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Water content and high temperature influence on the oxidation behavior of manganese and silicon thin films on iron matrix

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ABSTRACT

Mn and Si thin films were deposited by thermal evaporation on different Fe-substrates. The use of a mobile shutter during deposition allowed a thickness gradient to be obtained along each sample favoring thickness dependent annealing investigations of Mn and Si films on Fe. The annealing behavior of the prepared thin films was investigated at temperatures ranging between 750 and 950 °C under different atmospheric conditions. Not only the temperature, but also the O_2 partial pressure used as well as the film thickness influenced the oxidation behavior of the thin film samples during annealing. The Mn thin film deposited on the Fe substrate and annealed at varying conditions revealed a strong crystal growth. This depended on all annealing variables resulting in a grain size decrease with decreasing temperature, O_2 partial pressure and film thickness. The Si coated substrate showed a different oxidation behavior as compared to the Mn case, revealing mainly a thickness independent homogeneously oxidized surface. However, the heat treatment conditions were still evaluated as influencing factor for the Si thin film gradient because under specific conditions Fe diffusion through the Si thin film could be observed.

1. Introduction

The addition of Si and Mn as alloying elements is very popular in the steel industry. Both elements can induce specific properties to the steel when added within certain limits. A high amount of Si, for example, is added to electrical steels in order to ensure excellent magnetic properties, such as low core loss [1–4]. However, the maximum amount of Si in steel is limited to 6.5 wt.% because of the industrial production process, where more Si would result in a high brittleness of the steel [5–7]. In order to provide best magnetic but also best metallurgical properties, not only Si but also Mn is added to electrical steels in small amounts (<0.5 wt.%). A similar situation occurs for high Mn-steels. Higher strength and improved ductility during hot processing are only some of the properties that can be achieved by the addition of Mn [8,9]. Therefore, Mn in amounts of up to 30 wt.% is added e.g. to achieve TRansformation or TWinning Induced Plasticity (TRIP or TWIP) steels, in order to obtain both improved ductility and high-strength [10–13], or to produce Hadfield steels with increased wear and abrasion resistance [14, 15]. Additionally, Si is added to the TRIP and TWIP steels in order to provide superior impact strength [11]. The oxidation behavior of steels during annealing is highly relevant, possibly influencing the final properties. Both kinds of steels mentioned (high Mn-steels and high Si-steels) are industrially produced under H_2–N_2 atmospheres at temperatures of up to 1000 °C. These annealing atmospheres are protective for Fe but usually selective oxidation of Si and Mn can still occur since their oxides are thermodynamically more stable as compared to Fe oxides [16]. The dependence of the atmospheric conditions on the oxide layer formation was previously investigated [17–20]. This selective oxidation is detrimental since it can induce failures during the industrial production process which are more pronounced at an increased alloying content [5,21–26]. Especially the technology of coating the steel surfaces with Zn is of highest relevance for the steel industry but it is still problematic for these kinds of steels [13,23,27–29]. Previous investigations described in literature are usually performed on industrial or laboratory alloys and therefore limited by the abovementioned alloying contents.

An experimental approach via physical vapor deposition (PVD) was chosen in the present work for producing Fe–Si and Fe–Mn model samples. The preparation of both Fe–Mn and Fe–Si combinatorial thin films is described in literature, mainly by using complex chemical vapor deposition (CVD) and magnetron sputtering methods [6,30–32]. With those methods, the aforementioned alloying content restrictions in the steel are achieved without facing the challenges presented during hot-rolling. However, the alloying content restrictions are usually not exceeded. Overcoming these restrictions with the help of model samples

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might be an advantage for increasing the visible effect of the alloying content on the final material properties when considering the industrial production process with its specific annealing conditions. Therefore, a new approach was chosen in this work by using pure Si and/or Mn coatings deposited as thin films on the surface of Fe substrates. During this investigation, the elemental thin films were obtained as thickness gradients on Fe bulk substrates. The following step of annealing in different atmospheres and at different temperatures induced various diffusion and oxidation phenomena. Those effects were not only dependent on the annealing conditions but also on the thickness of each deposited thin film.

2. Experimental

Thin films of Si and Mn were deposited as thickness gradients via thermal evaporation along industrial Fe substrates (99.6% purity, supplied by voestalpine Stahl GmbH). The substrate material was a cold rolled and annealed material with a grain size of around 20 μm and a thickness of 1.4 mm. It was precut in a rectangular shape of 10×77 mm^2 for serving as substrate for the Si and Mn vapor condensation in vacuum. Before being used for thin film deposition, the surfaces of the substrates were ground using diamond paste with a 1 μm particle size. Both Si and Mn thin films were deposited from high purity materials (>99.9%, Alfa Aesar) using a self-developed thermal evaporator designed for combinatorial thin film library preparation. The particularity of the system is found in the evaporation geometry [33]. Three thermal sources can be used simultaneously, if desired, and each of them is positioned off-center with respect to the substrate. This leads to an accentuated thickness gradient along the substrate due to the cosine law of evaporation [34,35]. In the present study, only one source (Si or Mn) was used at a time for depositing thin films on the Fe substrates. In order to accentuate the obtained thickness gradient, a slowly moving shutter (with a speed of 0.8 mm s^{-1}) was used in front of the Fe substrates. A schematic cross section of this process is displayed in Fig. 1. The crucible with the evaporation powder (olive and green colored, respectively) is heated resistively. Even though the thickness of the deposited film depends on the deposition angle (obeying a cosine law), a significant thickness gradient along the substrate can be obtained only by using a moving shutter. This partly blocks vapor phase atoms from reaching the substrate due to the line-of-sight limitation of the evaporation process. The wedge-like structure is finally obtained on the substrate material. Crystal quartz microbalances (QCMs) positioned above each thermal source were used for in situ thickness measurements. For both deposited species, evaporation rates ranging from 0.4 to 0.5 nm s^{-1} were used leading to final thicknesses above 100 nm at the thicker end of the samples. The base pressure of the deposition chamber was in the range of 10^{-5} Pa and the thermal heat delivered to the samples during deposition due to radiation resulted in a temperature increase up to values of 80 °C for Si and 40 °C for Mn.

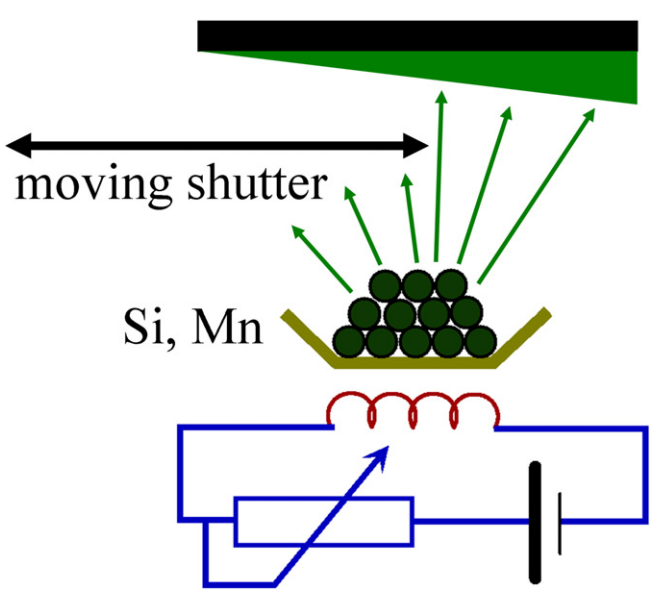

Fig. 1. Schematic illustration of the thermal evaporation method with the corresponding moving shutter in order to obtain a thickness gradient (wedge like structure) on the surface of the substrate.

After their deposition, the thin films were annealed using an IR-heated furnace. Due to the particularities of the setup, within the furnace it was possible to vary the annealing conditions in terms of temperature, atmosphere and water content. The annealing temperatures and atmospheres used are displayed in Table 1. For both conditions, the heating and cooling rates were in the range of 25 °C s^{-1} and −5 °C s^{-1}, respectively. The regulation of the water content in the atmosphere is a common method for precisely defining the O_2 partial pressure during an annealing procedure. Therefore, the annealing conditions indicated in Table 1 do not only give the content of H_2O but also the calculated partial pressure of O_2. Fig. 2 displays the Ellingham-type diagram revealing the correlation between the partial pressure of oxygen and the temperature. The equilibrium partial pressure for the metal-oxide equilibrium of the elements Fe, Mn and Si is given in the diagram. At the same time, the two annealing conditions 1 and 2 (described in Table 1) are also visualized. All these data were obtained using specialized software Factsage 6.3. The calculation was performed using the thermodynamically most stable phases within the database depending on the temperature.

The microstructures of the as-prepared and of the annealed thin films were evaluated by using scanning electron microscopy (SEM), energy-dispersive X-Ray (EDX) spectroscopy and glancing incidence X-Ray diffraction (GIXRD). The surface characterization via SEM was performed using a Field Emission Gun Microscope *Supra35* from ZEISS equipped with a secondary electron (SE) detector working at an acceleration voltage of 2 kV. The chemical composition was determined using an EDX system from EDAX with a Si(Li)-detector of 10 mm^2 and an acceleration voltage of 5 kV. The XRD characterization was accomplished with an X'Pert Pro system from PANalytical equipped with a Co Kα anode providing a wavelength of 0.178 nm. A voltage of 40 kV and a current of 40 mA were used while the divergence slit was set to 1/32° at an incidence angle of 0.5°.

3. Results and discussion

3.1. Thin film characterization before annealing

Both types of thin films prepared on the surface of polished Fe substrates were characterized before annealing using SEM, EDX and GIXRD. Figs. 3 and 4 present the SEM images describing the surface morphology of the Mn and Si gradient thin films before annealing, respectively. In the SEM images, both thin films reveal a smooth and homogeneous surface morphology, independent of the thickness of the film. The thickness (as previously measured in-situ by QCMs) varied from 150 nm to 25 nm for the Mn thin film (see Fig. 3a) and b), respectively) and from 100 nm to 25 nm for the Si gradient (see Fig. 4a) and b), respectively).

The pattern of straight lines visible in all images is a result of the polished substrate material where the scratch remnants from the substrate polishing procedure were not completely covered by the films due to their low thickness. Therefore, the effect is better visible at the thin end of each film. At the thick ends of both Mn and Si thin films (Figs. 3a) and 4a), respectively) not only the homogeneous surface morphology, but also small round grains were visible. Using EDX analysis of those grains it could be revealed that they contain high amounts of O_2 together with Mn and Si, respectively, as compared to the nearby surface regions. The low deposition pressure used did not allow a natural