JMEPEG (2003) 12:687-692

Research on Component Phases and Microstructure Shape of a Rapid Ion Nitriding Layer

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(Submitted 18 June 2003; in revised form 15 July 2003)

The properties of nitrided parts are closely related to the component phases of their compound layers and microstructure shape of their diffusion layers. Based upon the influence of nitriding temperature and nitrogen (N) potential on formation and decomposition of ion nitriding layer, the component phases and microstructure shape of ion nitrided layer, which was processed under cyclic N potential, was studied with x-ray diffraction (XRD) analysis and transmission electron microscopy (TEM). The mechanism of rapid ion nitriding is also discussed in this paper. The results show that if the rapid ion nitriding by the thermal cycling and the N potential cycling is controlled, the nitriding speed and nitrided layer thickness of materials can not only be enhanced compared to the conventional ion nitriding technique, but also the alloy nitrides can be obviously increased. The precipitation hardness phases of diffusion layer became more trivial and spread in all directions. It is very important to improve the quality of the nitrided layer and to enhance the properties of nitrided parts.

Keywords component phase, microstructure shape, nitrided layer, rapid ion nitriding

1. Introduction

The influence of the nitriding temperature and nitrogen (N) potential on formation and decomposition of nitrided layers is used to optimize nitriding technique parameters, to bring into play ion nitriding superiority of nitrided layer thickness linearly increasing with time rapidly during nitriding initial stage, to further accelerate N atoms inner diffusion, and to enhance ion nitriding speed and nitrided layer characteristics.[1-3] The surface properties of nitrided parts are closely related to the component phases of their compound layers and microstructure of their diffusion layers. Controlling the ion nitriding parameters can not only enhance nitriding speed, but also improve nitrided layer quality. Therefore, this paper reports research into the component phases and microstructure of nitrided layers of the multi-cycling rapid ion nitriding technique, which involves boosting N atoms at lower temperature and higher N potential combined with rapid diffusing at higher temperature and lower N potential. The study was conducted using by x-ray diffraction (XRD) analysis and transmission electron microscopy (TEM). The micro-mechanism employed by the new technique that speeds N diffusion is also discussed on thermodynamics and kinetics of rapid ion nitriding.

2. Experimental Materials and Methods

Samples include 40Cr, 25Cr2MoV, and 38CrMoAl steels preprocessed by oil quenching at 900 °C and tempering at 580 °C. The experimental equipment was a LD-25 glow ion nitriding furnace, and the nitriding atmosphere was dry cooled ammonia. According to conventional ion nitriding and cyclic N potential ion nitriding technique, all samples were processed for 10 h in the ion nitriding furnace. The main technique parameters were glow voltage 350-700 V, glow electric current 0.5-5 A, glow thickness 2-5 mm, nitriding temperature 350-570 °C, and ammonia flow 2-10 l/min.

An OLYMPUS-PMG3 metalloscope (Olympus Co., Japan) was used to observed microstructure of ion nitrided layer. A D/Max-1200 x-ray diffraction apparatus (Rigaku Co., Japan) was used to analyze their component phases and JEM-1200EX (JEOL Co., Japan) transmission electron microscope was also used to observe and take pictures for the microstructure of diffusion layer.

3. Results and Analysis

3.1 Microstructure of Ion Nitriding

The microstructure of ion nitrided layer was observed and pictures were taken with the OLYMPUS-PMG3 metalloscope. Figure 1 and 2 are metallography pictures of ion nitrided layers of 40Cr and 38CrMoAl steels, respectively. The N-ferrite α_N and alloyed nitrides of diffusion layer were easily corroded by 3% nitric acid alcohol and became dark. The color of nitrided layer became darker as its α_N and alloy nitrides increased. There was obvious difference between ion nitrided layer and

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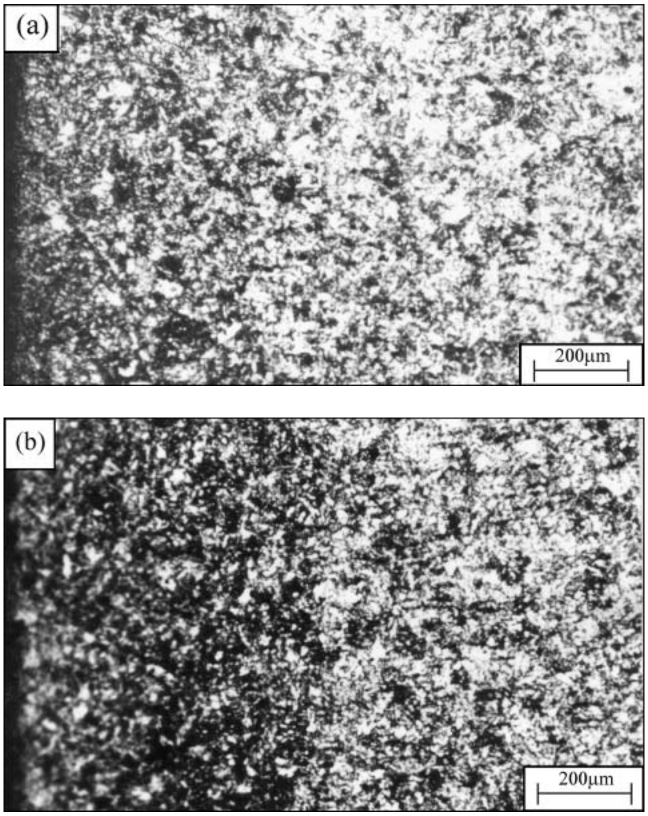

Fig. 1 Microstructure of ion nitrided layer of 40Cr steel (magnification, ×50): **(a)** conventional ion nitriding and **(b)** rapid ion nitriding

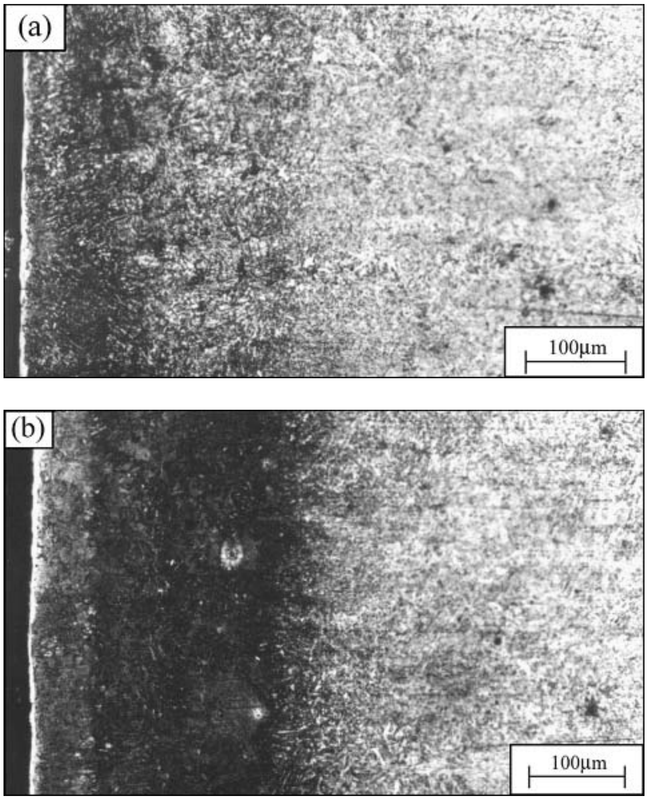

Fig. 2 Microstructure of ion nitrided layer of 38CrMoAl steel (magnification, ×100): **(a)** conventional ion nitriding and **(b)** rapid ion nitriding

the core. Compared with conventional ion nitriding, the diffusion layers of 40Cr and 38CrMoAl steels processed by the rapid ion nitriding under cyclic nitrogen potential were darkened and their nitrided layer thickness was increased. Generally, compared with the gas-nitriding technique, the superiority of ion nitriding lies in that the nitriding medium decomposes easily and the interface reaction accelerates,[4] which nitrides parts' surfaces to obtain high N potential during a short time and produces high-density dislocations by ion bombardment. The higher absorption rate of N atoms on part surfaces evidently quickens nitrided layer growth with at ion nitriding. The speed of ion nitriding is faster than that of the gas nitriding technique while the shortened time of the ion nitriding process occurs at the initial stage. However, the part surfaces are hardened during the deep ion nitriding processing, whose diffusion speed is mainly controlled by inner diffusion speed as gas nitriding is at subsequent stage. According to the second law of Fick $\partial c/\partial \tau = D(\partial^2 c/\partial^2 x)$, the ion nitriding speed is determined by diffusion factor D and N concentration gradient $\partial c/\partial x$, which are the parameters of nitriding temperature and atmosphere potential, etc. Hereby, the ion nitriding of higher N potential at lower temperature causes the surface of parts to have higher N absorption; the surface of the parts nitrided could adsorb and deposit more active N atoms or N ions, which is advantageous for formation of the nitrided layer. On the other hand, the processing of lower N potential at higher temperature can accelerate decomposition of the nitrided layer, eliminate the obstacle of inner diffusion of N atoms, enhance nitriding speed, make diffusion factor D and N concentration gradient $\partial c/\partial x$ increase, offer energy gurgitation and concentration gurgitation for interface reacts and inner diffusion rapidly, and improve driving force effectively. This is advantageous for rapid inner diffusion of N atoms. After multi-cycle nitriding, the nitrided layer will boost the nitrided parts' inner stage by stage, which would meet the need of rapid ion nitriding. Figure 1 and 2 show that cyclic N rapid ion nitriding is advantageous for quickening nitriding speed and increasing nitrided layer thickness.

3.2 Phase Component of Ion Nitriding Compound Layer

Figure 3, 4, and 5 are XRD patterns of conventional ion nitriding and rapid ion nitriding for 40Cr, 25Cr2MoV, and 38CrMoAl steels, respectively, which show that the compound layers are mainly γ' phase by conventional ion nitriding. They include a small ε phase and alloy nitrides, whose diffraction patterns are simple and sharp. However, after rapid ion nitriding, component phases and their relative content are evidently changed. Diffractive peaks of ε phase are higher than diffractive peaks of the γ' phase, and their main phases are ε phase, especially for 25Cr2MoV and 38CrMoAl steels. The kinds of alloy nitrides are increased obviously, and their diffraction patterns are complicated and interlaced. Table 1 shows the phase components of conventional ion nitriding and rapid ion nitriding.

The characteristic of conventional ion nitriding technique is that temperature and N potential are constant; the aim is to

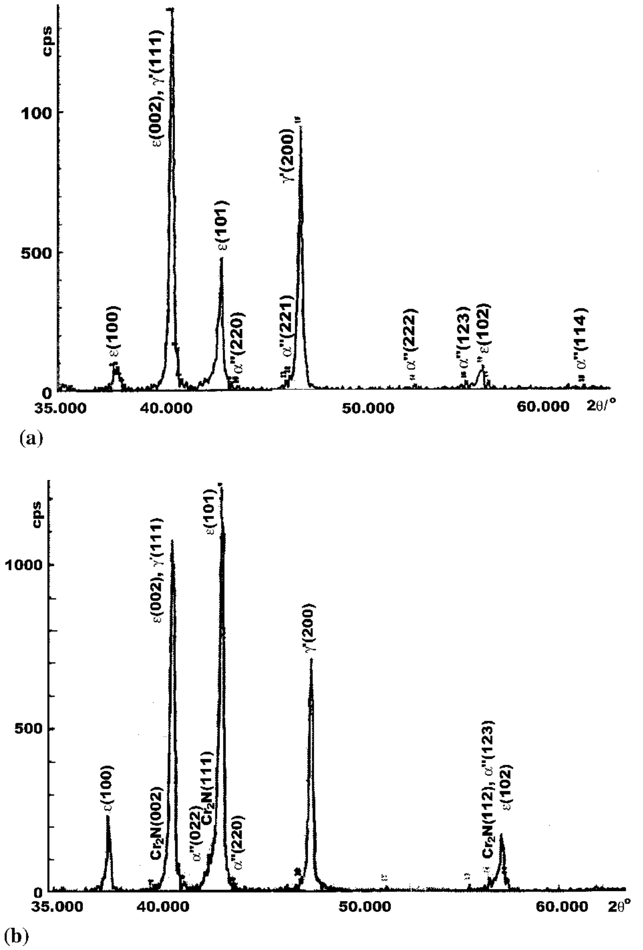

Fig. 3 XRD patterns of ion nitriding layer of 40Cr steel: (**a**) conventional ion nitriding and (**b**) rapid ion nitriding

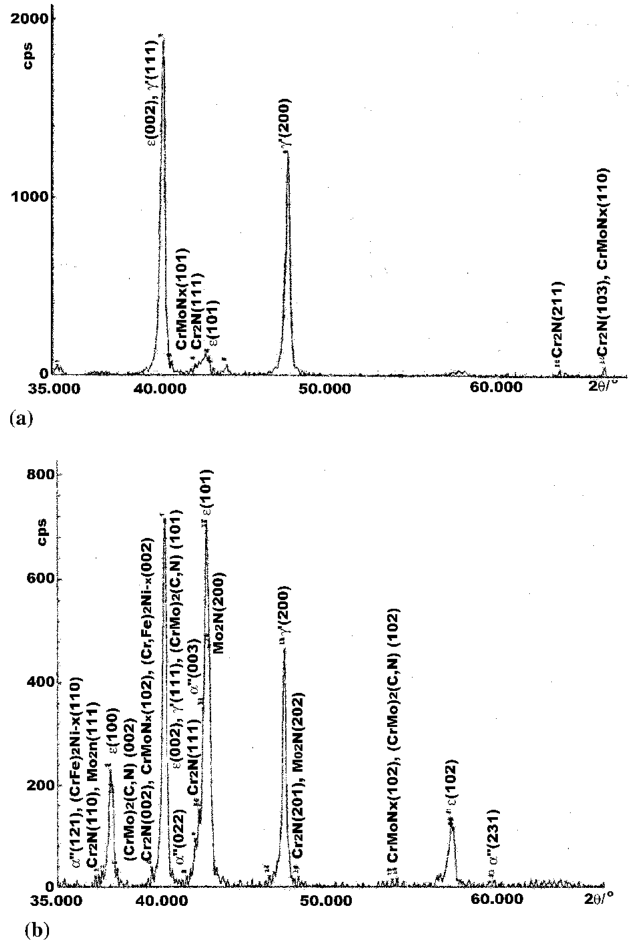

Fig. 4 XRD patterns of ion nitrided layer of 25Cr2MoV steel: (**a**) conventional ion nitriding and (**b**) rapid ion nitriding

avoid forming brittle nitrided layer by the technique of maintaining constant nitriding temperature and ammonia flow and lower N potential. The N solubility concentration inside the γ' phase is 5.30-5.75%, but 4.55-11.0% in ε phase, so the compound layers of conventional ion nitriding contain mainly γ' phase and less ε phase comparatively. Especially for 25Cr2MoV and 38CrMoAl steels, lower N potential could not provide enough active N atoms to form alloy nitrides for elements such as Cr, Mo, V, Al, so there are a few phases and fewer Cr_2N in compound layers; the diffraction peaks are certain sharp and simple.

Like rapid ion nitriding, the N diffusion speed can be quickened by cyclic control of boosting at lower temperature and higher N potential and diffusion at higher temperature and lower N potential. For the boosting stage of higher N potential at lower temperature, the atmosphere's N potential is higher, and N concentration gradient is great between surface and core of parts, which makes large active N atoms to diffuse into inner parts, which is advantageous for forming the ε phase of high nitrogen. The N concentration changes widely, and at the same time, it will provide conditions for forming alloy nitrides. Because alloy elements such as Cr, Mo, and Al have great appetency with N atoms and combine to form nitrides rapidly, the result would form poor N areas around them and lead to increased asymmetry of N concentration in local areas. The polymers of nitrided layers contain Fe_2N, ε-$Fe_{2\sim3}N$, Fe_3N, and γ'-Fe_4N, which cause diffraction lines to interlace and disperse.[6] However, for the diffusion stage of lower N potential at higher temperature, the marked decrease of N potential makes the high N ε phase of part of the surface change to γ' phase. The ε phase of the compound layer disappears rapidly in a short time, so some N atoms contained in ε phase will return nitriding atmosphere; the rest of the N atoms contained in the ε phase will rapidly diffuse into the inner parts, which will reduce the amount of N atoms on the surface and eliminate the ε phase as an obstacle to diffusion of N atoms.[7] On the other hand, if nitriding temperature is increased, the N atom diffusion factor will increase, which will increase diffusion speed of N atoms and diffusion distance. The poor N potential on part of the surface increases the surface activity, which will provide favorable conditions for ion nitriding of higher N potential at lower temperature in the next stage; at this time, the nitrided layer containing high N phases will form rapidly on part of the surface. After multi-cycle intensity-boosting diffusion ion nitriding, ageing lasts 1 h finally, which will greatly improve the quality, and the nitrided layer will disperse many kinds of alloy

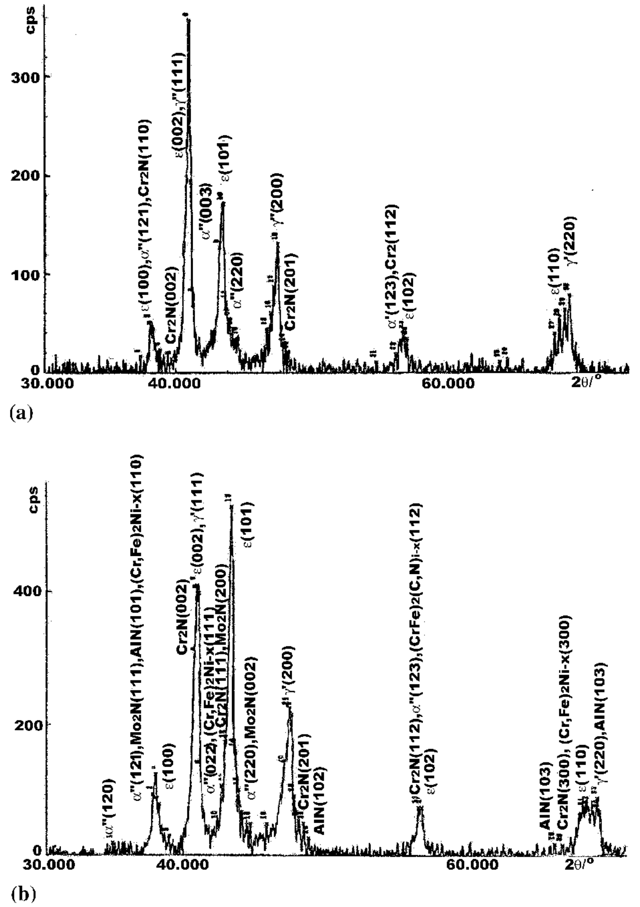

Fig. 5 XRD patterns of ion nitrided layer of 38CrMoAl steel: **(a)** conventional ion nitriding and **(b)** rapid ion nitriding

Table 1 Compound Layers' Phases of Conventional Nitriding and Rapid Ion Nitriding

Materials	Conventional Ion Nitriding	Rapid Ion Nitriding
40Cr	γ' (more), ε, α''	ε(more), γ', α'', Cr_2N
25Cr2MoV	γ' (more), ε, Cr_2N, $CrMoN_X$	ε(more), γ', α'', Cr_2N, Mo_2N, $(Cr,Mo)_2(C,N)$, $CrMoN_X$, $(Cr,Fe)_2(C,N)_{1\text{-}X}$
38CrMoA1	γ' (more), ε, α'', Cr_2N	ε(more), γ', α'', Cr_2N, Mo_2N, AlN, $(Cr,Fe)_2(C,N)_{1\text{-}X}$

nitrides. This will increase asymmetry of N atoms distribution; it will lead to diffraction line dispersion and an obvious spectrum side. Therefore, rapid ion nitriding not only creates a compound layer containing primarily ε phase, but it also increases the kinds of alloy nitrides, and makes the spectrum lines more complicated and interlaced. Evidently, due to the different nitriding technique, the difference between component phases on nitriding surface is great, and the existence of nitriding elements such as Cr, Mo, and Al will make the diffraction pattern more complicated.

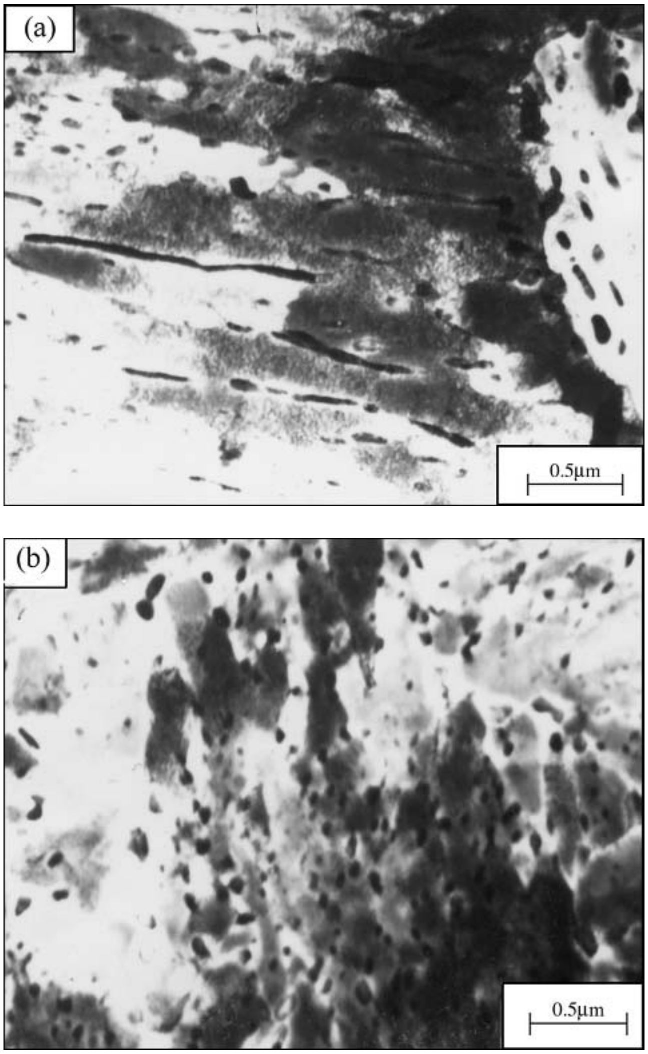

Fig. 6 TEM micrographs of ion nitrided layer of 40Cr steel: **(a)** TEM micrograph of the γ' phase in the diffusion layer of 40Cr steel via conventional ion nitriding and **(b)** TEM micrograph of the γ' phase in the diffusion layer of 40Cr steel via rapid ion nitriding

3.3 Microstructure Shape of Ion Nitriding Diffusion Layer

The white layer in the ion nitrided layer is very thin. It was corrupted when the TEM sample was made by the double-spray method. The status observed is mainly the microstructure shape of the subsurface diffusion zone. Figure 6 and 7 show the results observed from nitrided layers of 40Cr and 25Cr2MoV steels. Figure 6(a) indicates there are two forms of the γ' phase, such as spicula and clava, in the diffusion layer of 40Cr steel, which has white edge around it after conventional ion nitriding. This causes non-precipitation areas beside the grain boundary from diffusion of the cavity. It results from the appearance of a N-poor area after formation of the γ' phase. Figure 6(b) shows a TEM micrograph of the diffusion layer of 40Cr steel via rapid ion nitriding under cyclic N potential. The γ' phases in the diffusion layer were distributed with fine grains and precipitated with some punctate Cr_2N nitrides from the N-ferrite α_N, which were much tiny and dispersed than those of conventional ion nitriding.

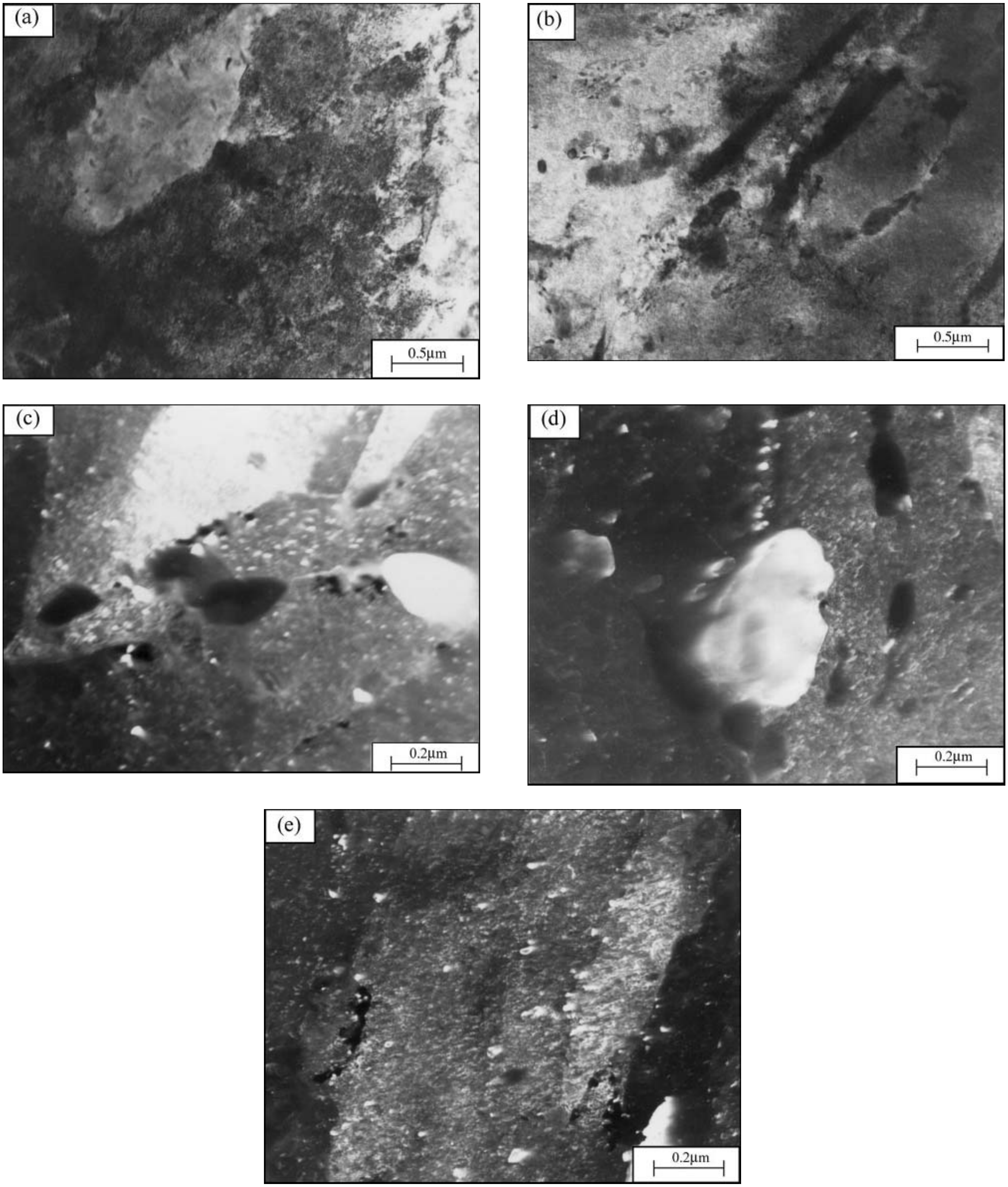

Fig. 7 TEM micrographs of ion nitrided layer of 25Cr2MoV steel: **(a)** TEM micrograph of diffusion layer via convention ion nitriding, **(b)** TEM micrograph of precipitation on sub-crystal boundary via convention ion nitriding, **(c)** TEM micrograph of γ' and $(Cr,Mo)_2(C,N)$ of rapid ion nitriding layer, **(d)** TEM micrograph of γ' and CrN of rapid ion nitriding layer, **(e)** TEM micrograph of precipitation inside ferrite of rapid ion nitriding layer

Figure 7(a) and 7(b) are TEM micrographs of the ion nitrided layer of 25Cr2MoV steel via conventional ion nitriding. By way of index for ion nitrided layers, not only were the precipitation particles along grain boundary Cr_2N and $CrMoN_X$ and the precipitation phases of sub-grain boundary α'' and CrN, but alloy nitrides were also distributed around the grain boundary and subgrain boundary of ferrite α_N as thick sheet or grains. TEM micrographs of the ion nitrided layer of 25Cr2MoV steel via rapid ion nitriding are shown in Fig. 7(c)-7(e). The precipitation nitrides of the diffusion layer were complex and were mainly α''-$Fe_{16}N_2$, γ'-Fe_4N, CrN, Cr_2N, $CrMoN_X$, MoN, $(Cr, Mo)_2(C, N)$, etc. There were quite difference for precipitation shape and location. For example, Fig. 7(c) and 7(d) illustrate that there are big grainy and nubby γ' phases, a great of small needle $(Cr, Mo)_2(C, N)$, and fine grainy CrN along grain boundary α_N. Figure 7(e) indicates the microstructure shape of small precipitation phases such as Cr_2N, MoN and $CrMoN_X$ from batten ferrite. The precipitation phases in diffusion layer of rapid ion nitriding are more profuse, and the alloy nitrides are smaller and more dispersed than those of conventional ion nitriding.

As the nitrides are easily conglomerated into large grains and distributed unevenly under longer and continuous nitriding, the preferential diffusion of N along inherent grain boundaries, subgrain boundaries, and batten ferrite inside parts leads to nitrides formation on inherent grain boundary and subgrain boundary mainly with conventional ion nitriding of constant temperature and constant N potential. However, the rapid ion nitriding is a technique involving temperature-change and N potential-change, for which multi-cycle between boosting of higher N potential at lower temperature and diffusion of lower N potential at higher temperature are used. In the stage of higher N potential at lower temperature, high N potential is helpful for increasing nitriding ability and N concentration asymmetry and increasing the atoms' diffusion driving force. This accelerates formation of nitrided layers containing mainly ε phase and alloy nitrides that are relatively fine and steady. In the stage of lower N potential at higher temperature, the precipitates formed will not grow up.[8] In the process at high temperature, the alloy nitrides formed remain finely distributed and low in N potential, which is helpful in accelerating decomposition of the ε phase in the nitrided layer and increasing the N diffusion ability further. This opens the path to N atoms and is advantageous for forming more alloy nitrides in more locations, which are formed not only at grain boundaries and subgrain boundaries, but also between ferrite battens or battens inside. The N concentration asymmetry provides conditions for formation of different types and location of nitrides, which makes precipitates of rapid ion nitriding more complicated than those of conventional ion nitriding. On the other hand, the fine alloy nitrides formed at higher temperature and lower N potential could become continuous cores of formation of ε and γ' phases during nitriding and could refine those in the diffusion layer further.

The results of 40Cr and 25Cr2MoV steels examined by TEM in Fig. 6 and 7 show that the technique of rapid ion nitriding under cyclic N potential can visibly refine the microstructure of nitrided layers and their precipitates, which will improve the quality of the nitrided layer and the performance of nitrided parts.

4. Conclusions

(a) Rapid ion nitriding not only makes the ε phase the main phase in compound layers, but also forms many types of alloy nitrides whose diffraction patterns are more complicated, interlaced, and overlapping.

(b) Compared with conventional ion nitriding, the phases in the diffusion layer are more profuse; their shape and locations are increased greatly. The precipitating phase and alloy nitrides precipitate more finely among grain boundaries, subgrain boundaries, ferrite battens, and ferrite grain interiors.

(c) The technique of rapid ion nitriding under cyclic N potential can accelerate nitriding speed and increase nitrided layer thickness effectively, and refine the phase of nitrided layer, which is helpful in improving quality of the nitrided layer and the performance of nitriding parts.

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