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Kinetics of Plasma Nitriding and Renitriding of 3% Cr-Mo-V Steel

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Kinetic studies of plasma nitriding of 3% Cr-Mo-V DIN 39CrMoV13.9 steel were performed at 538, 510, and 483 °C. It was found that the process obeys a parabolic law of diffusion for total case depth and is slower than parabolic for effective case depth formation. The kinetics of renitriding was found to be a continuation of the preexisting case growth. Mathematical equations were developed for the relationships. Long exposure to the nitriding temperatures had a negative effect on the hardness of the steel.

Keywords 3Cr-Mo-V steel, diffusion, microhardness, nitriding, surface engineering

1. Introduction

The kinetics of plasma (ion) and gas nitriding of different ferrous and austenitic steels has been the subject of extensive studies in the last couple of years. In the majority of articles published, the authors agree that the nitrided layer growth is controlled by a parabolic law.[1–3] This assumption is based on the internal oxidation model[3] and is successful in predicting the nitrided case depth of high alloy steels. However, in some of the studies, there were deviations reported from the parabolic growth for ferritic[4] as well as austenitic[5] steels. Most of the researchers concentrated their efforts on modeling of the gas or ion nitriding process, while only a few of them provided kinetic information for specific steels.[5–7] It seems to be rather obvious that the nitriding rate, or so-called total case depth formation, must obey the parabolic law if the process is carried out with a compound zone present on the surface.[1–3] Nevertheless, there is little practical data available for the various steels, which would allow, predicting with good accuracy, the nitriding time required for a specific case depth and nitriding temperature for a specific steel.

The other problem, which often needs to be addressed in industrial applications, is a prediction of effective case depth formation (case with a specific hardness). It may be controlled by a nonparabolic equation because of an effect of nitriding time on the hardness of the nitrided layer as well as on the hardness of the steel itself.[8] This especially applies to very long nitriding times used for exceptionally deep case formation, when a long exposure of the steel to the nitriding temperature may effect its mechanical properties.[10] In practice, the nitriding process may also need to be interrupted for different reasons, or products may need to be reprocessed to achieve a deeper case. It could be assumed that the kinetics of renitriding is a continuation of the interrupted process. Accordingly, attempts have been made in present research to investigate the nitriding behavior of a low alloy steel. The steel chosen is a 3% Cr-Mo-V alloy used for gear applications where an exceptionally deep case depth is required. The nominal composition of this steel is 0.35% C max, 3.00 to 3.5% Cr, 0.8 to 1.10% Mo, and 0.15 to 0.25% V.

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2. Experimental

2.1 Material

A quenched and tempered 3% Cr-Mo-V (DIN 39 CrMoV13.9) nitriding steel, similar to UNS K33585, was used for this evaluation. The Brinell hardness was 321 to 363. The test samples were 1 × 1 × 6 in. bars with a ground surface finish of Ra 125 or better. All new and rerun samples were blasted with 180-grit aluminum oxide before nitriding and renitriding.

2.2 Processing

The samples were configured in the circular patterns, as shown in Fig. 1. Fifteen bars were processed in each run. There was a minimum of five new samples used with each nitriding cycle. The remaining ten samples (except the first run) were rerun samples. There were a total of four thermocouples with one inserted into each of four of the bars. The maximum temperature variation observed during processing was 8 °C. Nitriding was carried out at nominal temperatures of 538, 510, and 483 °C. The nitriding times ranged from 4 to 400 h with the total renitriding time, achieved from a combination of the basic cycles on some of the samples, exceeding 1000 h. The nitriding was carried out in laboratory type equipment with a 0.6 × 0.6 × 0.75 m working space. A mixture of 30% nitrogen and 70% hydrogen and a pressure of approximately 3.2 mbar were used for each nitriding cycle.

2.3 Testing Procedure

The total and effective case depths were determined from microhardness profiles taken on cross sections of the nitrided

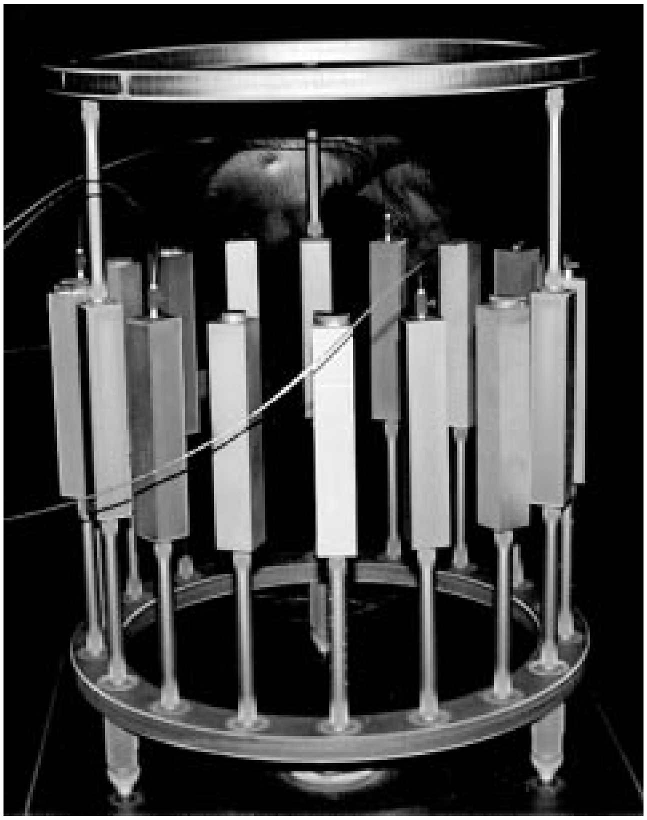


Fig. 1 Configuration of the samples in ion nitriding vessel. Note four thermocouple wires

bars. The microhardness was tested using a Vickers indenter and 200 g load (HV0.2). Each sample was tested in three different areas (three sides) resulting in 12 to 15 microhardness readings for each depth measurement. The effective nitriding depth was defined as the case depth where the hardness was 392 HV0.2. The total nitriding case depth was defined as the case depth where the hardness was core hardness plus 10%. The core hardness of every sample was tested with a Rockwell C method, and the selected samples were examined with an optical microscope.

3. Results and Discussion

The typical microhardness profile is shown in Fig. 2. The total and the effective case depths obtained from the microhardness curves were plotted in the form of CASE-TIME diagrams, as shown in Fig. 3 to 8. The total case depth formation data were fitted to a simple parabolic relationship $y = a + bx^{0.5}$, where y is the total case depth in millimeters and x is the nitriding time in hours. The coefficient of determination r^2 (a measure of the proportion of each other's variability that two variables share) shown in the figures is higher for nitriding at 538 °C since more data were available for this temperature. The coefficient a in the equation represents the case depth formed during the ramp up time. Its value is higher for the higher temperatures (0.1005 mm for 538 °C, 0.0912 mm for

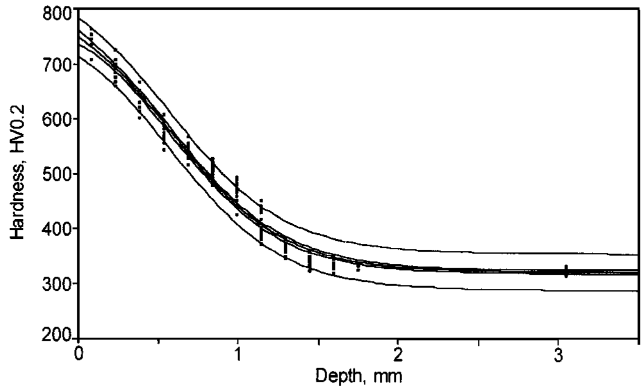


Fig. 2 Microhardness test results for sample nitrided at 538 °C for 400 h. The fit equation is $y = 322.1636 + 505.7495/\{1 + \exp[-(x - 0.5773)/(-0.3506)]\}$, $r^2 = 0.985$

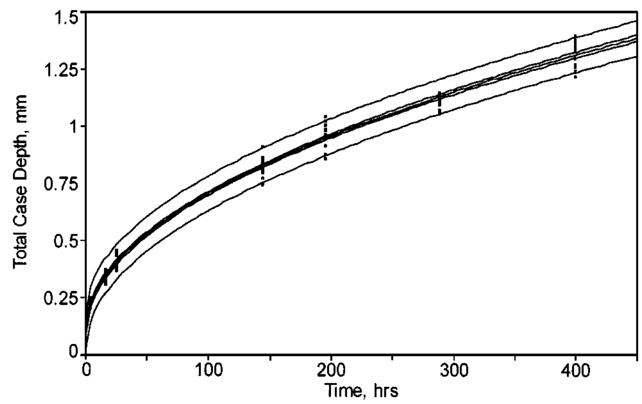


Fig. 3 Effect of nitriding time on total case depth formation at 538 °C. The fit equation is $y = 0.1005 + 0.0605x^{0.5}$, $r^2 = 0.991$

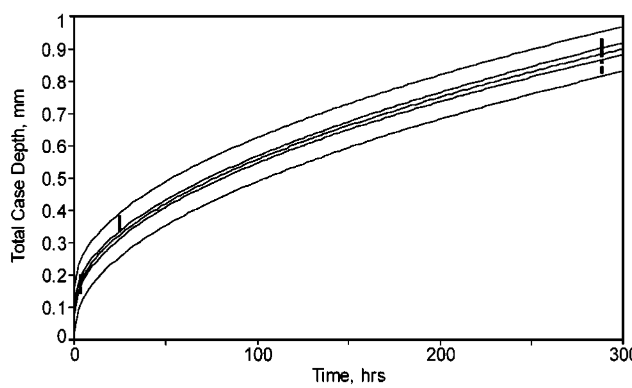


Fig. 4 Effect of nitriding time on total case depth formation at 510 °C. The fit equation is $y = 0.0912 + 0.0464x^{0.5}$, $r^2 = 0.989$

510 °C, and 0.0804 mm for 483 °C), which can be expected. The coefficient b represents the rate of nitriding and also has the highest value at 538 °C. The correlation using the parabolic equation is very good for all of the total case depth formation

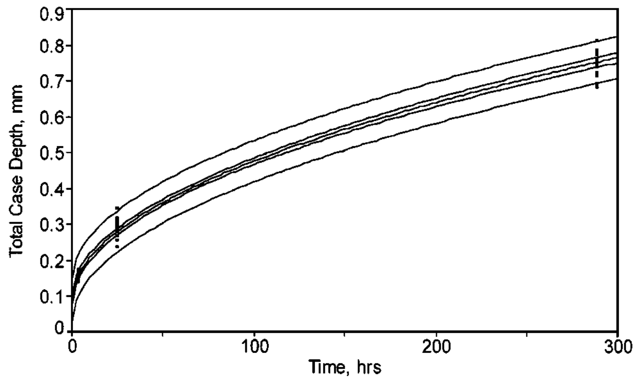


Fig. 5 Effect of nitriding time on total case depth formation at 483 °C. The fit equation is $y = 0.0804 + 0.0393x^{0.5}$, $r^2 = 0.989$

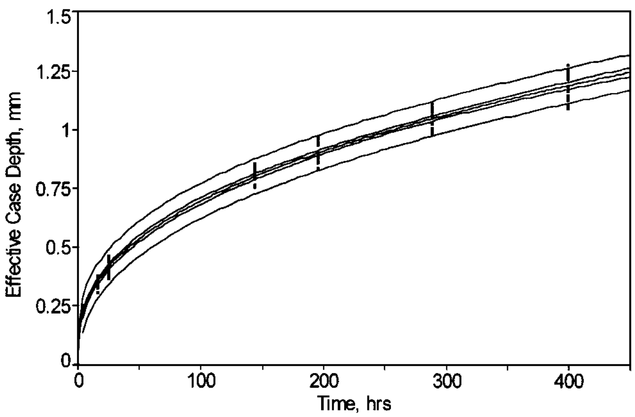


Fig. 6 Effect of nitriding time on effective case depth formation at 538 °C. The fit equation is $y = 0.0308 + 0.1045x^{0.401}$, $r^2 = 0.989$

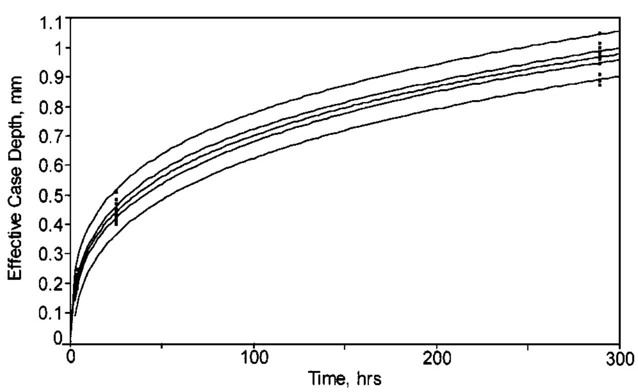


Fig. 7 Effect of nitriding time on effective case depth formation at 510 °C. The fit equation is $y = -0.1918 + 0.2834x^{0.249}$, $r^2 = 0.988$

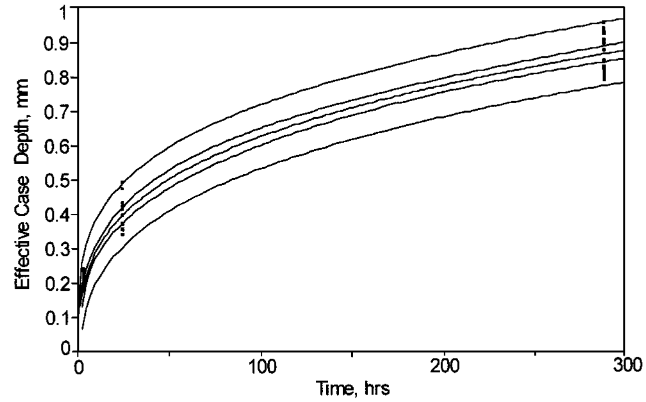


Fig. 8 Effect of nitriding time on effective case depth formation at 483 °C. The fit equation is $y = -0.1304 + 0.2288x^{0.258}$, $r^2 = 0.977$

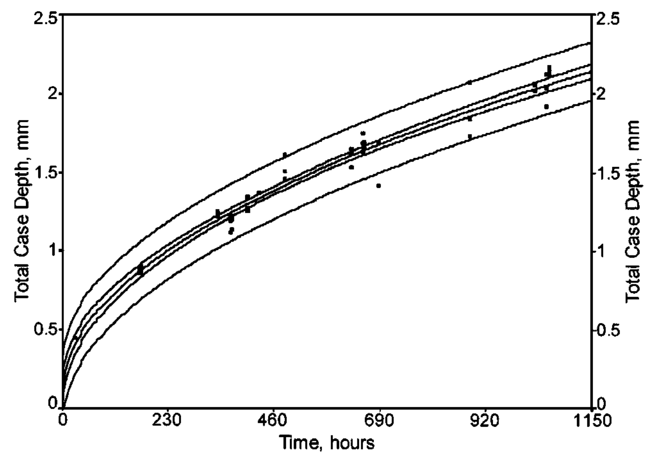


Fig. 9 Effect of renitriding time on effective case depth formation at 538 °C. The fit equation is $y = 0.0885 + 0.0606x^{0.5}$, $r^2 = 0.964$

curves, which, in fact, represent the diffusion rate of nitrogen into the steel (Fig. 4 to 6). The curves of the effective case depth formation did not fit well to the parabolic equation and therefore were fitted to a power-type equation $y = a + bx^c$ (Fig. 6 to 8). The effective case increases at a slower rate than the total case. This can possibly be explained by the fact that the specific hardness, which defines the effective case, depends not only on the rate of nitrogen diffusion but also on the hardness of the base steel as well as the structure of the nitrides.[8] The total case depth from samples rerun at 538 °C is presented in Fig. 9. Some of the samples were nitrided through several cycles to achieve long nitriding cycle times. The data could also be fitted to a simple parabolic equation. The coefficient a represents the total case formed during the total of several ramp up times. However, its value is not higher than in the equation for the uninterrupted cycle. This means that the total case depth accumulated from all of the ramp up steps to the temperature of the already nitrided steel is less than the one produced in a fresh (not pre-nitrided) steel. The coefficient b is the same as in the equation for the kinetics of the uninterrupted cycle for the same temperature; however, the coefficient of determination, r^2, for this equation is slightly smaller.

A summary of the kinetic data, in the form of three-dimensional graphs, is shown in Fig. 10 and 11. The surface equations were automatically chosen by a software program called Table Curve 3D.[9] These data allowed us to calculate the time and temperature needed for producing the required effective or total case depth.

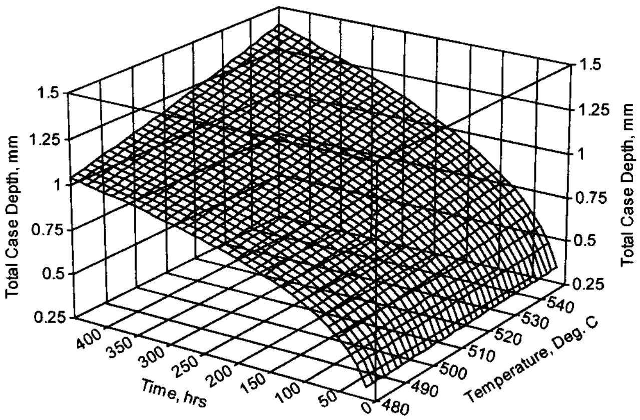


Fig. 10 Effect of nitriding time and temperature on total case depth formation. The fit equation is $z = (-4.441 + 82.29/x^{0.5} + 10.46/\ln y)^{-1}$, $r^2 = 0.991$; x—temperature (°C), and y—time (h). The individual experimental points are omitted for clarity of the graph

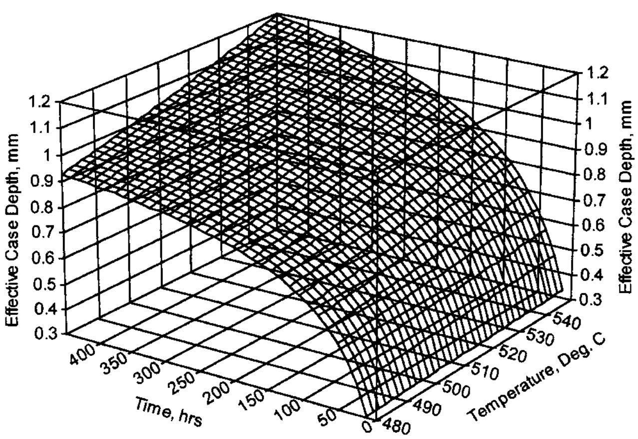


Fig. 11 Effect of nitriding time and temperature on effective case depth formation. The fit equation is $z = (-2.776 + 80.90/x^{0.5} + 12.06 \ln y/y)^{-1}$, $r^2 = 0.997$; x—temperature (°C), and y—time (h). The individual experimental points are omitted for clarity of the graph

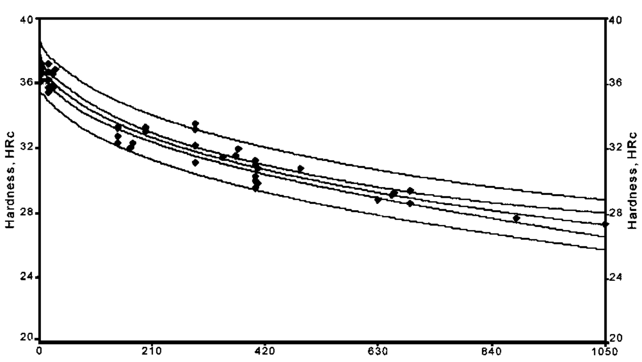
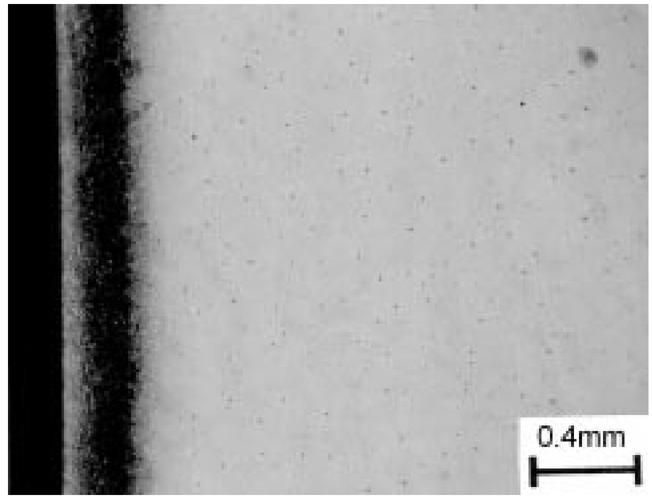
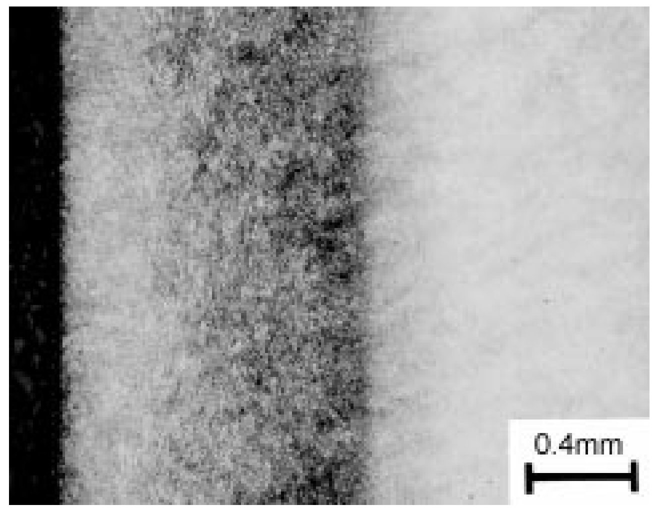


Fig. 12 Effect of nitriding time on (core) hardness of the steel at 538 °C. The fit equation is $y = 13.0885 + 24.1816/(1 + (x/1779.5719)^2)$, $r^2 = 0.951$



(**a**)



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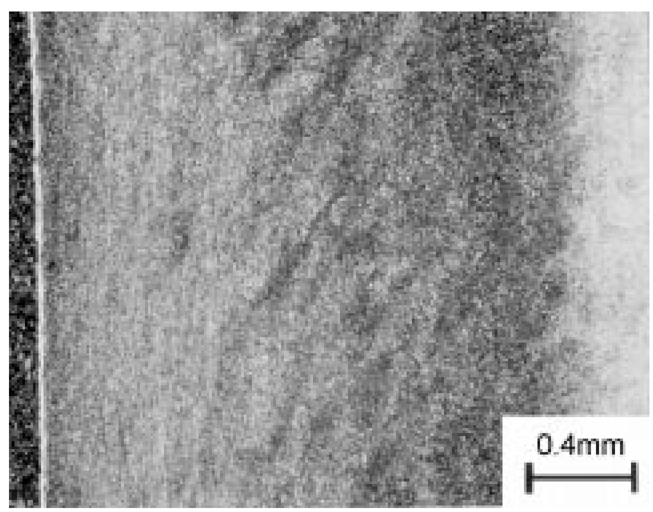
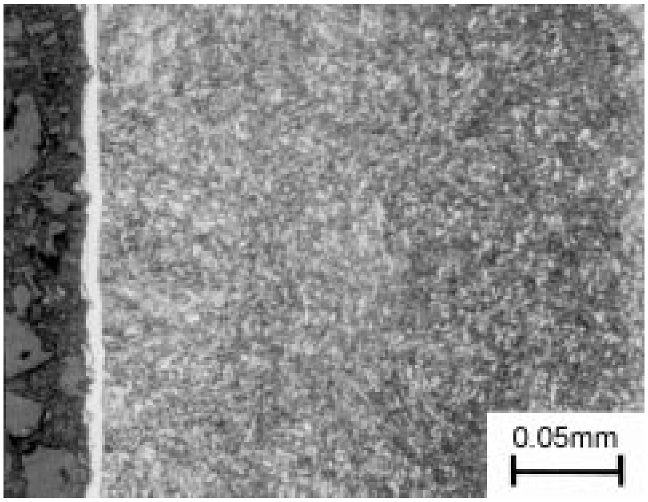


(**c**)

Fig. 13 Photomicrographs of the surface layer in the 3% Cr-Mo-V steel nitrided at 538 °C in a continuous cycle: (**a**) for 25 h, (**b**) for 400 h, and (**c**) in six interrupted cycles for a total of 1058 h. Etched with 2% nital



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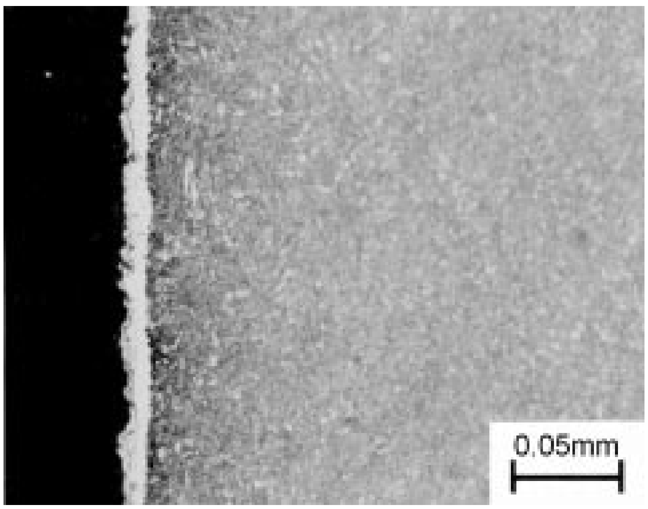

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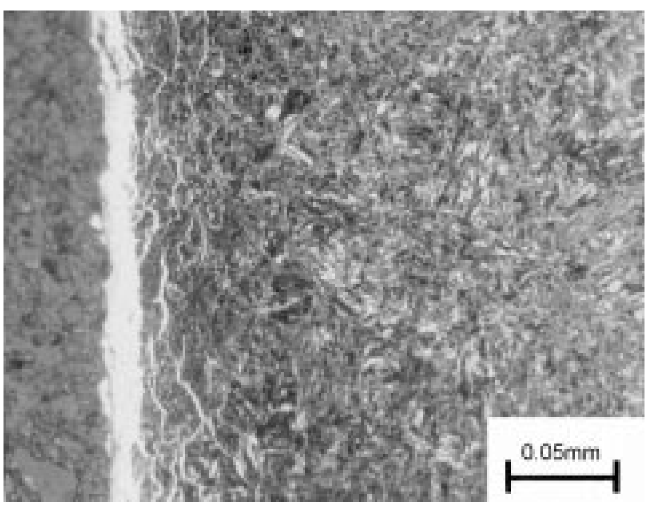
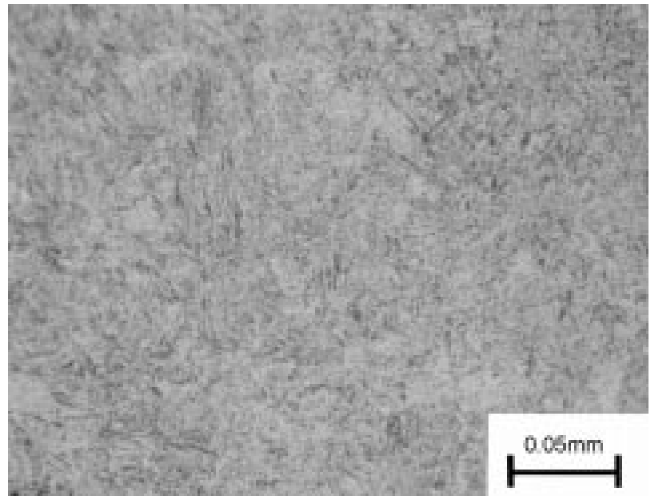


(**c**)

Fig. 14 Photomicrographs of the transition from the compound layer to the diffusion layer in the 3% Cr-Mo-V steel nitrided at 538 °C in a continuous cycle: (**a**) for 25 h, (**b**) for 400 h, and (**c**) in six interrupted cycles for a total of 1058 h. Etched with 2% nital



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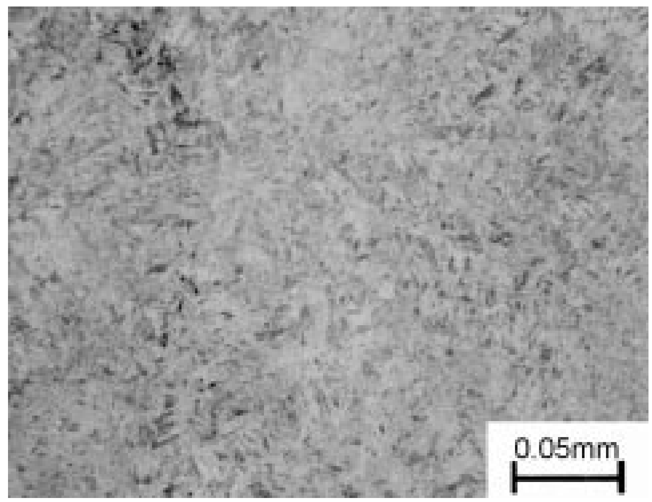

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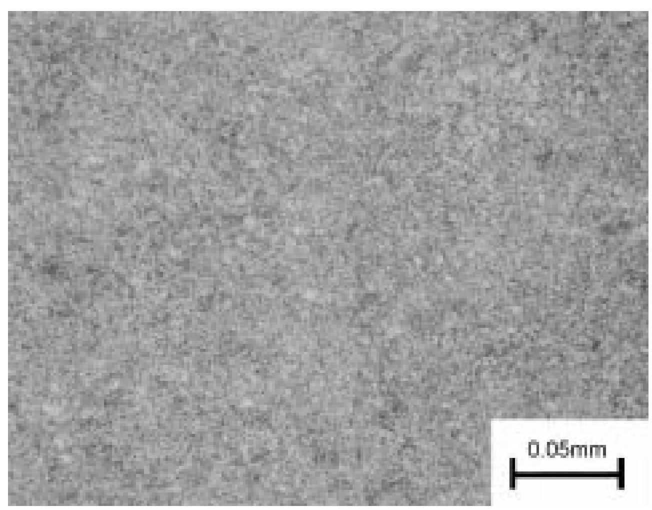

(**c**)

Fig. 15 Photomicrographs of the core structure of the 3% CrMoV steel samples nitrided at 538 °C in a continuous cycle for (**a**) 25 h, (**b**) 400 h, and (**c**) in six interrupted cycles for a total of 1054 h. Etched with Marble's reagent. Average Rockwell C hardness is (**a**) 36.4, (**b**) 30.4, and (**c**) 27.3

Figure 12 illustrates the effect of nitriding time on the core hardness of all of the samples nitrided and renitrided at 538 °C. As would be expected, very long exposures of the steel to the nitriding temperature resulted in a reduction of its mechanical properties, namely, hardness.[10] Although the 3% Cr-Mo-V steel is very resistant to tempering, its hardness drops to approximately 30 HRc after 400 h and to about 27 HRc after 1000 h of nitriding time. The optical microphotographs of the selected nitrided samples are presented in Fig. 13 and 14. The limit of the nitrided zone in the steel as revealed by etching does not correspond to any particular hardness, since that depends on the nitride-forming alloy content, the nitriding temperature and time, and the prior tempering treatment of the steel.[8,11] However, it does show the limit of the alloy nitride formation, which corresponds very well to total case depth. Higher (400×) magnification clearly shows the thickness of the compound zone in the nitrided layer. Even after nitriding times of 1058 h, it stays comparatively thin and does not exceed 20 μm. This fact may be explained by the sputtering effect during plasma nitriding, where development of the compound zone deviates from the parabolic law.[3,12]

Etching with Marble's reagent revealed the core structure of the steel samples, as seen in Fig. 15. The (a) and (b) photographs show a typical tempered martensite microstructure, while (c) shows an overtempered martensitic/spheroidal type structure with the presence of coalesced carbides. The metallographic information corresponds well with the hardness data in Fig. 12. The over-tempered structure of the steel, with the longest nitriding time, had the lowest hardness.

4. Conclusions

The long nitriding cycles employed in this study provided sufficient data to prove that ion nitriding of 3% Cr-Mo-V steel is a diffusion-controlled process. The kinetics of the total case depth formation at a constant temperature can be described by a simple parabolic relationship, while the effective case formation can be described by a power equation. A mathematical relationship between case depth, temperature, and nitriding time was developed based on the experimental data. It was also verified that interruption during the nitriding process does not have a detrimental effect on the ability of the steel to form a thicker nitride layer. Very long nitriding times have a detrimental effect on the mechanical properties of the steel, but more detailed studies are needed to determine the structural changes.

Note

Confidence and prediction intervals represent normal distribution and standard error (small internal) at 95% in Fig. 2 to 9 and 12. Intervals are tighter for 538 °C due to the number of samples available. This set of runs was used to determine the representative curve fit for the rest of the kinetic experiments.

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