



Surface nitridation of Ti and Cr in ammonia atmosphere

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Abstract

Surface nitridation of pure Ti and Cr was carried out by exposing them to ammonia atmosphere at optimum temperatures in a thermogravimetric analyzer–mass spectrometer (TGA–MS) system. The nitrided specimens were characterized by PXRD, GIXRD, SPM, surface and cross sectional SEM and Microhardness tester.

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1. Introduction

Transition metal nitrides, particularly TiN and CrN, display a wide spectrum of important physical properties which make them very useful for a variety of applications ranging from protective coatings, that require a high mechanical hardness combined with thermal and chemical stability, to decorative coatings. Owing to its superior mechanical properties, TiN coatings are widely used in many industrial applications where high hardness, high wear resistance and low friction coefficient are required [1,2]. Due to its glittering golden colour, it is also used as a decorative coating. TiN is biocompatible and is considered as a very effective substrate for the nucleation of the strongly bonded calcium phosphate bone phases under suitable oxidation conditions, which makes it an ideal material for orthopedic implants [3]. In recent years, CrN has also been attracting attention as a hard coating material due to its good wear, corrosion and oxidation resistance and high thermal stability [4]. Possibility of making thicker CrN coatings makes it an outstanding candidate to protect the base material from corrosion and hence extend its service life [5,6]. The ob-

served increase in hardness with coating thickness has been attributed to the increase in internal stress and decreased effect of substrate [6].

Some of the widely used methods to synthesize these TiN and CrN or other nitride coatings are, reactive or non-reactive magnetron sputtering [7], ion beam enhanced deposition [8], plasma assisted chemical vapour deposition [2], inductively coupled plasma assisted evaporation [9], plasma nitriding [10] etc. Although a high temperature process, thermal gas phase nitridation is often used to synthesize coatings [11–13]. This method has the advantages of being a non-line of sight, relatively less expensive and suitable for larger components. Active gases like nitrogen or ammonia is used for this purpose. In the present study, thermal gas phase nitridation of Ti and Cr specimens was carried out by exposing them to ammonia gas at high temperatures. Optimum nitriding temperatures were obtained by carrying out these nitridation experiments in a locally built TGA–MS facility [14] and investigating the process by in situ dynamic mass spectrometry of gaseous products while the weight gain of the specimen was obtained from TG. The nitrided samples were characterized by powder X-ray diffraction (PXRD), grazing incidence XRD (GIXRD), scanning electron microscopy (SEM), scanning probe microscopy (SPM) and microhardness tester.

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2. Experimental procedure

Pure specimens of Ti and Cr ($\sim 10 \times 10 \times 1$ mm) were metallographically polished up to 800 grit emery paper and ultrasonically cleaned in acetone prior to nitridation. The experimental TGA–MS system is provided with a mass flow controller based gas delivery to facilitate specimen exposures in a desired gas mixture of required composition. Prior to sample heating, the system was evacuated and purged with high pure Ar several times to minimize oxygen partial pressure. This was done to avoid surface oxidation. Initially the specimens were heated to a temperature up to 1200 °C by a linear temperature programme (ramp) in pure NH₃ (flow rate = 15 sccm) atmosphere. As a protective cover gas for the TG balance, high pure Ar flow (flow rate = 45 sccm) was also maintained in all our experiments. Continuous monitoring of weight gain by TG and decrease in concentration of NH₃ and the corresponding formation of nascent nitrogen and hydrogen by dynamic mass spectrometry were carried out. These runs were primarily used to obtain cracking temperature of NH₃ and temperature pertaining to maximum rate of nitridation. From this data, the optimum nitridation temperatures for Ti and Cr are found to be 1100 and 900 °C, respectively. Subsequently, a set of specimens were isothermally exposed to NH₃ atmosphere for different durations (5, 10, 20 h) at these optimized temperatures. The phase identification of the nitrided layers was carried out by PXRD and GIXRD (STOE X-ray Powder Diffractometer). The surface and cross sectional morphology of the specimens was investigated using SEM (Philips GX 30 ESEM). The surface topography was observed using SPM (Model: Solver Pro, NTI-Europe). Microhardness measurements were made at the surface as well as along the cross section using Vicker's hardness indenter (Leitz Wetzler, Germany).

3. Results and discussion

3.1. TGA–MS

A typical TGA–MS plot of nitridation of Ti by subjecting it to a linear heating program up to 1200 °C in NH₃ gas is shown in Fig. 1. The mass spectrometry data in the figure shows that the cracking of NH₃ starts around 600 °C as seen from the drop in partial pressure of NH₃ and the corresponding increase in the partial pressures of N, N₂ and H₂. This suggests the feasibility for onset of nitridation even at 600 °C. However, above 600 °C only a slow increase in weight is observed due to slow kinetics. Whereas, a rapid gain in weight was observed at temperatures above 1000 °C with a maximum rate at around 1100 °C. This was chosen as the optimum temperature for prolonged exposures. The overall

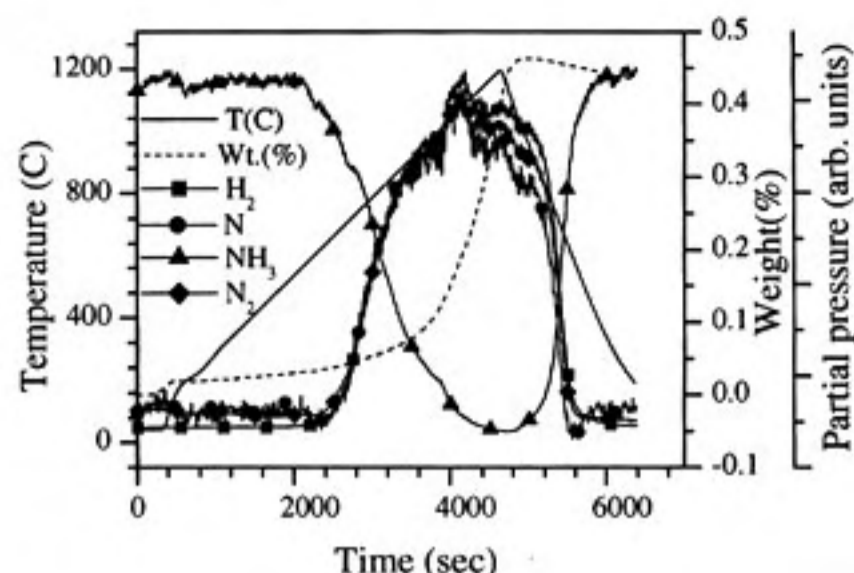


Fig. 1. TGA–MS spectra of nitridation of Ti in NH₃ gas exposed to linear heating up to 1200 °C.

weight gain for the 5 and 10 h treated Ti specimens was found to be 1.44% and 1.82%, respectively.

Similarly, Fig. 2 shows a typical TGA–MS spectra of pure Cr nitrided in ammonia up to 1100 °C. In this case, the cracking of NH₃ starts only above 700 °C. The cracking rate and the weight gain were maximum at temperature around 900 °C, which was taken as the optimum temperature for long exposure of 20 h. The commencement of NH₃ cracking at lower temperature in the case of Ti compared to Cr indicates the influence of surface catalytic activity of Ti. But the actual rate of Ti–N reaction peaks at higher temperature (i.e. 1100 °C), indicating higher activation energy required for this reaction. Though the onset temperature (i.e. 700 °C) of ammonia cracking is higher in the case of Cr, the rate of reaction peaks at around 900 °C, which is much less compared to Ti. This also shows the nitridation by this method may not be feasible for Ti and Cr below 600 and 700 °C, respectively unless pre-cracking mechanism or other catalytic material is used. However, Russell et al. [13] have claimed the formation of thin Cr₂N/CrN layer

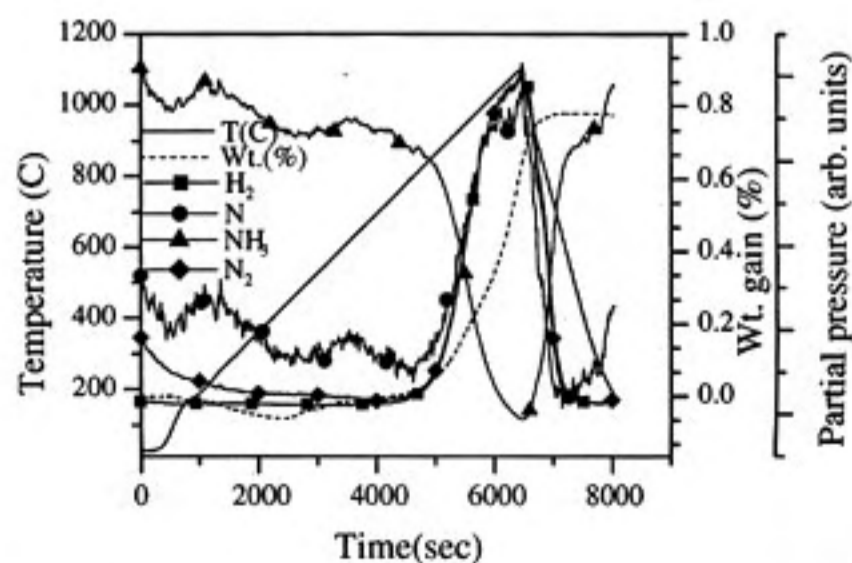


Fig. 2. TGA–MS spectra of nitridation of Cr in NH₃ gas exposed to linear heating up to 1100 °C.

even at 600 °C. The overall weight gain of our 20 h nitrided Cr specimen was found to be ~1.74%.

3.2. PXRD and GIXRD

Fig. 3a and b show the diffraction patterns of Ti nitrided at 1100 °C for 10 h, obtained by PXRD and GIXRD, respectively. All GIXRD patterns were taken at 1° incidence angle. From Fig. 3a it is evident that the nitrided layer constitute predominantly of TiN (PCPDF: 38-1420) with a noticeable contribution from Ti₂N (PCPDF: 17-0386). It is also seen that TiN has a preferred orientation in (111) plane. But GIXRD pattern of Fig. 3b, which gives more information on the sub-micron surface layer, shows the phase is almost pure TiN except for a very small peak corresponding to Ti₂N at $2\theta = 39.274$. These observations indicate that the specimen surface, where the availability of nascent nitrogen is maximum, is nitrogen rich TiN and towards interior region, the nitrogen deficiency is evident from the increase in concentration of Ti₂N. Prolonged nitridation could result in thicker stoichiometric TiN layer by the diffusion of nitrogen through the nitride matrix. Fig. 3c shows the GIXRD pattern of Ti nitrided for 5 h at 1100 °C. This also shows noticeable presence of Ti₂N along with TiN. When comparing Fig. 3b and c, one could conclude that as a function of nitridation time, the TiN phase grows at the expense of Ti₂N. Moreover, no trace of unreacted Ti was observed in the nitrided layer.

Fig. 4a and b show the diffraction patterns of Cr nitrided at 900 °C for 20 h, obtained by PXRD and GIXRD, respectively. The PXRD pattern (Fig. 4a) shows it is a mixture of CrN (PCPDF: 11-0065) and Cr₂N (PCPDF: 35-0803), but the GIXRD (Fig. 4b) indicates the surface to be of pure CrN phase. Absence of peaks corresponding to Cr (at $\theta = 44.39$, PCPDF: 6-0694) indicates that no unreacted Cr was left at the surface, which is a prerequisite for better corrosion resistance. Also it is

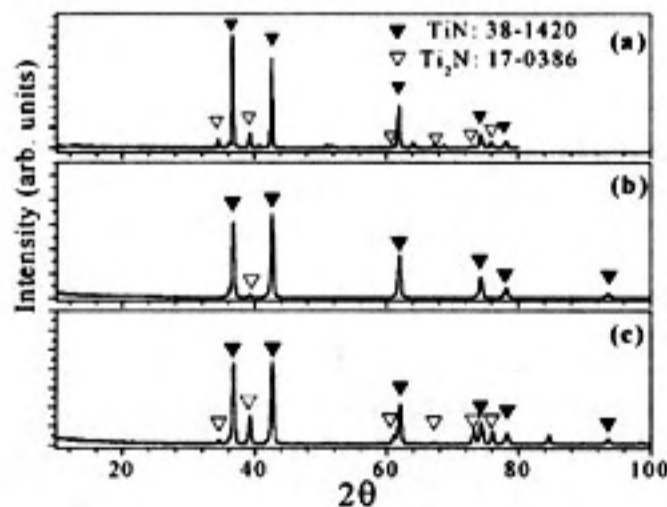


Fig. 3. (a) XRD pattern of Ti nitrided at 1100 °C for 10 h, (b) GIXRD patterns of Ti nitrided at 1100 °C for 10 h and (c) GIXRD pattern of Ti nitrided at 1100 °C for 5 h.

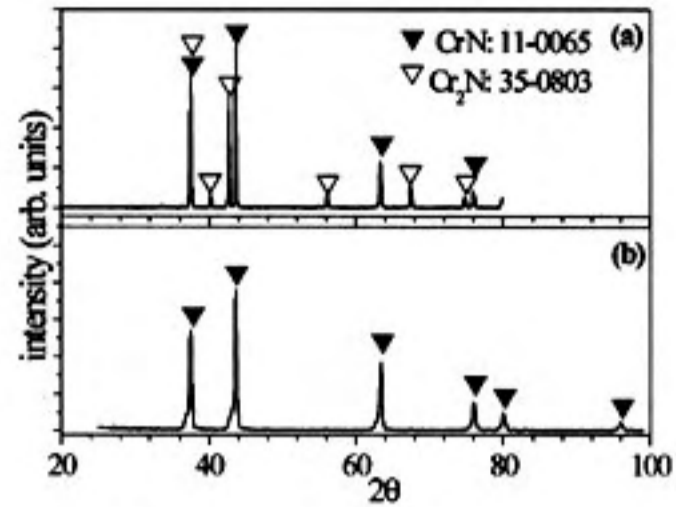


Fig. 4. (a) PXRD pattern of Cr nitrided at 900 °C for 20 h and GIXRD patterns of Cr nitrided at 900 °C for 20 h.

noticed that there is no Cr₂O₃ present in the nitride, though it is considered difficult to circumvent oxide formation during high temperature processes [15]. It could be due to the presence of high reducing nascent hydrogen atmosphere at the surface resulting in the instability of any oxide if formed in the case of both Ti and Cr.

3.3. SEM

Scanning electron microscopy was employed to understand the surface morphology and cross sectional microstructure of the nitrided specimens. Fig. 5a and b show the SEM images obtained in the back scattered electron mode of Ti specimens nitrided at 1100 °C for 5 and 10 h, respectively. The 5 h nitrided specimen shows smaller grain size and a porous morphology. Whereas, the 10 h treated sample shows larger grains (2–4 μm) and relatively denser surface.

The cross sectional microstructure of the 10 h nitrided specimen was also studied by SEM and is shown in Fig. 6. The clearly visible nitrided case is almost parallel to the sample surface and is about 80 μm thick (refer also Fig. 11a). Though it is a two phase nitride layer, as evident from XRD, there is no colour contrast observed in this layer.

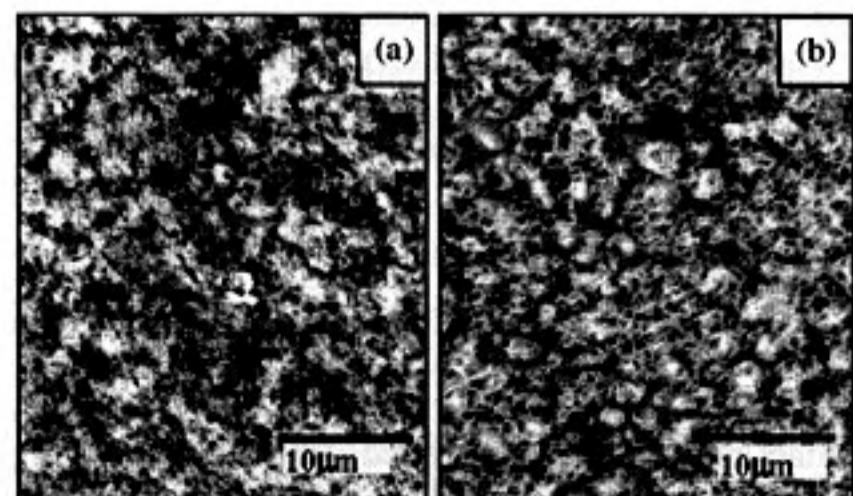


Fig. 5. SEM micrograph of Ti nitrided at 1100 °C for (a) 5 h and (b) 10 h.

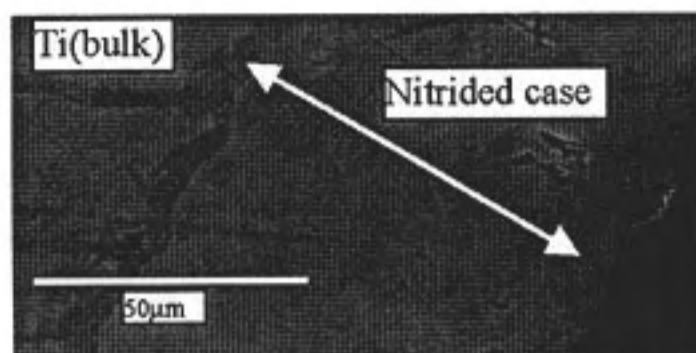


Fig. 6. Cross sectional SEM image of Ti nitrided at 1100 °C for 10 h.

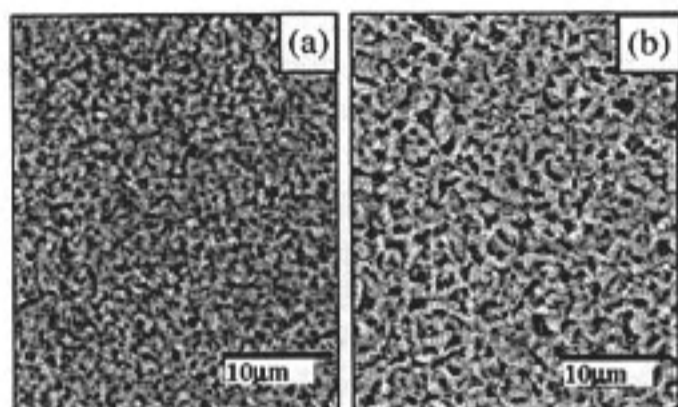


Fig. 7. SEM micrograph of Cr nitrided (a) to 1100 °C ramp and (b) at 900 °C for 20 h.

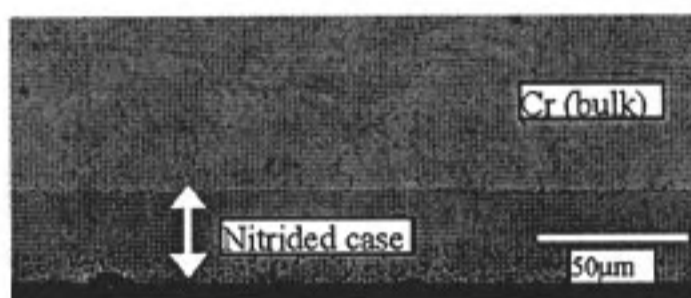


Fig. 8. Cross sectional SEM image of Cr nitrided at 900 °C for 20 h.

Fig. 7a and b show the surface morphology of nitrided Cr samples. The specimen, which was ramped to 1100 °C (corresponding to Fig. 2) showed grains with sizes nearly 0.5 μm (Fig. 7a), while the specimen nitrided at 900 °C for 20 h showed considerable grain growth with grains as big as 2–3 μm (Fig. 7b).

Fig. 8 shows the cross sectional microstructure of Cr nitrided at 900 °C for 20 h with a very clear contrast between the bulk Cr and the nitrided case.

The nitride layer is about 35 μm thick (refer also Fig. 11b) and it is observed that this layer is more denser towards the metal–metal nitride interface.

3.4. SPM

In order to study the surface topography, growth and roughness of the nitrided layers, scanning probe microscopy was employed. The SPM was operated in the semi-contact mode and the measured signal was height. Fig. 9a and b show the 3D surface image of Ti nitrided at 1100 °C for 5 and 10 h, respectively. Average surface roughness and the grain size were calculated from the

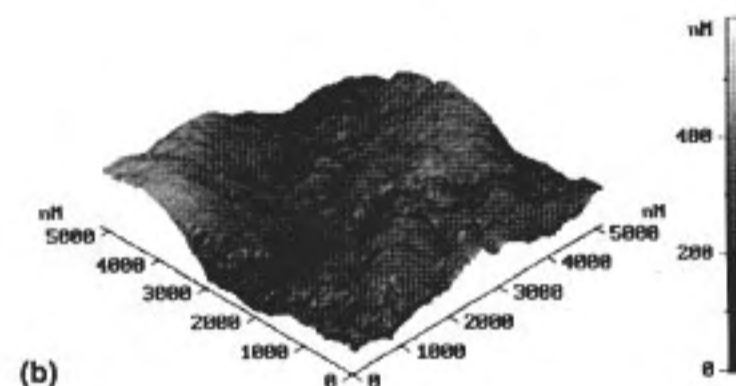
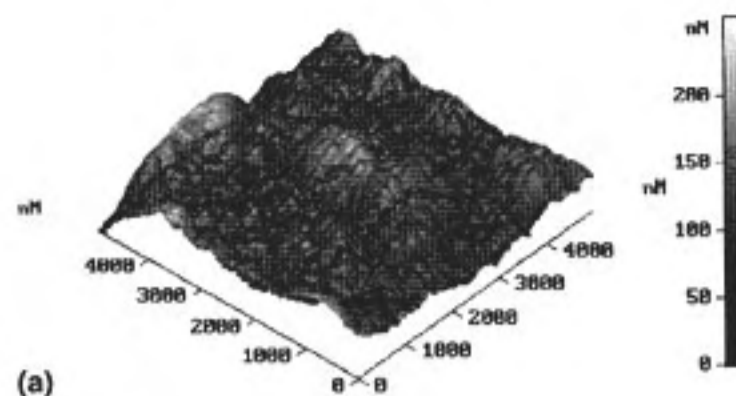


Fig. 9. 3D AFM surface image of Ti samples nitrided at 1100 °C for (a) 5 h and (b) 10 h.

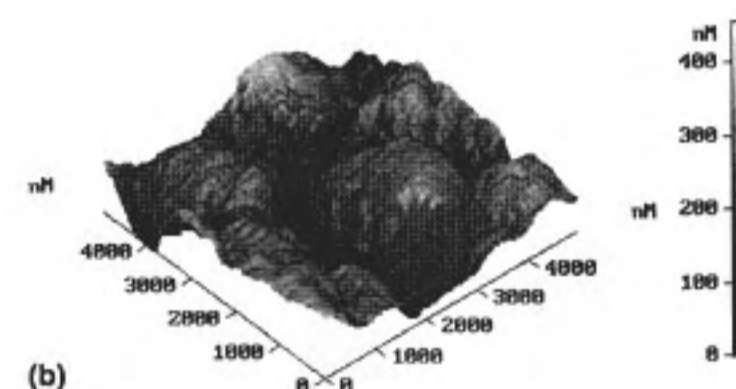
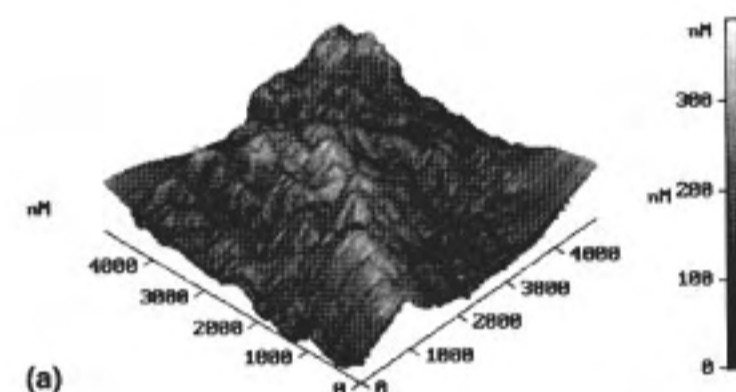


Fig. 10. 3D AFM surface image of Cr samples nitrided (a) to 1100 °C ramp and (b) isothermally at 900 °C for 20 h.

in-built software. It is observed that there is an increase in roughness as well as grain size with nitridation time. The roughness values were 32 and 108 nm for samples nitrided for 5 and 10 h respectively. The average grain size increased from 133 to 350 nm in the corresponding samples. The AFM topography (Fig. 9a and b) shows that grains observed in SEM (Fig. 5a and b) were actually agglomerates of smaller grains.

Fig. 10a and b show the 3D surface image of Cr nitrided by linear heating to 1100 °C and isothermally treated at 900 °C for 20 h, respectively. The average roughness values were measured to be 56 and 79 nm,

respectively and the corresponding grain sizes were calculated to be 152 and 270 nm. The 2–3 μm particles seen in Fig. 10b are in fact coalescing smaller grains of size ~ 250 nm.

3.5. Microhardness measurements

Microhardness measurements at the surface as well as along the cross sections were carried out using a Vicker's hardness tester with 50 g load. The hardness measurements at the surface did not yield consistent values due to surface roughness and high hardness. However, the hardness profile along the cross section was measured precisely and it is shown in Fig. 11. The hardness values of nitrided Ti layer are plotted against distance from the surface in Fig 11a. In this case we could not make measurements below 15 μm from the surface but the hardness profile could be extrapolated and found to be about 2000 kg/mm^2 at the surface and the hardness value approaches the bulk value above 80 μm from the surface. This matches well with the SEM case thickness. Though the hardness value of TiN vary substantially under different coating conditions, the literature value falls between 1700 and 2500 HV [2,6] and the measured value is well within this range. The lowering of hardness with depth (Fig. 11) could be due to the presence of unreacted Ti in the case. However, absence of any Ti peak in PXRD indicates their presence is only beyond the X-ray penetration depth (10–15 μm) and not at the surface. So one could conclude that the inner nitride layers might contain some unreacted Ti as well, whereas, the surface contains pure nitride. This is true in the case of Cr also. The Fig. 11b shows similar hardness profile for the CrN layer. The hardness values are higher compared to the TiN layer and if extrapolated to the surface, it could be well above 2400 kg/mm^2 and matches well with the reported data [6]. The hardness versus depth data cor-

roborate well with the thickness of nitride layers observed in cross sectional SEM.

4. Conclusion

Gas phase nitridation of Ti and Cr was achieved by exposing them to NH_3 atmosphere at optimized temperatures. The nitrided specimens were characterized by PXRD and GIXRD. The nitrided Ti layer is predominantly of TiN with a noticeable contribution of Ti_2N . The submicron surface layer is made up of almost pure TiN. In the case of Cr, the nitride layer is an even mixture of CrN and Cr_2N with the outermost surface layer constituted only by CrN. The thickness of nitrided layers are found to be about 80 and 35 μm in Ti and Cr, respectively. Absence of pristine Ti and Cr indicates formation of uniform nitride layer covering the entire sample surface, which is a prerequisite for better tribological and corrosion properties. The presence of hydrogen as a cracking product and high processing temperature ensures the reduction of any undesired oxides in the nitrided layers. SEM images of these samples show grain growth and densification of the nitrided layer with increase in nitridation time. The achieved thickness of the nitrided layer is quite high compared to many other synthesis methods. SPM observations have shown increase in the average surface roughness with nitridation time and grain growth by coalescence of smaller grains. Microhardness values of nitrided Ti and Cr are found to be about 2000 and 2400 kg/mm^2 , respectively and matches well with the literature values. This method of nitridation could be duplicated, without any modification, to Ti or Cr plated structural materials and studies on Cr plated steel are underway. Efforts are being made to reduce the process temperature by using NH_3 cracking catalyst or using pre-cracked ammonia. The reduction in temperature is anticipated to give fine grained and nanostructured coating which are reported to have superior properties.

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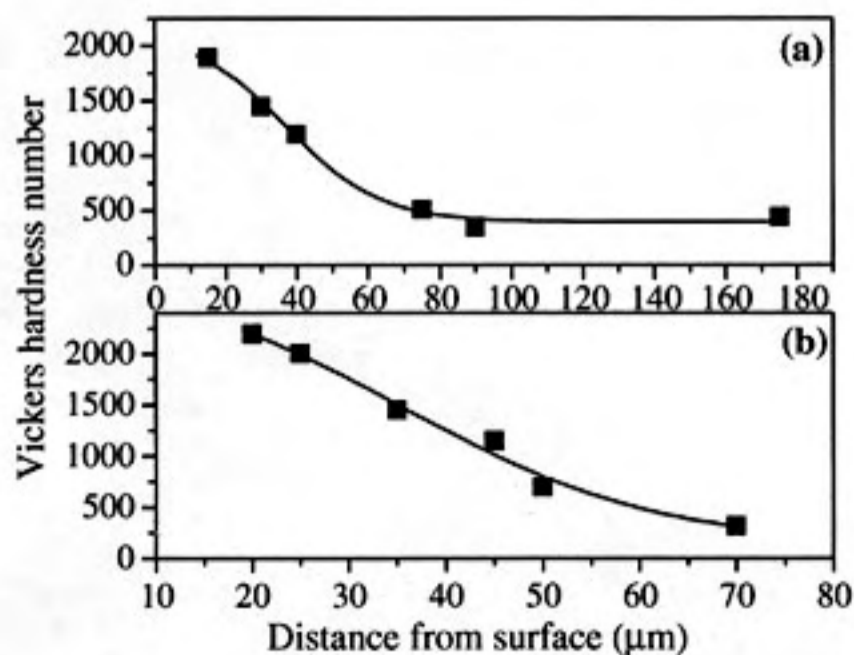


Fig. 11. Cross sectional hardness profile of (a) Ti nitrided at 1100 $^{\circ}\text{C}$ for 10 h and (b) Cr nitrided at 900 $^{\circ}\text{C}$ for 20 h.

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