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THE STUDY OF PHASE STRUCTURES AND SURFACE HARDNESS VALUES OF ION NITRIDED AISI H13 STEEL UNDER VARIOUS TEMPERATURES

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Abstract

In this study, temperature dependence phase structure and hardness values of water quenched-tempered AISI H13 tool steel and its ion nitrided form has been investigated. Surface hardness of the steel has been considerably increased by ion nitriding due to formation of Fe_2N, Fe_3N and Fe_2-3N phases. Hardness values of the water quenched-tempered steels gradually decreased from the surface to inner part whereas it was dramatically reduced immediately after the surface in ion nitriding steels in which it was almost equal to that of water quenched-tempered steels. Hardness values reduced with increasing applied temperature in water quenched-tempered steels. The hardness values of nitrided steel was not altered considerably at lower temperatures (up to 300ºC), slightly reduced at temperatures between 400 ºC and 500 ºC and yielded almost equal hardness value with water quenched-tempered steel at 600 ºC. The hardness values of the both water quenched-tempered and nitrided steels decreased at 800 ºC in which they showed the same hardness values.

Keywords: Hot work tool steel, ion nitriding, phase structure, hardness

1. Introduction

The occurrence of material loss in machine parts due to friction, i.e. wear was a subject which is constantly being examined in recent years. It was known that wear decreases the life of machine parts; this causes economically and technically substantial losses. Especially, wear which occurred in high temperatures hot forging die that adequate strength was expected and constantly works under impact load is one of the interests of researchers [1]. The factors such as selection of material used, production process, heat treatment applied and place of use were important in terms of wear [2]. Because that wear occurred on the surface, one of the approaches was to increase hardness on the surface [3]. The surface hardening was provided the advantage of high wear resistance and high toughness of material’s matrix.

The most important feature expected from hot work steels was toughness and high temperature strength [1-4]. Ion nitriding process was applied to improve surface properties, to surface harden, to increase wear, corrosion and fatigue strength [5-11]. In ion nitriding, it was known that nitrides occurred on the material surface, especially chrome and iron nitrides (Fe_2N, Fe_3N, Fe_4N-γ' phase, $Fe_{2-3}N$-ε phase) was shown high hardness and wear resistance [12-16].

Özbaysal et al. [17], have studied ion nitriding of tool steels and examined the variations in microstructure. Tang and Plumtree [18] have studied fatigue fracture of hot work tool steels in various temperatures. Karamış [19] has researched some properties of ion nitriding in layer properties. Devi and Mohanty [20] have studied ion nitriding of tool steels in wear fatigue based on impact and rolling process. On the other hand, Stappen et al. [21] have researched surface variations in ion nitrided tool steels.

In addition to this, especially as a result of ion nitriding of AISI H13 hot work tool steel, surface hardness values in different temperatures have not been examined in detail. Therefore, the aim of this study is to examine phase structures and their surface hardness of ion nitrided AISI H13 hot work tool steel in different

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temperatures.

2. Experimental Studies

In experimental studies, AISI H13 hot work tool steel has been used. The chemical composition of quenched and tempered AISI H13 steel is given in Table 1. For chemical composition analysis ARL 3460 spectrometer has been used.

Table 1. Chemical composition of quenched-tempered AISI H13 steel

%C	%Mn2	%P	%S	%Si	%Cu	%Cr	%Ni	%Mo
0.3750	0.3857	0.0213	0.0045	0.9703	0.1159	4.950	0.2945	1.273
%Sn	**%Al**	**%As**	**%Ca**	**%Ta**	**%V**	**%W**	**%Co**	**%Fe+**
0.0108	0.0274	0.0107	0.0006	0.0254	0.9494	0.0656	0.0182	90.53

Samples have been prepared in 50 mm diameter and 5 mm thickness. As first the samples have been pre-annealed between 350-400°C and the second pre-annealed between 800-820°C in inert atmosphere. After, the samples have been austenizated at 1040°C for 20 minutes, then quenched in hot bath (500-520°C) and cooled in ambient temperature. Finally, the sample has been tempered three times in 560°C for 2 hours.

For ion nitriding process, the samples and the apparatus which the samples included have been cleaned with trichlorethylene and the samples have been replaced in a chamber. After the vacuum chamber has been cleaned and after silicon has been applied for tightness, it has been scattered with hydrogen for half an hour. The ion nitriding experimental conditions were %25N_2 + %75H_2 gas mixture (1 l/min ± %10 gaseous flow rate, 500 ± 50V voltage), 500°C temperature, 10 hours time and 10 Torr pressure. Nitrogen analysis has been done with LECO TC-436 device. Total nitrogen amount has been found as %0.02716.

The samples have been prepared for microstructure examinations by being cut in 15x10x5mm dimensions in numerically controlled wire erosion machine. Hardness measures have been done by taking the average of three values measured under 50 gf loads with Karl Frank and ATS DMH-2 Vickers microhardness devices. The surface hardnesses of quenched and tempered steel and ion nitrided steel have been measured at the different temperatures (200°, 300°, 400°, 500°, 600° and 800°C) for 2 hours. For X–ray diffraction analysis, Rigaku 2050/32 RINT X-Ray diffractometer has been used. Diffraction has been done with 40kV voltage, 20 mA current by using CoK_α ray between 6-80° with 10°/min scanning speed. In the study, optical microscope and scanning electron microscope (SEM- JSM-840) have been used for microstructure analysis.

3. Results and Discussion

In Figure 1, the microstructure of quenched and tempered AISI H13 steel which is taken by optical microscope and electron microscope and in Figure 2, X-ray diffraction of the same steel are shown. In optical microscope and scanning electron microscope (SEM) microstructures of quenched and tempered AISI H13 steel, typical small carbides have been detected. Which can be understood from the X-ray diffraction analysis shown in Figure 2, these carbides were the phases of Fe_3C and Cr_7C_3. In a study [17], it was reported that small carbides spreading a wide range were seen and searched in X-ray diffraction $(Fe, Cr)_7C_3$ in microstructure research of AISI H13 steel, but since the carbides were small it could not be determined. In another study [18], it is reported that nodular chrome carbide has been seen in ferritic matrix in the structure of the same steel which was pre-heated at 1040°C and oil quenched which was tempered at 600°C for 2 hours and 580°C for 1 hour.

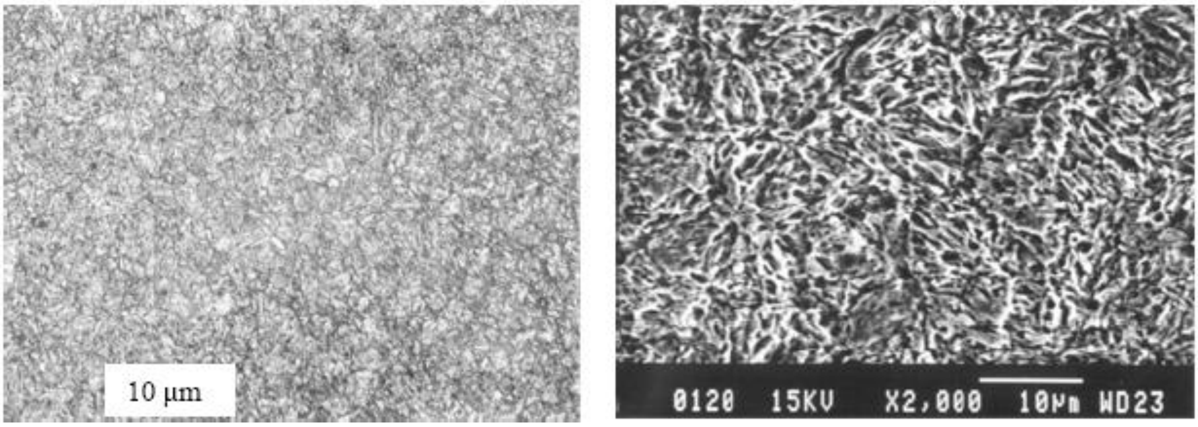


Figure 1. Microstructures of quenched-tempered AISI H13 steel; a)Optical microscope, b) Scanning electron microscope (SEM)

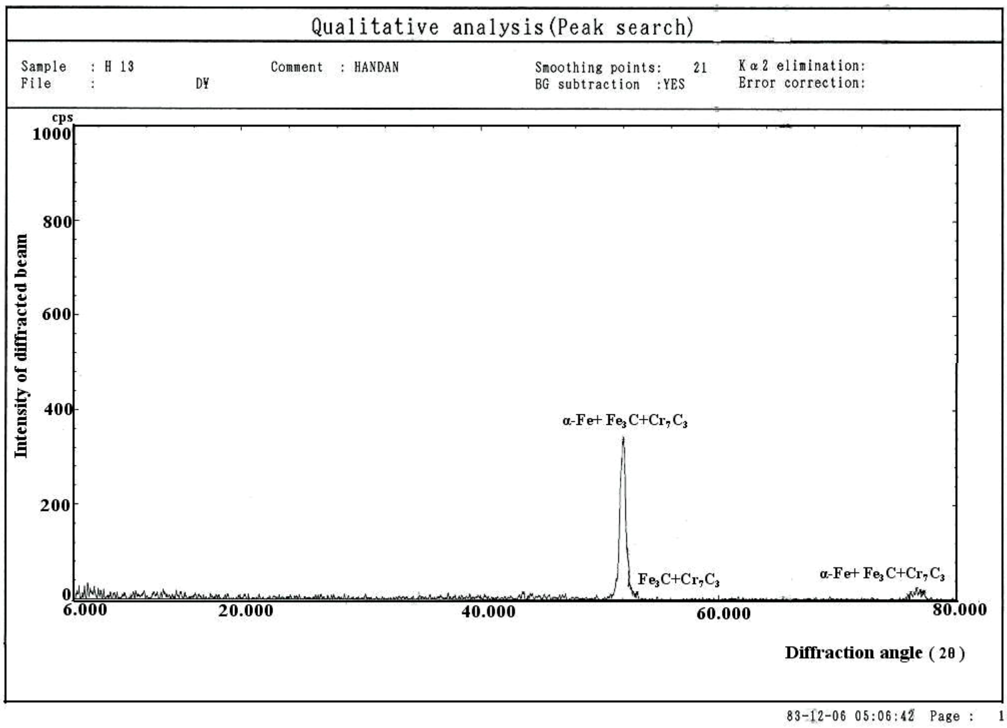
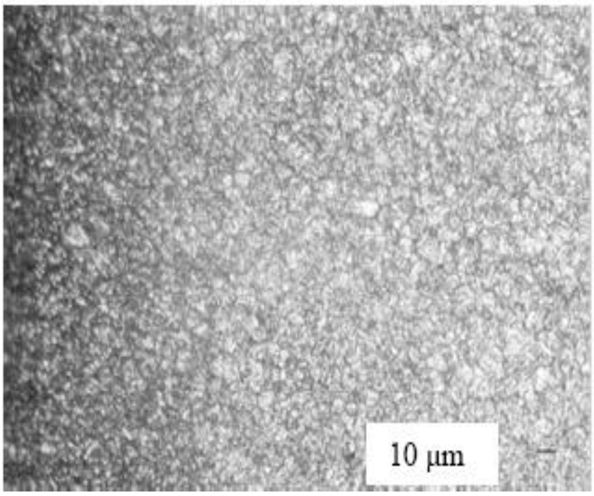
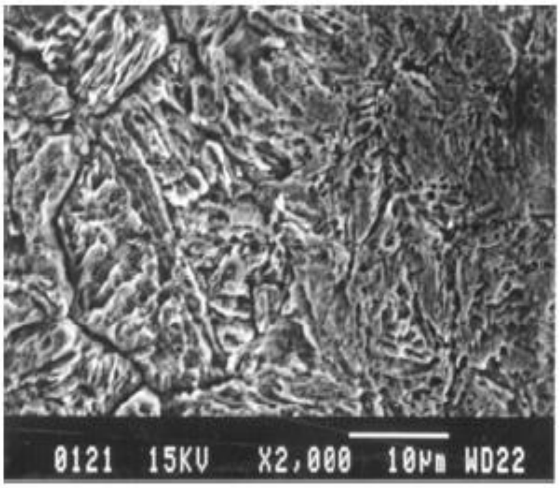


Figure 2. X-Ray diffraction of quenched-tempered AISI H13 steel

In Figure 3, the microstructures of AISI H13 steel taken by optical microscope and SEM are shown a diffusion layer without the white layer on the surface of steel. In the core region of the steel, relatively big carbides have been seen according to only quenched and tempered steel. In microstructure shown by SEM, lath martensite structure in transition region and small nitride precipitates in diffusion layer have been seen. In X-ray diffraction analysis (Figure-4), α-Fe, Fe_3C, Fe_2N, Fe_3N, $Fe_{2-3}N$ mixture phase has been determined. In an article [17], it was reported that CrN has been determined in ion nitrided AISI H13 steel was performed at 480°C for 7 hours. In another article [19], it was reported that there is $Fe_{2-3}N$ + Fe_4N mixture phase in the structure of the same steel which ion nitrided in 550°C for 16 hours by using ammoniac. In a research [20], it was noted that the period of ion nitriding was formed compound layer phase. It was reported that to the same steel, $Fe_{2-3}N$ phase was formed when ion nitrided at 530°C for 12 hours and Fe_4N phase was formed when ion nitrided for 24 hours. This formation has been attached to the release of molecular nitrogen [20].



a)



b)

Figure 3. Microstructures of ion nitrided AISI H13 steel; a) Optical microscope, b) Electron microscope (SEM)

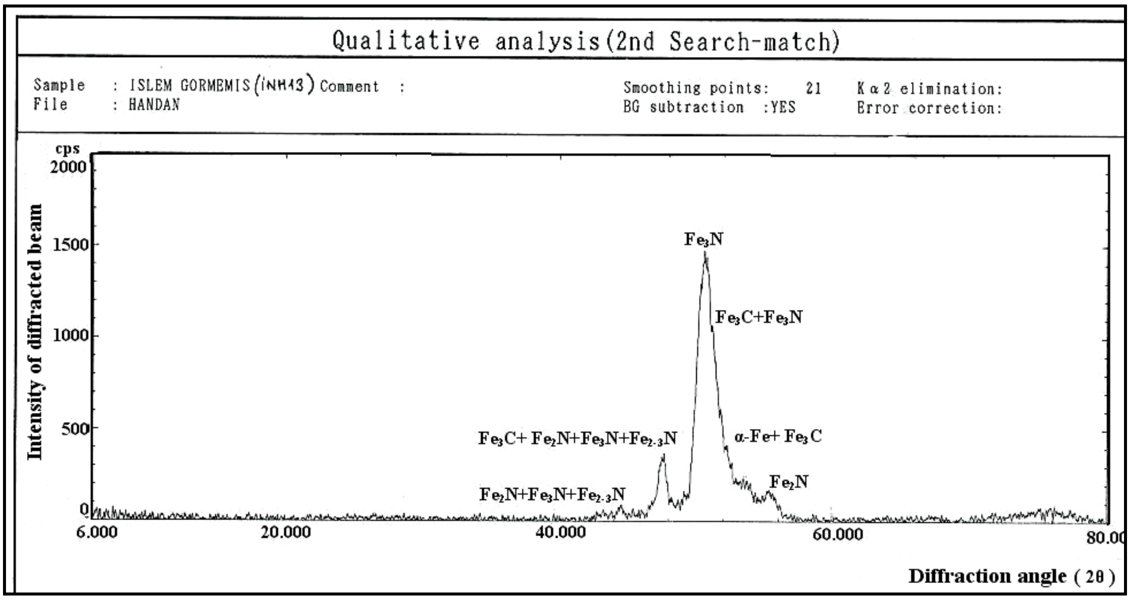


Figure 4. X-Ray diffraction analysis of ion nitrided AISI H13 steel

In Figure 5, it was shown that the surface hardness of quenched and tempered H13 hot work steel is 621 $HV_{0.05}$ and the surface hardness increases to 1300 $HV_{0.05}$ when ion nitrided to this steel and the hardness decreases distance from surface and the hardness values (515 $HV_{0.05}$) does not change in 175μm depth.

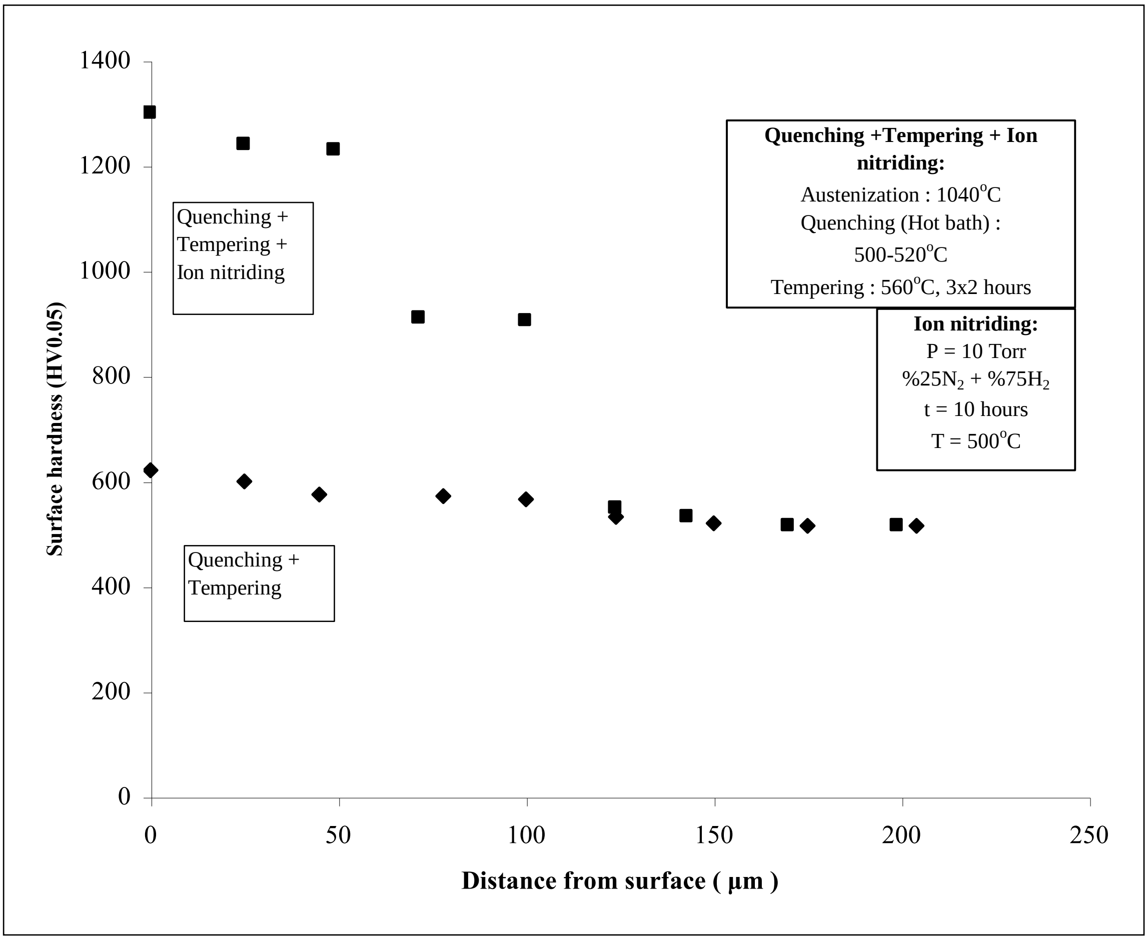


Figure 5. The hardness distributions of quenched and tempered AISI H13 steel and ion nitrided AISI H13 steel distance from the surface to the inside

In consideration of these explanations in literature and these results, it is understood that hardness is high on the surface which is included high amount of nitrogen, nitrogen amount decreases from surface to the inner part and hardness decreases. Since nitrides formed in ion nitriding increase the hardness, nitrogen diffusion is an important matter. In literature [17, 21], it have been reported that martensite lates were caused high nitrogen diffusion in steel. Also, it have been noted that nitrogen replaces by carbon in nitride diffusion layer and this replacement is a function of distance from surface of the material [22]. In another study [23], it has been expressed that nitrogen diffusion for AISI H13 steel was reached the highest value on the surface and decreases as the distance increases from the surface. Also in a study it have been indicated that [24], $Fe_{2\text{-}3}N$ phase generally was formed in grain boundaries in low process temperatures for AISI H13 steel and was formed at the grain boundary in medium process temperatures less than 420°C and there was nitrogen diffusion in the grains in high process temperatures. The hardness of AISI H13 hot work tool steel was approximately two times more than quenched and tempered steel. Also, approximately to 175µm depth, the hardness of ion nitrided steel was higher than only tempered steel. In deeper, the hardness of both steels was the same.

The increase of working temperature changes the steady state of material and causes the occurrence of different properties in the material. Experimentally, the change of surface hardnesses of quenched and tempered AISI H13 steel with the same ion nitrided steel at 20 ^{o}, 200 ^{o}, 300 ^{o}, 400 ^{o}, 500 ^{o}, 600 ^{o} and 800 ^{o}C for 2 hours are examined (Figure 6). It has been seen that the hardness value of quenched and tempered steel hold in furnace at 200 ^{o}C for 2 hours decreases to 524 HV0.05 from 621 HV0.05 and surface hardness decreases little more (482-480 HV0.05) within the steel hold at 300o and 400 ^{o}C for 2 hours. It was determined that surface hardness increases some more in the steel hold at 500 ^{o}C for 2 hours (524 HV0.05). The martensite hardness decreases at this temperature. But as a result of carbide formation, the secondary hardness was occurred and hardness increase was observed. Surface hardness of the steel hold at the 600 ^{o}C temperature for 2 hours is decreased a little more (445 HV0.05) and surface hardness is measured as 255 HV0.05 at 800 ^{o}C.

When the change of surface hardness of the ion nitrided steel was examined according to the temperature, it was determined that hardness decrease slightly at 200 °, 300 °, 400 ° and 500 ° C. In X-ray diffraction analysis (Figure 7), it was revealed phases of nitrides (Fe2N, Fe2-3N, CrN) given high hardness to the structure and carbides (Fe3C, Fe7C3, Cr7C3, Cr23C6) in the structure. At this point, it was reported nitride phases decreases as the temperature increases so that hardness values decrease. In an article [25], when surface hardness of ion nitrided AISI 5140 steel at between 100-500 ° C for 4 hours is measured, it was reported the hardness decreases as the temperature increases and this decrease is related to the density of alloy nitrides was occurred in diffusion layer.

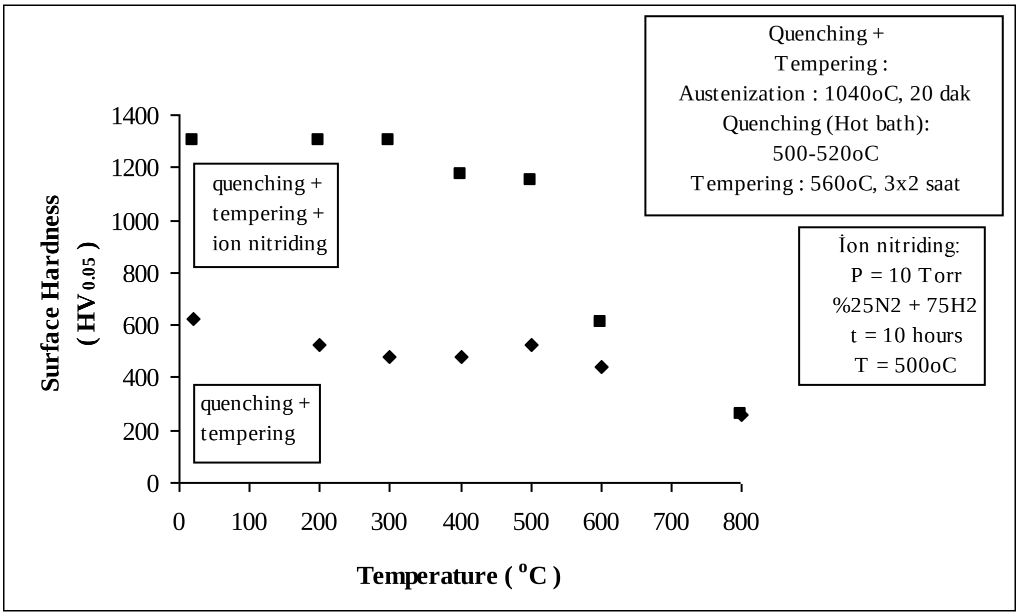


Figure 6. The surface hardness distributions of quenched and tempered AISI H13 steel and ion nitrided AISI H13 steel (20 °, 200°, 300°, 400°, 500°C – 2 hours).

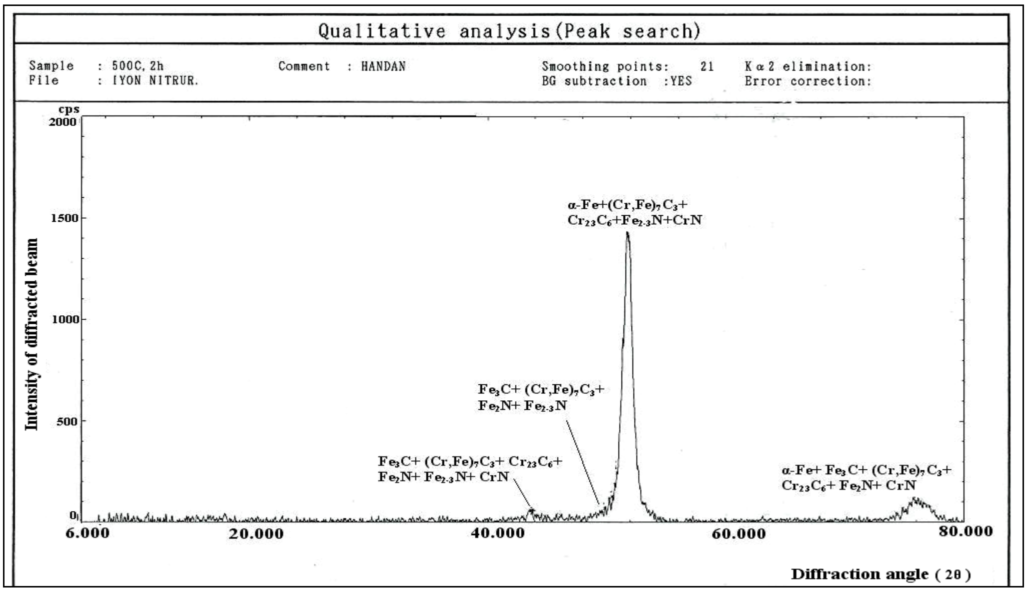


Figure 7. X-ray diffraction analyse of ion nitrided AISI H13 steel (500°C – 2 hours).

Dramatically decrease (605 HV0.05) has been determined in the surface hardness of ion nitrided steel hold at 600 ° C for 2 hours. When it was compared with quenched-tempered steel, it can be said that very few amount of nitride effect stays in this material. A layer was seen in microstructure analysis but nitride phase was not seen in X-ray diffusion and only Fe3C and (Cr,Fe)7C3 was seen. For this reason, it was thought that nitride precipitates were in very small size.

The hardness was the same in ion nitrided steel (260 HV0.05) and in quenched and tempered steel (260 HV0.05) at 800 ^{o} C. As a result, it can be said that nitride effect does not exist at 800 ^{o} C temperature. X-ray diffraction analyses were confirmed in this comment. Only Fe3C and (Cr,Fe)7C3 were seen in the structure. Although there are alloy elements such as Al, Cr, Mo, V within AISI H13 steel (Table 1), nitrides of these alloy elements which is affinities with nitrogen is more than iron were not seen in X-ray diffraction analysis in ion nitrided steel. But at the different temperatures, CrN structure was seen in the steel which is hold for a certain period. This result indicates that better diffraction results are obtained if the factors such as diffraction tube (CoKα), scanning speed (10o/min.) used in the study is changed. But in researched literatures [17, 19, 24, 29], other nitrides of alloy elements have not been, except Cr in ion nitrided H13 steel.

In a study [26], it was reported that CrN was formed in high chromic steels containing %12-18Cr because of high affinity of chrome to nitrogen and Cr4N and Cr2-3N was formed in low chromic steels (%1Cr). Also, according to Fe-Cr-N isothermal phase diagram, it was seen CrN was seen stable at 550 ^{o} C and less amounts than %1.6 nitrogen and CrN is less stable with the increase of γ′-(Fe,Cr)4N or ε-(Fe,Cr)2-3N in the surface that nitrogen amounts are high [27]. In this study, CrN was seen in the diffractions taken by ion nitrided AISI H13 steel which contains %5Cr and hold at 200 ^{o} C and higher temperatures (Figure 7). Because total nitrogen amount is % 0.02716 in ion nitrided steel, it can be expected that CrN is stable at the temperature effect. It was reported in the literature that much of nitrogen in CrN precipitates is in nitride layer in high chromic steels and nitrogen distribution solutes in ferrit is so small that can be ignored for total nitrogen in the layer [28].

When system is stable with minimum energy and activation energy of H13 steel is 19.5 kcal/mol in nitriding is considered, it can be said that AIN is stable, VN and CrN is metastable and Fe4N is unstable. Also, it was reported that free energy increases depending temperature and AIN and CrN don’t exist in the structure at 800 ^{o} C [28]. In an article, it was reported the solubility of nitrogen in ferrit decreases with the temperature [30]. In another article, it was reported that because of solubility of nitrogen in the γ-phase is about 28 times as much as in the α-phase, Fe3N can saved its structure at high temperatures [31]. Also, it was reported that after fast cooling of a temperature above 700 ^{o} C with vacuum, Fe3N and Fe4N phase was not seen in X-ray diffraction. This result was supported the study has been done. Sato et al. [32] were expressed that there were so much incorporated nitrogen atoms by ion nitriding in austenitic matrix. Also the nitrogen atoms were accommodated in the octahedral vacancies of FCC lattice with chemical reactions. In another article, it was reported that there was α-Fe (BCC) was formed in the structure bigger than 600 ^{o} C temperature by phase diagrams and in this structure, the biggest interstitial vacancy was on (110) plane. When the requested calculations were done, it was reported interstitial solid solution radius is 0.078nm which shall be accommodated in this vacancy. So the nitrogen which its atom radius is 0.071nm can possibly be accommodated as interstitial solid solution in α-Fe (BCC) due to distortion result.

As a result, it can be said that the hardness considerably increases with ion nitriding process of AISI H13 hot work tool steel which is generally used as hot forging die and it has high hardness values under the temperature effect to 600 ^{o} C and so wear rate decreases and the life of material increases.

4. Conclusions

There has been considerably increase in the surface hardness value of ion nitrided AISI H13 hot work tool steel. The hardness of ion nitrided steel is two times more than only quenched-tempered steel has been determined. The increase in the hardness has been based on the essences of Fe2N, Fe3N and Fe2-3N complex phases.

The decrease in hardness values from the surface is less in quenched-tempered steels; the hardness in ion nitrided steels on the surface has dramatically decreased to inner sides (approximately 175μm depth) and has been equalized with quenched-tempered steel.

The decrease has been observed in the hardness values of quenched-tempered steel with the temperature applied. While considerable decrease has not been observed in ion nitrided steel up to 300oC, the hardness has decreased a little more in 400-500 ^{o} C and in 600 degrees it reached the almost same value with quenched-tempered steel. At 800 ^{o} C, the surface hardness values of both quenched-tempered steels and ion nitrided steels have considerably been decreased; they have showed the same hardness values.

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