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# Ion-Beam Nitriding of Steels

Joshua Salik  
*Lewis Research Center*  
*Cleveland, Ohio*

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## ION-BEAM NITRIDING OF STEELS

Joshua Salik<sup>1</sup>  
National Aeronautics and Space Administration  
Lewis Research Center  
Cleveland, Ohio 44135

### SUMMARY

The application of the ion-beam technique to the nitriding of steels is described. Preliminary results indicate that the technique can be successfully applied for this purpose. Some of the structural changes obtained by this technique are similar to those obtained by ion-nitriding. The main difference is the absence of the iron nitride diffraction lines. The dependence of the resultant microhardness on beam voltage for super nitralloy was found to be different from that of 304 stainless steel.

### INTRODUCTION

Nitriding of steel is a well-established surface treatment used extensively in the metal industry. The main purpose of this process is to increase hardness and wear resistance without sacrificing the bulk properties. Traditionally this process has been done at high temperatures (around 540° C) using either molten salt bath or reactive gases.<sup>1</sup> These processes are costly as well as time consuming. This is the reason which led to the development of an alternative process called ion-nitriding. This process is accomplished in a vacuum chamber at a pressure of several torrs of the nitriding gas which is usually a mixture of N<sub>2</sub> and H<sub>2</sub>. A voltage (either rf or negative dc) is applied to the workpiece thus causing a discharge which results in nitriding of the workpiece. Although relatively few studies of this process have been reported<sup>2-6</sup> it has found industrial

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<sup>1</sup>NRC-NASA Research Associate.

application<sup>6</sup> as it decreases the cost and process time (from some 20 to 6 hr) and also allows for lower substrate temperatures during ion-nitriding.

The process described herein, namely nitriding by means of ion beams is different from the ion-nitriding process in several aspects. The ion-beam technique was used extensively for deposition of thin films but was rarely employed for chemical modification of surfaces.<sup>7,8</sup> Here preliminary results obtained upon applying it to the nitriding of steels are reported.

#### Some Features of the Ion-Beam Nitriding Process

The process is carried out in a vacuum system sketched in Figure 1 in an  $N_2$  atmosphere at a pressure of  $3 \cdot 10^{-4}$  torr, i.e. four orders of magnitude lower than that employed in ion-nitriding. This low pressure will have a beneficial effect in that the introduction of undesirable impurities into the workpiece will be reduced. This may be of significance since ion-nitriding is usually done in a  $N_2-H_2$  atmosphere. The combination of relatively high  $H_2$  partial pressure with high workpiece temperature may cause diffusion of hydrogen into it with the detrimental result of embrittlement.

Production of ions is done by the use of the ion source rather than by discharge throughout the whole chamber as is the case in ion-nitriding. This may be also significant in reducing the introduction of impurities into the workpiece.

Another advantage of the use of ion source is avoidance of the discharge instability problem often encountered in ion-nitriding.<sup>5,6</sup> This problem is due to the fact that ion-nitriding is done in the region of abnormal glow discharge where voltage and current increase simultaneously thus tending to change into arc discharge. Since arc discharge is concentrated around isolated spots

it can cause overheating, melting and thereby result in damage to the workpiece.

Yet another advantage of the ion beam technique is the ability to control beam voltage and current independently and thus reach optimal conditions. This is not possible in ion-nitriding where voltage and current are inter-dependent at a given pressure.

## MATERIALS

The nitridability of steel depends on its alloy content. Although most steels are capable of yielding iron nitride if exposed to nitrogen at suitable temperatures, the best results are obtained with steels which contain one or more of the nitride-forming alloying elements. Among the common alloying elements the strongest nitride formers are aluminum, chromium, molybdenum and vanadium.<sup>1</sup>

For the present study two types of steel containing different nitride forming elements were selected: Super nitralloy which is a grade specifically manufactured for nitriding in which the nitride forming element is aluminum and 304 stainless steel in which the nitride forming element is chromium.

The nominal compositions of these steels are given in Table II.

## RESULTS AND DISCUSSION

Several techniques were used to characterize the nitrided samples.

### Microscopy

Metallographic cross sections of the two types of steel are presented in Figs. 2 and 3. It is seen in Fig. 3 that in the case of 304 stainless steel the interface between the nitrided layer and the core is sharp and that the nitrided layer is shallow and brittle. This, however, is by no means

unique to the present technique and was reported for steels containing more than 5 wt. percent chromium upon both conventional<sup>9</sup> and ion-nitriding.<sup>10</sup>

Another feature to be noted in these micrographs is the absence of the compound layer usually observed in conventionally<sup>1</sup> and ion-nitrided<sup>10</sup> steels. This may be due to sputtering of this layer by the impinging ions. As can be seen in Fig. 4 the process results in a severely etched surface and it is possible that any compound layer which might have been formed was removed by sputtering.

### X-ray Diffraction

X-ray diffraction patterns obtained from the two types of steel under several conditions are presented in Figs. 5 and 6. Examination of the patterns obtained from super nitralloy (fig. 5) reveals that the (200) diffraction line of  $\alpha$ -Fe at  $2\theta = 65.10^\circ$  is missing in the nitrided sample, indicating that the process causes some structural change in the near-surface layers. The same phenomenon is revealed upon examination of the diffractograms reported by Spalvins<sup>10</sup> for ion-nitrided AISI 4140 steel. In order to check whether this structural change is due to the nitriding reaction or to the bombardment of the workpiece by the ions, another sample of the same material was bombarded with argon rather than nitrogen ions and examined by X-ray diffraction. The diffraction pattern obtained from this sample is presented in Fig. 5(c) and it is seen that none of the lines which appear in the as-received sample are missing. It can thus be concluded that the structural change is due to the nitriding reaction. The same phenomenon is observed in the case of 304 stainless steel (fig. 6) where nitriding results in the disappearance of three of the  $\gamma$ -Fe diffraction lines - the (200) line at  $2\theta = 50.46^\circ$ , the (220) line at  $2\theta = 74.56^\circ$ , and the (311) line at  $2\theta = 90.4^\circ$ .

There is a major difference, however, between the diffraction patterns reported by Spalvins<sup>10</sup> for ion-nitrided AISI 4140 steel and the present results. The diffractograms reported by Saplvins clearly indicate the presence of two iron nitrides –  $\text{Fe}_4\text{N}$  and  $\epsilon\text{-Fe}_{2-3}\text{N}$  whereas no such observaton was made in our case. The reason for this discrepancy probably lies in the absence in our case of the compound layer which was discussed earlier. It is probably this layer which contains the iron nitrides and thus its absence in our case is compatible with the absence of the iron nitride diffraction lines.

#### Microhardness

The microhardness of the nitrided surfaces was measured by means of a Vickers tester with a load of 500 gm. The results obtained for the two types of steel under different conditions are presented in Figs. 7 and 8. It is seen that with increasing processing time the hardness first increases, reaches a maximum and then decreases. The reason for this behavior has not been studied yet.

Another striking feature of the results is the different effect of beam voltage on the surface microhardness attained with the two types of materials. This also is not yet understood.

#### CONCLUSIONS

The main conclusion of this study is that the ion-beam technique can be successfully applied to nitriding of steels.

Some of the structural changes obtained by this technique are similar to those obtained by ion-nitriding. The main difference is the absence of iron nitride diffraction lines.

The dependence of the resultant microhardness on beam voltage was found to be different for the two types of steel used.

## REFERENCES

1. Metals Handbook, vol. 2, 8th edition, American Society for Metals, Metals Park, Ohio, 1964.
2. M. Hudis, J. Appl. Phys. 44 (1973) 1489.
3. B. Edenhofer, Heat Treat. Met. 1 (1974) 23-28; 2 (1974) 59-67.
4. G. G. Tibbets, J. Appl. Phys. 45 (1974) 5072.
5. P. C. Jindal, J. Vac. Sci. Technol. 15 (1978) 313.
6. A. M. Staines and T. Bell, Thin Solid Films 86 (1981) 201.
7. W. J. Moore, S. R. Logan, L. C. Luther, and S. N. Brown in "Ionic Bombardment Theory and Applications," ed. by J. J. Trillat, Gordon and Breach, New York, 1964.
8. C. Weissmantel, G. Reisse, H. J. Erler, F. Henny, K. Bewilogua, U. Eberslack and C. Schuer, Thin Solid Films 63 (1979) 315.
9. B. J. lightfoot and D. H. Jack, Source Book on Nitriding, American Society for Metals, Metals Park, Ohio, 1977, pp. 248-254.
10. T. Spalvins, Thin Solid Films 108 (1983) 157-163.



TABLE I. - COMPARISON OF THE ION-NITRIDING AND ION-BEAM NITRIDING PROCESSES

	Ion-nitriding	Ion-beam nitriding	Advantages
Pressure	Several torrs	$3-10^{-4}$ torr	Lower impurity (mainly hydrogen) introduction
Ion production	Glow discharge	Ion-beam source	Avoidance of discharge instability problems  Lower impurity introduction
Voltage and current control	Voltage and current are interdependent	Voltage and current are independently controllable	Better process control

TABLE II. - COMPOSITION OF WORKPIECE  
MATERIALS

	Super nitralloy	304 Stainless steel
Al	2.06	-----
Cr	.58	18-20
Ni	5.16	8-12
C	.24	0.08 max
Mn	.25	2.00 max
Si	.22	1
Mo	.26	-----
V	.12	-----
P	.005	0.045 max
S	.003	0.03 max
Fe	Balance	Balance

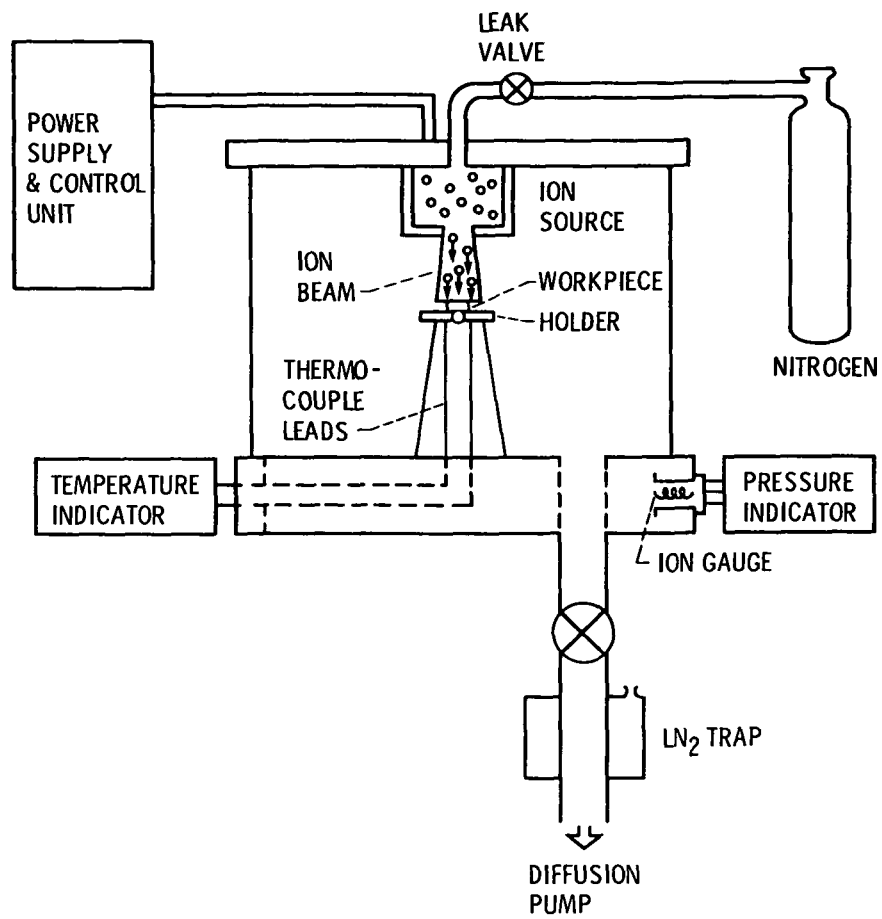


Figure 1. - Schematic of the ion beam system.

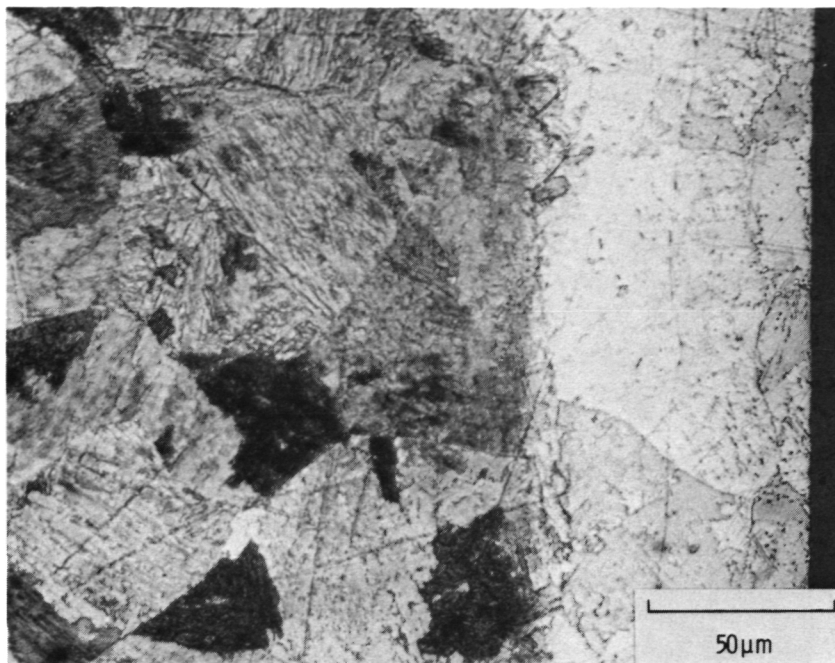


Figure 2. - Metallgraphic cross-section of super nitralloy nitrided with ion beams at 1000 V, 30 mA for 50 minutes.

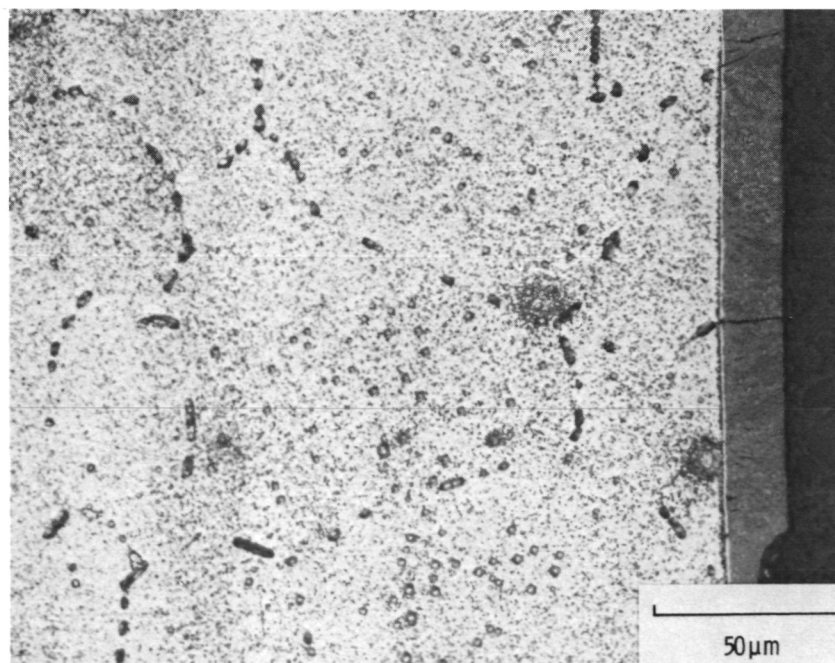


Figure 3. - Metallgraphic cross-section of 304 stainless steel nitrided with ion beams at 1000 V, 30 mA for 50 minutes.

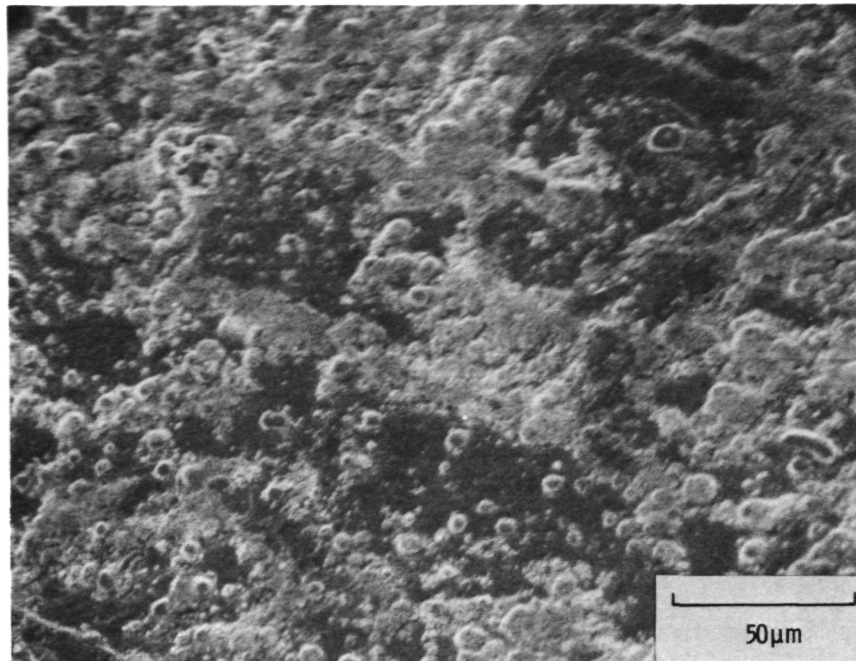


Figure 4. - Surface of super nitralloy nitrided with ion beams at 1000 V, 30 mA for 90 minutes.

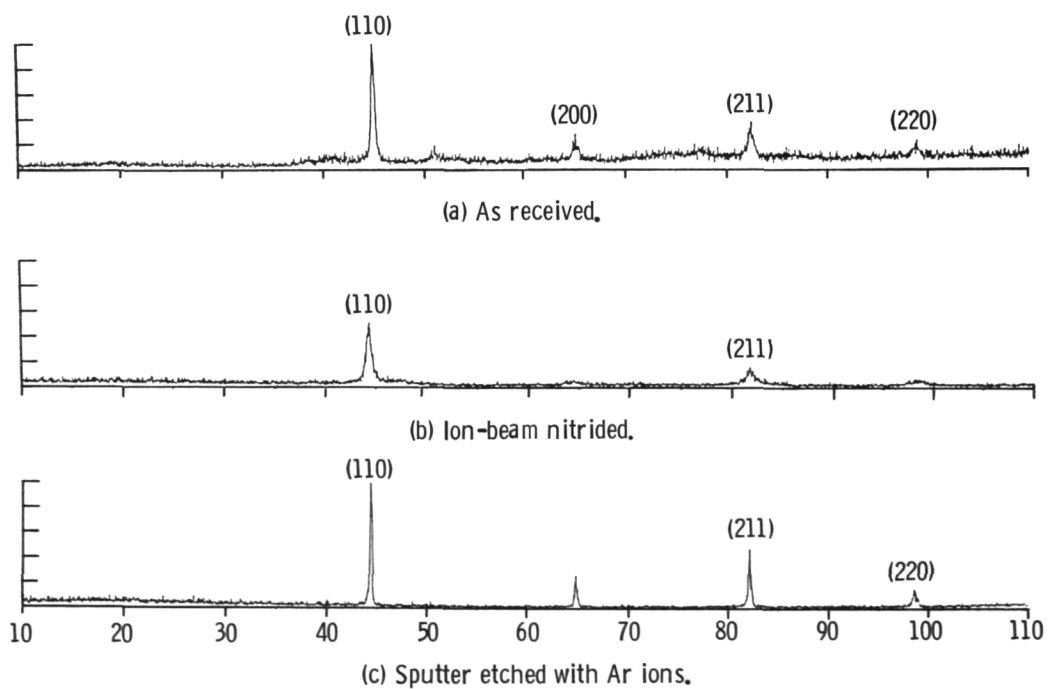


Figure 5. - X-ray diffractograms of super nitralloy.

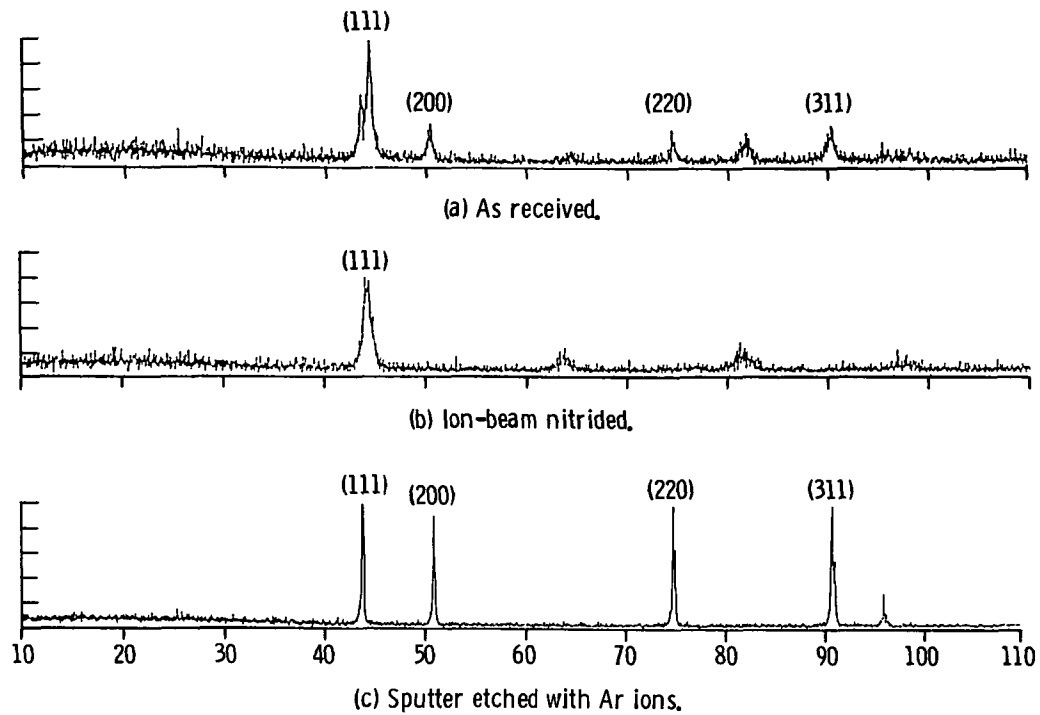


Figure 6. - X-ray diffractograms of 304 stainless steel.

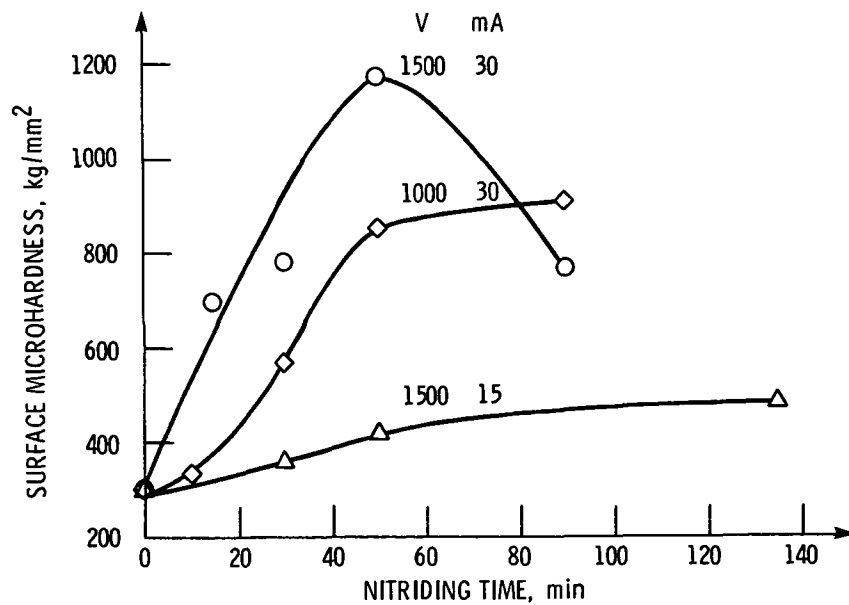


Figure 7. - Microhardness of super nitralloy nitrided by ion beams under various conditions.

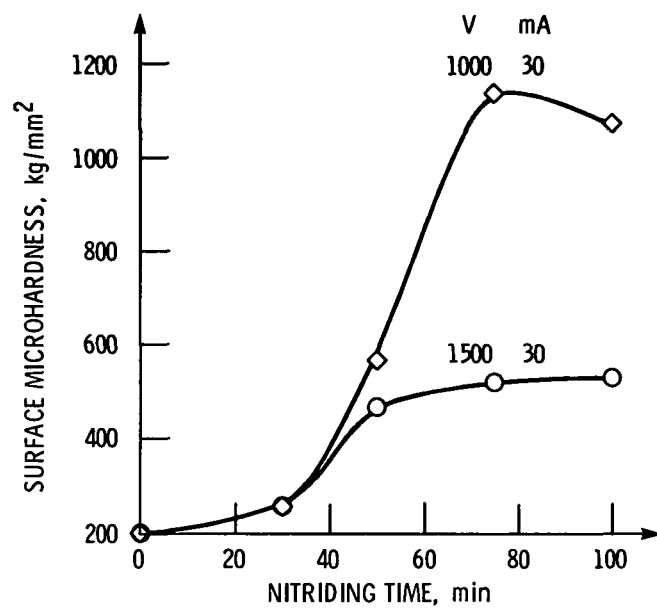


Figure 8. - Microhardness of 304 stainless steel nitrided by ion beams under various conditions.

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