in passing a given specimen through a pair of rolls to reduce its thickness until the desired value. This technique is generally used in the case of ductile materials like aluminium [8]. Non-ductile materials (like titanium) can also be rolled but thermal treatments between each pass are necessary to reduce internal stresses [9].

Others techniques based on vacuum deposition can also be considered: it consists in depositing a metal on a substrate and then peeling it off. This type of technique has already been studied by Hughes [10] and Smith et al. [11] who have managed to produce titanium alloy foils by electron-beam evaporation. However, these techniques remain quite difficult to control due to potential interactions between the deposited metal and the substrate which can prevent the peeling off. Therefore, appropriate process parameters (like substrate temperature, substrate roughness, release agent, etc.) have to be used and adapted to each case.

In the present work, the feasibility of the technique exposed above has been studied. A process of vacuum deposition recently developed by ArcelorMittal (Self-induced Ion Plating) has been used to produce thin copper and zinc foils. Microstructural and mechanical characterizations on foils obtained either by self-induced ion plating or by conventional techniques have also been carried out in order to compare their characteristics.

2. EXPERIMENTAL DETAILS

2.1. Self-induced ion plating (S.I.P) process

The S.I.P process [12, 13] is a combination between evaporation and magnetron sputtering processes, which allows obtaining high deposition rate (few micrometers per second) with great coating quality. The principle consists in ionizing argon gas (under high vacuum) between a target at a negative potential and a substrate at ground potential (Fig. 1).

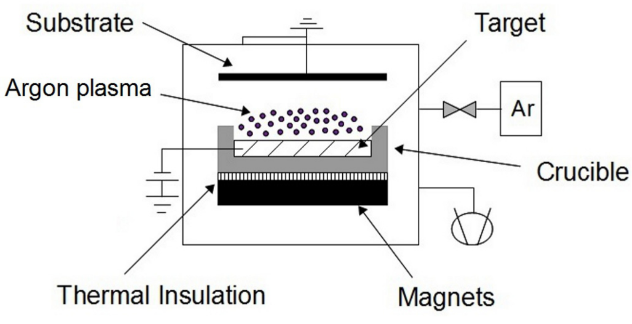

Fig. 1. Sketch of the self-induced ion plating (S.I.P) process

Argon ions are thus accelerated by the electrical field towards the target and bombard it with high energy. This bombardment leads to heating and evaporation of the target since the target is not cooled but thermally insulated. The metallic vapor is then condensed on a substrate which has a continuous displacement at a few centimeters above the target. The presence of magnets under the target crucible allows confining the argon plasma near the target by generating a magnetic field and thus improving the

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bombardment (magnetron effect) while keeping a reasonable substrate temperature.

2.2. Semi-industrial pilot

A semi-industrial pilot batch from ArcelorMittal has been used to perform vacuum depositions. As shown in Fig. 2, this pilot is divided into a superior and an inferior part with a pair of shutters between them. The S.I.P system as described in Fig. 1 is located in the inferior part while the substrate holder is located in the superior part. It consists in a drum on which a metallic substrate with a length about 3 m and a width about 0.5 m is attached. The rotation rate of the drum can be regulated in order to uniformly deposit the metal and reach the desired thickness in a reasonable time. The shutters are opened when the evaporation rate is satisfactory. Foils have then been manually peeled off from the substrate. Due to substrate size, foils of great dimension can be obtained.

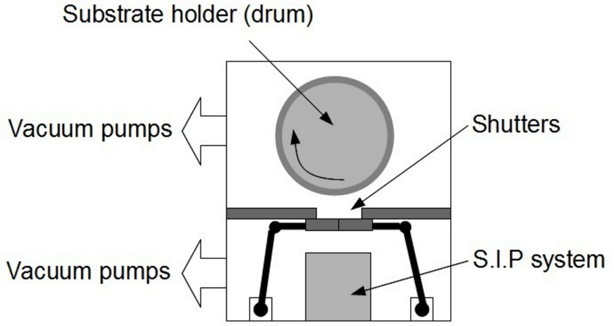


Fig. 2. Sketch of the semi-industrial pilot used for the deposition by S.I.P

2.3. Process parameters

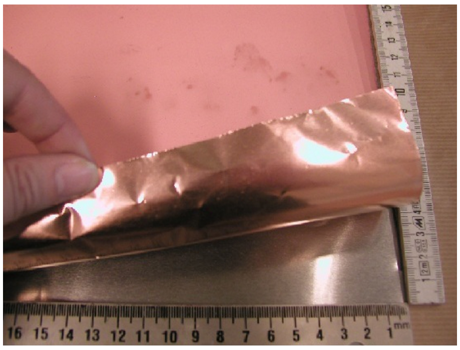
Targets are made of pure copper or pure zinc. They are heated above their evaporation temperature (i. e. above 2330 °C and 900 °C respectively) thanks to ions bombardment. Black steel (i. e. untreated steel) substrate has been used. Its temperature has not exceeded 200 °C during the deposition process. Several dozen micrometers of copper or zinc have been deposited by using a deposition rate about 3 µm/min.

2.4. Microstructural and mechanical characterizations

Foils microstructures have been observed by using a scanning electron microscope (SEM) while mechanical properties (like Young's modulus and hardness) have been determined by performing nanoindentation tests. These tests are quite difficult to perform on thin foils in regards to their weight which is not high enough to avoid the presence of voids between them and the substrate holder: some errors can thus happen during measurements. A solution consists in carrying out nanoindentation tests on one side of the foil which has been previously coated and polished. A Berkovich shaped diamond tip has been used. The indenter has been advanced into the foil through 500 nm with a strain rate target about 0.05 s^{-1}. The load-displacement data has been collected and once the desired depth has been reached, the indenter has been gradually withdrawn, unloading the specimen. The reproducibility of this experiment has been checked by performing about ten tests by specimen on different zones.

3. RESULTS AND DISCUSSION

Results show that foils with a thickness less than 40 µm can be easily produced: foils in copper and in zinc of 35 µm in thickness are shown in Fig. 3.



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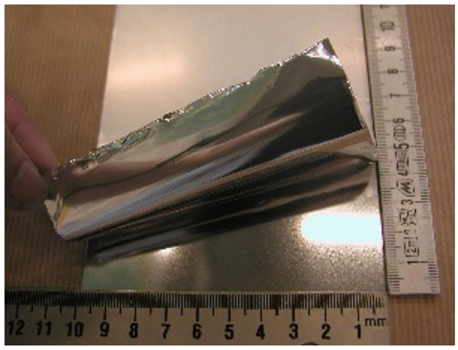

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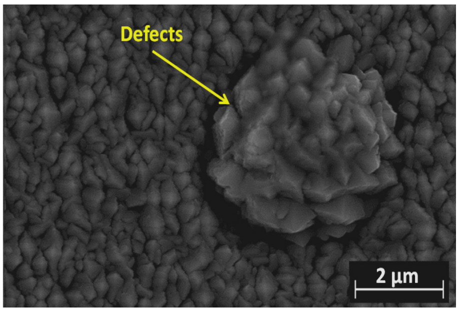
Fig. 3. Foil in copper (a) and in zinc (b) obtained by vacuum deposition on steel

No release agent is necessary between the deposited metal and the substrate to allow the peeling off. The phenomenon of diffusion bonding is indeed quite limited in our study due to the confinement of the plasma near the target. The substrate temperature remains low during the deposition preventing any atoms diffusion between the substrate and the deposited layer and thus the formation of any metallurgical bond. Consequently a vast range of substrates can be used.

3.1. Microstructural characteristics

Foils obtained by S.I.P exhibit porous columnar microstructure (Fig. 4). Grain size is relatively homogeneous and doesn't exceed 1 µm but some defects, due to the presence of few irregularities on the substrate surface, can be observed.

This grain morphology is typical of those encountered in thin layers deposited by evaporation or sputtering. Movchan et al. [14] have indeed shown that three different grain morphologies can be obtained in thin layers deposited by evaporation. Their classification (called SZM or Structure Zone Model) depends on the homologue temperature T/T_m where T is the substrate temperature and T_m the melting temperature of the deposited metal. The morphology changes from columnar structure with smooth surface, coarse grains and good density, to dense equiaxed structure when T/T_m is about 0.5. For thin layers deposited by sputtering, Thorton [15] has also shown that gas pressure has an impact on the grain morphology. Therefore, by varying process parameters like gas pressure and homologue temperature, foils can exhibit various morphologies of grains as illustrated in Fig. 5.



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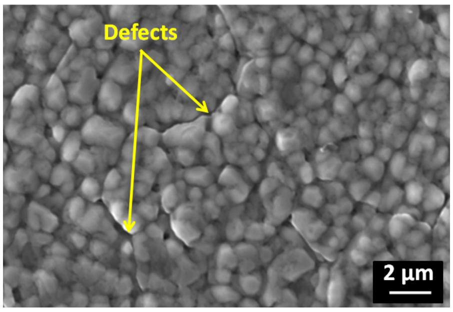

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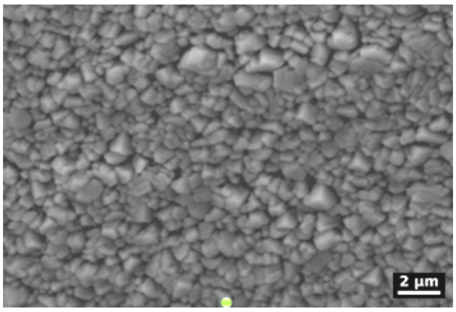
Fig. 4. SEM observations of the microstructure of copper (a) and zinc (b) foils obtained by vacuum deposition



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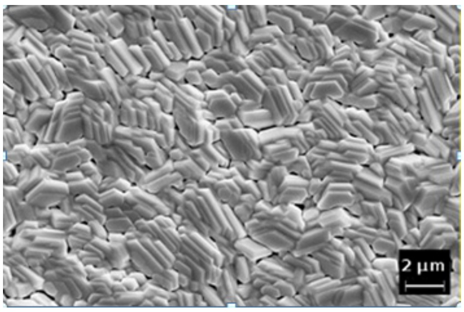


b

Fig. 5. Illustration of copper foil microstructures obtained by varying process parameters (SEM observations)

Microstructure of copper foils obtained by increasing substrate temperature or gas pressure is shown in Fig. 5, a, and Fig. 5, b, respectively. It can be noticed that some changes have occurred compared to morphologies shown in Fig. 4.

The ability to peel off a foil from its substrate depends on its microstructure. Porous morphology leads to brittle foil which can break in several pieces during the peeling off. Thus, dense microstructure must be privileged. However, this condition does not allow avoiding the formation of some cracks into the foil (as shown in Fig. 4, b). It may be explained by the small foil thickness coupled with a manual peeling off.

3.2. Mechanical characteristics

Typical indentation load-depth curves obtained after nanoindentation tests on the different foils are shown in Fig. 6. These tests have been performed on foils exhibiting the microstructures shown in Fig. 4.

Reproducibility is correct for both foils: an average standard deviation in load of about 0.8 mN was found at the maximum indentation depth when same testing conditions were used. Young's modulus of the material being indented has been determined from the slope of the unloading curves (not represented on Fig. 6). Hardness has been found by computing the mean pressure under the indenter at the point of maximum load. The results are summarized in Table 1.

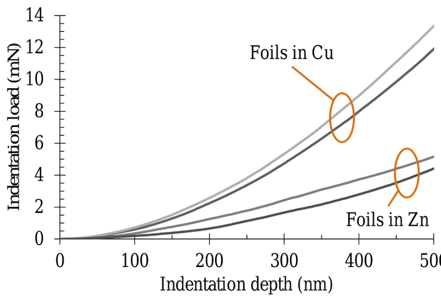


Fig. 6. Indentation load-depth curves for foils in copper and in zinc obtained by S.I.P

Table 1. Mechanical characteristics of copper and zinc foils obtained by using S.I.P technique

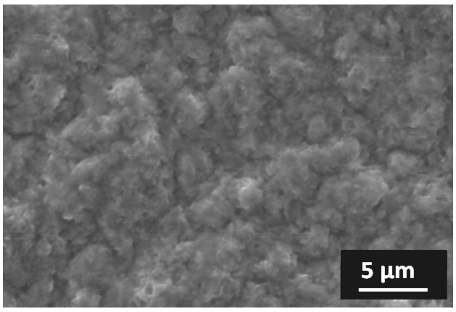
Mechanical characteristic	Copper foil	Zinc foil
Young's modulus (GPa)	113	58
Hardness (GPa)	2.8	0.9

Elastic moduli of foils are inferior to moduli of bulk materials which are equal to 145 GPa for pure copper [16] and 84 GPa for pure zinc [16]. This point is quite surprising since several studies during last decades have shown that thin films tend to exhibit similar Young's modulus that bulk material [3, 5]. This peculiar behavior may be explained by the surface roughness of the foils. Indeed, Jiang et al. [17] have shown that elastic moduli of rough thin films are much lower than that of smooth thin films. By improving the surface roughness of the foil, it would thus be possible to reach the elastic modulus of bulk materials.

Hardness of foils is quite different from hardness of bulk material which is about 1.77 GPa for bulk copper [16] and 0.84 GPa for bulk zinc [16]. These differences are due to size effect. As explained by Arzt [6], dislocations motion and arrangement are influenced by the small dimensions of the specimens. Under a given thickness, the size constraint, rather than the microstructure, controls most of the properties: mechanical properties such as yield stress and hardness are thus generally improved when film thickness decreases. This point is confirmed by the hardness values given by the nanoindentation tests. However, the contribution of microstructural constraints to the improvement in hardness when decreasing material thickness is not well defined. It is generally assumed that a superposition of size effect, Hall-Petch effect (decrease in grain size) and Taylor hardening (contribution from dislocations) occurs.

3.3. Comparison with foils obtained by conventional techniques

Microstructures of copper and zinc foils (of 35 µm in thickness) obtained by electroplating and rolling respectively are shown in Fig. 7 while Young's modulus and hardness deduced from nanoindentation tests are summarized in Table 2.



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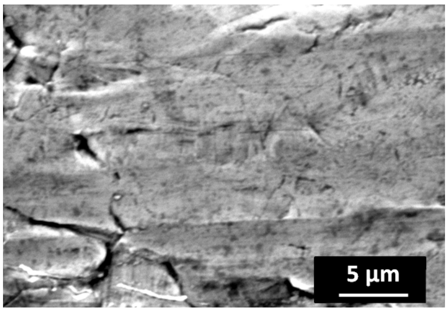

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Fig. 7. SEM observations of the microstructure of: copper foils obtained by electroplating (a) and zinc foils obtained by rolling (b)

Table 2. Mechanical characteristics of copper and zinc foils obtained by conventional techniques

Mechanical characteristic	Copper foil	Zinc foil
Young's modulus (GPa)	120	75
Hardness (GPa)	2.5	1.1

By comparing Fig. 4 and Fig. 7, it can be noticed that foils morphologies obtained with conventional elaboration techniques are quite different from those obtained by using S.I.P technique: (i) denser and smoother structures are formed and (ii) coarser grains are present. Copper foil obtained by electroplating and zinc foil obtained by rolling exhibit grains about 2 µm and 50 µm respectively. The grains size for zinc foil has been determined by microscopic observation on foil previously polished and etched with HCl solution.

The presence of smoother structures in both foils leads to an increase in elastic modulus (see Table 2): it tends towards the Young's modulus of bulk materials. This result confirms the study of Jiang et al. [17] on the effect of surface roughness on Young's modulus of thin films.

The hardness values are relatively close to those obtained on foils produced by vacuum deposition: a standard deviation of 0.18 GPa is found for copper and zinc foils. Due to this low deviation, it is difficult to conclude on the effect of the elaboration technique i. e on the effect of the grain morphology on hardness. However, some trends can be underlined. For copper foils, it can be noticed that hardness appears dependant of grain size: hardness increases when decreasing grain size, which is due to the Hall-Petch effect. For zinc foils, a decrease in grain size leads to a decrease in hardness, which underlines a break-down in the Hall-Petch behaviour. This phenomenon has already been studied in numerous studies [18, 19]. The Hall-Petch effect is valid only for grains sizes higher than a critical value which depends on the material. Consequently, most of the nanocrystalline materials are generally affected and exhibit an "inverse" Hall-Petch effect. In view of the results obtained with the nanoindentation tests, it may be possible to assume that this critical value has been reached in the case of zinc foils produced by S.I.P technique but not for copper foils whatever the technique of elaboration considered.

4. CONCLUSIONS

The feasibility to produce thin foils by using vacuum technology has been investigated. A recent process developed by ArcelorMittal and called Self-induced Ion Plating has been employed and has led to the production of copper and zinc foils of 35 µm in thickness. Compared to foils obtained by conventional techniques, smaller grains are obtained but rougher surfaces are also present. These differences have an impact on the mechanical characteristics of foils. Depending on grain size, foils can indeed exhibit a Hall-Petch behaviour or an inverse Hall-Petch behaviour. Depending on surface roughness, foils can exhibit an elastic modulus more or less close to the one obtained for a bulk material.

Acknowledgments

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