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COMPOSITION COMPOUND OF Cr-N COATING DEPOSITED ON AN ALUMINUM PRELIMINARY IRRADIATED WITH NITROGEN IONS

A.G. Guglya, I.M. Neklyudov, V.A. Shkuropatenko, A.F. Vanzha, V.D. Virich

National Science Center "Kharkov Institute of Physics and Technology", Kharkov, Ukraine

Ion-beam assisted technology was used for deposition of Cr-N coating on aluminum under simultaneous irradiation with 30 keV nitrogen ions at temperatures 200 and 300°C. Distribution of metal components in the coating and in the coating-substrate mixing zone was studied as regards process temperature and the degree of pretreatment of aluminum surface with nitrogen ions to doses of $1{,}7.10^{17}$ and $3{,}4.10^{17}$ ions/cm^2. The results obtained with the use of secondary ion mass spectrometry prove that ion pretreatment of aluminum substrate causes drastic changes in distribution of metal components in the intermixing zone. As the dose of preirradiation of the substrate increases, we observe intermixing of Al with Cr. Besides, we have recorded an expanded peak of AlCr precipitation in the intermixing zone. The chromium coating contains some admixtures of CrN and Cr_2N uniformly distributed in the depth, with their maximum near the mixing zone. Thus, the effect of penetration of those elements grows stronger with the increase of process temperature. A possible diffusion mechanism of metal and gaseous components into the coating is discussed.

INTRODUCTUON

At present ion-beam technologies are widely used for modification of structural material properties. Under traditional applications of those technologies (at a pressure of residual gases in working chamber oat the level of $5.10^{-2}…1.10^{-5}$ Pa), ion beam assisted physico-chemical processes of interaction between molecules of residual gases and the surface under treatment can occur to some degree. In particular, the results of ion implantation showed a significant increase of carbon and oxygen content in the materials being treated in the near-surface areas [1-3]. Ion bombardment of surface on the growing coating is accompanied, in turn, by desorption of adsorbed particles, stimulation of heterogeneous chemical reactions, sputtering of coating materials, defect formation and implantation of bombarding ions into the layer being formed.

The use of ion beam assisted technologies (IBAD method) enables to obtain a high-quality adhesion of the coating, concomitant with intense penetration of the material deposited into the substrate, due to formation of a wide intermixing zone. However, in the proposed method the degree of intermixing and the composition of the coating-substrate transition zone can be changed by means of an additional, prior to deposition, treatment of the substrate. One of the ways to realize this idea can be a preliminary, prior to deposition, bombardment of the substrate surface with a beam of ions.

There are few publications devoted to the study of effect of preliminary ion bombardment on the peculiarities of distribution of metal and gaseous components in the coating-substrate transition zone. In [4] it has been shown that preliminary irradiation of aluminum with nitrogen ions in the range of doses $1.10^{17}…1.10^{18}$ ions/cm^2 with subsequent deposition of an AlN coating results in substantially improved adhesion of a given coating, is its wear resistance and microhardness becoming better as well. Increased oxygen content in the transition zone was observed; that can be explained by the fact that pretreatment and subsequent deposition were performed using different equipment. Moreover, the use of identical material (Al) in the coating and in the substrate do not permit to reveal the effect of preliminary irradiation on composition and expanse of the intermixing zone.

The authors of [5] studied the dose effect for the case of silicon substrate preliminarily bombarded with 50 keV argon ions on penetration depth of silver, being deposited under simultaneous irradiation with 125 keV argon ions. It has been shown that the increase of the preliminary irradiation dose from 2.10^{14} to 1.10^{15} ions/cm^2 leads to a subsequent increase of Ag penetration depth into Si. The effect of silicon penetration into silver coating was not studied.

The authors of [6], prior to deposition of a Ti+N coating onto Al-11Si substrate, performed preliminary cleaning of this substrate by the beam of nitrogen ions with energy of 20 keV. As a result, aluminum penetration throughout the coating thickness (1.2 μm) was observed. Unfortunately, they give no data on the ion cleaning duration, and, consequently, on preliminary irradiation dose.

The purpose of present work was to study the dose influence, in the case of preliminary bombardment of aluminum with nitrogen ions, and the substrate temperature influence on the composition and expanse of the coating- substrate intermixing zone.

EXPERIMENTAL PROCEDURES AND RECEARCH METHODS

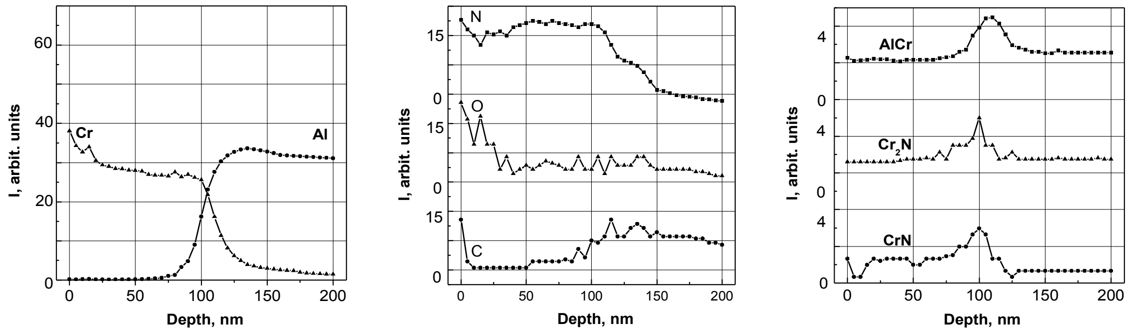
Experiments on deposition of chromium coatings onto aluminum substrate were performed at ARGO-1 ion beam assisted deposition unit [7]. Chromium was evaporated from electron-beam evaporator at a rate of 0.1 nm/s. Simultaneously with chromium deposition bombardment with 30 keV nitrogen ions was performed at ion beam density of 2.10^{14} ions /cm^2.s. Coatings were deposited in vacuum of 5.10^{-4}Pa created by a turbo-molecular and a magnetodischarge pumps. The substrate temperature was 200ºC and 300ºC. The thickness of coatings made 100…150 nm. High purity aluminum (<99.999 mas %.) was used as a substrate.

To study the influence of preliminary irradiation onto metal and gas components distribution in the transition zone some specimens, prior to deposition, were bombarded with nitrogen ions of energy 30 keV up to doses of 1,7 and $3,4.10^{17}$ ions/cm^2 at the same temperatures. After reaching the indicated doses deposition itself was performed, irradiation being continued.

Layer-by-layer analysis of coatings was carried out using MS-7201M industrial mass-spectrometer of secondary ions equipped with a quadrupole analyzer. Primary ions were Ar^+ with energy of 6 keV and current density from 0.5 to 5 mA/cm^2.

RESULTS AND DISCUSSION

Fig. 1,a,b,c demonstrates the spectra of secondary ion emission of Cr, Al O, N, C and their compounds depending on the depth of layer being etched for the case of chromium deposition without preliminary bombardment (Fig.1,a) and after bombardment up to doses 1,7 and $3,4.10^{17}$ ions/cm^2 (Fig.1,b,c) respectively. The coating thickness is 100 nm, substrate temperature being 300°C.



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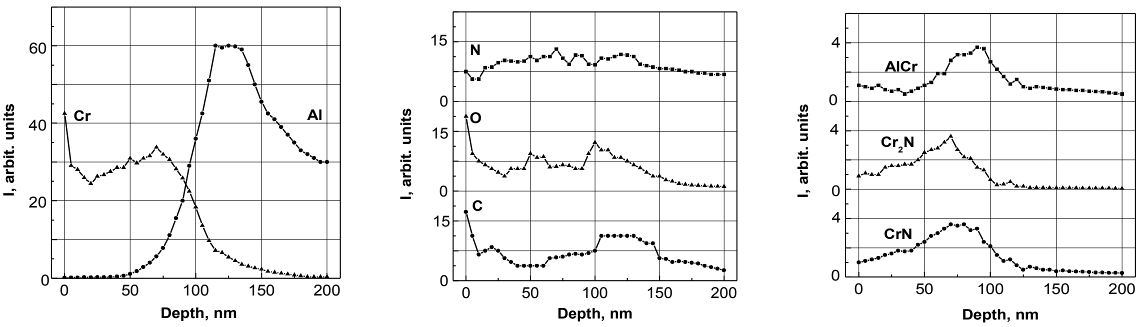

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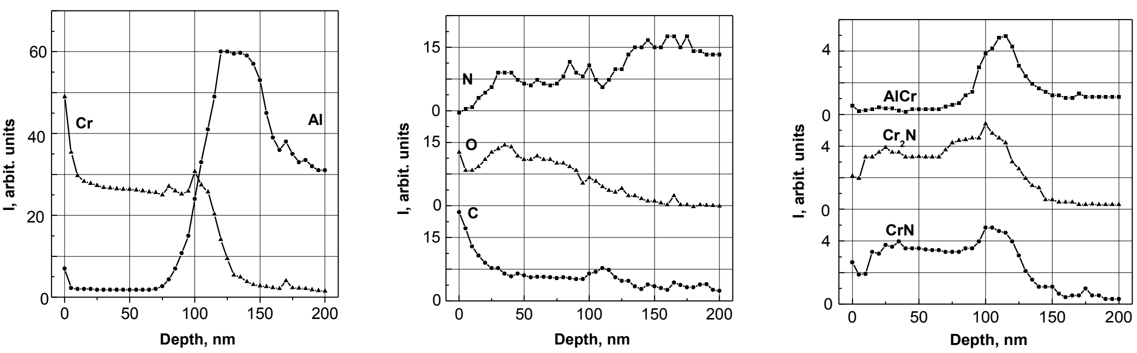


c

Fig. 1. SIMS depth profiles of constituents in the Cr film deposited on Al-substrate: a – without previous ion bombardment; b –with previous ion bombardment. D=1,7.10^{17} ions/cm^2; c – with previous ion bombardment, D=3,4.10^{17}ions/cm^2. T = 300ºC

As we can see, for case Fig.1,a the intermixing zone is non-symmetric due to a deeper chromium penetration into aluminum, as compared to the case of aluminum penetration into chromium. The zone width does not exceed 60…

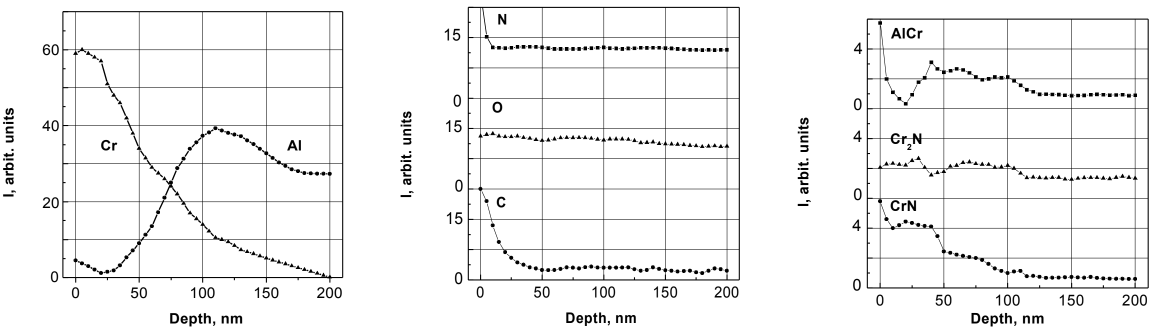
70 nm. Distribution of AlCr intermetallide, for the most part, is within the limits of this zone. Its deeper penetration into aluminum is in correlation with similar chromium propagation. Chromium nitrides CrN and Cr_2N are distributed rather uniformly in the coating and the substrate, except transition zone, where some maxima are observed. Also, we should note increased carbon content in the substrate as compared to the coating.

Preliminary irradiation of aluminum with nitrogen ions up to dose of $1{,}7.10^{17}$ ions/cm^2 (Fig.1,b) leads, first of all, to a significant propagation of Al and AlCr into the coating throughout its thickness. Distribution of N, C and O becomes more uniform throughout the entire coating-substrate thickness. In addition, an appreciable increase of CrN and Cr_2Ncontent in the coating takes place as well as a shift of their maxima from intermixing zone into the coating.

On the other hand, penetration of Cr and AlCr into the substrate remained actually unchanged as compared to Fig. 1,a. We estimate the width of transition zone to be at least 100 nm. Enhancement of signal from aluminum at the substrate surface (depth of 120…150 nm) is explained by formation of AlN compound after ion bombardment in this area, its sputtering coefficient being higher than that of aluminum.

Increase of the dose of preliminary bombardment up to $3{,}4.10^{17}$ ions/cm^2 (Fig. 1,c) does not change substantially the distribution pattern of Al, Cr and AlCr. The only distinction is a gradual increase, from Fig. 1,a to Fig. 1,c, of the value of AlCr compound distribution maximum. At the same time nitrogen distribution is characterized by increase of nitrogen content in the substrate in conformity with increasing preliminary bombardment dose. Also, our attention is drawn to the significant increase of chromium nitrides concentration in the coating. Their content is actually uniform throughout the coating thickness.

Similar experiments at 200°C (Fig. 2,a,b,c) have shown that a decrease of the temperature of ion beam assisted deposition stimulates the effect of preliminary irradiation on the intermixing of coating and substrate elements.



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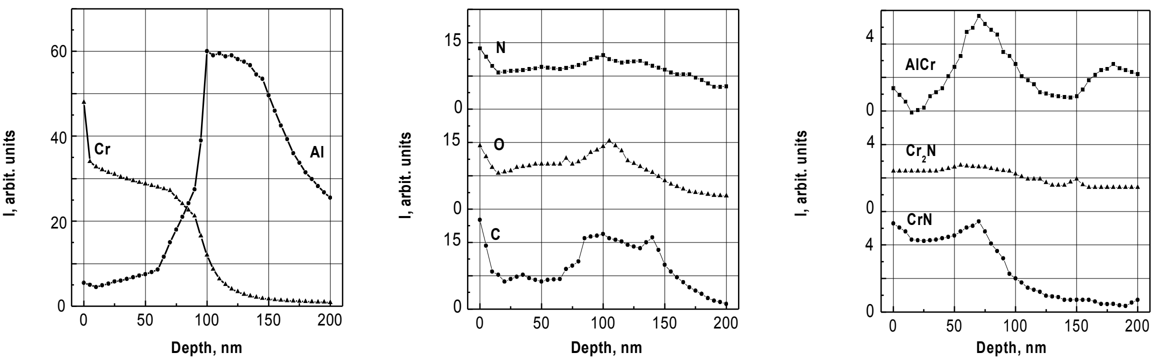

b

ВОПРОСЫ АТОМНОЙ НАУКИ И ТЕХНИКИ. 2005. № 3.
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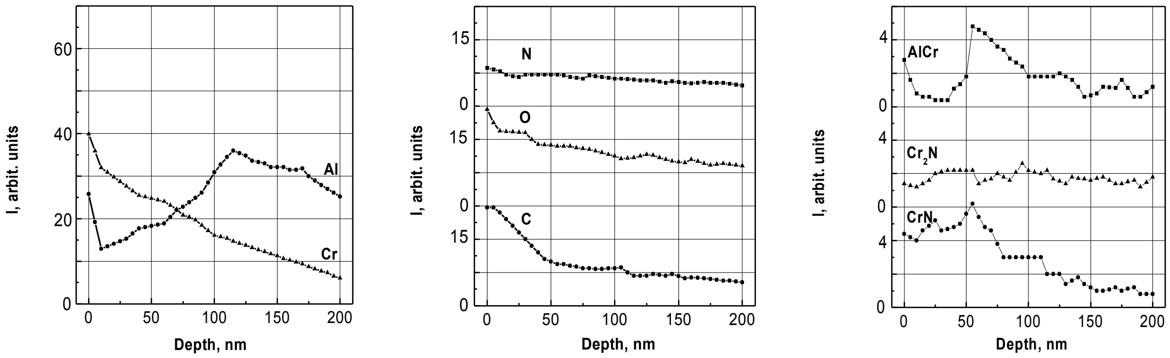

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Fig. 2. SIMS depth profiles of constituents in the Cr film deposited on Al-substrate: a – without previous ion bombardment; b – with previous ion bombardment, D=1,7.10^{17} ions/cm^2; c – with previous ion bombardment. D=3,4.10^{17} ions/cm^2. T = 200ºC

Even without pretreatment (Fig. 2,a) the width of intermixing zone attains ≈100 nm, and an appreciable presence of Al and AlCr intermetallide is observed throughout the thickness of the coating. Moreover, the maximum of AlCr distribution takes place not in the aluminum substrate, as it does at 300°C, but in the chromium coating. In distributions of CrN and Cr_2N no maxima were found at coating-substrate interface.

The preliminary bombardment up to 1,7.10^{17} ions/cm^2 (Fig. 2,b) increases still more the content of aluminum and AlCr in chromium coating. CrN content in the coating is also substantially increased. The most impressive is the effect of aluminum penetration into chromium after preliminary bombardment up to 3,4.10^{17} ion/cm^2 (Fig. 2,c). In distributions of aluminum and, even more, of chromium no bends are found at coating-surface interface, all concentration transitions being smooth. The concentration of chromium nitrides increases gradually, in the substrate as well.

Thus, the performed study has shown that the preliminary ion bombardment of substrate before coating deposition results in a substantial redistribution of both metal and gaseous components in the coating-substrate system. Besides, the effect is more and more pronounced with implantation dose increasing and substrate temperature decreasing. The explanation of this phenomenon can lie in the fact that ion bombardment, at doses used in this study, leads to nitrogen implantation into a limited area near the substrate surface, its concentrations attaining as high values as N/Al = 0.5 and 1 [9]. This circumstance, as well as the fact that irradiation to such doses leads to creation of a high level of defect presence in the same zone, promote the formation of fields of increased stress in the near-surface zone. The level of these stresses will increase with growing implantation dose and with process temperature reducing [10-12]. Relaxation of such stresses is possible either by annealing of the stressed state, or by creation of a powerful sink for defects and interstitial atoms together with some mechanism for their diffusion. In our experiment such a sink is movable surface of the chromium coating. This sink cannot actually be saturated due to a permanent inflow of deposited atoms and molecules. A low rate of deposition, combined with high vacancy supersaturation, which is a consequence of ion bombardment, creates conditions for intense aluminum atoms diffusion into the chromium coating using vacancy mechanism. Nitrogen atoms are too much smaller than those of aluminum; therefore, they can diffuse more intensely into the chromium coating in the course of its deposition. The proof of this reasoning is visibly more substantial increase of content of chromium nitrides in the coating after preliminary ion bombardment as compared to the growth in Al and AlCr content.

In order to study the effect of newly found phenomenon on tribological characteristics we have measured aluminum microhardness without coating, with coating deposited otherwise than ion assisted irradiation, deposited after nitrogen ion bombardment and deposited subsequently to preliminary nitrogen implantation up to dose 3,4.10^{17} ions/cm^2. Coating thickness was 1 μm. The temperature was 200ºC. Vickers microhardness indenter showed 5 gm load. The results obtained are shown in the Table.

Microhardness of Al after different kinds of coating deposition

The kind of substrate's performance	Microhardness, MPa
Al substrate without coating	(230 ± 2,5)%
Cr coating deposited on Al without N^+ bombardment	(550 ± 2)%
Cr coating deposited on Al with N^+ bombardment	(400 ± 1,5)%
Bombardment of Al (3,4.10^{17} ions/cm^2) + Cr coating deposited with N^+ bombardment	(255 ± 1,5)%

As we can see, in spite of neglectable coating thickness the method of its deposition defines quite substantial differences. Aluminum coated without ion assisted bombardment shows maximum hardness, whereas the hardness of aluminum with coating deposited after preliminary bombardment turns to be the least, though higher that that of uncoated aluminum. The data obtained are in registry with Al and AlCr distribution (Figs. 2a,b,c) in coatings. Gradually increasing content of those elements in a hard Cr-N coating should lead to a reduction of its hardness which is confirmed by results in the Table.

CONCLUSION

As a result of our study it has been established that a preliminary bombardment of substrate with heavy ions of mean energies leads to a significant expansion of coating-substrate intermixing zone. The basic mechanism responsible for this effect is relaxation of prestresses in the substrate at the expense of intense ion bombardment in the course of coating deposition by ion beam assisted technology. The use of this technique enables a substantial improvement of adhesion characteristics of deposited coatings as well as extended possibilities of the technology of ion beam assisted deposition at the expense of an insignificant increase in duration of the process.

At the same time selection of such a soft material as aluminum for substrate leads to reduced coating hardness. We chose aluminum due to its purity excluding the effect of other metal additives on the phenomenon under study as well as its low initial microhardness. Nevertheless, the use of preliminary bombardment enables obtaining multi-component coatings with acceptable tribological characteristics such as wear resistance and friction coefficient.

Acknowledgements

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ЗАКОНОМЕРНОСТИ ОБРАЗОВАНИЯ Cr-N-ПОКРЫТИЯ НА АЛЮМИНИЕВОЙ ПОДЛОЖКЕ ПРЕДВАРИТЕЛЬНО ОБЛУЧЕННОЙ ВЫСОКОЭНЕРГЕТИЧНЫМИ ИОНАМИ АЗОТА

А.Г. Гугля, И.М. Неклюдов, В.А. Шкуропатенко, А.Ф. Ванжа, В.Д. Вирич

Покрытие Cr-N осаждалось на алюминий с использованием имплантационно-стимулирующей технологии в условиях облучения ионами азота с энергией 30 кэВ при температурах 200 и 300ºС. Исследовалось распределение металлических и газовых элементов в покрытии и зоне перемешивания покрытие-подложка. Для исследования влияния роли предварительной обработки поверхности подложки на адгезию покрытия подложка предварительно облучалась ионами азота с той же энергией до доз $1{,}7.10^{17}$ и $3{,}4.10^{17}$ ион/см^2. Полученные с использованием вторичной ионной масс-спетроскопии результаты показали, что предварительное ионное облучение приводит к кардинальным изменениям в распределении металлических элементов в зоне перемешивания. Увеличение дозы предварительной обработки ведет к увеличению перемешивания Al и Cr. Кроме этого, наблюдается расширение пика распределения AlCr в данной зоне. Распределение нитридов хрома – CrN и Cr_2N становится однородным по глубине покрытия с максимумов в зоне смешивания. Снижение температуры процесса приводит к усилению данного эффекта. Обсуждается возможный механизм данного явления.

ЗАКОНОМІРНОСТІ СТВОРЕННЯ Cr-N-ПОКРИТТЯ НА АЛЮМІНІЄВІЙ ПІДКЛАДЦІ, ЯКА БУЛА ПОПЕРЕДНЬО ОПРОМІНЕНА ВИСОКОЕНЕРГЕТИЧНИМИ ІОНАМИ АЗОТУ

О.Г. Гугля, І.М. Неклюдов, В.О. Шкуропатенко, О.Ф. Ванжа, В.Д. Вірич

Покриття Cr-N осаджувалося на алюміній з використанням імплантаційно-стимульованої технології в умовах опромінення іонами азоту з енергією 30 кеВ при температурах 200 та 300°C. Досліджувався розподіл металевих та газових елементів у покритті та зоні змішування покриття-підкладка. Для вивчення впливу попередньої обробки поверхні підкладки на адгезію покриття підкладка попередньо опромінювалася іонами азоту з тією ж енергією до доз $1,7.10^{17}$ и $3,4.10^{17}$ іон/см^2. Здобуті з використанням вторинної іонної мас-спектрометрії результати показали, що попереднє іонне бомбардування призводить до кардинальних змін у розподілі металевих елементів у зоні змішування. Зростання дози попереднього опромінення веде до збільшення ступіні змішування Al та Cr. Крім цього, мале місце розширення пику розподілу AlCr у даній зоні. Розподіл нітридів хрому - CrN та Cr_2N стає однаковим по всьому покритті з максимумом в зоні змішування. Зниження температури процесу призводить до посилення даного ефекту. Обговорюється можливий механізм даного явища.