Low-Temperature Siliconizing of Surface-Nanocrystallized Silicon Steel Thin Strips: Influence of Parameters (Postprint)

Authors: Liu Gang, Mo Chenggang, Yuhui Sha, Zhao Xiang, Zuo Liang

Date: 2023-03-18T00:00:00+00:00

Abstract

Shot peening, cold rolling, and solid powder siliconizing were sequentially performed on silicon steel, and the microstructure, phases, and composition of the surface layer were characterized. The results indicate that after shot peening, nanocrystals with a size of approximately 10 nm were generated in the silicon steel surface layer, and 91% cold rolling caused a slight increase in the size of these surface nanocrystals. Cold-rolled samples (in silicon powder + halide) could be siliconized at 500°C; increasing the siliconizing temperature or extending the holding time at elevated temperatures both increased the compound layer thickness, whereas the halide content had minimal influence. After siliconizing at lower temperatures, the compound layer consisted of a single Fe3Si phase; with increasing temperature, prolonged time, and increased halide content, the FeSi phase content increased.

Full Text

Low-temperature Siliconizing of Silicon Steel Thin Strip with a Nanostructured Surface Layer and Effect of Treatment Parameters

LIU Gang[1], MO Chenggang[1], SHA Yuhui[2], ZHAO Xiang[2], ZUO Liang[2]

[1]Key Laboratory of Electromagnetic Processing of Materials, Ministry of Education, Northeastern University, Shenyang 110819, China

Abstract

Silicon steel thin strip was subjected to surface shot peening, cold rolling, and finally siliconizing by pack cementation process. The microstructural evolution of the steel during treatment was examined. Results show that shot peening induces the formation of nanocrystalline grains (approximately 10 nm in size) in the top surface layer; the grain size increases slightly after cold rolling. A compound layer can be obtained after siliconizing at 500°C in Si powder + halide on the shot-peened and cold-rolled steel strip. Its thickness increases with increasing temperature and holding time, while the halide content exhibits little effect. After siliconizing at lower temperature, the compound layer consists of single-phase Fe_3Si. The formation of FeSi phase is promoted by increasing temperature, holding time, and halide content.

KEY WORDS metallic materials, silicon steel, shot peening, siliconizing, structure

Introduction

Silicon steel is primarily used for iron cores in motors, transformers, relays, and other electrical instruments, accounting for over 90% of total magnetic material consumption. The magnetic properties of silicon steel determine the efficiency and energy consumption of electromechanical equipment. When silicon content increases to 6.5% (mass fraction, hereinafter the same)—referred to as high-silicon steel—the material exhibits excellent comprehensive magnetic properties including high magnetic permeability, low iron loss, and near-zero magnetostriction coefficient [1-3]. Consequently, high-silicon steel represents an ideal core material for the development of high-efficiency, low-energy-consumption, miniaturized, and low-noise electromechanical equipment. However, high silicon content also renders its room-temperature elongation nearly zero [4,5], making large-scale industrial production via conventional cold rolling impossible.

Currently, various methods have been proposed for preparing high-silicon steel, including chemical vapor deposition (CVD) [6] and hot-dipping-diffusion [7] for siliconizing-diffusion on 3% Si steel substrates, as well as special rolling [8], rapid solidification [9], powder rolling-sintering [10], and direct casting [11] for Fe-6.5%Si alloys. Among these, only the CVD method enables small-scale continuous production.

The CVD process requires siliconizing steel strips at high temperatures (~1250°C) in media with high halide content (N_2 or Ar + ~35 vol.% $SiCl_4$ gas) [1,12]. The elevated temperature increases energy consumption, while the high halide concentration severely corrodes equipment and steel surfaces. Additional issues include complex subsequent temper rolling operations, significant iron loss from steel strips, and environmental pollution from $FeCl_2$. Extensive experimental research has been conducted to reduce siliconizing temperature and halide content, but with limited success. Since siliconizing involves reaction and diffusion between the environmental medium and steel strip, optimizing the surface structure of the steel strip could potentially simplify siliconizing conditions. Surface nanocrystallization technology, which has developed rapidly in recent years, enables such surface structure optimization.

Surface nanocrystallization (SNC) technology induces severe cyclic plastic deformation on metal surfaces to form nano-micro gradient structures [13]. The high volume fraction of interfaces between surface nanocrystalline grains can accelerate surface chemical reactions and provide diffusion channels for atoms, significantly reducing the temperature and time required for chemical treatment [14-16]. Preliminary studies have shown that after surface nanocrystallization of 2.2 mm thick silicon steel hot-rolled plates, pack siliconizing can be performed at 550-650°C in silicon powder with 3% halide content [17], demonstrating the feasibility of using surface nanocrystallization to simplify siliconizing conditions. Since the magnetic properties of hot-rolled silicon steel plates are far inferior to those of cold-rolled plates, this study combines surface shot peening (SP) and cold rolling (CR) to obtain large-sized 3% silicon steel thin strips with nanostructured surface layers. Low-temperature siliconizing was then performed under various parameters (temperature, time, and halide content), and the feasibility of low-temperature siliconizing on silicon steel thin strips, initial conditions, and parameter effects were investigated through analysis of microstructure, phase composition, and elemental distribution.

Experimental

The experimental material was 3% silicon steel hot-rolled plate with a thickness of 2.2 mm and chemical composition (mass fraction, %) of: Si 3.035, Mn 0.338, Al 0.441, P <0.005, S <0.005, C 0.004, Fe balance.

Plates were cut into samples measuring 100 mm × 50 mm × 2.2 mm. Mechanical vibration shot peening (SP) was performed on both sides of the samples in vacuum. The processing parameters were: shot diameter 8-10 mm, mechanical vibration frequency 50 Hz, distance between shot and sample 15 mm, processing time 60 min. The shot-peened samples were cold rolled (CR) at room temperature with a reduction of 91% through six passes, resulting in a final strip thickness of 0.20 mm. The surfaces of the SP+CR samples were cleaned with 3% hydrochloric acid alcohol solution to remove oxide layers. Pack siliconizing was performed with the following parameters: holding temperature 500-700°C, holding time 1-8 h, siliconizing agent composition of silicon powder + 1-5% halide, heating rate 10°C/min.

Phase analysis of sample surfaces was conducted using X-ray diffraction (Pert Pro PW3040/60, XRD). Cross-sectional backscattered electron images of siliconized samples were observed using scanning electron microscopy (JEOL-JSM 6360LV, SEM), and silicon distribution along the depth direction was measured using energy-dispersive spectroscopy (EDS). Microstructures on the surface and along the depth direction of shot-peened and cold-rolled samples were observed using field-emission transmission electron microscopy (JEOL-JEM2100F, TEM). Sample preparation involved mechanical grinding of the treated surface to the desired depth, followed by mechanical grinding from the back side to 30 m thickness, and finally single-sided ion milling from the back until perforation.

2.1 Structural Characteristics of Surface Nanocrystallization

Figure 1 [Figure 1: see original paper] presents TEM images and corresponding selected-area electron diffraction (SAED) patterns of the shot-peened sample surface and at 20 m depth. After shot peening, nanocrystalline (nc) grains approximately 10 nm in size formed on the surface. The uniform diffraction rings in the SAED pattern indicate random orientation of the nanocrystalline grains (Fig. 1a). At a depth of 20 m from the treated surface, the grain size was approximately 100 nm, and the discontinuous diffraction spots on the SAED rings indicate medium to large orientation differences between grains (Fig. 1b). TEM observations reveal that shot peening creates randomly oriented nanocrystalline grains on the sample surface with a nanocrystalline layer thickness of approximately 20 m. This gradient structure is similar to that of industrially pure iron processed by surface mechanical grinding [18].

Figure 2 [Figure 2: see original paper] shows TEM images and corresponding SAED patterns of the shot-peened + cold-rolled sample surface and at 20 m depth. After cold rolling, the surface remained nanocrystalline but with increased grain size (approximately 20 nm). The uniform diffraction rings in the SAED pattern indicate that the nanocrystalline grains maintained random orientation (Fig. 2a). At 20 m depth, the microstructure consisted of submicron grains/dislocation cells 100-300 nm in size, with irregularly distributed diffraction spots in the SAED pattern indicating small orientation differences between submicron grains/dislocation cells (Fig. 2b).

Comparison of Figs. 1 and 2 reveals that shot peening produces nanocrystalline grains on the sample surface, which are retained after subsequent cold rolling, though with slightly increased grain size. This occurs because shot peening creates a gradient structure along the depth direction, while cold rolling brings some slightly larger grains from the subsurface to the surface. At 20 m depth, the shot-peened sample exhibits nanocrystalline grains with medium to large orientation differences, whereas the cold-rolled sample shows submicron grains/dislocation cells with small orientation differences and significantly larger size. This indicates that cold rolling preserves the nanocrystalline structure induced by shot peening on the sample surface while increasing the variation in gradient structure along the depth direction.

2.2 Initial Conditions for Siliconizing

In pack siliconizing using silicon powder as the silicon source, halides are essential catalysts but also corrode equipment and steel strips. Therefore, halide content should decrease as temperature increases. Figure 3 [Figure 3: see original paper] shows cross-sectional morphology and silicon distribution along the depth of shot-peened + cold-rolled samples after siliconizing. After siliconizing at 500°C for 4 h, a compound layer approximately 3 m thick formed on the sample surface. SEM-EDS measurements revealed a surface silicon content of 11.89%. The silicon content within the compound layer changed little with increasing depth but dropped sharply at the compound layer/substrate interface to match the substrate composition (Fig. 3a). After siliconizing at 550°C for 4 h, the surface compound layer thickness increased to approximately 16 m with a surface silicon content of 15.48%. The silicon content decreased slightly within the compound layer and dropped sharply at the interface (Fig. 3b).

Figure 4 [Figure 4: see original paper] presents XRD patterns of sample surfaces before and after treatment. The original hot-rolled plate showed single-phase α-Fe (Fig. 4a). After shot peening, diffraction peaks broadened significantly due to grain refinement and increased microstrain (Fig. 4b). After cold rolling, peak width decreased because X-rays have certain penetration depth—the surface nanocrystalline size increased slightly while grain size in the depth direction grew rapidly. Additionally, the relative intensity of diffraction peaks changed noticeably, indicating that cold rolling induced texture changes (Fig. 4c). Pack siliconizing of SP+CR samples in Si + 5% halide at 500°C for 4 h produced XRD patterns dominated by α-Fe with weak Fe_3Si diffraction (Fig. 4d). Siliconizing in Si + 3% halide at 550°C for 4 h resulted in complete disappearance of α-Fe peaks and appearance of both Fe_3Si and FeSi phases (Fig. 4e).

These results demonstrate that silicon steel thin strips with nanostructured surface layers obtained by combining shot peening and cold rolling can undergo pack siliconizing. The initial siliconizing temperature is approximately 500°C, with the initial compound layer phase being Fe_3Si. The measured surface silicon content of 11.89% is slightly lower than the theoretical Si content of Fe_3Si (14.29%) because the thin initial compound layer allows XRD to penetrate both the compound layer and underlying α-Fe substrate. As siliconizing temperature increases, compound layer thickness grows significantly and FeSi phase begins to appear. The surface silicon content reaches 15.48%, intermediate between Fe_3Si and FeSi phase compositions (33.33%). XRD phase analysis and EDS composition results are fully consistent.

2.3 Effects of Siliconizing Parameters

The initial siliconizing temperature is approximately 500°C, while surface nanostructure coarsening begins at 650°C in steel [19]. Therefore, siliconizing temperatures of 550-700°C were selected. Cross-sectional SEM observations, EDS composition analysis, and surface XRD phase analysis were performed after siliconizing under various parameters to investigate the effects of temperature (T), time (t), and halide content (x) on compound layer thickness and phase composition.

Figure 5 [Figure 5: see original paper] presents histograms showing the influence of siliconizing parameters on compound layer thickness. Increasing temperature significantly increases compound layer thickness (Fig. 5a), particularly at higher halide contents (e.g., 3%). This indicates that temperature is the key factor affecting compound layer thickness. Extending holding time facilitates silicon diffusion, but at lower temperatures (e.g., 600°C) diffusion is slow, limiting the effect of holding time. Only at higher temperatures (e.g., 650°C) with faster diffusion does holding time become significant (Fig. 5b). Increasing halide content has little effect on compound layer thickness at different temperatures (Fig. 5c), as halides tend to corrode thin strips and equipment. Therefore, further reduction of halide content may be possible.

Figure 6 [Figure 6: see original paper] shows the effect of siliconizing parameters on compound layer phase composition. Generally, at lower temperatures (e.g., 550°C and 600°C), the compound layer consists of single-phase Fe_3Si. As temperature increases (e.g., to 650°C), silicon diffusion accelerates. At low halide content (e.g., 1%), the relatively low concentration of active silicon in the siliconizing agent results in only Fe_3Si phase formation. As halide content increases (e.g., to 3%), the concentration of active silicon increases, allowing formation of both Fe_3Si and FeSi phases. When temperature, time, and halide content are all high (e.g., 650°C, 4 h, and 3%), the high active silicon concentration and rapid diffusion cause transformation of Fe_3Si phase to FeSi phase due to increased silicon content.

In summary, low-temperature siliconizing can be achieved on silicon steel thin strips with nanostructured surface layers obtained by combining shot peening and cold rolling. Compared with CVD siliconizing, solid-state low-temperature siliconizing based on surface nanocrystallization offers several advantages: siliconizing temperature is reduced from ~1250°C to 550-700°C, decreasing energy consumption; halide content is reduced from ~35% (volume fraction) to 1-5%, significantly reducing corrosion of substrates and equipment as well as environmental pollution; and silicon powder as the silicon source can be reused continuously, avoiding silicon loss with gas flow in CVD. Thus, using surface nanocrystallization to simplify siliconizing operations is feasible.

Conclusions

1. Shot peening of silicon steel produces nanocrystalline grains approximately 10 nm in size on the surface layer. After subsequent 91% cold rolling, the surface structure remains nanocrystalline but with slightly increased grain size, and the variation in gradient structure along the depth direction increases.
2. Shot-peened and cold-rolled silicon steel samples can form a compound layer through pack siliconizing in silicon powder + halide at 500°C. Increasing siliconizing temperature or extending holding time at higher temperatures significantly increases compound layer thickness, while halide content has little effect.
3. After siliconizing at lower temperatures, the compound layer consists of single-phase Fe_3Si. With increasing temperature and halide content, the compound layer comprises both FeSi and Fe_3Si phases, and forms single-phase FeSi when temperature, time, and halide content are all high.

References

1. H. Haiji, K. Okada, T. Hiratani, M. Abe, M. Ninomiya, Magnetic properties and workability of 6.5% Si steel sheet, Journal of Magnetism and Magnetic Materials, 160, 109(1996)
2. Y. F. Liang, F. Ye, J.P. Lin, Y. L. Wang, G. L. Chen, Effect of annealing temperature on magnetic properties of cold rolled high silicon steel thin sheet, Journal of Alloys and Compounds, 491, 268(2010)
3. T. P. P. Phway, A. J. Moses, Magnetostriction trend of non-oriented 6.5% Si-Fe, Journal of Magnetism and Magnetic Materials, 320, 611(2008)
4. T. Ros-Yáñez, D. Ruiz, J. Barros, Y. Houbaert, R. Colás, Study of deformation and aging behaviour of iron-silicon alloys, Materials Science Engineering, A447, 27(2007)
5. B. Viala, J. Degauque, M. Fagot, M. Baricco, E. Ferrara, F. Fiorillo, Study of the brittle behaviour of annealed Fe-6.5wt%Si ribbons produced by planar flow casting, Materials Science and Engineering, 212, 62(1996)
6. Y. Takada, M. Abe, S. Masuda, J. Inagaki, Commercial scale production of Fe-6.5wt.% Si sheet and its magnetic properties, Journal of Applied Physics, 64, 5367(1988)
7. T. Ros-Yáñez, Y. Houbaert, V. G. Rodríguez, High-silicon steel produced by hot dipping and diffusion annealing, Journal of Applied Physics, 91, 7857(2002)
8. LIN Junpin, YE Feng, CHEN Guoliang, WANG Yanli, LIANG Yongfeng, JIN Jinan, LIU Yan, Fabrication technology, microstructures and properties of Fe-6.5wt.% Si alloy sheets by cold rolling, Frontier Science, 2, 13(2007)
9. N. Tsuya, K. I. Arai, Magnetostriction of ribbon-form amorphous and crystalline ferromagnetic alloys, Journal of Applied Physics, 50, 1658(1979)
10. K. Kusaka, T. Imaoka, T. Kondo, Relationship between properties and Si-content sintering conditions of Fe-Si type magnetic alloys, Journal of the Japan Society of Powder and Powder Metallurgy, 47(2), 195(2000)
11. J. S. Shin, Z. H. Lee, T. D. Lee, E. J. Lavernia, The effect of casting method and heat treating condition on cold workability of high-Si electrical steel, Scripta Materialia, 45, 725(2001)
12. S. C. Combe, S. Audisio, J. Degauque, J. L. Porteseil, E. Ferrara, M. Pasquale, F. Fiorillo, The magnetic properties of Fe-Si 6.5wt% alloys obtained by a $SiCl_4$-based CVD process, Journal of Magnetism and Magnetic Materials, 160, 151(1996)
13. K. Lu, J. Lu, Nanostructured surface layer on metallic materials induced by surface mechanical attrition, Materials Science Engineering, A375,

38(2004)

14. W. P. Tong, N. R. Tao, Z. B. Wang, J. Lu, K. Lu, Nitriding iron at lower temperatures, Science, 289, 686(2003)
15. W. P. Tong, Z. Han, L. M. Wang, J. Lu, K. Lu, Low-temperature nitriding of 38CrMoAl steel with a nanostructured surface layer induced by surface mechanical attrition treatment, Surface & Coatings Technology, 202, 4957(2008)
16. Z. B. Wang, N. R. Tao, W. P. Tong, J. Lu, K. Lu, Diffusion of chromium in nanocrystalline iron produced by means of surface mechanical attrition treatment, Acta Materialia, 51, 4319(2003)
17. MO Chenggang, LIU Gang, HUANG Pu, ZUO Liang, Siliconizing behavior in surface nanostructure of non-grain oriented silicon steel, Iron and Steel, 47(3), 65(2012)
18. N. R. Tao, Z. B. Wang, W. P. Tong, M. L. Sui, J. Lu, K. Lu, An investigation of surface nanocrystallization mechanism in Fe induced by surface mechanical attrition treatment, Acta Materialia, 50, 4603(2002)
19. WANG Aixiang, LIU Gang, ZHOU Lei, WANG Ke, YANG Xiaohua, LI Ying, Thermal stability of structure and hardness of the surface layer of 316L stainless steel after surface mechanical attrition treatment, Acta Metallurgica Sinica, 41(6), 577(2005)

Note: Figure translations are in progress. See original paper for figures.

Source: ChinaXiv —Machine translation. Verify with original.