



GAS PHASE NITRIDATION OF CHROMIUM PLATED STAINLESS STEEL

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ABSTRACT

To enhance the high temperature hardness and wear resistance of chrome plated 316 LN austenitic stainless steel, gas phase nitriding in a home-assembled TGA-MS system has been investigated. The sluggish diffusion kinetics of nitrogen in chromium and the presence of a thin oxide layer at the surface are the major constraints towards adopting a low temperature gas nitriding process. This paper attempts to bring out a detailed correlation of the effect of nitriding environment, ammonia dissociation rate, substrate temperature and catalytic role of nickel layer, on the nitriding characteristics. XRD, SEM and AFM investigations unambiguously reveal the morphology and the distribution of CrN and Cr₂N phases formed.

Key-words: Chrome plating, gas nitriding, Chromium nitride, texturing, AFM

1.0 INTRODUCTION

Hard chrome plating has been a widely adopted practice for surface hardening of materials for several applications in automotive, heavy equipment, aerospace and other engineering sectors. The relative ease of obtaining uniform coatings over large components and the low costs have favored their large-scale industrial adaptability. Although chrome plating can result in a hardness of about 800-1000 VHN at room temperature, they suffer from poor hot-hardness. Also the room temperature hardness is drastically reduced after elevated temperature exposure even for short durations [1]. These constraints restrict the application of chrome plated steels for elevated temperature service conditions. Also, several through-thickness microcracks are often observed in the chromium case of the as-plated steels [2]. The presence of such cracks can limit the wear resistance under aggressive conditions.

CrN has been reported to exhibit good hot hardness properties and thereby offers interesting possibilities for engineering applications [3]. However, the large difference in the thermal expansion coefficient between CrN and steel, leads to the build up of very high residual stresses at the interface. This can result in early delamination of the hard nitrides during elevated temperature service and thermal fatigue conditions, limiting the life of such coatings on steel substrates.

Nitriding of chromium plated steels is therefore a potential alternative for elevated temperature applications. The lack of a sharp transition interface as a result of the formation of a gradient nitride microstructure by diffusion nitriding of chromium at the surface aids in better stress accommodation. Also, chromium has a thermal expansion coefficient in between that of the austenitic steel and the chromium nitride. Hence, the presence of un-nitrided chromium sandwiching between the nitride case and the steel results in enhanced adhesion, capable of

withstanding the induced thermal stresses. Apart from improving the room and elevated temperature wear resistance, chromium nitride is also reported to have better corrosion resistance in acidic environments compared to chromium plated layer [4].

Although, gas nitriding is a well established technique mainly for steel components [5,6], nitriding of chromium necessitates careful optimization of several parameters. The high affinity of chromium to oxygen, results in the presence of a thin adherent surface oxide layer on the chromium plated steel. This acts as a diffusion barrier to the transport of nitrogen and poses a major constraint in nitriding of chromium. In-situ reduction of the chromium oxide layer is therefore essential prior to nitriding. This is also the reason for gas nitriding to be done preferentially in a reducing atmosphere particularly for such oxide forming substrates. Further the slow diffusion kinetics of nitrogen in chromium, demand high nitriding temperatures to achieve the required case thickness in reasonable time period. The need for such high gas nitriding temperatures for chromium plated steel, can however result in significant distortion of large components or sensitization of steel if exposed in that temperature range. Also, once a thin nitride layer is formed, it acts as a diffusion barrier reducing the nitriding kinetics further.

Nitriding of chromium is reported to result in a gradient microstructure with a CrN case at the surface, CrN/Cr₂N layer beneath and a Cr₂N/Cr layer close to matrix [7]. Such a microstructure results in a continuous gradient in microhardness and physical properties, leading to improved thermal stress accommodation capabilities. Buijnsters et al., have suggested that Cr₂N phase is the first to form on nitriding chromium and that subsequent nitridation of this phase leads to formation of CrN layer at the surface [8]. It is known in general that nitriding of chromium occurs only at temperatures higher than about 600°C. Nitridation at temperatures between 600 – 700 °C was reported to form only a mixture of Cr and Cr₂N [9]. However, at higher temperatures (700 – 1050 °C) the formation of the Cr₂N and CrN phases has been observed. Above 1050 °C, destabilisation of the CrN phase leads to its dissociation resulting only in the single Cr₂N phase at the surface. It has also been observed by Taguchi et al., that the formation of a two-phase structure with Cr₂N and CrN results in a low current density in the anodic polarisation measurement and shows improved corrosion resistance in 1 kmol m⁻³ H₂SO₄ at 100 °C [10]. Further, it has been observed that with increasing fraction of CrN at the surface, the corrosion resistance improves. The present study aims to investigate several key factors like, surface catalytic activity, role of reducing environment, substrate temperature etc., on the nitriding kinetics and morphology, with an objective to optimize the key parameters and to innovate a low temperature gas nitriding process for chromium plated steels.

2.0 EXPERIMENTAL PROCEDURES

Metallographically polished ASTM type 316LN austenitic stainless steels were electrolytically plated with a chromium layer of approximately 100 - 200 microns. The gas phase nitriding experiments were carried out on specimens of size 10 x 10 x 3 mm, in a home-assembled Thermogravimetric Analyser-Mass Spectrometry (TGA-MS) system [11]. 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. Nitriding was done in three different environments namely, NH₃, 60 % NH₃-H₂, and 10% NH₃ - H₂. Prior to sample heating, the system was evacuated and purged with high pure Ar several times to minimize oxygen partial pressure. As a protective cover gas for the TG balance, high pure Ar flow (flow rate = 45 sccm) was also maintained. 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 to arrive at optimum conditions for subsequent extended duration isothermal exposures. The specimen weight change and the change in the concentration of NH₃, H₂ and nascent nitrogen were continuously monitored. From the mass spectrometry data on dissociation of NH₃ and formation of nascent nitrogen, the cracking temperature of ammonia and the

optimum isothermal temperatures for subsequent nitriding runs were derived. Nitriding was studied at three different temperatures namely, 700, 800 and 900 °C. For sake of comparison, nitriding of pure chromium and titanium sheet metals were also investigated.

The microstructures of the as-nitrided surface, as well as the cross-section of the specimens were investigated using a scanning electron microscope (Philips GX 30 ESEM). The phases formed at the surface on Nitriding were characterized using a Powder X-ray Diffraction (PXRD) and Glancing Incidence XRD (GIXRD) (STOE X-ray powder diffractometer). Microhardness measurements were made at the surface as well as along the cross-section using a Vicker's hardness indenter (Leitz Wezzler, Germany). Surface topography was observed using Atomic Force Microscope (Solver Pro, NTI-Europe, The Netherlands).

3.0 RESULTS AND DISCUSSIONS

3.1.1 Effect of Surface Activity

A typical TGA-MS plot obtained on nitriding pure Ti and Cr specimens subjected to a linear heating program up to 1200 and 1100 °C respectively, at a heating rate of 10C/min., in a 100% NH₃ environment is shown in Fig.1. The ammonia cracking temperature is found to be strongly dependent on the specimen surface. The mass spectrometry data suggests, by way of observable decrease in concentration of NH₃, that ammonia cracking starts around 600 °C for Ti, while the same is above 700 °C for Cr. The difference in the ammonia cracking temperature of Cr and Ti surfaces can be attributed to the differential catalytic effects. Thus use of suitable catalysts could be an interesting possibility to reduce the feasibility temperature for nitriding. Nickel and nickel oxide are also known to be good catalysts for ammonia dissociation. Hence, the effect of a thin nickel flash coating on Cr-plated stainless steel was also investigated in the present study.

3.1.2 Ni coating on Cr-plated steel

TGA-MS plot obtained on nitriding of chromium plated steel shows a small loss in weight of specimen around 400 – 500 °C. This is attributed to the reduction of the surface chromium oxide film by hydrogen ion radicals formed by the dissociation of ammonia in the nitriding environment. This is further confirmed by a corresponding increase in water signal observed by mass spectrometry. Although, considerable decrease in ammonia concentration is seen only at temperature above 700°C on Cr, a measurable increase in partial pressure of hydrogen ions are observed even at temperatures as low as 350 °C. (It is easier to observe even a slight increase in H₂ and N₂ partial pressures by mass spectrometry as their initial concentrations in the system is very low. In contrast, the initial concentration of NH₃ is considerably high and hence a corresponding small reduction is difficult to observe). It may be noted that reduction of this oxide layer, which otherwise acts as a diffusion barrier is essential for enhancing the kinetics of nitriding chromium plated steels. While the peak reduction temperature of the oxide is about 500 °C for the as-plated steel, the same is about 420°C for a nickel coated Cr-plated steel. This decrease could again be ascribed to the catalytic effect of nickel in aiding the dissociation of ammonia resulting in increased fraction of hydrogen ion radicals at the surface.

SEM micrographs of a chromium plated steel, nitrided at 900 °C, with and without a nickel flash coating at the surface, are shown in Fig.2 (a,b). In the as plated steel specimen nitrided at 900 °C for 10 hours, delamination is observed in a few regions, as can be seen from Fig.2(b). EDAX analysis from the delaminated regions suggest that the exposed surface is only chromium and not iron. This shows that delamination occurs only at the nitride/Cr interface and not at the Cr/Steel interface. In contrast, the nickel plated steel, does not show any delamination as can be seen from Fig 2(a). Also, the nickel film is seen to restructure into localized islands of about 500 nm at the surface subsequent to nitriding (Fig. 3). The darker phase regions in the SEM image

corresponds to CrN, the greyish region represents the Cr₂N and the brighter spots are represented by pure Cr or pure Ni. The presence of such soft nickel phase interspersing between the hard nitrides at the surface may result in the reduced cracking and delamination of the nitride film at the surface. Flash coating of a thin layer of nickel is therefore suggested to be beneficial in nitriding of chromium plated steel to decrease the propensity of surface delamination as well as for the reduction of surface Cr₂O₃ layer.

3.1.3 Effect of nitriding temperature

The typical TG plots obtained on nitriding Cr plated steels at three different temperatures of 700, 800 and 900 °C for 10 hour duration are given in Fig. 4. It can be seen from the figure that the percentage weight gain corresponds to 0.21, 0.31 & 0.51 % on nitriding at 700, 800 and 900°C respectively. This correlates well with the expected increase in nitride case depth with increasing temperature.

Fig 5 (a,b) shows the bulk PXRD and GIXRD patterns of Cr plated stainless steel. The PXRD results show the presence of both CrN and Cr₂N peaks in all the three samples. The ratio of the XRD intensity peaks of CrN to Cr₂N is strongly dependent on the nitriding temperature, increasing from a value of 0.124 at 700 °C to 1.3 at 800 °C and further decreasing to 0.376 on nitriding at 900 °C. With increasing temperature, the extent of ammonia dissociation and hence the nitrogen activity at the surface increases, resulting in an increased tendency for CrN formation. However, once a thin layer of CrN is formed, they act as diffusion barriers for nitrogen diffusion. The rate of nitrogen flux available at the austenite/nitride interface is slower than the incubation period for Cr₂N precipitation. Hence further growth of the case is predominantly consistent of Cr₂N. These two opposing tendencies of nitriding temperature can explain the observed tendency of peaking of the relative CrN fraction at an intermediate temperature of 800 °C. Also, the intensity of the oxide peaks can be seen to reduce with increasing temperature from the PXRD patterns. This could be due to the higher dissociation efficiency of ammonia at higher temperatures resulting in a more reducing atmosphere. This suggests that increasing the hydrogen content of the nitriding gas may result in reducing the oxide phase content even at lower nitriding temperature.

GIXRD patterns show the surface layers are predominantly consist of only the CrN phase although the bulk PXRD patterns show high intensity of the Cr₂N phase. It may be noted that no Cr peaks are observed in the GIXRD patterns, suggesting the complete nitridation of the surface layer. The intensities of the Ni peak are very small in agreement with the thin nickel layer at the surface. The Cr₂O₃ peaks are observed only as the glancing incidence angle is increased from 1° to 6°. This indicates that the oxide phases are present at sub-surface levels. These phases are therefore not expected to be from the surface oxide layer of chromium. Small oxygen impurities in the nitriding gas can result in the formation of such subsurface oxide phases. The increase in reducing capability of the environment with increasing temperature, results in the decrease in oxide phase intensity at higher temperatures. This emphasizes the need for using high purity gas and leak tight, oxygen free nitriding chambers with higher reducing environment for such oxide forming specimens.

Microhardness measurements show a peak hardness at the surface of nearly 2200 VHN (Fig. 6). The 900°C nitrided Cr plated stainless steel specimen shows a nitrided case of about 20 micron, compared to a Cr plating thickness of over 100 microns. The decreasing hardness profile along the nitrided case indicates the decreasing nitrogen concentration profile as we move away from surface. It can be seen that the high temperature exposure during nitriding, results in a significant drop in hardness of electroplated chromium from about 900 VHN to about 250 VHN. This clearly demonstrates the need to nitride the Cr plated specimens for high temperature wear applications.

3.1.4 Texturing Of Nitrided Phase

From theoretical considerations, based on structure factor calculations, $\{111\}$ phase of Cr_2N is expected to be the maximum intensity peak while the $\{300\}$ peak intensity is 15% for a randomly oriented structure. However, from the XRD studies in the present investigation, the $\{300\}$ peaks of Cr_2N is seen to be 15-30 times more intense than its $\{111\}$ phase. This many fold increase clearly suggests a very strong tendency for texturing of the Cr_2N phase on nitriding of chromium. The interplanar spacing of $\{300\}$ plane of the Cr_2N phase is close to that of the $\{200\}$ plane of Cr, resulting in a compressive stress of about 3.67 %. In contrast, the orientation of the Cr_2N $\{111\}$ plane with the $\{100\}$ plane of Cr, would result in a tensile stress of about 4.4 %. Since the precipitation of the nitride phase is expected to result in significant additional tensile stress due to volume misfit considerations, the preferential texture along $\{300\}$ planes of the Cr_2N phase observed in the present study can be understood.

Similarly for CrN the intensity of the $\{111\}$ peak is expected to be about 80% of that of the most intense peak of $\{200\}$ as calculated from structure factor calculations. It can be seen from the Table-I that nitriding at 700 & 800 °C result in a nearly randomly oriented CrN structure at the surface. However, significant tendency for texturing of CrN along $\{111\}$ is observed at 900 °C. Further studies are in progress to understand this phenomenon of preferential texturing on high temperature nitriding.

3.1.5 Influence of hydrogen concentration of nitriding gas

Increasing the hydrogen concentration in the NH_3 carrier gas from 0 % to 40 %, is found to have little effect on the type and morphology of nitride phases formed. However, nitriding with a 10% NH_3 –90% H_2 is found to exhibit little increase in the weight change detected in the TG system, since the nitriding kinetics depends on the availability of the ammonia gas in the environment and is inversely related to H_2 gas concentration. Table II below shows the relative intensity of the XRD peaks between Cr_2O_3 and Cr_2N , as a function of the nitriding environment (0 % and 40% H_2) and the substrate temperature. The oxide peak intensities are very low on nitriding at 900 °C and hence could not be compared. It can be seen from the table that increasing the hydrogen concentration decreases the relative oxide fraction in the nitrided case. The oxide fraction obtained on nitriding at 700 °C with NH_3 -40% H_2 gas is equivalent to that obtained at 800 °C without H_2 gas. Hence an equivalent advantage of about 100 °C is expected by increasing the H_2 concentration by 40 %, from the consideration of oxide phase elimination alone. To optimize between the kinetics of nitriding which reduces with decreasing ammonia concentration in the carrier gas and the oxide phase formation, further studies to optimize the NH_3 concentration in between 10 % to 60 % is under way. The effect of Hydrogen in the nitriding gas mixture can be significantly observed on nitriding at 800°C .

3.1.6 AFM studies of nitrided surface morphology

The surface topography, grain size and roughness of the nitrided layers, were investigated by an scanning probe microscope. The AFM was operated in the semi-contact mode and the measured signal was height. The average roughness as well as the grain size is found to increase with increase in nitriding temperature. The average grain size increases from about 500 nm after nitriding at 700 °C for 10 h to 770 nm on nitriding at 900 °C for 10 h and the corresponding roughness values varied from 165 nm to 212 nm respectively. Fig.7 shows the 3D surface topography of the specimen nitrided at 700 °C for 10 hrs. It is observed that domains of about 1-2 microns as observed in SEM consist of agglomerates of smaller grains of 500 nm. Roughness profiles measured across the grains, also showed the presence of nano-features of dimensions of about 60 nm and about 4-10 nm in height. These could possibly indicate nano-

facetting of the nitride grains, due to localized surface relief phenomenon. Although, such nano-facetting is in general a high energy process and hence not an equilibrium surface morphology, the very high strain effects associated with the formation of nitrides can induce such non-equilibrium nano features.

4.0 CONCLUSIONS

- i) Gas nitriding of chromium plated steels in the temperature range from 700 – 900 °C, results in the formation of CrN and Cr₂N phases. GIXRD results show the complete nitridation of the surface, with a predominantly CrN phase.
- ii) The presence of a thin Ni layer over chromium is seen to aid early and faster reduction of the thin surface chromium oxide layer, as well as to promote adhesion of the nitride layer.
- iii) Role of hydrogen to provide a reducing environment during nitriding to prevent the formation of oxide phases has been illustrated. However, considering the already sluggish kinetics of nitriding chromium, careful optimization of the hydrogen content is essential.
- iv) A preferential strong tendency for texturing of Cr₂N along {300} is observed and is attributed to strain minimization effects. In contrast, a tendency for CrN texturing is seen only on nitriding at 900 °C and the same is absent on lower temperature nitriding.
- v) SPM investigation show that each microscopic feature observed in SEM is in reality constituted of nano grains of the nitride phase. Also features to suggest nano-facetting of the nitride phases of about 60 nm in width and 4-10 nm in height have been observed and are attributed to surface strain relief phenomenon.

5. REFERENCES

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TABLES

Table – I : Analysis of PXRD pattern showing relative tendency of texturing of CrN and CrN as function of Nitriding temperature

100 % NH ₃	700 °C	800 °C	900 °C
Cr ₂ N {300}/ {111}	15.2	13.8	31.8
CrN {111}/ {2000}	0.814	0.71	1.666

Table II : Relative XRD peak intensities of nitride and chromium oxide phases

Cr ₂ N/ Cr ₂ O ₃	700 °C	800 °C
	C	C
100 % NH ₃	8.3	7.4
60 % NH ₃	7.42	35.96

FIGURES

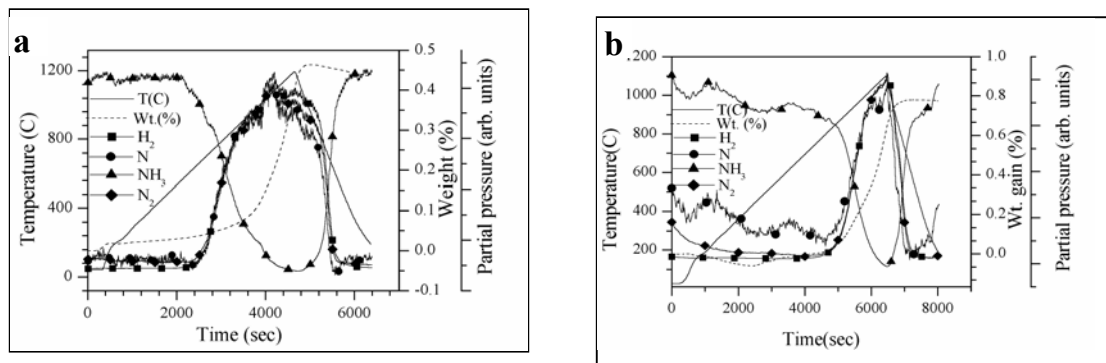


Fig 1. Typical TGA-MS spectra of nitridation in ramp mode of (a) pure titanium and (b) pure chromium

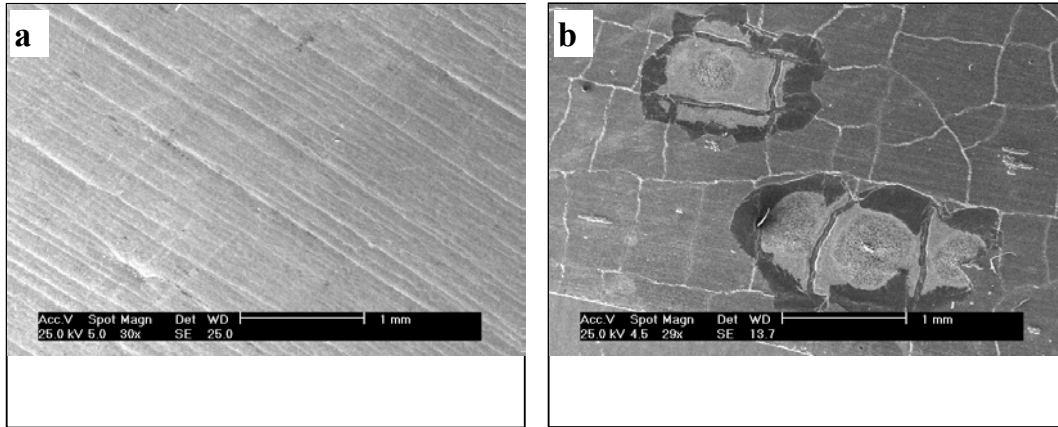


Fig. 2. Surface SEM micrographs of Cr – plated steels (a) with Ni flash coating and (b) without Ni

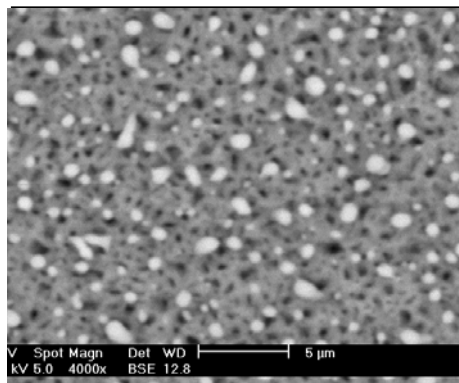


Fig. 3. Typical SEM micrograph of specimen nitrided at 900 °C showing Ni as bright phases.

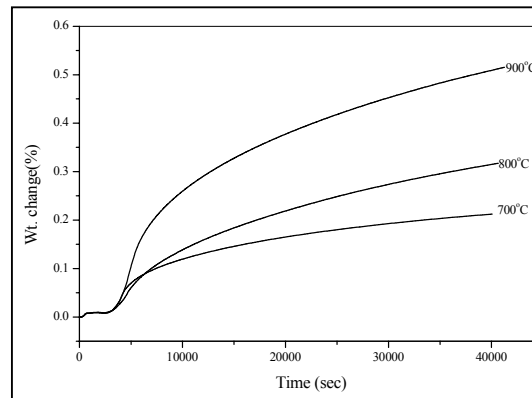


Fig. 4. TGA weight gain plots for specimens nitrided at three different temperatures.

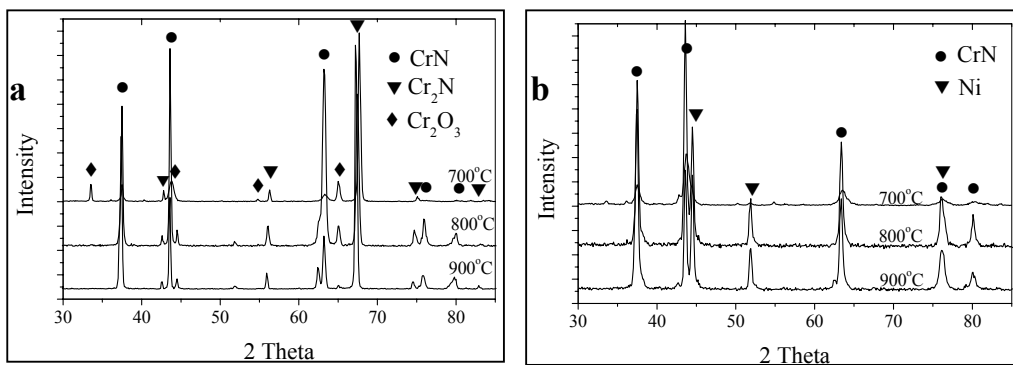


Fig. 5.(a) PXR and (b) GIXRD patterns of specimens nitrided at three different

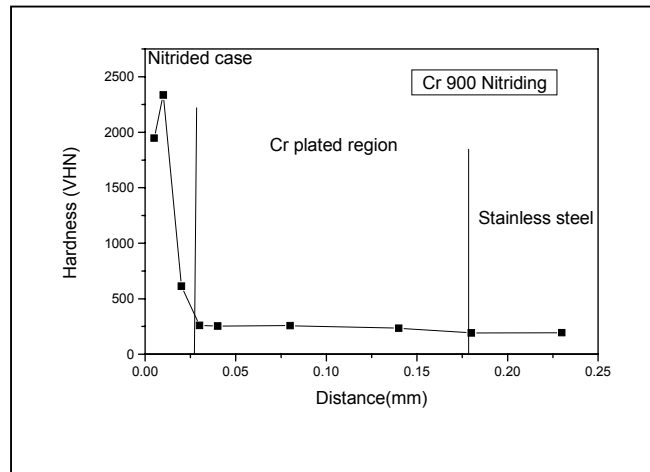


Fig.6 : Cross-sectional microhardness profile along a specimen nitrided at 900 ° C

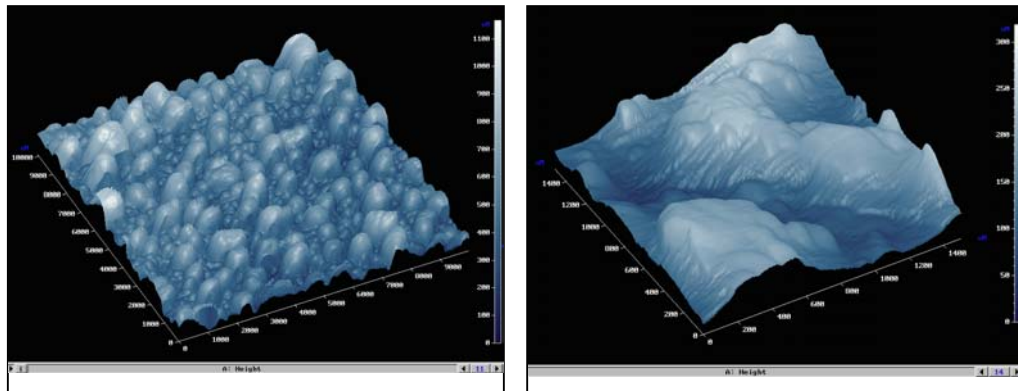


Fig. 7. The AFM topography of nitrided specimens at (a) 700 °C (b) 800 °C