Corrosion study of ZrN coated Ti6Al4V alloy in Normal Saline (0.9% NaCl) Solution

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ABSTRACT: *Titanium and Ti6Al4V alloy are widely used as biomaterial for implants. However, leaching out of V and Al in a physiological environment constitute the main limitation for their applications. Zirconium nitride (ZrN) coating started to attract more attention for its excellent corrosion resistance and biocompatibility which exhibits suitable properties for great varieties of industrial applications. Here, electrochemical corrosion behaviour in normal saline solution of ZrN coated Ti6Al4V alloy, coated by cathodic arc physical vapour deposition with parameters; substrate bias voltages of -50V, -200V, -350V and -500V; nitrogen gas pressure 10 mtorr; duration of coating 20 minutes is studied. ICPAES was used to determine amount of Al leached out when immersed in normal saline solution. The crystallographic orientation and surface morphology was studied using X-ray diffraction and Scanning Electron Microscope (SEM/EDAX). Microhardness was carried out using Vickers method by applying 10g load. ZrN coating improves corrosion resistance, microhardness and elemental out-diffusion resistance.*
Keywords: biomaterials; cathodic arc PVD; electrochemical corrosion; microhardness.

I. INTRODUCTION

Ti6Al4V alloy has been used extensively in biomedical applications such as hip replacements and dental implants due to its attractive combinations of mechanical properties, corrosion resistance and biocompatibility [1-5]. However, despite of its favorable mechanical properties, physicians still have concern against this alloy because of leaching out of Al and V from the surface of implants and their allergic reaction, toxicity and carcinogenicity. Aluminum is well known as to cause certain bone diseases and neurological disorders. For these reasons there are a lot of studies and attempts are made, in one hand to improve tribological and corrosion properties and in other hand to improve biocompatibility of the material. In order to improve corrosion resistance, various surface modification technique are used. The physical vapour deposition (PVD) coating is widely used in biomedical materials in current decade because of this good tribological and an anti-corrosion performance is achievable [6-13]. Zirconium nitride (ZrN) coating started to attract more attention for its excellent corrosion resistance and biocompatibility. It has been reported that ZrN coating showed higher corrosion resistance compared to that of TiN coating [14, 15]. Stoichiometry of ZrN is the only stable phase with a gold-like colour due to its metallic band structure. This coating appears to have substantial potential in aero engine, industrial and biological application [16]. In the present study, ZrN is selected for coating on Ti6Al4V alloy using cathodic arc physical vapour deposition in order to improve corrosion performance and the surface properties.

II. EXPERIMENTAL

2.1 Sample preparation

Table1
Chemical composition (wt. %) of Ti6Al4V

C	Ni	Mn	Mo	V	Ti	N	Sn	Fe	Al
0.036	0.001	0.008	0.004	4.08	89.56	0.008	0.011	0.25	5.97

Ti6Al4V in sheet form with thickness 0.5mm was used as samples for this study. The sheet was cut in small pieces with dimensions of 12mm X 12mm. The samples were polished using silica carbide paper of 1000, 1500, 2000 and 2500 grit. Final mirror polish was done using 0.5μm diamond pest in order to produce scratch free mirror polished surface. The polished samples were subsequently cleaned in acetone and deionized water. They are further subjected to ultrasonic cleaning in acetone for 20 minutes, rinsed in deionized water and dried in air.

Cathodic arc physical vapor deposition technique was used to produce ZrN coating on samples with process condition of substrate bias voltages of -50V, -200V, -350V, -500V, reactive nitrogen gas pressure 10 mtorr; deposition time 20 minutes.

2.2 Corrosion test (Electrochemical test)

The electrochemical corrosion test was carried out using conventional three-electrode cell of 300 ml capacity by using Gamry- potentiostat/Galvanostat reference 3000 and Tafel extrapolation method. The cell was fitted with working electrode, saturated calomel electrode (SCE) as the reference electrode and the platinum as a counter electrode. The studies were carried out in Normal Saline (0.9% NaCl) solution at 37 ± 1^0 C with scan rate 0.166 mV/s and electrode potential was raised from -800 mV to 1000 mV. The solution was de-aerated with pure argon (Ar) gas throughout the experiment. The critical parameters like $E_{corr,}$ $I_{corr,}$ β_a, β_c and corrosion rate in mpy were evaluated from the Tafel plots.

2.3 Dissolution test

In the dissolution test, six samples of surface area 1 cm^2 were immersed in 50ml of Normal Saline solution in polypropylene bottles. The bottles were evacuated and closed tightly and incubated in thermostatic chamber at 37 ± 1^0C for sixteen weeks. All bottles were shaken and rotated with a speed of 72 rpm. After 4th, 8th and 16th weeks the solutions were analyzed by Inductive Coupled Plasma Atomic Emission Spectroscopy (ICPAES) to determine amount of Al leached out from samples.

2.4 SEM and EDAX

Film surface morphology was studied using SEM/EDAX and XRD which was carried out at low angle.

2.5 Microhardness

The microhardness test was carried out to measure hardness of bare and ZrN coated samples at 10g load using Vickers method. Each measurement was repeated at three different locations on six samples of each type in order to avoid the statistical fluctuations.

III.   RESULTS AND DISCUSSION
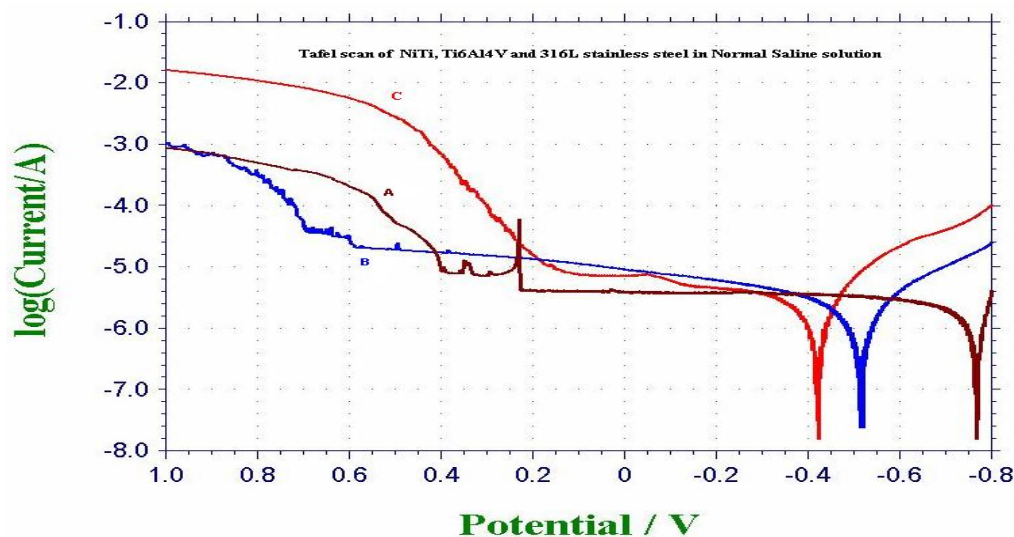
3.1 Corrosion behavior

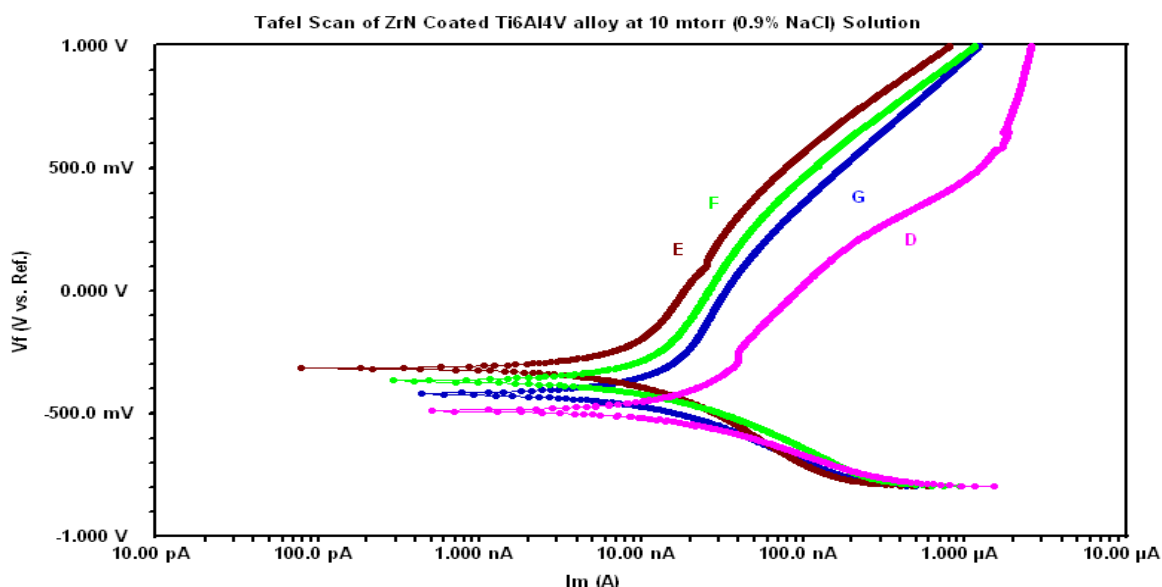Fig 1 Tafel plot of NiTi, Ti6Al4V and 316L Stainless Steel in Normal Saline solution.

Fig.2 Tafel scan of ZrN Coated Ti6Al4V alloy in Normal Saline solution.

Table 2 Corrosion rate of ZrN coated Ti6Al4V by Tafel extrapolation method in NS solution

Sample code	Sample	Bias Voltage	Pressure	β_a V/decade	β_c V/decade	E_{corr} mV	I_{corr}	Corrosion Rate in mpy
A	Ti6Al4V	--	--	--	--	-763.0	1.603 µA	1.00
B	NiTi	--	--	--	--	-512.7	1.563 µA	0.82
C	316L SS	--	--	--	--	-419.4	1.128 µA	0.51
D	Ti6Al4V	-50 V	10 mtorr	812.5	$254.5\ e^{-3}$	-486.6	23.56 nA	$14.78\ e^{-3}$
E	Ti6Al4V	-200 V	10 mtorr	1.328	$416.1\ e^{-3}$	-315.1	11.01 nA	$7.001\ e^{-3}$
F	Ti6Al4V	-350 V	10 mtorr	1.415	$277.5e^{-3}$	-365.1	11.28 nA	$7.172e^{-3}$
G	Ti6Al4V	-500 V	10 mtorr	1.223	$218.0e^{-3}$	-416.8	12.27 nA	$7.801e^{-3}$

The corrosion resistance of ZrN coated Ti6Al4V in Normal Saline solution was studied and compared with untreated Ti6Al4V, NiTi and 316L stainless steel. Present studies showed that uncoated 316L stainless steel had lower corrosion rate than NiTi and Ti6Al4V in Normal Saline solution. The order of corrosion rate obtained,   316L stainless steel < NiTi < Ti6Al4V. Sample E showed high E_{corr} and low I_{corr} than the samples D, F and G. The sample E showed more improvement in the corrosion resistance than the samples D, F, and G. The order of corrosion rate obtained, Samples E < Samples F < Samples G < Samples D. All the coated samples showed high corrosion potential E_{corr}, low corrosion current density I_{corr} and low corrosion rate than the uncoated samples. ZrN coating by cathodic arc physical vapour deposition method effectively improved the corrosion resistance of Ti6Al4V alloy. Substrate bias voltage affects the corrosion rate as shown in Fig 3. The substrate

bias voltage of -200V showed less corrosion rate. The substrate bias voltage of -200V is the best bias voltage to improve coating quality which results in improved corrosion resistance.
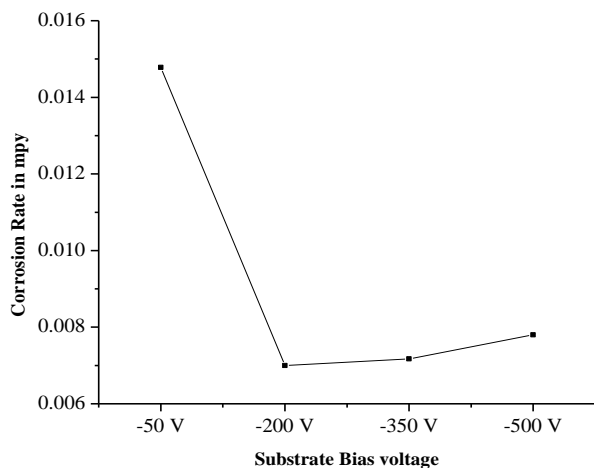

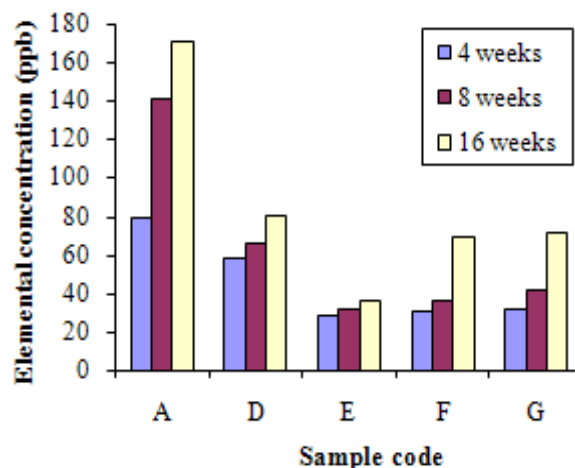Fig. 3 Substrate bias voltage dependent corrosion rate.

Fig. 4 Elemental concentration of Al leached out in dissolution test

3.2 Dissolution test

The dissolution test after continuous evaluation at the end of 4th, 8th and 16th week using ICPAES is shown in Fig. 4. At every stage of evaluation, uncoated Ti6Al4V showed high amount of Al leached out from the surface than coated Ti6Al4V. ZrN coating increased the elemental out-diffusion resistance. Sample-E (substrate bias voltage of -200V, nitrogen gas pressure 10 mtorr), showed less leach-out diffusion of Al in Normal Saline solution as compared to all other samples.

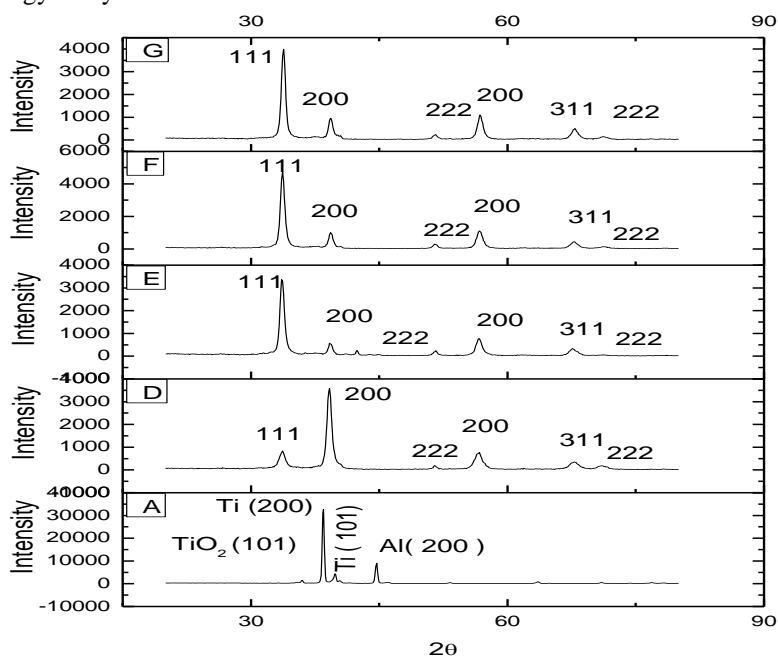3.3 Surface morphology analysis

Fig. 5 XRD pattern of ZrN coated Ti6Al4V.

Fig. 5 shows the XRD pattern of samples coated at nitrogen pressure 10 mtorr with different bias voltages. By means of XRD technique, the different phases present in the film were identified. For sample-D (-50V, 10mtorr), ZrN[200] peak is dominant indicating that the preferred orientation is ZrN[200]. For samples E (-200V, 10mtorr),   F (-350V, 10mtorr), G (-500V, 10mtorr), ZrN[111] peak is dominant indicating that

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preferred orientation is ZrN[111]. The preferred orientation changes from ZrN[200] to ZrN [111] with increase in substrate voltage from   -50V to -200V.
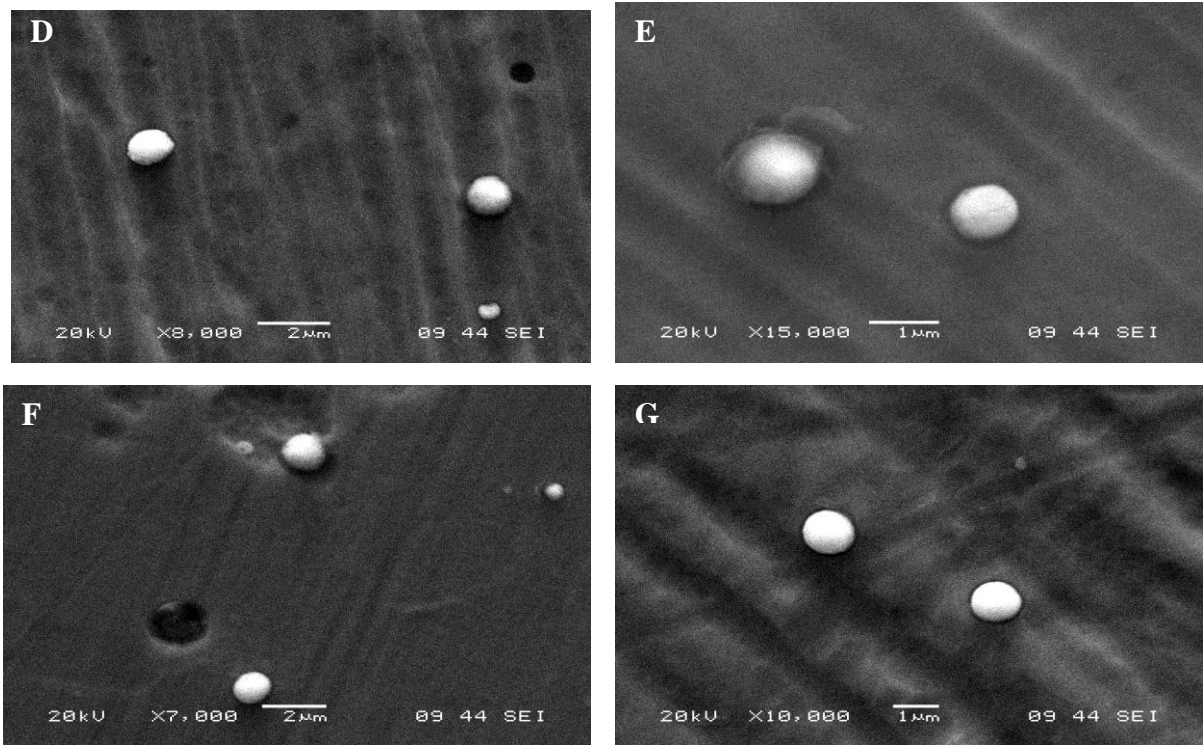

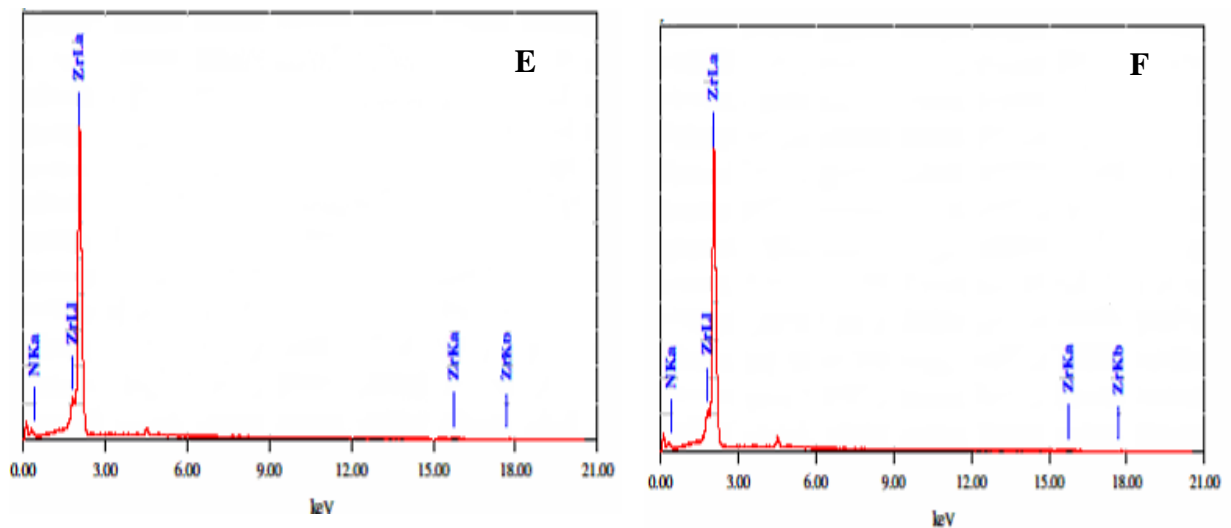Fig.6 SEM micro graph of ZrN coated Ti6Al4 alloy.

Fig.7 EDAX spectrum for ZrN coated Ti6Al4V samples.

SEM micrograph of ZrN coated Ti6Al4V shows droplets like defects recognized as macro-particles and black spot recognized as cavities or pinholes. The substrate bias voltage affects the density of macro-particle. The samples coated at bias voltage of -200V showed less density of micro-particles and pinholes. EDAX and XRD studies confirm the formation of ZrN coating on samples. The EDAX spectrums for samples E and F are shown in Fig. 7. N/Zr (wt. % ratio) increases, indicating elemental concentration of nitrogen increases in film stoichiometry which results in increase in microhardness of film.

Table 3
Wt. % ratio obtained from EDAX study

Sample code	Wt. % of N	Wt. % of Zr	N/Zr(Wt. % ratio)
E	32.88	67.12	0.49
F	37.07	62.93	0.59

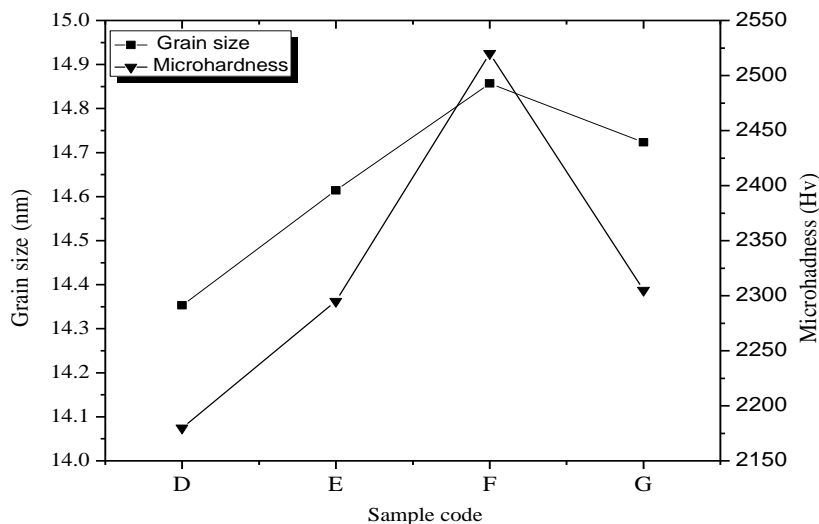## 3.4 Grain size and microhardness studies

Fig. 8 Microhardness and grain size of ZrN coated Ti6Al4V.

The average grain size were estimated from full-width at half-maximum (FWHM) of peaks in XRD patterns by Sherrer formula, $D = k\lambda/\beta cos\theta$, where λ is wave length ($1.540600\ A^0$ in this case), β the full- width with half maximum of dominating peaks and θ the diffraction angle. The average grain size increases with increase in substrate bias voltages in step of -50V, -200V, -350V but for -500V it decreases. The grain size was found between 14.35 nm to 14.85 nm. The film microhardness increases with increase in bias voltage from -50V to -350V but for bias voltage of -500V, microhardness of the film decreases. This decrease in grain size and microhardness is due to resputtering of Zr ion from surface at high bias voltage -500V.

IV. CONCLUSION

The ZrN coating increases corrosion resistance, the elemental out-diffusion resistance and surface microhardness. The substrate bias voltage affects the corrosion resistance, elemental leaching out concentration from surface, microhardness, grain size and droplet like defects. The substrate bias voltage of -200V is the best bias voltage to improve coating quality which results in improved corrosion resistance, the elemental out-diffusion resistance and microhardness. The preferred orientation changes from ZrN[200] to ZrN [111] with increase in substrate voltage from -50V to -200V.

VI. REFERENCES

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