

# Study on the Penetration of Al into Fe-3 %Si Thin Sheet Using PVD Method and Its Application in Preparing Fe-6.5 % (Si+Al) Alloy

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**Keywords:** Fe-6.5 % (Si+Al) alloy; Magnetron-sputtering; Diffusion annealing; Penetration mechanism of Al.

**Abstract.** Fe-6.5 %Si alloy has excellent soft magnetic properties but is hardly able to being produced by conventional hot-cold rolling processes. It is well known that a small amount of Al adding into Fe-Si alloys is benefit to enhancing the alloy's soft magnetic properties and its working performance. In the present work pure Al layers were deposited onto Fe-3 %Si thin sheets using direct current (DC) magnetron sputtering and followed by diffusion annealing to promote Al penetrating into low-Si steel substrates. Based on the experimental and simulation results, the mechanism of Al penetrated into low-Si steel substrate was subjected to rate-controlling and Si uphill diffusion only occurred under the influence of penetrated Al being gradient distributed. As deposited Al layer's thickness reached to 32  $\mu\text{m}$  onto 0.23 mm Fe-3 %Si substrate and followed by a diffusion annealing at 1200  $^{\circ}\text{C}$  for 6 h, Fe-6.5 % (Si+Al) alloy can be achieved. Electron dispersive spectroscopy (EDS) analyses showed that both Si and penetrated Al profiles were evenly distributed along the depth of the prepared Fe-6.5 % (Si+Al) alloy, and the microstructure was also uniform and density. The resistivity of Fe-6.5 % (Si+Al) alloy was close to that of Fe-6.5 %Si alloy, but the working performance of the former was observed evidently better than the latter.

## Introduction

Fe-6.5 % (weight percentage, hereinafter) Si alloy has excellent soft magnetic properties such as higher permeability, higher saturation magnetization, near to zero magnetostriction and lower core loss than conventional Fe-3 %Si steel sheets. However, due to the appearance of ordering brittle phases such as B2 or DO<sub>3</sub>, the high-Si alloys are hardly able to being produced by conventional hot-cold rolling processes [1-5]. Several techniques were developed to overcome the drawbacks, in an attempt to produce Fe-6.5 %Si thin sheets [6-9], but only chemical vapor deposition (CVD) realized low-scale commercial production, which is still far away from meeting the great demands required by electromagnetic applications [4]. Many researchers found that silicon steel sheets with a small amount of Al could optimize its magnetic properties and working performance. A. H. Kasama et al prepared Fe-3 %Si-3.5 %Al alloy by spray-formed approach, and found its magnetic properties were very well when compared with binary Fe-6.5 %Si. Claudemiro Bolfarini studied the magnetic properties of spray-formed Fe-6.5 %Si-1.0 %Al alloy and found that 1 % of Al added to the Fe-6.5 %Si alloy could suppress the generation of B2 structure and improve the Fe-Si alloy ductility [10]. J. Barros, et al assessed the feasibility of increasing the concentration of (Si, Al) in low-Si steel sheet by hot dipping and diffusion treatment [11]. All the above researches concluded that Al alloying into Fe-Si binary systems being advantage to its properties, but whether Fe-Si-Al alloys, especially Fe-6.5 % (Si+Al) alloy could be prepared by penetrated Al into Fe-3 %Si thin sheet was less reported, and what's the interaction effect between penetrated Al and solved Si in Fe matrix was still not very clear. This work started from depositing pure Al layers onto Fe-3 %Si steel substrates by PVD method and followed by a diffusion annealing at high temperature in vacuum, to evaluate the feasibility of preparing Fe-6.5 % (Si+Al) alloy, and clarify the penetration mechanism of Al into low-Si steel substrate.

## Experimental

0.23 mm thick commercial Fe-3 % Si steel sheet was degreased and cut into 10 mm × 20 mm for starting substrates. Al layers (Al target with purity of 99.99 %) were deposited on the starting substrates by using direct current (DC) magnetron sputtering. Table 1 presents the deposition parameters. The as-deposited samples were annealed with a heating rate of 10 °C/min in a vacuum of  $8 \times 10^{-4}$  Pa at temperatures ranging from 950 to 1200 °C and holding for 0.5-6 hours. Structure of the samples were characterized by X-ray diffractometer (XRD) XPERT-PRO with Cu Ka radiation ( $\lambda=0.1540598$  nm). Composition and microstructure along the sample cross-section were analyzed by Quanta 450 FEG scanning electron microscopy (SEM) equipped with electron dispersive spectroscopy (EDS). The micro-hardness was measured by HVD-1000IS digital micro-hardness tester along the polished cross-section with a load of 100 g and the imprinting time of 10 seconds. The electrical resistivity was measured using a four-probe technique.

TABLE 1. Detail parameters of deposition processes.

Ar pressure	Power density	Target-substrate distance	Substrate temperature	Deposition rate
0.8 Pa	6.3 W/cm <sup>2</sup>	80 mm	200°C	137 nm/min

## Results and Discussion

The effect of annealing temperature and time on the penetration of Al into low-Si steel substrates was investigated firstly. Fig.1a exhibits Al concentration profiles of the samples started with depositing 8 μm thickness Al layers and annealed at 950 °C, 1000 °C, 1100°C and 1200 °C for 2 h, respectively, where all the symbols represent experimental results and same color curves represent their Gauss-fitting. With the elevation of annealing temperature, the concentration gradients of Al declined, but the penetration depths increased gradually, annealing at 1200 °C for 2 h led to Al penetrating throughout the substrate thickness and almost being homogeneous distribution. Considering of possible evaporation of Al at higher temperatures in vacuum [12], the annealing temperature didn't exceed more than 1200 °C in the experimental.

The inset table in Fig. 1a lists the corresponding integrated areas between Al concentration profile curves and abscissa axis, which can be used to assess the dependence of annealing temperature on the total Al amount penetrated into the starting substrate. As temperature is increased from 950 °C to 1100 °C, the integrated areas increase from 147 (here ignoring its unit) to 188, meaning that more amount of Al penetrated into the substrate from deposited Al layers at higher temperatures. As annealing temperature is up to 1100 °C and 1200 °C, the integrated areas reach to nearly a constant of 188, implies that annealing above 1100 °C promises all or the most of the deposited Al penetrated into the substrates. For the reason of the deposited Al layer being finite as diffusion source, the concentration-depth profiles can be described by the thin-film solution of Fick's Second Law [13]:

$$C(x,t) = \frac{S}{2\sqrt{\pi Dt}} \left[ e^{-\frac{x^2}{4Dt}} + e^{-\frac{(x-2d)^2}{4Dt}} + \dots \right] \quad (1)$$

Where  $S$ ,  $x$ ,  $d$ ,  $D$  and  $t$  represent the Al amount as diffusant source, the distance of Al penetration, the thickness of the substrate, diffusion coefficient and annealing time, respectively. Based on trial method, when we try to set  $S$  value as 410,  $t$  equals to 7200 s, and  $D$  values being  $4.2 \times 10^{-13}$  m<sup>2</sup>/s at 1100 °C and  $1.5 \times 10^{-12}$  m<sup>2</sup>/s at 1200 °C, Al concentrations after diffusion annealing at 1100 °C and

1200 °C for 2 h can be calculated according to formula (1) and displayed in Fig. 1b. It can be seen that the calculated values were in good agreement with the experimental results. Thus, from Arrhenius equation:

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \quad (2)$$

We can furthermore achieve the activation energy  $Q$  of Al penetrated into low-Si steel sheet being about 214 kJ/mol. The value also is in well agreement with previous reports [14]. Based on the experimental and simulation results, the mechanism of Al penetrated into Fe-3 %Si substrate can be concluded being subjected to rate-controlling.

Fig. 2 demonstrates annealing time dependence of Al concentration profiles for samples coated with 8  $\mu\text{m}$  Al layer and annealed at 1200 °C. The penetration depth of Al increased with the annealing time. Meanwhile, the gradient of Al content decreased with annealing time, showing a homogeneous diffusion characterization.

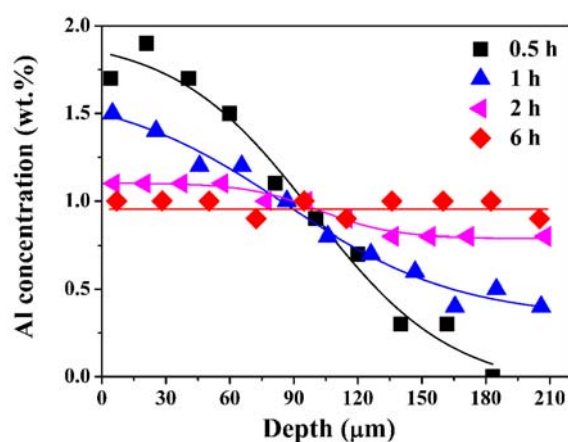


Figure 2. Cross-sectional Al concentration profiles for samples deposited with 8  $\mu\text{m}$  Al layers and annealed at 1200 °C for various time.

To clarify the interaction effect of Al and Si during diffusion annealing, both Si and Al distribution profiles along the cross-section for the samples processed by coated with 8  $\mu\text{m}$  thickness Al layer and subsequent annealing at 1200 °C for 10 min, 2 h and 6 h were displayed in Fig. 3, at where the black dotting line refers to the starting content of Si in the substrate. It can be found in Fig. 3a that after only 10 minutes annealing at 1200 °C, Al penetrated into the substrate nearly 80  $\mu\text{m}$  depth and having a steep decline distribution. Meanwhile, Si distribution in the substrate exhibits a very different profile, which can be divided along the depth into three regions. Region “I”, Si content increases with the depth but lower than the starting value of 3%. Region “II”, there is a maximum peak of Si content about 3.8 % in the depth near the diffusion front edge of Al. Region “III”, Si content keeps a constant value of about 3.3 % where no Al atoms can be detected.

In fact, the diffusion couple in the present work consisted of Fe-3 %Si alloy and pure Al layer. When the as-deposited samples were heated up over than Al melt point of 660°C, the pure Al layers would be molten as liquid layer coated on the Fe-Si substrates. Thus the system can be classified as solid/liquid diffusion couple. At the start of annealing, a solid/liquid interface formed at the plane of initial contact and a number of binary and ternary phases formed due to the diffusion flux of Fe and Si in Al liquid and an opposite flux of Al in solid Fe-3 %Si substrate. Therefore, Si content in region “I” in Fig. 3a being lower than the starting value of 3 % can be explained as Fe and Si atoms diffused into Al liquid layer and simultaneously penetrated Al having a dilution effect on the content of Si. In region “II”, Si content improved and deviated greatly from the starting value should be attributed to the uphill diffusion of Si under the repulsive effect of penetrated Al which changed the chemical potential in Fe-Si-Al ternary system, similar phenomenon also occurred in

literatures [14] and [15]. In region “III” no Al atoms can be detected but Si content kept greater than the starting value of 3 %, we guess it results from the diffusivity of Fe in liquid Al being greatly quicker than that of Al in solid Fe-Si substrate [16, 17], a net flux of Fe diffusing from the bulk substrate to liquid layer and leading correspondingly to a Si-rich than the starting value region “III” formation.

Until after 6 h annealing at 1200 °C as shown in Fig. 3b, with the penetrated Al became uniform distribution along the depth of the substrates, the distribution profiles of Si resumed evenly. However, the average content of Si was still bigger than the starting value. The interaction between Al and Si may demonstrate that Si uphill diffusion in Fe-Si-Al ternary system only occurred under the influence of Al being gradient distributed.

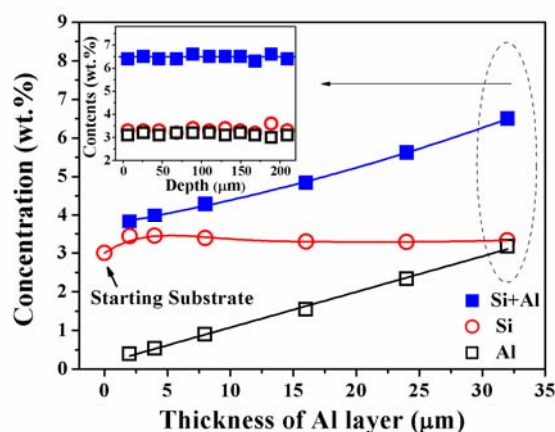


Figure 4. Dependence of the average contents of Al and Si and meanwhile their sum on the deposited Al amount. The inset shows both Si and Al were homogenously distributed in the prepared Fe-6.5 % (Si+Al) alloy

To investigate the dependence of Al and Si concentrations on the deposited Al amount, the starting substrate deposited with various thickness of Al layers and all followed by annealing at 1200 °C for 6 h. EDS measurement results shown that after 6 h annealing at 1200 °C, all the penetrated Al and Si in the substrates were homogenously distributed across the sections. Thus the average contents of Si and Al in the processed alloys were demonstrated in Fig. 4 with the abscissa axis exhibiting corresponding thickness of deposited Al layers. It can be found that the penetrated Al concentration increased linearly with the deposited Al layer thickness. The average contents of Si elevated up to a maximum value of 3.45 % when Al content was near 0.5 %, and then declined slowly. As deposited Al layer's thickness reached to 32 μm (cross-sectional image showed in Fig. 5a) and after diffusion annealing (cross-sectional image showed in Fig. 5b), the average content of Al increased to 3.17 % and Si average content was 3.33 %, meaning that Fe-6.5 % (Si+Al) alloy was achieved. The inset in Fig. 4 exhibits that both Si and penetrated Al profiles were evenly distributed along the depth of the prepared Fe-6.5 % (Si+Al) alloy, meanwhile Fig. 5b demonstrates that its microstructure was also uniform and density after cleaning the residual layer attached in the surface.

The change of Si average contents in Fig. 4 also can be verified from the microstructures of the processed alloys. Fig. 6 shows the XRD patterns of the starting substrate of Fe-3 %Si sheet (sample “A”), the processed alloys with penetrated Al reaching to 0.9 % (sample “B”, Si content being at 3.39 %) and 3.17 % (sample “C”, Si content being at 3.33 %), respectively. The inset in Fig. 6 displays the magnified diffraction profiles in the range of 43.5°- 47° and corresponding lattice constants calculated according to the 2θ positions at (110) peaks which were indexed as α-Fe(Si) or α-Fe(Si,Al) solution. It can be seen that the two processed alloys were vastly different with the starting substrate in the positions of (110) peaks and their lattice constants. The (110) peak of sample “C” with greater amount of penetrated Al shifted toward lower angle side, and its lattice constant of 0.2884 nm was bigger than that of the starting substrate of 0.2874 nm. But the ones of sample “B” penetrated with 0.9 % Al varied to opposite direction, higher angle side and its lattice constant being smaller. This could be interpreted from the difference of atomic sizes: the atomic

radius of Al is the biggest and that of Si is the smallest among the ternary system of Fe-Si-Al (Fe: 0.124 nm, Si: 0.118 nm, and Al: 0.142 nm) [18], therefore in sample “C” with the penetration of Al atoms into Fe-Si matrix substituting Fe atoms and/or Si atoms, the lattice should be expanded with the increment of Al content. In contrast, smaller amount of Al penetrated into the starting substrate such as sample “B”, Al content was only 0.9 %, as discussed above, the increment of Si from 3 % to 3.39 % may compensate the influence of Al and play a dominant role in its microstructure, thus the lattice constant was smaller than that of the starting substrate.

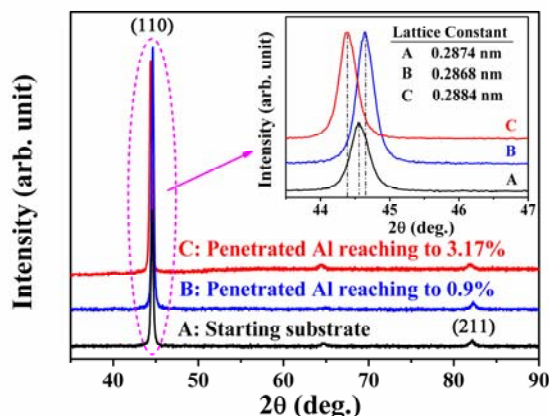


Figure 6. XRD patterns for (A) starting substrate, (B) and (C) with penetrated Al concentration reaching to 0.9 % and 3.17 %, respectively. The inset magnifies their diffraction profiles in the range of 43.5-47° and lists the corresponding lattice constants.

Fig. 7 demonstrates the electrical resistivity and the micro-hardness of the processed alloys with various sum contents of (Si+Al). It can be seen that with the increasing of the sum content of Si and Al in the processed alloys, both its resistivity and micro-hardness elevated almost linearly. The resistivity and micro-hardness of Fe-6.5 %Si also were displayed in the figure [2]. It can be found that the resistivity of Fe-6.5 % (Si+Al) alloy is very close to that of Fe-6.5 %Si alloy. Higher resistivity of soft magnetic material can be expected being beneficial to reducing its eddy loss, especially at high frequency. As comparing the hardness of Fe-6.5 % (Si+Al) alloy with Fe-6.5 %Si alloy, it can be seen the micro-hardness of Fe-6.5 % (Si+Al) alloy is obviously less than that of Fe-6.5 % Si alloy, which can be beneficial to its working performance. This has been proved by the photo inserted in Fig. 5b up-right corner that the prepared Fe-6.5 % (Si+Al) alloy can be cut by scissors at ambient temperature and bended to a right angle, which is hardly possible to Fe-6.5 %Si alloy. Better working performance of the Fe-6.5 % (Si+Al) alloy may be attributed to the presence of Al improving the alloy's ductility by producing changes in stacking fault energy and influencing its micro-structural behavior in the order/disorder transformation [19].

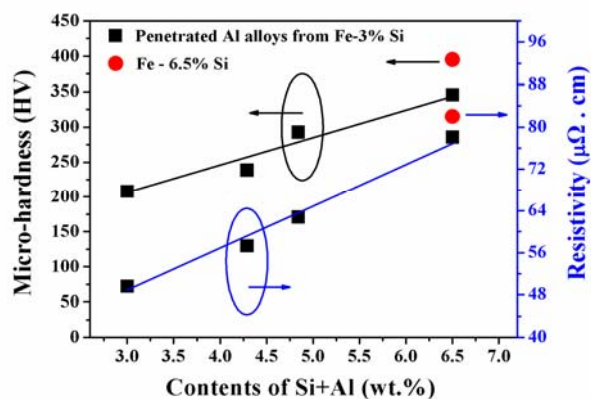


Figure 7. Dependence of the micro-hardness and resistivity for the processed alloys on the sum contents of Si and Al.



## Conclusions

Pure Al layers were deposited onto low-Si steel substrates using DC magnetron sputtering method and subsequent diffusion annealing was conducted led to penetration of Al into the substrate. The penetration mechanism of Al into low-Si steel sheets is subjected to rate-controlling, and its activation energy can be evaluated about 214 kJ/mol, in good agreement with literatures. Si uphill diffusion in the processed Fe-Si-Al system only occurred under the influence of Al being gradient distributed. The resistivity of the prepared Fe-6.5 % (Si+Al) alloy was close to that of Fe-6.5 %Si alloy and its working performance was observed evidently better than the latter.

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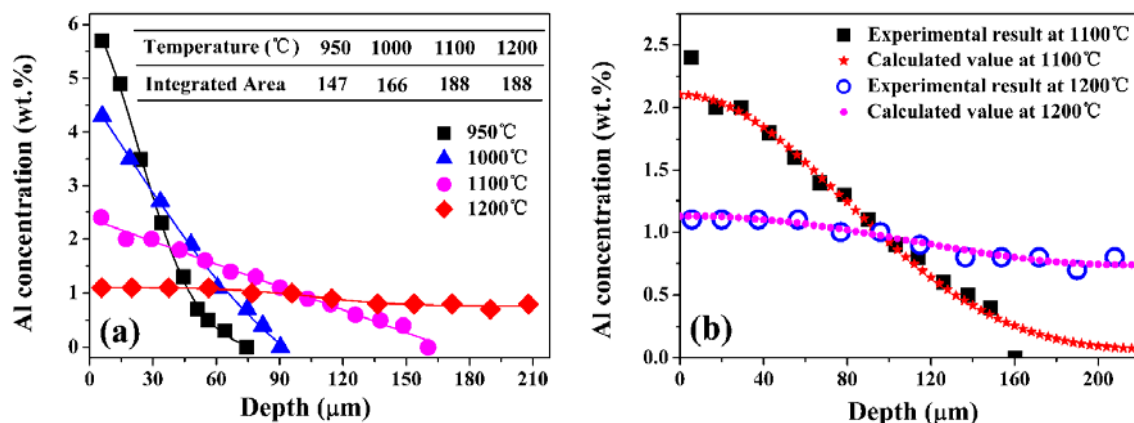


Figure 1. (a) Cross-sectional Al concentration profiles for samples deposited with 8 μm Al layers and annealed at different temperatures for 2 h. The inset lists the integrated areas under the Gauss-fitting curves representing penetrated Al amounts. (b) Comparing of calculated Al concentration with experimental results in (a).

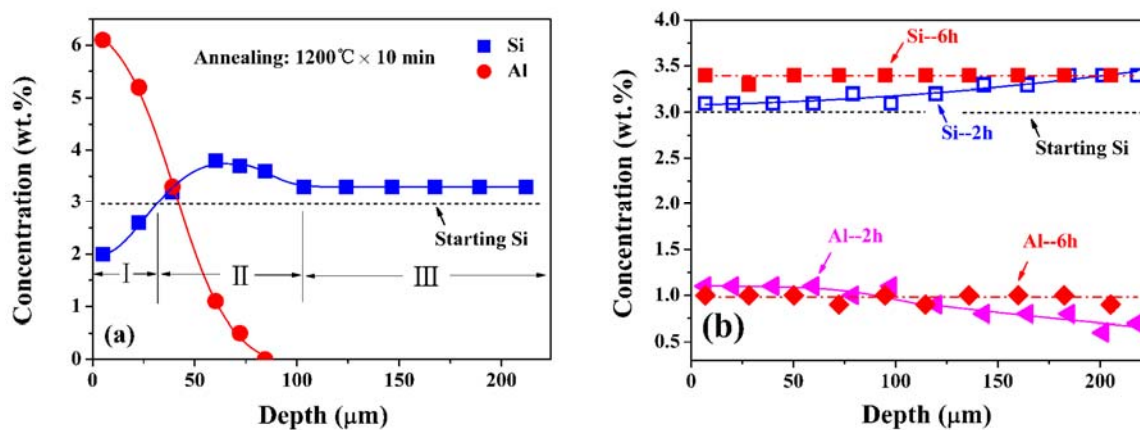


Figure 3. Both Si and Al distribution profiles along the cross-section for samples processed by coated 8 μm Al layer and annealed at 1200 °C for: (a) 10 min, (b) 2 h and 6 h. The dotting lines refer to Si content in the starting substrate.

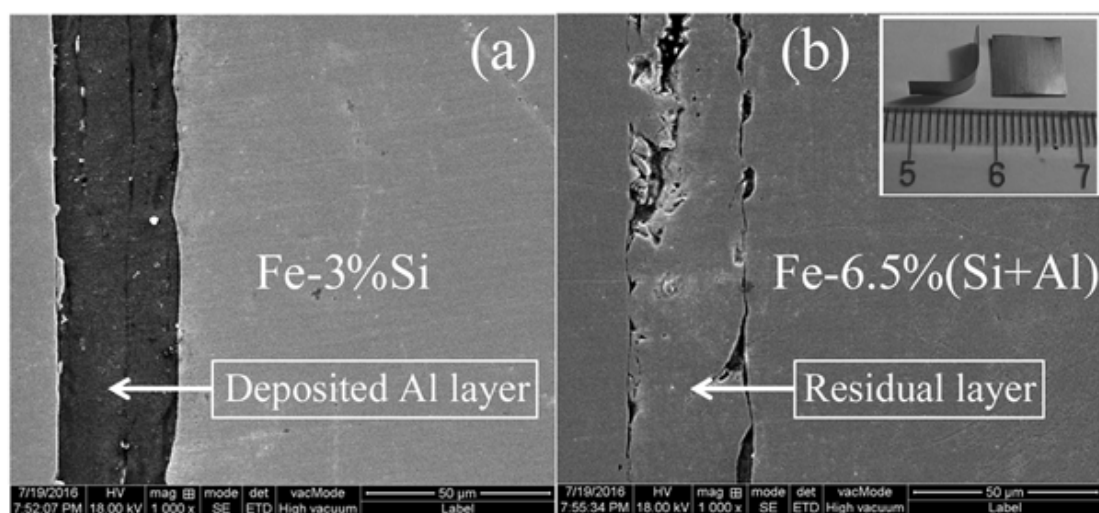


Figure 5. Cross-sectional images of as-deposited Fe-3%Si substrate with 32  $\mu\text{m}$  Al layer (a) and as-annealed Fe-6.5 % (Si+Al) alloy (b). The inset shows the workability of prepared Fe-6.5% (Si+Al) sheet being cut at ambient temperature and bend near to a right angle.