Nickel Powders Modified Nanocoating Strengthened Iron Plates by Surface Mechanical Attrition Alloy and Heat Treatment

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ABSTRACT

Added with Ni powders, an enhanced thick Fe–Ni alloy nanocoating was fabricated mechanically on pure iron plate by using cycling surface mechanical attrition alloy treatment (SMAAT). The nanocoatings were analyzed and characterized by optical microscope (OM), X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectra. The hardness of the nanocoating was tested. Owing to the combination of deposition, wear, deformation and defect-enhanced diffusion processes, the repeated heat treatment combined with SMAAT can effectively increase the thickness and improve the performance of the nanocoatings. The process not only refined the surface crystallinity of Fe–Ni alloy, but also promoted the fabrication of the FeNi3 and NiFe2O4 alloy phases. As a result, the average thickness of the nanocoatings has been doubled after the process of 3-cycle treatment. The microhardness in the near-surface region and bonding between coating and target was considerably enhanced.

KEYWORDS: Surface Mechanical Attrition Treatment, Microhardness, Thickness, Crystallinity, Alloys Coatings.

1. INTRODUCTION

At present, surface mechanical attrition treatment (SMAT) is regarded as an effective surface modification approach to produce a surface nano-crystalline (NC) layer with higher hardness and intensity, which has been successfully applied in Fe, low carbon steel, medium carbon steel, Cu, Ti, Mg alloy, Al, Fe–Ni alloy, Cu–Zn alloy, Mg–Gd alloy, Co and stainless steel. The large grain boundary misorientation, dislocation blocks, micro-bands and inter-diffusion of alloying elements can be found in the surface layer of the treated target during the impacts of SMAT. The metal surface properties can be improved by chemical activity, which promotes the effectiveness of subsequent treatments such as chromizing, nitriding, ion implantation, and synchronous mechanical alloying.

Similar to the mechanical alloying (MA) process, simultaneous plastic deformation, fragmentation and cold welding were also observed in the process of SMAT. Either favorable phases such as solid solution phase or hard inter-metallic compounds may also form during SMAT. To improve the process of alloy, the surface mechanical attrition alloying treatment (SMAAT) had been realized...
by adding metal powders. The strengthening effectiveness could be the key to enlarge the application of this technology. It has been found that, with the increase of attrition duration, the thickness of alloy coatings tended to increase to a certain value and could not acquire the desired enhancement.

The development and application of materials science has promoted the progress of human society. Since the 21st century, material science has entered a period of advanced materials with small sizes, high dimensions, and functionalization. Advanced materials including ceramics, polymers, composites, semiconductors, and superconducting materials have excellent mechanical, transmission, optical, electrical, magnetic, and thermal properties, and gradually replaced the traditional materials in many applications. However, traditional materials still have their advantages in a certain range of applications. Compared with polymers or other organics, the inorganic coating can give stronger complex and capability to be used at higher temperatures. One major challenge is the thin thickness of the alloy modified layer fabricated with the current technologies.

In this paper, the thickness of the alloy layer was successfully increased by using cyclical surface mechanical alloy attrition combined with high-temperature heat treatment. A thick and enhanced coating on the pure iron plate had been fabricated. The microstructure evolution and mechanical properties of the surfaces were investigated. The optimum process parameters and the mechanism of the process were revealed. And the enhanced Ni–Fe alloy coating on the iron plate would further promote the use of pure iron in equipment metal-ceramic manufacturing, electric power, polymer maker, corrosion and protection, and other industrial applications.

2. EXPERIMENTAL DETAILS

2.1. Apparatus
A high energy shot peening apparatus has been carried out in the mechanical attrition alloying process. During the treatment process, the high frequency vibration would be generated and around a hardened steel cylindrical reflecting chamber with the diameter of 20 mm and the height of 15 mm would be vibrated. The hard steel balls would be resonated simultaneously. The balls shot the plate which has been fixed under the cover of the chamber. The frequency of vibration is 50 Hz, approximate amplitude of 35 mm, and a maximum velocity of 12 m/s.

2.2. Procedures
The SMAAT process can be described briefly as follows. The steel balls (GCr15, with 8 mm diameter) and Ni powders (About 5 mg, with particle size of 200 meshes) were placed at the bottom of the cylindrical chamber, and the target (commercial pure iron plate 100 mm × 100 mm × 3 mm with a purity of 99.95 wt%) was fixed tightly at upper side of the cylindrical chamber. The attrition duration used was 100 min, by which the acquired coating could reach the optimum value. To eliminate the effects of mechanical deformation, the homogeneous coarse grains with an average 100~150 μm in grain size had been used, thus the iron plate was annealed at 950 °C for 2 h in vacuum before treatment. The basic process of one cycle is 2-hour vacuum annealing at 950 °C accompanied with 100-min SMAAT. The coatings were performed as the following treatment conditions. One coating sample was prepared using one cycle added with low temperature (450 °C) annealing treatment. The other two coating samples were made using 1 and 3 basic cycles separately. During SMAAT, the reflecting chamber was always filled with argon as the protective atmosphere.

2.3. Characterizations
The surface and cross-sectional microstructures were observed by a JEOL scanning electron microscopy (SEM, JSM-66700F) at its backscattered electron (BSE) mode. The samples were embedded in epoxy. The cross-sections of the coatings were carefully polished mechanically for the analysis of micro-structure. The quantitative elemental analysis was carried out by energy dispersive X-ray (EDX) spectra analysis. In order to study the phase constitutions, the Rigaku D/max-2400 X-ray diffract meter was used to test alloy coatings, using Cu-Ka radiation in θ–2θ geometry, from 20° to 90° in steps of 0.02°. The measurements were carried out on the layers with different depth to the treated surface. The interval depth between the adjacent data acquisition layers was 20 and 40 μm for the two samples fabricated by 1 and 3 basic cycles respectively.

The mechanical tests were carried out on the cross-section using an HVS-1000 device. The applied constant load was 10 g. Five indentations were made on each sample to obtain an average value of microhardness. The test was carried out following the testing standard: GB/T 4340.1-2009. The dynamic Vickers micro-hardness (HV) was calculated using the Oliver–Pharr method.

3. RESULTS AND DISCUSSION
Figure 1 shows the cross-sectional OM observations (a, b) and the surface SEM scans (c, d) of the samples fabricated by 1 and 3 basic cycles respectively. As can be seen in both Figures 1(a) and (b), the lamellar structure in the top-surface layer and a thickness of gradient fine-grain structure can be seen clearly. It can be seen obviously that the depth of surface coating is 30~60 μm for the just SMAAT 100 min sample (Fig. 1(a)). The interface between the coating and the matrix is clear but uneven, from which it can be concluded that the bonding between coating and target was formed in the mechanical welding.

The significant uneven plastic deformation
is evident in the surface layer of iron, within which the grain boundaries could hardly be identified under optical microscopy (Fig. 1(a)). A closer observation reveals the presence of a large number of traces of plastic flow in the top surface layer, implying that the nickel powders and the matrix pure iron experienced severe plastic deformation process. The alloy layer has been embedded in the pure iron surface. After three cycles of high-temperature annealing combined with SMAAT, the thickness of the coating increased obviously to ∼140 μm, within which the grain boundaries become more chaotic and unclear, showing very small clutters. And the coverage on the surface became compacted (Fig. 1(b)). The crystallization, the diffusion process, and the degree of alloying would be accelerated by the annealing treatment. At the same time, the interface between the coating and the substrate became fuzzy. The mutual diffusion may further ensure the tight bonding between coating and target.

It can be seen that the just SMAAT 100 min sample surface (Fig. 1(c)) has been equably welded with Ni powders. Many powders can be observed on the surface, which is understandable that the Ni powders were embedded into the iron plate by the peening balls. The surface appears to be very coarse and loose, and looks like toughened state arising from repeatedly beaten by the colloidal mud for a long time.22 Correspondingly, from the cross-section view (Fig. 1(a)), the clusters of nickel powders are not tight. The Ni powders have been welded and bonded each other locally by the severe plastics deformation. A nickel-rich surface layer has been formed and shows a flat shape. Different surface morphologies (Fig. 1(d)) can be seen after three cycles of high-temperature annealing combined with SMAAT. Many mini cauliflower shape particles can be seen on the surface, indicating much more Fe–Ni alloys formed during the treated process.

Figure 2 shows the cross-sectional SEM morphologies (serial of a) and backscattered electron images (serial of b) of the samples. The general view of the SMAAT process can be inferred from the SEM and back dispersion images taken on the cross section. As can be seen, the average thickness of the coating for the SMAAT 100 min sample is about 40 μm, which is accompanied with some porosity.22 The lamellar structure near the target and some adhesion defects can be seen clearly, which has been also shown in Figures 1(a) and (c). It can be explained that either the surface was kneaded heavily by the impacts, or the layered composite particles were attached to it from the loose powder.22,26 The initial development of a lamellar microstructure can still be observed by the clear sign of surface shearing and folding on the top surface. The interface between target and coatings is rough, suggesting the embedding of nickel powders in the iron during the process of wear and deformation.

In the single cycle of SMAAT process, a simple model was proposed to explain the main features of the formation of alloy coatings. There are 3 steps by which the Ni powders had been attached to the iron surface. The first, earlier peening of steel balls on the relatively soft Fe target resulted in surface roughening and significant wear, and some debris had been produced from the iron surface. Secondly, Ni powders, which are mixed some abraded Fe (debris), adhered to the surface of the steel balls and the
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Fig. 2. Cross-sectional SEM morphologies (a) and back scattered electron image (b) of the SMAAT sample (a1, b1 just SMAAT 100 min samples; a2, b2 SMAAT 100 min plus low-temperature annealing samples; a3, b3 three cycles of high-temperature annealing combined with SMAAT samples).

chamber wall. At last, with the impact between the balls and iron plate, the Ni powders and debris had been transferred into the Fe target. Owing to the higher hardness of Ni than Fe, the Ni powders were pressed into the iron target with the peening balls. The initial coating with unalloyed components has been formed with the deposition of Ni powders.

Further treatment results in mixing and alloying, which happens in part by plastic deformation at the surface of the Fe target. Much of the mixing has been taken place in the powder phase, which is mixed with debris abraded from the iron surface. The more uniform alloy particles, on which the iron debris had been re-deposited, were pressed into the target. These micron-scale processes are supplemented by defect-enhanced diffusion and rearrangement of clusters on the atomic scale. The coating gets thicker with increasing the treatment time. After a certain time of impact, the coarse lamellar structure can be seen as in Figures 1(a) and 2(a1), which is a ductile system of the early stages of mechanical alloying. It is shown that the coatings were built up via a combination of grain refinement, deposition, wear, chemical reaction and synchronous defect-enhanced diffusion processes.

Different scenes in the sample can be found after low temperature (450 °C) annealing treatment. The thickness of the coatings has been increased to about 60 μm and the coverage of the surface compacted (Figs. 2(a2 and b2)), implying that anneal treatment accelerates the diffusion process and increases the degree of alloying. The significant grain refinement is evident in the surface coating,
which may be caused by the recrystallization during low-temperature annealing. A very narrow gap along interface between target and coatings can be seen, which may be caused by different coefficients of thermal expansion between coating and matrix. Therefore, low temperature (450 °C) annealing treatment can increase the coating depth, but the effectiveness is limited.

After three cycles of high-temperature annealing and SMAAT, the thickness of the coating has been enlarged evidently to about 140 μm (Figs. 2(a3 and b3)). It can be seen from back dispersion images Figure 2(b3) that the diffusion traces between the coating and the substrate target is clear. The disappeared interface indicates that Ni has been evidently diffused to the pure iron substrate during the high-temperature heat treatment, and strong bonding was further ensured.

The supplemental EDX analysis taken by the line scan of the coatings has been shown in Figure 3. The variation of the Ni and Fe contents was relatively evident across the thickness of the coatings. A thorough mixing of these two elements due to the intense mechanical working can be seen clearly. There is an increase of Fe concentration and decrease of Ni close to the substrate-coating interface in all the samples. The measurement showed that the thickness of as-fabricated coatings is 45, 55 and 130 μm for the as-treated three samples of just SMAAT 100 min, SMAAT 100 min plus 450 °C annealing treatment and three cycles treated sample respectively if the thickness of the coatings has been defined as the depth of the substrate-coating interface. However, after multiple heat treatments at high temperature, the gradient of Ni and Fe concentration in the interface was obviously slowed down (Fig. 3(c)). The sufficient diffusion and resulted alloying in the inter-facial region would promote effectively the tight bonding between the coating and the substrate.

Figures 4(a) and (b) shows two series of XRD patterns, obtained from the layers with various depths from the alloy surface. The coatings prepared by one (Fig. 4(a)) and three cycles of SMAAT (Fig. 4(b)) were measured. The shifting and the broadening of Bragg peaks in different degree in both Figures 4(a) and (b) suggest that, accompany with SMAAT, solid solution phases with Fe or Ni coherent lattice may be formed. The refined grain and/or large microstrain can be detected in both two samples surface layer. There are some important differences between these two series of diffraction curves due to different fabricating conditions. Figure 4(a) reveals the presence of some Fe (PDF no. 06-0696) close to the surface, probably from Fe fragments that were abraded from the surface at the beginning of the preparation and re-deposited at later process. The peaks of FeNi3 and FeNi (PDF no. 38-0419 and 37-0474) were also visible down to the depth of 80 μm. The existence of new FeNi3 and FeNi phases suggested that the interaction between nickel and iron had been accompanied with SMAAT process. The presence of new phases not only close to the free surface but also deep into the iron base in the single circle sample indicates that the alloying process is synchronized with the SMAAT process.

Figure 4(b) suggests that a thicker top surface was fabricated after 3-cycle annealing and SMAAT. The peaks of Fe-Ni alloy phase are also visible down to the depth of 200 μm, implying the accelerated alloying process by the anneal treatment. The new peaks of NiFe2O4 (PDF no. 54-0964) were shown, which proved again that
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**Fig. 4.** X-ray diffraction patterns at various depths from two sample surfaces: Just SMAAT 100 min sample (a); three cycles of high-temperature annealed combined with SMAAT one (b).

High-temperature heat treatment had accelerated the alloying process.\(^{11,28}\) The peaks of FeNi\(_3\) and FeNi were shown enhanced and narrowed, implying the existence of more alloys. As can be proved, after 3-cycle annealing and SMAAT, the increased thickness of the coatings is properly identical with the conclusion obtained by Figures 1–3.

Figure 5 shows the variation of coating depths along the treating duration and number of cycles in the SMAAT samples. As can be seen, with the increase of SMAAT duration, the thickness of coatings increases. After the treatment of 80 min, the increase of thickness tends to be gentle. The coating depth is no longer increased as the treatment reaches 100 min.\(^{105}\) Annealing at high-temperature of 950 °C for 2 h and then being treated by 100 min SMAAT once more can effectively enlarge the coating depth. After three-cycle annealing and SMAAT, the thickness of the coatings has been increased to about 140 μm. It is understandable that the depth of coating would increase with increasing the number of cycles. However the depth increasing will be less and less with the increase of cycle number owing to the equilibrium between wear and deposition at the target.\(^{26,27}\) and the three cycles may be the optimization parameter of the effective increase of coating thickness.

In fact, the thickness of the modified coating is not always proportional to the amount of available powders. It has been shown that much larger amount of powders added could only result in limited increase of the coating thickness.\(^{18,26}\) And the thickness of alloy coating tended to increase to a certain value of about 60 μm when the treating duration increased up to 100 min. The main reason is that the work hardening may slow down the wear. The free surface of the coating is much smoother than the substrate-coating interface, which prevents the increase of the coating thickness. It seems that the thickness was determined more by the equilibrium between wear and deposition at the target than by the amount of the available powders.

The low-temperature annealing can accelerate the recovery and re-crystallization, the reduction of the dislocation density and the degree of strain hardening,\(^{3,18,24}\) which partly enhance the thickness of alloy coating and the refinement of the grain process of alloying. Therefore, the latter annealing at 950 °C for 2 h has effectively eliminated the work hardening of the SMAATed sample. Subsequently, a surface softened and partly alloyed plate with coarse grains has been obtained once more, which is helpful to increase the thickness of alloy layer in the latter SMAAT. Consequently, 3-cycle annealing at 950 °C for 2 h and SMAAT 100 min, the alloyed coating has

**Fig. 5.** Coatings depths variation along the treating duration and number of cycles.
target was further formed. The cyclical process not only refined the surface layer of Fe–Ni alloy, but also promoted the fabrication of the FeNi2 and NiFe2O4 alloy phase. The enhancement of hard layer in the near-surface region overall improved the mechanical properties of materials.

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References and Notes
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81. A. Alippi, A unique timely moment for embedding intelligence in robotic systems. Talanta 70, 143, 324 (2007).


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83. X. Zhang, H. Gao, M. Guo, G. Li, Y. Liu, and D. Li, A study on key technologies of unmanned driving. CAAI Transactions on Intelligence Technology 1, 4 (2016).


