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Development of Nitriding Technology by Optimizing Steel Composition and Processing Conditions

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Abstract

The hardness of nitrocarburized S40C and SCr420 was measured to investigate the effects of pre-treatments on hardening ability of nitrocarburizing. The hardness of the diffusion layer in S40C with normalizing was lower than that without normalizing. In the case of SCr420, normalizing did not affect the hardness of the diffusion layer. The observation with transmission electron microscopy suggested that the clustering of α"-$Fe_{16}N_2$ contributes to lower hardness of the diffusion layer in normalized S40C. Quenching and tempering and low-temperature annealing caused a decrease in hardness of the diffusion layer in SCr420. This decrease in hardness was caused by a decrease in the amount of Cr dissolved into the matrix.

1. Introduction

Mechanical parts used for automobiles, industrial machinery, and construction machinery are sometimes subjected to various types of surface-hardening heat treatment in order to improve their fatigue strength. Surface-hardening heat treatments are broadly divided into carburizing, induction hardening, and nitriding (nitrocarburizing). Among these, in carburizing and induction hardening, martensitic transformation is applied by quenching from high temperature, which forms deep hardened layers easily but, on the other hand, distortion by transformation is large. Meanwhile, nitrocarburizing is performed at a low temperature of 600°C or lower, therefore distortion is very small as compared with other surface-hardening heat treatments.

Vehicles with internal combustion engines have been replaced with EVs and HVs in recent years. Under these circumstances, customers have started demanding parts that have new characteristics, such as low noise and low vibration, different from conventional characteristics.[1] To improve such characteristics of engines and transmissions for HVs, it is effective to improve the accuracy of the dimensions of parts. Therefore, nitrocarburizing with small distortion is appropriate for these needs.[2] To utilize the characteristics of nitrocarburizing involving small distortion to expand the application, the fatigue strength and wear resistance need to be further improved.

Nippon Steel Corporation has been developing steel products with excellent nitrocarburizing characteristics by optimizing alloy contents by drawing on its strong points as a material manufacturer. However, the nitrocarburizing characteristics of steel can change due to the influence of various factors such as the components of steel products, microstructure, and pretreatment. Therefore, to allow steel subjected to nitrocarburizing to fully exert its capability, it is necessary to clarify the mechanism of various parameters affecting nitriding characteristics and make proposals of steel products to users including their optimum way of use.

2. Relationship between Pretreatment before Nitrocarburizing and Nitrocarburizing Characteristics

When steel is nitrocarburized, a layer called a compound layer with a thickness of a few micrometers to approximately 30 μm mainly consisting of iron nitride is formed on the outermost surface. The matrix immediately under the compound layer is called a diffusion layer, which is hardened due to the interaction with nitrogen. It is widely known that alloying elements affect the hardening characteristics of the diffusion layer during nitrocarburizing. When alloying elements that easily form compounds with nitrogen in steel (e.g., Cr) are contained, the higher the content of such elements is, the larger the hardness increment of the nitrocarburized layers is.[3–5]

Factors other than steel products' components also affect nitrocarburizing characteristics. Parts to be subjected to nitrocarburizing are manufactured through various manufacturing processes such as forging, heat treatment, and machining before nitrocarburizing. Some researchers have reported that these upstream processes affect

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the nitrocarburizing characteristics. Egashira et al. have reported that normalizing before nitrocarburizing reduces the hardness after nitrocarburizing.[6] Miwa et al. produced steels which have various types of microstructure by heat treatment and nitrocarburized them: They have reported that the surface of the outer layer of bainite steel is harder than that of ferrite, pearlite, and martensite steels and the hardened depth of the bainite steel is deeper than that of ferrite, pearlite, and martensite steels.[7] Takase et al. have reported that cold-working makes the diffusion depth shallow and they considered that the reason could be nitrogen trapping due to dislocation.[8]

These reports have revealed the qualitative influence of upstream processes on the nitrocarburizing characteristics. However, it cannot be said that the mechanism of these upstream processes affecting the nitrocarburizing characteristics has been fully clarified. Therefore, it is sometimes difficult to generally apply the knowledge about the effect of upstream process to steel products with various components. This paper introduces study examples of the influence of heat treatment and forging conditions before nitrocarburizing on the hardness of nitrocarburized layers and their mechanisms.

3. Influence of Normalizing on Nitrocarburizing Characteristics

Steel is sometimes normalized before nitrocarburizing to homogenize microstructures. As mentioned previously, it has been reported that normalizing decreases the hardness of the diffusion layers and that the lower the normalizing temperature is, the larger influence is.[9] This section studies how normalizing affects the hardness of diffusion layers and describes the study results of the influence of steel grades on hardness reduction behavior by normalizing.

3.1 Influence of steel on hardness reduction behavior by normalizing

Two steels were used, S40C (0.4C-0.2Si-0.8Mn) and SCr420 (0.2C-0.2Si-0.8Mn-1.0Cr), containing the nitride formation element, Cr. Steel ingots were made from them by vacuum melting and they were formed into round bars with a diameter of 50 mm by hot forging. The forged S40C round bar was held at 850°C for one hour and the SCr420 round bar was held at 900°C for one hour. Then, they were air-cooled (normalized). A square bar test specimen of 10×10×80 mm was prepared from each normalized round bar. The test specimens were nitrocarburized at 580°C for two hours and then quenched in oil (nitrocarburized). The microstructure of the cross sections near the surfaces of the nitrocarburized specimens was observed and the hardness was measured.

Figure 1 shows optical micrographs of the outer layers of the nitrocarburized steel. The non-pretreated S40C has a ferrite-pearlite structure. On the normalized steel, the volume of pro-eutectoid ferrite increased and the size of pro-eutectoid ferrite grains and pearlite became finer. From the perspective of microstructure, the microstructure of normalized steel consists of ferrite and pearlite and is qualitatively the same as the non-pretreated steel. In the microstructure of the non-pretreated SCr420, bainite was included in addition to ferrite and pearlite. It seems that, on the normalized steel, the microstructure became finer and the volume fraction of the bainite is smaller than that of the non-pretreated steel.

Figure 2 shows the influence of normalizing on the hardness profile near the surface of the nitrocarburized S40C. The hardness of the surface of the normalized steel is lower than that of the non-pretreated steel by approximately 40 HV. **Figure 3** shows the influence of normalizing on the hardness profile of the diffusion layer of the nitrocarburized SCr420. For the SCr420, normalizing has no influence on the hardness of the surfaces.

3.2 Mechanism of normalizing affecting the hardness of diffusion layers

As described in the previous section, the influence of normaliz-

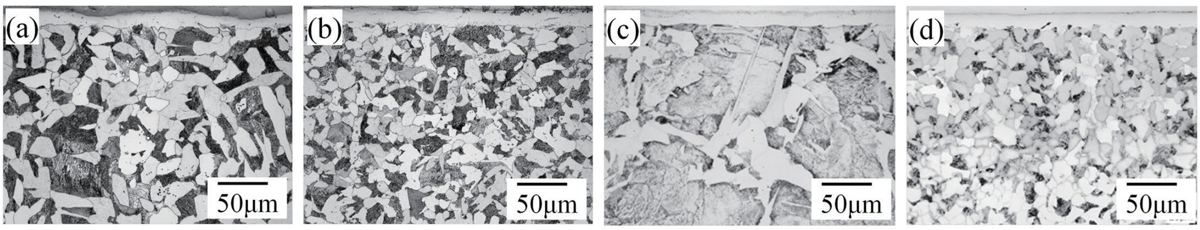

Fig. 1 Optical micrographs of the cross sections of the nitrocarburized surface in (a) Non-pretreated S40C, (b) S40C normalized at 1373 K, (c) Non-pretreated SCr420 and (d) SCr420 normalized at 1123 K

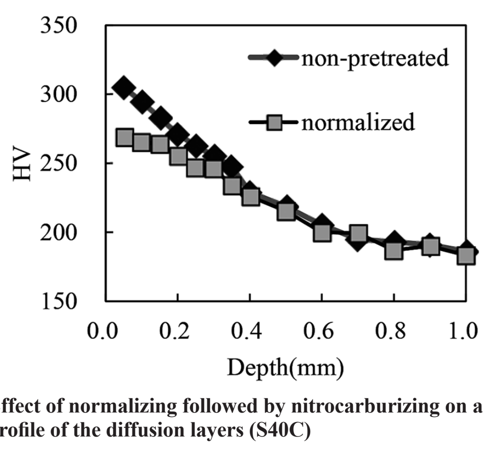

Fig. 2 Effect of normalizing followed by nitrocarburizing on a hardness profile of the diffusion layers (S40C)

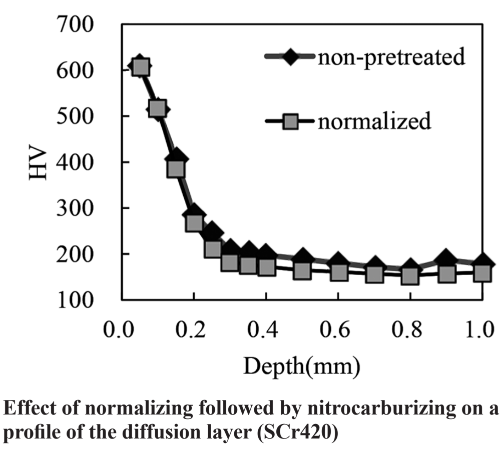

Fig. 3 Effect of normalizing followed by nitrocarburizing on a hardness profile of the diffusion layer (SCr420)

ing on the hardness profile varies between steel grades. To clarify the reason for this difference, the authors focused on the controlling factor of the hardness of the diffusion layers for both steels. The sample whose hardness was measured was observed by transmission electron microscopy (TEM). A thin sample was prepared from each nitrocarburized test specimen whose hardness was measured, such that the location 75 μm deep from the nitrocarburized surface became the observation section.

Figure 4 shows TEM images of precipitates observed in the S40C diffusion layer. The precipitates observed in the non-pretreated S40C steel are metastable iron nitride α"-$Fe_{16}N_2$.[10] These nitrides precipitated during the process of cooling from the nitrocarburizing temperature.[11] The crystal structure of the α" phase is similar to that of the matrix. The misfit between α" and the matrix is small and the thickness of α" is only a few nanometers. Due to these structural characteristics, these nitrides can contribute to precipitation hardening.[12, 13] When focusing on the size of α", the length of α" in the non-pretreated steel is several tens of nanometers while the length of α" in the normalized steel seems to exceed 200 nm and the width seems to exceed 10 nm. This is a cluster of α"[14] and the size of an individual α" grain is not very different from that in the non-pretreated steel. The number density of α" in the normalized steel is clearly lower than that in the non-pretreated steel. Therefore, the amount of precipitation hardening with α" in the non-pretreated steel may be larger than that in the normalized steel. The decrease in the number density of α", as a result of clustering, is assumed to reduce the hardness of a diffusion layer in normalized steel.

Figure 5 shows TEM images of the SCr420 diffusion layer. The precipitates have a B1 crystal structure and they may be CrN.[5] The length of the minute precipitates considered to be CrN is 10 nm or smaller and no 100-nm or longer α" was seen although such α" was seen on the S40C. The size and number density of the CrN did not change depending on whether normalizing was performed. This corresponds to the fact that the hardness profiles did not change depending on whether normalizing was performed.

3.3 Changes in the dispersion state of α"-$Fe_{16}N_2$

To study why the dispersion state of α" changed in the S40C with normalizing, X-ray diffraction analysis was performed with Co-K_α radiation. The full width at half maximum (FWHM) of the {211} ferrite peak was analyzed for the core region of the nitrocarburized samples. The FWHM of the {211} plane of the non-pretreated steel is 0.200° and that of the normalized steel is 0.180°. That is to say, the ferrite of the non-pretreated steel has more lattice defects or elastic strain than that of the normalized steel. It may be considered that the defects and strain field become nucleation sites of α" during cooling from the nitrocarburizing temperature. On non-pretreated steel with many such defects and much strain, α" can precipitate on the matrix uniformly. On the other hand, normalized steel with few defects and less strain does not have sufficient nucleation sites. Then, in the late stage of precipitation of α", α" precipitates on the strain field formed by α" precipitating in the early stage. This variation of nucleation promoted clustering of α". **Figure 6** schematically illustrates the influence of defects and strain field on the precipitation behavior of α".

The results above show that the hardness of a diffusion layer decreases with normalizing because the number density of α" decreases. When the diffusion layer is hardened mainly with alloy nitrides, normalizing may not affect the hardness.

4. Influence of Quenching/Tempering and Low-temperature Annealing on Nitrocarburizing Characteristics

The previous chapter described the influence of normalizing. Some parts for nitrocarburizing are annealed at low temperatures or quenched and tempered before use. The influence of these types of heat treatment was studied.

4.1 Influence of quenching/tempering and low-temperature annealing on the hardness of diffusion layers

Some of the S40C and SCr420 round bars with a diameter of 50 mm were held at 650°C for two hours (low-temperature annealing).

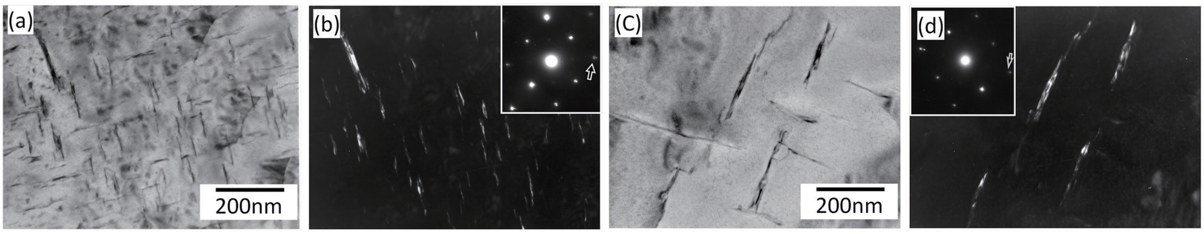

Fig. 4 TEM images taken in diffusion layer of the nitrocarburized S40C
(a) Bright field image of the non-pretreated specimen, (b) Dark field image of the non-pretreated specimen, (c) Bright field image of the normalized specimen, (d) Dark field image of the normalized specimen

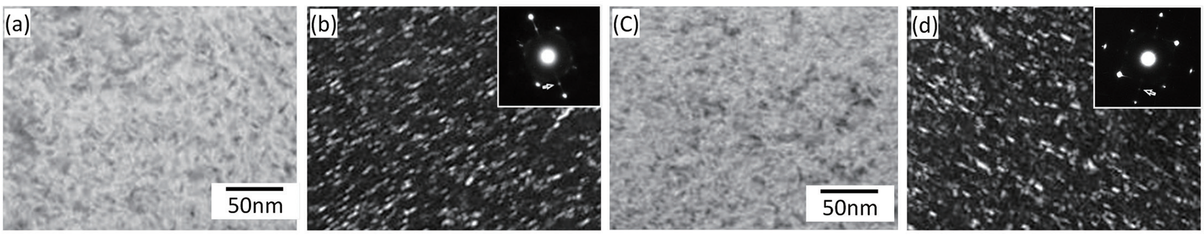

Fig. 5 TEM images taken in diffusion layer of the nitrocarburized SCr420
(a) Bright field image of the non-pretreated specimen, (b) Dark field image of the non-pretreated specimen, (c) Bright field image of the normalized specimen, (d) Dark field image of the normalized specimen

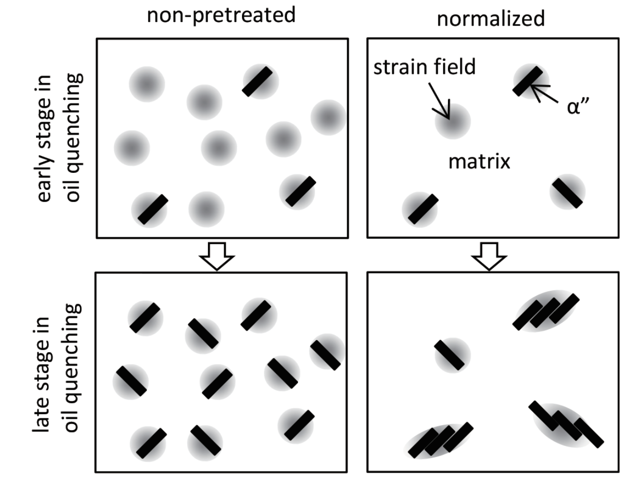

Fig. 6 Schematics of behavior of α” precipitation during oil quenching in the non-pretreated specimen and the normalized specimen

Some other bars were heated at 860°C and quenched in water and heated at 620°C for one hour (quenching/tempering). Block test specimens were made from these round bars and they were nitrocarburized under the conditions described in the previous chapter.

Figure 7 shows the influence of the low-temperature annealing and quenching/tempering on the hardness profiles of the S40C. The figure shows that both types of heat treatment decreased the hardness of the diffusion layers. When steel is annealed at low temperature and then nitrocarburized, clustering of α” occurs as is the case with normalizing, which reduces the number density of α”.[14] Therefore, the reason for the decrease in the hardness of nitrocarburized layers may be the same as that for normalized steel.

Figure 8 shows the influence of low-temperature annealing and quenching/tempering on the hardness profiles of the SCr420. The figure shows that the hardness of the SCr420 did not change by normalizing, but that low-temperature annealing and quenching/tempering reduced the hardness.

4.2 Mechanism of quenching/tempering and low-temperature annealing affecting the hardness of diffusion layers

The diffusion layer of the SCr420 was strengthened mainly by the precipitation hardening of minute CrN. If the amount of Cr that contributes to precipitation hardening decreases for steel annealed at low temperature or quenched and tempered steel, that can explain why the hardness increment decreases. Therefore, to check whether the amount of effective Cr that contributes to precipitation hardening changes, an additional test was performed. A 50-mm-long test specimen with a diameter of 10 mm was prepared from each of the round bars made from non-pretreated steel, steel annealed at low temperature, and quenched and tempered steel that has not been nitrocarburized. The surfaces of the test specimens were electrolyzed and filtered using a 0.2-μm filter. The amounts of Cr in the residues were measured by ICP atomic emission spectrometry.

Assuming that, in the state before nitrocarburizing, undissolved Cr is present as a part of cementite in place of Fe, it can be said that the values obtained by analysis of the residues are the concentrations of Cr in the cementite. Once the Cr concentrates into cementite, even if cementite dissolves during nitrocarburizing, the distribution of Cr remains because the diffusion velocity of Cr is slow at the nitrocarburizing temperature. It may be considered that, even when Cr in such a dispersion state precipitates as CrN, the size is coarse

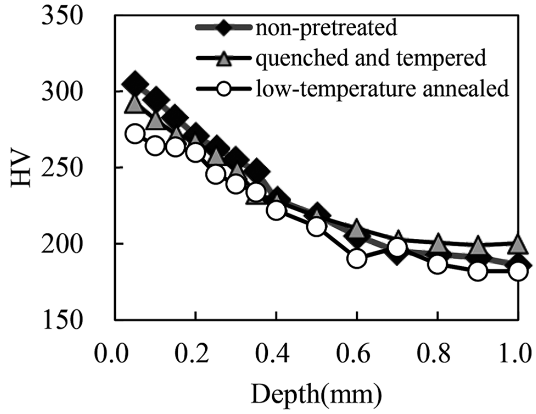

Fig. 7 Effects of quenching-and-tempering and low-temperature annealing followed by nitrocarburizing on hardness profiles of the diffusion layers in S40C

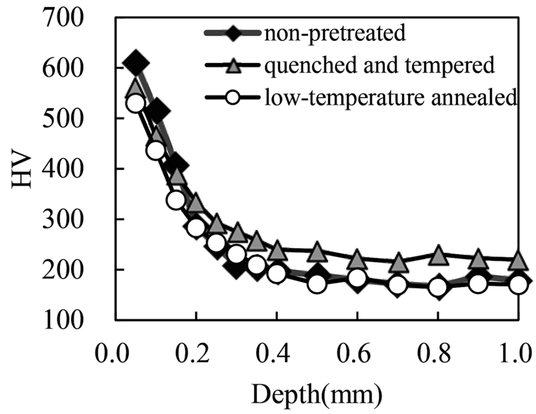

Fig. 8 Effects of quenching-and-tempering and low-temperature annealing followed by nitrocarburizing on hardness profiles of the diffusion layers in SCr420

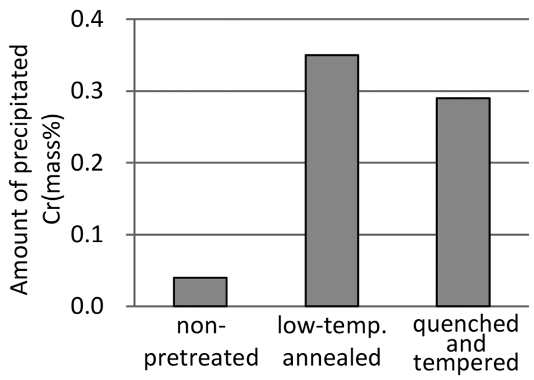

Fig. 9 Effects of the pre-heat treatments on amount of Cr precipitated as a part of cementite

and the number density is low. That is to say, Cr present in cementite before nitrocarburizing may hardly contribute to hardening in nitrocarburizing.

Figure 9 shows the influence of each type of heat treatment on the concentration of Cr in the cementite in a state before nitrocarburizing. The figure shows that, for the non-pretreated steel, the amount of Cr precipitating in the cementite is small at 0.05%, while for the quenched and tempered steel and steel annealed at low temperature, 0.2% or more Cr is present in the cementite. When regarding the amount of dissolved Cr that contributes to hardening during nitrocarburizing as the difference between the total Cr content and the amount of Cr in the cementite, it can be said that the amounts of dissolved Cr are small in the quenched and tempered steel and steel annealed at low temperature. Therefore, arguably, the reason for the decrease in the hardness increments in nitrocarburizing for the quenched and tempered SCr420 steel and the SCr420 steel annealed at low temperature is the decrease in the amount of dissolved Cr.

5. Influence of Forging Temperature on Nitrocarburizing Characteristics

This paper has so far shown that, when the microstructure changes as a result of heat treatment before nitrocarburizing, the nitrocarburizing characteristics vary even between steel products with the same chemical composition. The microstructure and nitrocarburizing characteristics of steel can change according to the forging conditions in addition to heat treatment.[15] This chapter describes the study results of the influence of forging temperature on nitrocarburizing characteristics examined using steel whose structure was changed by controlling the forging temperature.

As the test steel, S40C was used. Vacuum-melted ingots were forged into square bars with a side of 75 mm. Then, they were heated at 1523 K for 30 minutes and forged into a round bar with a diameter of 50 mm by hammer forging. At this time, some square bars were forged immediately after being taken out of the furnace. Some other square bars were forged after the surface temperature decreased to 1413 K or 1293 K. The surface temperatures were measured by a radiometer. Block test specimens were prepared from these materials and they were nitrocarburized at 853 K to study the structure and hardness.

Figure 10 shows optical microscope images of the microstructure after forging. The figure shows that the lower the forging start temperature is, the finer the microstructure is, and the higher the fraction of ferrite is.

Figure 11 shows the influence of the forging start temperature on the hardness profiles. The figure shows that the lower the forging temperature is, the lower the hardness increment in the nitrocarburizing is. The lower the forging temperature is, the higher the transformation temperature in the following cooling becomes. Owing to the high transformation temperature, the dislocation density in the microstructure may decrease. Therefore, it is estimated that, in steel forged at low temperature with low hardness of the diffusion layer, clustering of α'' occurs as is the case with normalized steel.

6. Conclusions

This paper shows that the forging and heat treatment conditions prior to nitrocarburizing affect the nitrocarburizing characteristics using some study cases.

(1) When steel is normalized before nitrocarburizing, for S40C, the hardness increment in nitrocarburizing decreases, but for SCr420, it does not decrease. One reason for the decrease in the hardness increment for S40C may be the clustering of α''.

(2) When steel is quenched and tempered before nitrocarburizing or annealed at low temperature before nitrocarburizing, the hardness increment in nitrocarburizing decreases for both S40C and SCr420. The reason for the decrease in the hardness increment for SCr420 may be the decrease in the amount of dissolved Cr that can contribute to precipitation hardening.

(3) Lowering the forging temperature also decreases the hardness increment in nitrocarburizing for S40C.

We will deepen our knowledge of the combinations of steel products and manufacturing methods to contribute to the development of high-strength nitride parts.

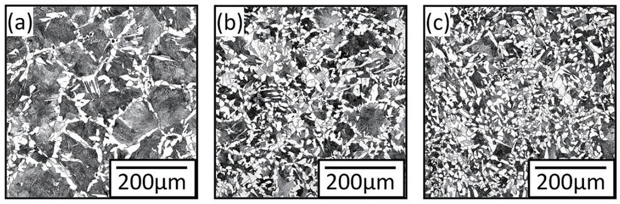

Fig. 10 Optical micrographs of cross sections of the core matrix (a) Forged at 1523 K, (b) Forged at 1413 K, (c) Forged at 1293 K

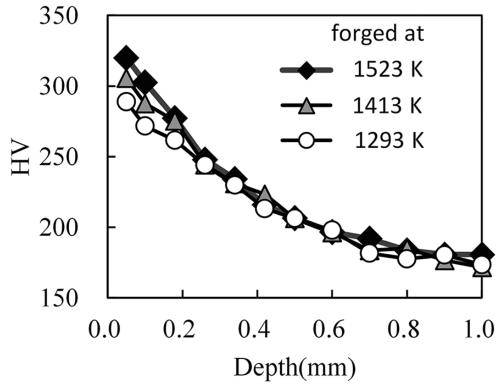

Fig. 11 Effect of forging temperature on hardness profiles of the diffusion layers

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