

complete  $\alpha$  to  $\gamma$  transformation has occurred and partly in the deeper ( $>500$  nm) layers where the nitrogen concentration is also low.

The values of the ratio  $F_{\gamma_0}/F_{\gamma_N}$  fractions derived from the fitting procedure were used for semi-qualitative estimation of the character of the interaction between the nitrogen atoms present in the austenitic phases. To do this, we considered two models discussed first in [9].

In model A, we assume that the occupation of each of 6 octahedral sites occurs in the random way, *i.e.* there is no interaction between nitrogen atoms in the nearest neighbour positions of an iron atom. In model B, we assume, following [9], that strong repulsive forces act between both first- and second-nearest nitrogen atoms. So they tend to separate from each other.

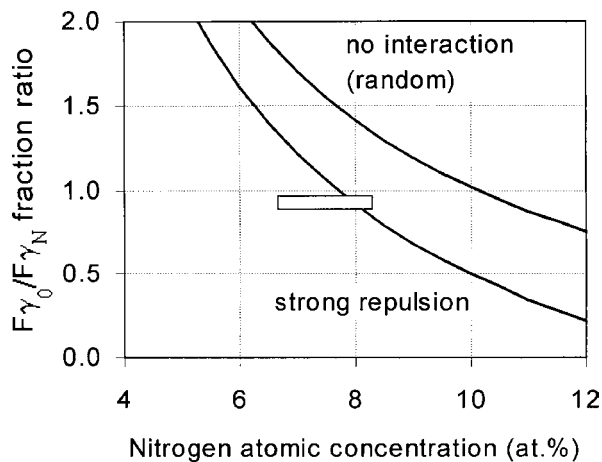


Fig. The box represents value of  $F_{\gamma_0}/F_{\gamma_N}$  fraction ratio observed experimentally in Armco sample after 20 pulses of nitrogen plasma. The horizontal sides represent the range of experimentally measured concentrations, the vertical sides represent the estimated error of the  $F_{\gamma_0}/F_{\gamma_N}$  fraction ratio. The solid lines show theoretical predictions assuming no interaction and strong repulsion between nitrogen atoms in nearest-neighbour positions.

In Figure, we depicted the calculated ratio of  $F_{\gamma_0}/F_{\gamma_N}$  vs. nitrogen atomic concentration in the range of interest, *i.e.* from 4 to 12 at.% for cases A and B using the formulae given in [9]. Range of experimentally measured concentrations is represented by the horizontal sides of the box. The ver-

tical sides represent the estimated error of the experimental  $F_{\gamma_0}/F_{\gamma_N}$  fraction ratio. The position of the box has been established under the following assumptions: Firstly, we assume that all nitrogen atoms introduced into the sample are distributed in fcc structure. Such assumption seems to be justified by the fact that, according to Fe-N phase diagram, the nitrogen does not practically dissolve in the  $\alpha$ -Fe phase. Secondly, we disregard the role of  $\alpha'$  (martensite) and  $\alpha''$  ( $\text{Fe}_{16}\text{N}_2$ ) phases since their fraction identified by CEMS analysis is very small. The length of the box on the nitrogen concentration scale is deduced from the analysis of the nitrogen concentration. As it is seen in Fig., the experimental result is definitely much closer to the data predicted by model B than by model A. Therefore, we conclude that strong repulsion forces act between both, the first and the second-nearest-neighbour nitrogen atoms in the fcc austenitic structure formed as a result of nitriding of pure iron by intense nitrogen plasma pulses.

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## References

- [1]. Blawert C., Mordike B.L., Jirásková Y., Schneeweiss O.: Surf. Eng., **15**, 469 (1999).
- [2]. Özturk O., Williamson D.L.: J. Appl. Phys., **77** (8), 3839 (1995).
- [3]. Blawert C., Mordike B.L., Jirásková Y., Schneeweiss O.: Surf. Coat. Technol., **116-119**, 1891 (1999).
- [4]. Menthe E., Rie K.T., Schultze J.W., Simon S.: Surf. Coat. Technol., **74-75**, 412 (1995).
- [5]. Piekoszewski J., Langner J., Białoskórski J., Kozłowska B., Pochrybniak C., Werner Z., Kopcewicz M., Waliś L., Ciurapiński A.: Nucl. Instrum. Meth. Phys. Res., **B80/81**, 344 (1993).
- [6]. Sartowska B., Piekoszewski J., Waliś L., Szymczyk W., Stanisławski J., Nowicki L., Ratajczak R., Kopcewicz M., Barcz A.: Modification of the near surface layer of carbon steels with intense argon and nitrogen plasma pulses. Vacuum, in press.
- [7]. Gulaiev A.P.: Metallovedenie. Izdatil'estwo "Metallurgiya", Moscow 1977, in Russian.
- [8]. Saker A., Leroy Ch., Michel H., Frantz C.: Mater. Sci. Eng., **A140**, 702 (1991).
- [9]. Oda K., Umezū K., Ino H.: J. Phys. Condens. Matter, **2**, 10147 (1990).

## PRETREATMENT OF AlN CERAMIC SURFACE PRIOR TO DIRECT BONDING WITH COPPER USING ION IMPLANTATION TECHNIQUE

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According to the recent literature, the direct bonding (DB) of ceramic substrates, especially alumin-

ium nitride (AlN) to the conductor is considered as the most promising technique for electronic appli-

cations in high power density packing. In DB technique, the metal is joined immediately to the ceramics with only a very thin transition layer between metal-ceramic interface. In one of the pioneering works [1], it was shown that satisfactory results of AlN-Cu bonding can be achieved by addition of 1-1.5 at.% of oxygen as an active element to AlN-Cu system without intentional modification of surfaces of the joint components. Our previous, preliminary experiments with implanted titanium, iron and oxygen ions into AlN substrates were aimed at the replacement of the conventional process of thermal oxidation. The results obtained suggested that the best shear strength could be expected for relatively low energy of titanium ions [2]. In the present work, more systematic studies on this subject have been undertaken. Titanium, iron and oxygen ions were used at acceleration voltages of 15 and 70 kV in the dose range between  $10^{16}$  and  $10^{18}$  ions/cm<sup>2</sup>. The metallic ions, *i.e.* titanium and iron, were implanted into commercial (Goodfellow) AlN substrates of  $12 \times 3 \times 0.63$  mm<sup>3</sup> with roughness of about  $R_a = 0.1$   $\mu$ m, using MEVVA type TITAN implanter with direct beam, described in detail elsewhere [3]. Oxygen ions were implanted with non-mass separated beam in a home made semi-industrial implanter. In both cases to avoid overheating effects the samples were clamped onto a water-cooled stainless steel plate. The ion current densities were kept be-

- Oxygen implantation gives consistently better results than iron.
- For all elements, the lower energy of (15 kV) implantation leads to shear strength greater by a factor of about 2 than implantation at higher energy (70 kV).
- The best results are attained for titanium implantation with the optimum corresponding to a dose of  $5 \times 10^{16}$  cm<sup>-2</sup>. The shear strength of such joints equal to about 70 kG/cm<sup>2</sup> exceeds by a factor of 5 the value (14 kG/cm<sup>2</sup>) obtained using conventional isothermal oxidation AlN pretreatment process [2].
- For 70 kV, the shear strength is low and shows a weak dependence on ion dose. Searching for the reason of such distinct difference in behaviour of the joint, careful scanning electron microscopy (SEM) observations were performed on the fractured surfaces of both components of the joints.

The results of this inspection can be summarised as follows.

The strongest joints are of adhesive type over the entire surface. Over 90% of the copper surface in contact with the ceramics shows neither changes, nor inhomogeneities. The joint has a continuous and homogeneous structure. Only insignificant copper grooves are observed at the grain boundaries. They are associated with copper oxidation prior to the

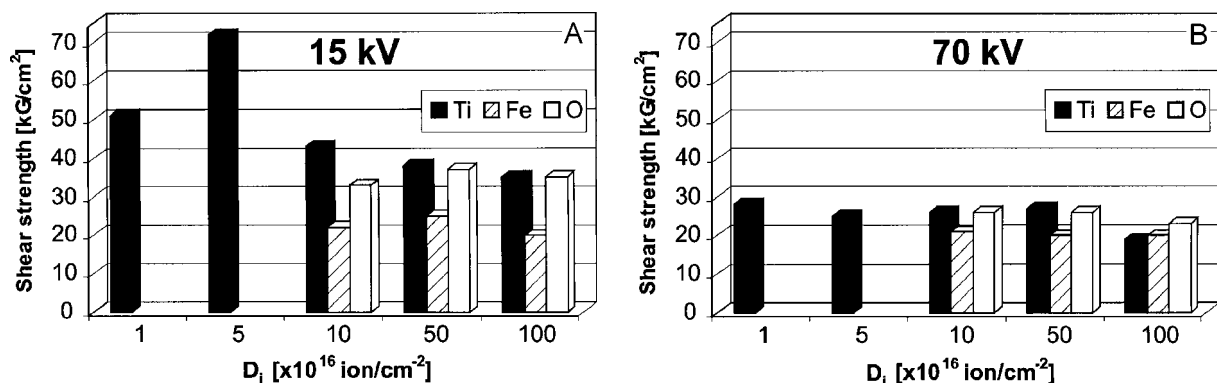


Fig.1. Summarized results of shear strength tests for various implantation conditions *i.e.* for 15 (A) and 70 kV (B) of acceleration voltage.

low  $10 \mu$ A/cm<sup>2</sup>, so the substrate temperature did not exceed 200°C. The metallic component of the joint, *i.e.* oxygen-free copper in the form of strips of  $30 \times 3 \times 0.3$  mm<sup>3</sup> was first annealed at 600°C for about 30-40 min in flowing nitrogen containing 1.5 ppm of oxygen. Subsequently, the copper component was oxidized in air at 380°C for 3 min. Following this preparatory procedure, the conventional DB process was performed and the resultant joints were examined with respect to their mechanical properties and microstructure. Figure 1 shows a dependence of the observed shear strength for different implantation conditions. The measured shear strengths were between 20 and 70 kG/cm<sup>2</sup> depending on implanted element, dose and energy. The implantation program started with higher dose range and since the best results were obtained for titanium ions the tests in lower dose range were continued only for this element. The following regularities can be inferred from these results:

joining process. The ceramic surface has a homogeneous compact grain structure. The grain surfaces are covered homogeneously with nanoprecipitates. Small quantities of needle-shape precipitates are also present. An increase of titanium ion dose results in a growth of the number of needle-shape precipitates and in appearing of a new phase in the form of multifaceted crystals. On the other hand, an increase of both energy and dose of titanium ions gives rise to a growth of a grain-like phase.

With regard to the other implanted ions, AlN/O-Cu joints are formed on no more than 30% of the surface. Copper ruptures together with the surface layer of the ceramic and the remaining copper surface exhibits deep surface morphology changes. Similar changes are observed at the AlN/Fe-Cu joint surfaces, the number of new phase precipitates being much greater than in the case of oxygen and the joint being with a laminar structure. Although as much as 60% of the surface is ruptured together

with the ceramic surface layer, these joints exhibit the lowest shear strength which means that the presence of iron atoms in the near surface layer of AlN deteriorates its mechanical toughness.

Both, iron and oxygen implantations, do not lead to substantial changes of the microstructures at the joint surfaces of ceramics and copper for different implantation conditions. Such effects are seen only for titanium.

In conclusions, ion implantation seems to be ideally suited for DB process. As it was shown, the optimised implantation process leads to much better results than a conventional process at a comparable processing time. The advantages of ion implantation include:

- potentially fast processing time, for instance, for ion beam intensities in the 100 mA range, the

processing time would be of the order of minutes instead of tens of minutes in the conventional process;

- accuracy in creating an appropriate dopant content;
- flexibility in tailoring the desired distribution of the introduced atoms at nanometer depth range;
- ability to form non-equilibrium compounds.

## References

- [1]. Entezarian E., Drew R.: *Mat. Sci. Eng.*, **A212**, 206, (1996).
- [2]. Piekoszewski J., Olesińska W., Jagielski J., Kaliński D., Chmielewski M., Werner Z., Barlak M., Szymczyk W.: *Solid State Phenom.*, **99-100**, 231 (2004).
- [3]. Bugaev S., Nikolaev A., Oks E., Schanin P., Yushkov G.: *Rev. Sci. Instrum.*, **10**, 3110 (1994).