
Volume 204, Number 3, 25 October, 2009
ISSN 0257-8972
ELSEVIER
SURFACE & COATINGS TECHNOLOGY
Editors
A. Matthews
J. Patscheider
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Available online at
ScienceDirect
www.sciencedirect.com
http://www.elsevier.com/locate/surfcoat

Surface & Coatings Technology 204 (2009) 386–390

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

# Modification of nitride layer on cold-work tool steel by laser melting and friction stir processing

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ARTICLE INFO

*Article history:*
Received 11 June 2009
Accepted in revised form 30 July 2009
Available online 8 August 2009

*Keywords:*
Friction stir processing
Laser melting
Nitriding
Tool steel
Microstructural refinement

ABSTRACT

The microstructural control of the nitrided case on a cold-work tool steel (SKD11) plate by laser melting and friction stir processing (FSP) was studied. The laser melting and the FSP were used as a pretreatment for the nitriding to refine the microstructure of the SKD11. The diffusion zone of the nitrided case on the SKD11 plate contained thick brittle boundary lines consisting of local formed nitride particles. On the other hand, the microstructure of the diffusion zone was very uniform and the thick brittle boundary lines disappeared as a result of the combined treatment of the laser melting and the FSP before the nitriding process.


## 1. Introduction

Nitriding is widely used for various ferruginous products to improve their surface properties such as hardness, wear resistance, etc. [1–4]. It is well known that the diffusion zone formed by nitriding can effectively enhance the life time of the products because of its excellent resistance against wear and heat check cracking. Surface modification by nitriding has mainly been studied, based on the nitriding conditions and material composition. It is reported that a solution of nitrogen into the matrix and the formation of the nitride particles lead to the hardening of the diffusion zone [5,6]. Thus, chromium, aluminum, and molybdenum, which are conductive to forming nitrides, are added to the nitriding steels.

However, it is difficult to form a diffusion zone of uniform depth and microstructure in the cold-work tool steels which contain large amounts of alloying elements, such as chromium. Although chromium and carbon are integral elements for the formation of the carbides which increase the mechanical properties of the cold-work tool steels, the coarse chromium carbides and the segregated chromium carbides on the grain boundary of the matrix lead to the heterogeneous structure in the diffusion zone. The diffusion zone becomes brittle due to the local formation of the nitride particles formed by the reaction between the nitrogen and the chromium carbides. The local formed nitride particles become the starting point of the heat check cracking and exfoliation of the nitrided case. Additionally, the diffusion of nitrogen during the nitriding is prevented by the large carbide particles. For these reasons, nitriding cannot be used for the cold-work tool steels. The uniform fine structure of the material must effectively fabricate a sound diffusion zone without any brittle boundary lines. However, there has been no useful method to refine the microstructure of the tool steels because of their high plastic deformation resistance. Usually, the conventional severe plastic deformation processes cannot be used for the tool steels to refine the microstructure.

Authors have studied the microstructural refinement of tool steels and revealed that the size of the carbide particles and the matrix grains can be drastically decreased by the combined treatment of laser melting and friction stir processing (FSP) [7]. FSP is a new approach for surface modification due to plastic flow [8–12]. A rotating tool is inserted into a substrate and produces a highly plastically deformed zone. It is well known that the frictioned zone consists of fine and equiaxed grains produced due to dynamic recrystallization. The sizes of the primary crystal chromium carbide particles and the matrix grains are reduced to nanometer-sizes. In addition, the very fine chromium carbide particles are uniformly dispersed in the matrix. The laser melting and FSP pretreatment of the nitriding seem to be effective in controlling the microstructure and the mechanical properties of the diffusion zone for cold-work tool steels. In this study, the effect of the microstructural change of the cold-work tool steel by the laser melting and the FSP on the diffusion zone is investigated.

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0257-8972/$ – see front matter 
doi:10.1016/j.surfcoat.2009.07.043

**Table 1**
Chemical composition of the as-received SKD11.

| C | Si | Mn | P | S | Cu | Cr | Mo | V |
|---|---|---|---|---|---|---|---|---|
| 1.48 | 0.29 | 0.35 | 0.25 | 0.01 | 0.09 | 11.74 | 0.85 | 0.22 |

Unit: mass%.

## 2. Experimental procedure

A commercially available plate of SKD11, which is the representative cold-work tool steel, was used. The chemical composition of the SKD11 is shown in Table 1. Fig. 1 shows a flow diagram for the preparation of the various nitrided samples. The surface of the SKD11 plate was melted by multi-pass laser heating (1 kW, LASERLINE LDF-1000-750) to produce a rapidly solidified zone. The scanning rate of the laser beam and the beam diameter at the surface of the plate were 1000 mm/min and 1 mm, respectively. The overlap between the beam paths was 0.3 mm. The as-received SKD11 and the laser treated SKD11 were modified by FSP. The FSP tool made of hard metal (WC–Co) had a columnar shape ($\phi$ 12 mm) without a probe. The shape of the tool end was flat. The FSP tool without a probe was effective to form the large treated area on the SKD11 plate which had a high plastic deformation resistance. A constant tool rotating rate of 400 rpm was adopted and the constant travel speed was 400 mm/min. A tool tilt angle of 3° was used. The process was conducted by a single pass. Nitriding was carried out using a mixture of nitrogen (flow rate: 1 L/h) and ammonia (flow rate: 3 L/h) at 540 °C for 5 h. Hydrogen disulfide gas was used to activate the surface of the SKD11 plate for 1 h at the beginning of the nitriding.

Transverse sections of the as-received and the variously treated SKD11 specimens were mounted and then mechanically polished. The microstructures of the samples were observed by optical microscopy and TEM (JEOL JEM-2100) at an accelerating voltage of 200 kV. The crystal phase of the samples was identified by XRD (Rigaku RINT2500V). The microhardness was measured using a micro-Vickers hardness tester (Akashi HM-124) with a load of 100 g.

## 3. Results and discussion

### 3.1. Microstructural change in the SKD11 by pretreatment for nitriding

The representative SKD11 plate treated by the combination of laser melting and FSP before nitriding is shown in Fig. 2. The rapidly solidified zone formed by laser melting and the stir zone formed by FSP can be clearly confirmed. No texture was observed in the stir zone using the optical microscope. The thicknesses of the rapidly solidified zone and the stir zone were about 700 μm and 200 μm, respectively. Both thicknesses were sufficient to evaluate the effect of the microstructural change of the SKD11 on the nitrided case.

Fig. 3 shows the microstructural change in the SKD11 by laser melting and FSP. There were many coarse chromium carbide particles in the matrix of the as-received SKD11 as shown in Fig. 3(a). On the other hand, no coarse carbide particles could be confirmed in the rapidly solidified zone as shown in Fig. 3(b). The laser melting formed a fine dendritic structure consisting of fine carbide particles with sizes of less than 1 μm. Several coarse carbide particles, which were about 10 μm in size could be confirmed in the stir zone without the laser melting as shown in Fig. 3(c). The size of the refined carbide particles

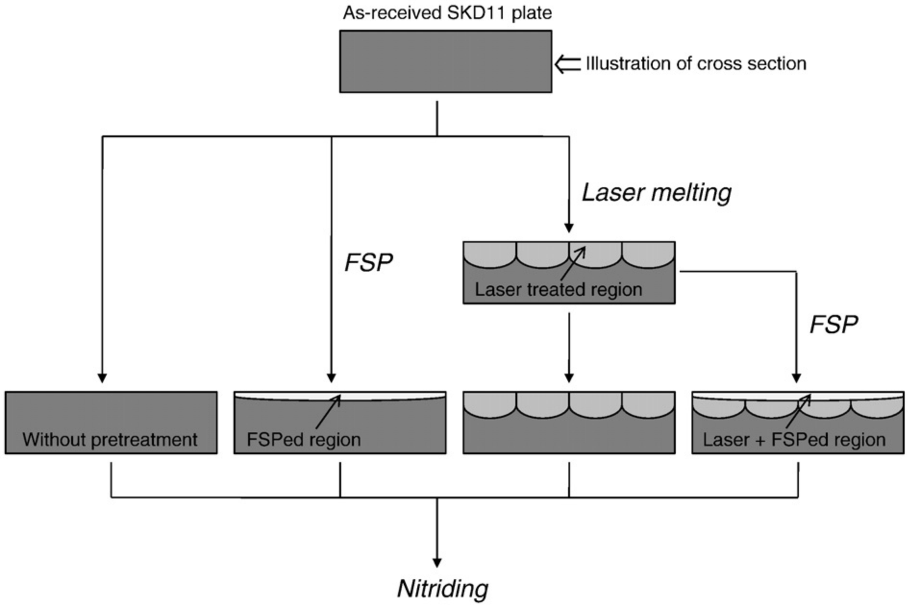


**Fig. 1.** A flow diagram for the preparation of the various nitrided samples.

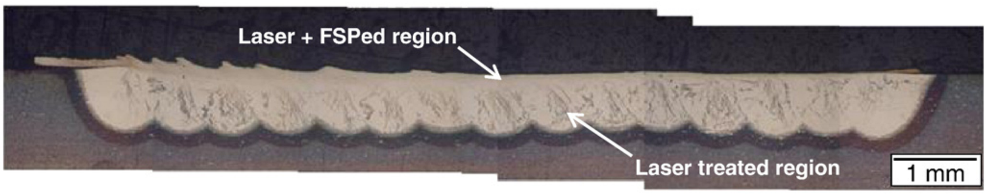


**Fig. 2.** OM images of a cross-section of the SKD11 treated by the combination of laser melting and FSP.

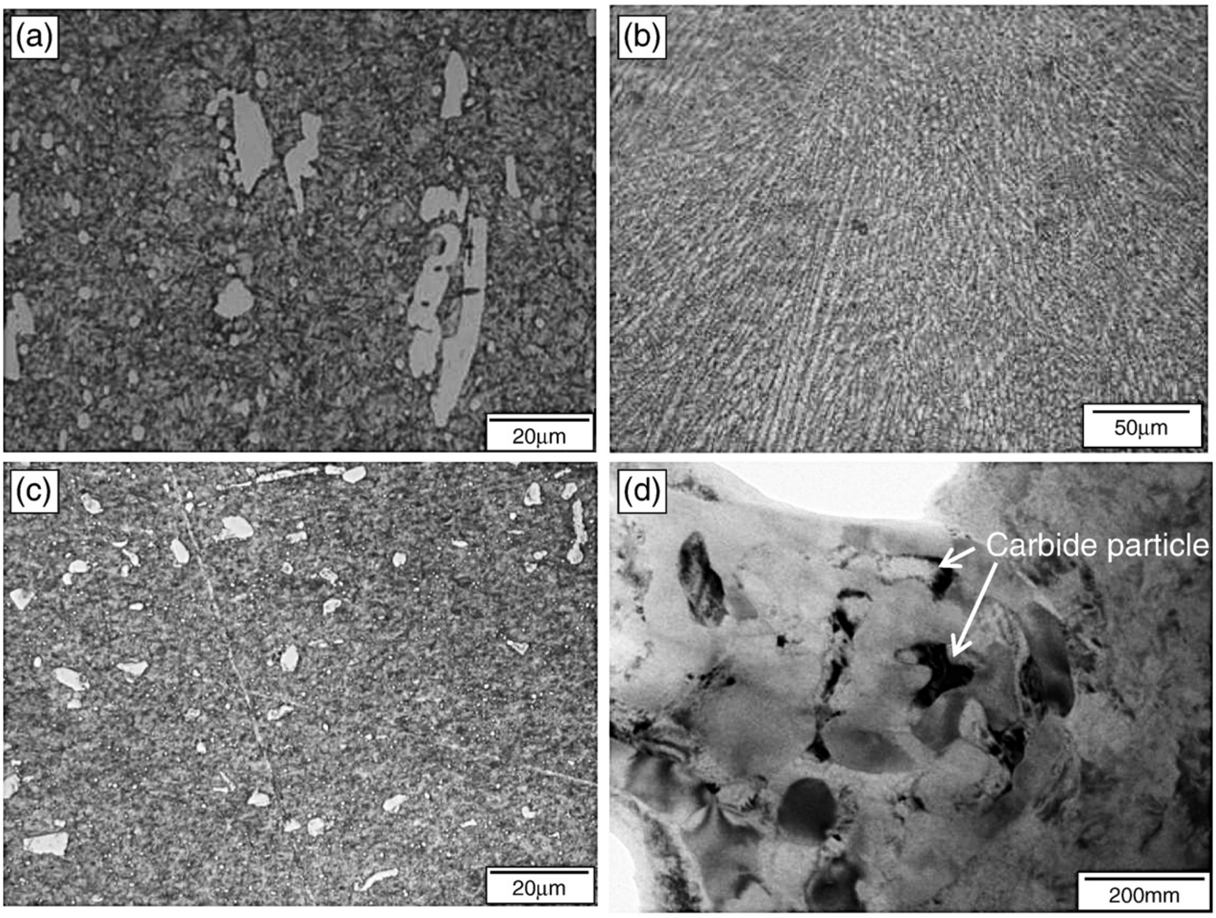


**Fig. 3.** Microstructural change of the SKD11 by laser melting and FSP. (a): OM image of the as-received SKD11, (b): OM image of the laser treated SKD11, (c): OM image of the FSPed SKD11, and (d): TEM image of the SKD11 treated by the combination of laser melting and FSP.

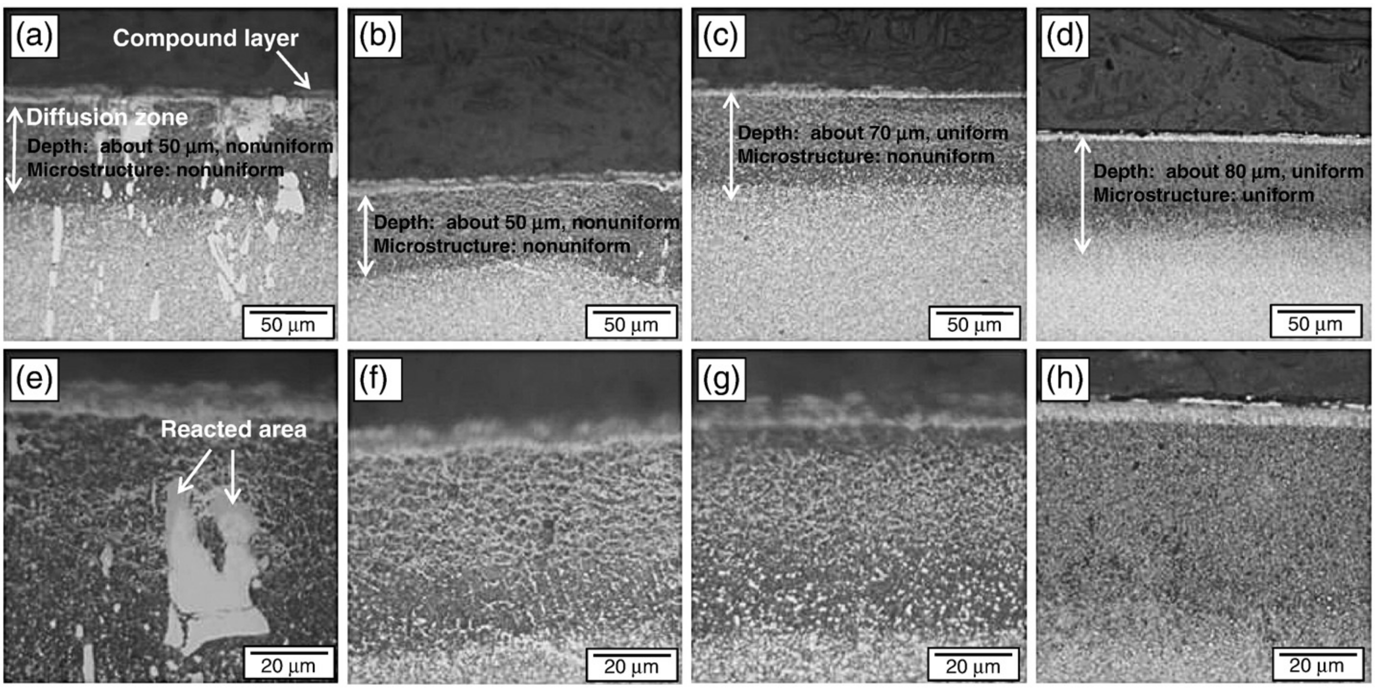


**Fig. 4.** OM images of the cross-section of the nitrided SKD11 samples. (a) and (e): as-received SKD11, (b) and (f): laser treated SKD11, (c) and (g): FSPed SKD11, and (d) and (h): SKD11 treated by the combination of laser melting and FSP.

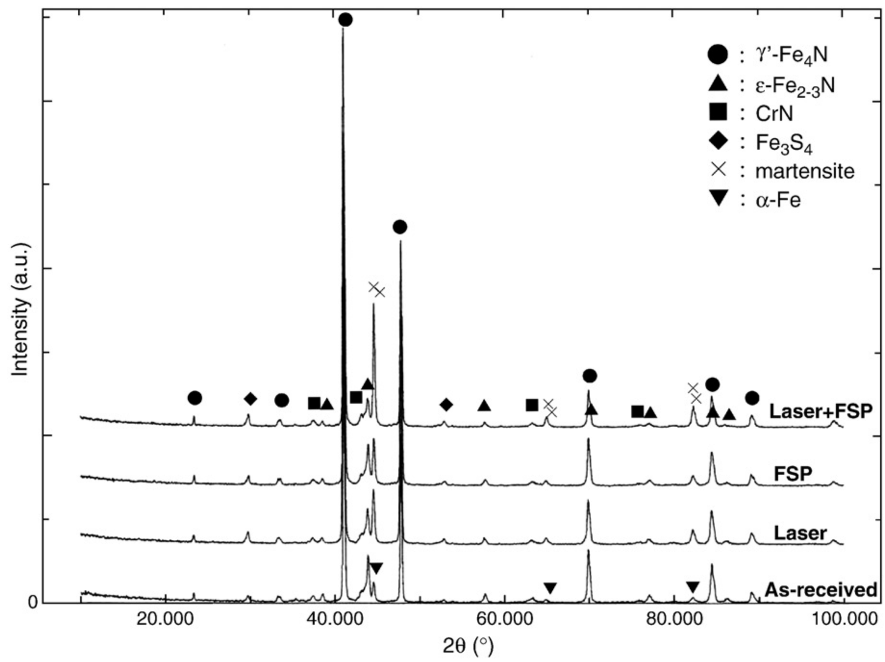


**Fig. 5.** XRD patterns of the nitrided SKD11 samples.

by FSP was also relatively coarser when compared to the SKD11 treated by the combination of laser melting and FSP as shown in Fig. 3(d). There were no coarse carbide particles and dentritic carbide structure in the FSPed zone with laser melting. The carbide particles and the grains of the matrix became much smaller with sizes of 100 nm and 200 nm, respectively. The microstructural change in the SKD11 by the laser melting, FSP, and the combination of laser melting and FSP were explained in detail elsewhere [7].

### 3.2. Microstructure and microhardness of the diffusion zone

Fig. 4 shows cross-sections of the nitrided SKD11 plates. The diffusion zone of the SKD11 without the pretreatment contained many thick boundary lines consisting of local formed nitride particles. The reacted area could be confirmed on the outer surface of the coarse chromium carbide particles. The uniform diffusion of nitrogen into the SKD11 plate was inhibited by the reaction with the coarse carbide particles. The diffusion zone of the sample treated by the laser melting was also nonuniform. It is considered that the reaction between the small chromium carbide particles on the grain boundary of the matrix and nitrogen led to the local formed nitride particles. On the other hand, the diffusion zone of the samples treated by FSP was relatively uniform compared with the sample treated by laser melting and without any pretreatment. The grain refinement of the matrix by FSP increased the path for the diffusion of nitrogen through the grain boundary. Additionally, the uniform dispersion of the chromium

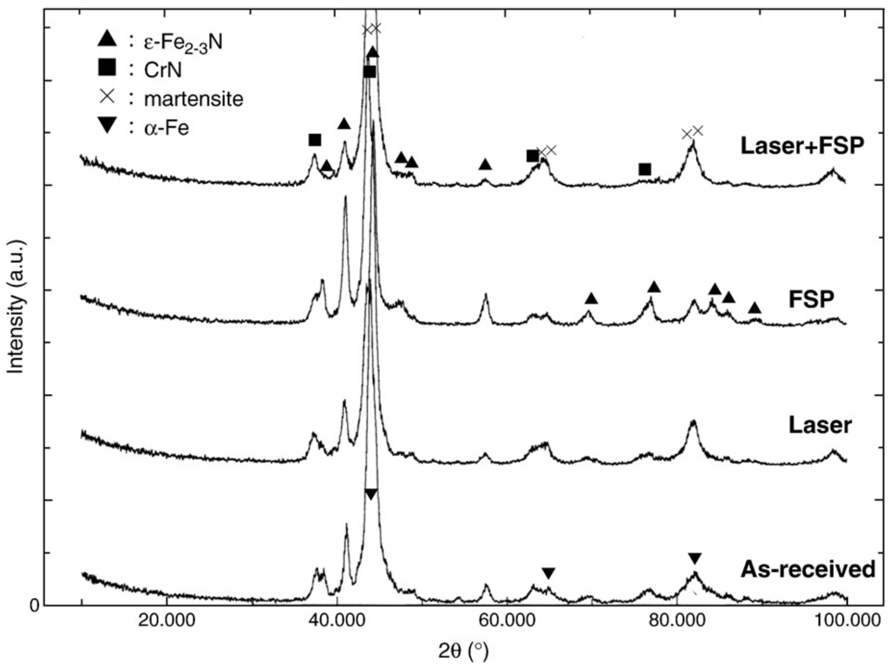


**Fig. 6.** XRD patterns of the nitrided SKD11 samples without the compound layer.

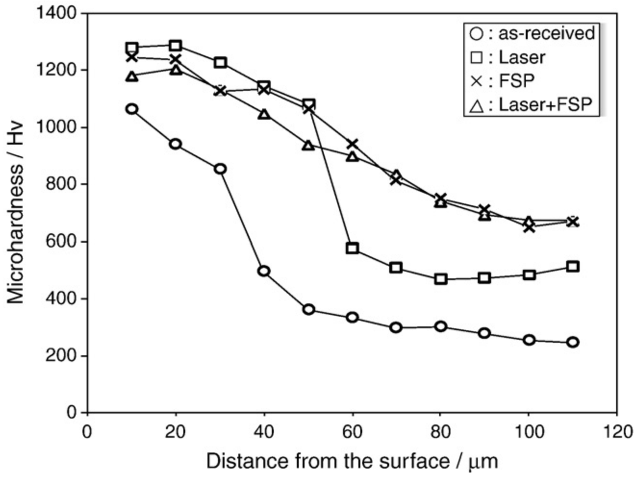


**Fig. 7.** Microhardness depth profiles of the cross-section of the nitrided samples.

particles prevented the local formation of the nitride particles. There was no conspicuous local formed nitride particle in the diffusion zone for the sample treated by the combination of laser melting and FSP. The uniform nanostructure of the SKD11 realized such a homogeneous diffusion zone due to the many fine grain boundaries and the uniform dispersion of the nanometer sized chromium carbide particles.

XRD patterns for the nitrided samples with and without the compound layer are shown in Figs. 5 and 6, respectively. The compound layer was removed using #1500 emery paper after the first XRD measurement. The compound layer could be identified as $\gamma'$-$Fe_4N$ because strong peaks attributed to $\gamma'$-$Fe_4N$ in Fig. 5 had disappeared in Fig. 6. $\varepsilon$-$Fe_{2-3}N$ and CrN were formed in the diffusion zone of all samples. It was confirmed that the crystal phase of the compound layer and the nitride particles formed in the diffusion zone were not affected by the microstructure before the nitriding.

Fig. 7 shows the microhardness depth profiles of the diffusion zone for the nitrided samples. The thickness of the diffusion zone varied by the microstructural modification of the SKD11 before the nitriding. The depth of the diffusion zone of the nitrided SKD11 without the pretreatment was about 50 µm and the microhardness was sharply decreased from the surface. Although the microhardness of the nitrided SKD11 after laser melting was higher than that of the other samples, it suddenly decreased to the same microhardness as the SKD11 without the nitriding at about 50 µm in depth. It is considered that the consumption of nitrogen by the reaction with the segregated fine chromium carbide particles led to the thin diffusion zone with a high microhardness. Compared with these two nitrided samples, the diffusion zone of the nitrided samples with FSP was thicker and reached about 80 µm. Additionally, the nitrided samples with FSP showed an ideal change in the microhardness which gradually decreased from the surface. The grain refinement by FSP enhanced the path for the diffusion of nitrogen to form the thick diffusion zone. Furthermore, there were no local formed nitride particles in the diffusion zone for the nitrided sample treated by the combination of laser melting and FSP. These results revealed that the combination of laser melting and FSP was an effective pretreatment for the SKD11 to form an excellent diffusion zone.

## 4. Conclusions

The microstructural control of the nitrided case on the SKD11 plate by laser melting and FSP was studied. The obtained results can be summarized as follows.

(1) The diffusion zone of uniform depth and microstructure without any local formation of the nitride particles can be obtained for the SKD11 by the combined pretreatment of laser melting and FSP.
(2) The crystal phase of the nitride is not influenced by the microstructural modification by laser melting and FSP. The compound layer is $\gamma'$-$Fe_4N$, and the nitride particles in the diffusion zone are $\varepsilon$-$Fe_{2-3}N$ and CrN for all the nitrided samples.
(3) The microstructural modification of the SKD11 leads to differences in the thickness and the microhardness of the diffusion zone for the nitrided samples. The FSP before the nitriding increases the thickness and decreases the change in the microhardness from the surface.

## Acknowledgements

The authors wish to acknowledge the financial support of a Grant-in-Aid for Young Scientists (B) and a Grant-in-Aid for Science Research (B) from the Ministry of Education, Culture, Sports, Science and Technology. One of the authors (HF) also appreciates the financial support from the Global COE Programs.

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