Microstructure and Wear Resistance of Ti/TiN Multilayer Films Deposited by Magnetron Sputtering (Postprint)

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Abstract

Ti/TiN multilayer films were deposited on Ti6Al4V alloy substrates with a fixed Ti interlayer thickness and varied TiN layer thicknesses, to investigate the influence of the number of cycles on the phase structure, surface morphology, adhesion, hardness, and friction and wear behavior in simulated body fluid. The results revealed that, compared with monolithic TiN film, the TiN phase in Ti/TiN multilayer films changed from (111) preferred orientation to (200) preferred orientation, while the surface roughness, hardness, and adhesion were significantly improved. Increasing the number of cycles reduced the surface hardness of Ti/TiN multilayer films, but improved the bonding strength. The strengthening and toughening of multilayer Ti/TiN films mainly derived from grain refinement strengthening of TiN layers and coherent interface strengthening effects. When the thickness ratio of TiN to Ti layer was 30 and the number of cycles was 3, the Ti/TiN multilayer film exhibited excellent comprehensive performance, with a hardness of 15.8 GPa, bonding strength of 50 N, friction coefficient of 0.35, and volumetric wear rate lower than 4.0$×10^{-6}$ mm^3/(N·m).

Full Text

Preamble

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Abstract

Ti and Ti alloys with low elastic modulus, good mechanical properties and biocompatibility have been widely used for dental implants, arthroplasty and internal fixation material in spinal fusion. But the poor wear resistance of Ti and Ti alloys generally results in the aseptic loosening of the implants. TiN coating has good chemical stability and biocompatibility in physiological environment and plays an important role in improving the corrosion wear performance of Ti and Ti alloys. However, the adhesion strength of TiN film prepared by traditional technologies does not meet the requirement of long service life of the implants. In this work, the alternating Ti/TiN multilayer films were prepared by magnetron sputtering technology with constant Ti layer thickness and varying TiN layer thickness. The cycling periods were designed to be 1, 3, 6, 9, and 12. The total depositing time was 185 min. The main aims of this investigation were to clarify the effects of the cycling periods on the surface morphologies, hardness, bonding strength, friction and abrasion behavior in simulated body fluid of Ti/TiN multilayer films. The results show that the total thickness of Ti/TiN multilayer film is in the range of 5.5~6.0 mm. (111)TiN preferred orientation is found in TiN monolayer film, and (002)TiN preferred orientation is found in Ti/TiN multilayer films. In comparison with TiN monolayer film, Ti/TiN multilayer films exhibit lower surface roughness, higher hardness, bonding strength and wear resistance. The strengthening and toughening of Ti/TiN multilayer films result from the refinement of columnar crystals and interface coherent effect between Ti and TiN layer. The increase of cycling period decreases the hardness of Ti/TiN multilayer film, but is beneficial to enhancing the bonding strength to the substrate. The rupture and exfoliation of thin TiN layer at outer surface promote the abrasive wear and oxidation wear. At the condition of layer thickness ratio 30 for TiN and Ti and 3 cyc, the Ti/TiN multilayer film has good combined mechanical properties. Hardness is 15.8 GPa, adhesion strength is 50 N, coefficient of friction is 0.35, and volume wear rate in Hank's solution is less than 4.0$×10^{-6}$ mm^3/(N • m).

Keywords

Ti/TiN multilayer film, magnetron sputtering, cycling period, microstructure, wear resistance

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Titanium alloys are widely used in load-bearing medical applications such as spinal fixation devices and artificial joints due to their low elastic modulus, excellent biocompatibility, and suitable mechanical properties. However, the poor wear resistance of titanium alloys makes implants susceptible to wear during long-term service, and the resulting wear debris can cause aseptic loosening, severely compromising implant longevity. TiN exhibits outstanding chemical stability, wear resistance, and good biocompatibility, and has been designated as a coating material for cardiac, dental, and orthopedic implants [1]. TiN coatings deposited by magnetron sputtering on titanium alloy surfaces feature smooth surfaces, dense structures, and high hardness, making them an effective approach for improving the wear resistance of titanium alloys [2,3].

Nevertheless, as medical implant devices cannot be replaced as readily as conventional engineering components, higher quality requirements must be imposed on TiN thin films. Both film-substrate adhesion strength and surface friction coefficient are critical considerations for the long-term wear performance of TiN coatings. Monolithic TiN films prepared by conventional magnetron sputtering exhibit high internal stresses and poor adhesion to the substrate, failing to meet the wear resistance requirements for medical titanium alloys. Current improvement methods typically involve depositing a Ti interlayer before TiN deposition to reduce residual stresses and enhance coating adhesion. However, even with this approach, TiN delamination and spalling can occur due to direct load transfer to the low-hardness Ti interlayer [4]. Studies [5-7] have shown that depositing (Ti/TiN) multilayer nanocomposite coatings with alternating soft and hard layers on medical metallic materials such as titanium alloys, Ni-Ti alloys, and stainless steel using physical vapor deposition can improve coating toughness and substrate adhesion while maintaining hardness, thereby enhancing tribological and fretting fatigue performance.

For Ti/TiN multilayer films, the cycling period, individual layer thicknesses within each period, and the Ti/TiN thickness ratio significantly influence surface roughness, microstructure, hardness, and adhesion strength, which in turn directly affect friction and wear behavior. Most literature reports to date have focused on Ti/TiN multilayer films prepared using single processes, with limited in-depth investigation into the correlation between microstructural characteristics and mechanical behavior [8-10]. Moreover, few studies have reported on the friction and wear behavior of Ti/TiN multilayer films in physiological environments [11-16].

In this work, Ti6Al4V alloy was selected as the substrate material, and Ti/TiN multilayer films were deposited on its surface using magnetron sputtering. By fixing the Ti layer deposition time and varying the TiN layer deposition time, we investigated the effects of cycling periods on the phase structure, morphology, hardness, adhesion strength, and corrosive wear performance of Ti/TiN multilayer films. Comparative analysis with monolithic TiN films was conducted to elucidate the hardening and wear resistance mechanisms of multilayer films, providing an experimental basis for improving the quality of Ti/TiN multilayer coatings on medical titanium alloys and their wear resistance in physiological environments.

1 Experimental Methods

Ti/TiN multilayer composite films were prepared using a CD-800 multifunctional vacuum coating system, with 1 mm thick Ti6Al4V alloy plates as substrates. Samples were ultrasonically cleaned in acetone and deionized water, then placed in the vacuum chamber. A 99.9% purity Ti target (mass fraction, %) was used as the radio-frequency cathode. Prior to deposition, the sample surfaces were bombarded with Ar^+ for approximately 10 minutes for cleaning, followed by deposition of a 10-minute Ti transition layer. N_2 gas was then introduced to deposit TiN. The flow rates of Ar and N_2 gases were 30 mL/min and 8 mL/min, respectively. Ti/TiN multilayer films were deposited alternately by switching the N_2 supply on and off. The cycling periods were set to 1, 3, 6, 9, and 12 cycles, with the Ti deposition time fixed at 5 minutes per cycle and the corresponding TiN deposition times being 175, 55, 25, 15, and 10 minutes, respectively. The total deposition time was 185 minutes, with a working pressure of 0.38 Pa, current of 1.5 A, voltage of 350 V, and substrate temperature of 300 °C.

The cross-sectional morphology of the multilayer films was observed using an SSX-550 scanning electron microscope (SEM). Phase composition was analyzed using a SmartLab X-ray diffractometer (XRD) with CoKα radiation at a scanning rate of 3°/min. Microhardness was measured using a 401MVD digital micro-Vickers hardness tester with a load of 25 g and dwell time of 30 s. The adhesion strength of Ti/TiN films was determined using a WS-2005 automatic scratch tester. In this test, a diamond indenter of specific geometry moves across the film surface under continuously increasing load. The critical load (Lc) corresponds to the onset of acoustic emission signals generated when the coating fractures or delaminates from the substrate, which is determined in conjunction with scratch morphology observation. Each sample was tested three times, and the final adhesion strength was taken as the average of the three measurements.

Ball-on-disk corrosive wear tests were conducted using a CSM-Tribometer precision friction and wear tester in Hank's solution with the following composition: 8 g/L NaCl, 0.4 g/L KCl, 0.1 g/L $MgSO_4 \cdot 7H_2O$, 0.1 g/L $MgCl \cdot 6H_2O$, 0.14 g/L $CaCl_2$, 0.154 g/L $NaHPO_4$, 0.06 g/L KH_2PO_4, and 1000 mL deionized water. The counterface material was a 6 mm diameter Si_3N_4 ball. The test parameters were: load 10 N, frequency 1 Hz, stroke length 20 mm, and duration 2 h. The original surface morphology of Ti/TiN films was examined using a JSM-7001F field-emission SEM (FE-SEM), while wear track morphology was observed using an SSX-550 SEM. Energy-dispersive spectroscopy (EDS) attached to the SEM was used for micro-area composition analysis, and an OLS 3100 laser confocal microscope was employed to measure wear track depth.

2.1 Phase Structure and Morphology of Multilayer Films

Figure 1 [Figure 1: see original paper] shows the XRD patterns of monolithic TiN and Ti/TiN multilayer films. Both monolayer and multilayer films consist primarily of TiN with minor Ti. The monolithic TiN film exhibits a strong (111) preferred orientation, whereas the multilayer films show a pronounced (200) preferred orientation. Additionally, the intensity of Ti diffraction peaks gradually increases with increasing cycling periods, reflecting the increasing volume fraction of Ti layers. The (002)Ti diffraction peak slightly deviates from the standard angle, likely due to lattice distortion in the extremely thin Ti interlayers caused by growth stresses from the TiN layers.

Figure 2 [Figure 2: see original paper] presents the cross-sectional morphology of monolithic TiN film and a Ti/TiN multilayer film at 3 cycles. The monolithic TiN film exhibits columnar crystal growth with a thickness of approximately 5.6 m. The columnar crystals are tightly bonded without defects such as pores or microcracks reported by Jeong et al. [3] in their prepared films. In contrast, the multilayer film shows significantly refined TiN columnar crystal length and width due to the Ti interlayer interruption. The monolayer film surface appears uneven due to varying growth rates among columnar crystals, while the multilayer film exhibits uniform growth rates as columnar crystals renucleate on each Ti interlayer, resulting in a very smooth surface. Figures 3a [Figure 3: see original paper] and 3b show FE-SEM images of the surfaces of monolithic TiN film and the 3-cycle multilayer film, respectively. The monolayer surface displays a "fish-scale" morphology formed by exposed coarse columnar crystals. With scale thicknesses of 30-50 nm and 90° sharp corners, the monolayer surface is extremely rough. The multilayer film exhibits significantly reduced scale dimensions (<20 nm thickness), with many sharp corners becoming rounded arcs, substantially improving surface roughness. Figures 3c and 3d show cross-sectional morphologies of 3-cycle and 9-cycle multilayer films, respectively. Good bonding is observed between Ti and TiN layers as well as between the Ti transition layer and substrate, with uniform layer thicknesses. The measured Ti and TiN layer thicknesses for various cycling periods are listed in Table 1 . The average Ti interlayer thickness is 60 nm, and the TiN/Ti thickness ratio decreases with increasing cycling periods, though the rate of decrease gradually slows. This variation significantly influences the mechanical behavior of the films.

2.2 Effect of Cycling Period on Hardness and Adhesion Strength of Multilayer Films

Table 2 lists the surface microhardness values of monolithic TiN and Ti/TiN multilayer films. The microhardness of all multilayer films exceeds 11.0 GPa, higher than the 10.8 GPa of the monolithic film. The 3-cycle multilayer film achieves the highest hardness of 15.8 GPa. With increasing cycling periods, the surface hardness of multilayer films gradually decreases. The hardness variation pattern correlates closely with the Ti and TiN layer thicknesses in each period. In the monolithic film, the TiN layer thickness far exceeds that of the Ti adhesion layer, so the TiN layer hardness dominates the overall film hardness. In this case, the coarse TiN columnar structure offers low resistance to dislocation motion, resulting in relatively low hardness. In multilayer films, the columnar structure is refined and the increased Ti/TiN interface density enhances resistance to plastic deformation, leading to significant work hardening and higher hardness than monolithic films. As cycling periods increase, the cumulative thickness of hard TiN decreases while that of soft Ti increases. Under applied load, stresses on TiN layers can be transferred to Ti layers, where internal stresses are relieved, causing the multilayer hardness to gradually decrease. However, at 12 cycles, the TiN/Ti thickness ratio is only 5 and the single TiN layer thickness reduces to 322 nm. At this point, the micro/nanoscale effect of TiN increases resistance to dislocation generation and motion, and this strengthening effect outweighs the influence of reduced TiN cumulative thickness, resulting in slightly higher hardness for the 12-cycle multilayer compared to the 9-cycle film.

Table 2 also presents the adhesion strength of monolithic TiN and Ti/TiN multilayer films measured by scratch testing. The monolithic film exhibits an adhesion strength of 47 N, while all multilayer films show higher values that increase with cycling periods. The maximum adhesion strength occurs at 6 cycles, showing an opposite trend to hardness variation. This demonstrates that Ti interlayers effectively serve as stress buffers, inhibiting crack propagation and improving fracture toughness of the coating.

2.3 Effect of Cycling Period on Wear Performance of Multilayer Films

Figure 4 [Figure 4: see original paper] shows the variation of friction coefficients for monolithic TiN and Ti/TiN multilayer films in Hank's solution under a 10 N load over time. Due to the presence of incompletely ionized Ti droplet particles on the outermost surface, the friction coefficient initially increases then decreases during initial wear. In the steady-state stage, the 3-cycle multilayer film exhibits the lowest and most stable friction coefficient of 0.35. The monolithic film and 9-cycle multilayer film show the highest friction coefficients of 0.50 and 0.52, respectively. The 6-cycle and 12-cycle multilayer films show intermediate but unstable friction coefficients that decrease initially then increase.

Figure 5 [Figure 5: see original paper] displays the wear track morphologies of monolithic TiN and Ti/TiN multilayer films at various cycling periods. The monolithic film shows a wear track width of 460 m, while multilayer films exhibit widths between 380-410 m, with the 3-cycle multilayer having the smallest width. Black areas within the wear tracks contain high oxygen content according to EDS analysis, resulting from oxidation of the exposed Ti interlayer after the surface TiN layer was worn away in the simulated body fluid. Gray areas represent the original TiN layer. The damage morphology and extent vary with cycling periods. The 3-cycle multilayer surface shows only compression and scratching marks in the central wear track with minimal damage and slight plowing in undamaged regions. The 6-cycle multilayer exhibits large-area damage covering approximately 1/4 of the wear track. The 9-cycle multilayer shows damage exceeding 80% of the wear track area, with local TiN layer spalling indicated by arrows in Figure 5d. The 12-cycle multilayer shows damage covering about 1/2 of the area. The friction coefficients and wear track characteristics correlate well with hardness and surface roughness variations. The high surface roughness and low hardness of the monolithic film directly lead to high friction coefficient and poor wear resistance. The 3-cycle multilayer film, with minimal surface roughness and highest hardness, consequently shows the lowest friction coefficient and best wear resistance. In 6-12 cycle multilayer films, the reduced TiN layer thickness not only decreases composite hardness but also makes the surface TiN layer prone to fracture and delamination during sliding, increasing the friction coefficient and surface wear.

Based on the ball-on-disk wear volume calculation formula, the wear rates of monolithic and multilayer films can be estimated:

$$K = \frac{\Delta V}{P \cdot S} = \frac{h^2}{P \cdot S}\left(w - \frac{h}{3}\right)$$

where K is the volumetric wear rate (mm^3/(N · m)), ΔV is the wear volume (mm^3), P is the load (N), S is the sliding distance (m), h is the wear track depth (mm), w is the wear track width (mm), and r is the wear track radius (mm). Laser confocal microscopy measurements show the maximum wear depth of the monolithic film is approximately 1 m, yielding a calculated wear rate of 4.0$×10^{-6}$ mm^3/(N · m). The wear depths of multilayer films are extremely small and beyond the instrument's measurement precision, suggesting wear rates below 4.0$×10^{-6}$ mm^3/(N · m), classifying them as completely wear-resistant materials.

3.1 Hardening Mechanism of Ti/TiN Multilayer Films

Since the 1970s, the mechanical enhancement effects of transition metal nitride heterostructured multilayer films have attracted widespread attention in the international academic community [17-20], and such hardening effects significantly influence coating wear performance. Researchers have proposed several hardening mechanisms for multilayer films, including the Hall-Petch effect, coherency strain effect, and composite strengthening theory, with multiple mechanisms potentially acting simultaneously for a given multilayer structure [21-23]. This study demonstrates significant differences in columnar orientation, growth morphology, surface roughness, and hardness between monolithic TiN and Ti/TiN multilayer films deposited on Ti6Al4V alloy by magnetron sputtering, leading to superior friction and wear performance of multilayer films in Hank's solution. The hardening mechanisms originate from several aspects. First, monolithic TiN columnar crystals exhibit (111) preferred orientation, while multilayer TiN shows (200) preferred orientation. When the loading direction is perpendicular to the film surface, the multilayer (200)TiN orientation provides more equivalent slip systems and larger maximum Schmid factors than the monolithic film, favoring multiple slip systems and promoting work hardening. Second, the alternating Ti interlayers reduce TiN columnar crystal length to 1/3-1/12 of that in monolithic films, producing significant grain refinement strengthening. Third, complete coherent matching can be achieved between hcp (0001)Ti and (111)TiN, creating a coherent stress field at phase interfaces that strongly impedes dislocation motion. The combined effects of work hardening, grain refinement strengthening, and coherent strengthening significantly enhance multilayer film hardness. However, it should be noted that as cycling periods increase, the cumulative thickness of Ti layers with good plastic deformation capability gradually increases, offsetting the hardening effect of TiN layers to some extent but improving coating toughness and adhesion strength. Achieving optimal matching of hardness and adhesion strength in multilayer films requires comprehensive consideration of these competing factors.

3.2 Corrosion-Wear Mechanism of Ti/TiN Multilayer Films

According to corrosion-wear theory for metallic materials, the total corrosion-wear loss (T) in corrosive solutions consists of three components: pure mechanical wear (W), pure chemical or electrochemical corrosion (C), and the synergistic effect of corrosion on wear (Wc) plus wear on corrosion (Cw), expressed as:

$$T = W + C + Syn$$

TiN possesses much higher hardness than Ti6Al4V substrate alloy and exhibits excellent corrosion resistance in simulated body fluid [24]; therefore, the W and C terms in Equation (3) contribute little to the T value. Literature [25] indicates that the Syn/T ratio for Ti/TiN films in simulated body fluid is approximately 0.77, demonstrating that the synergistic effect of corrosion and wear is the primary cause of coating failure in physiological environments.

Compared with monolithic films, the TiN columnar crystal size in multilayer films is reduced from 300-600 nm to approximately 100-200 nm. Grain refinement not only enhances hardness but also promotes rapid passivation of the coating in corrosive environments due to the high surface energy of nanocrystalline structures, reducing corrosion rates and effectively inhibiting the mutual enhancement between electrochemical corrosion and mechanical wear [26].

TiN layer thickness significantly influences wear behavior in multilayer films. As shown in Table 1, the TiN/Ti thickness ratio (dTiN/dTi) decreases substantially with increasing cycling periods. At small cycling periods, moderate TiN layer thickness yields high coating hardness. When the counterface ball contacts micro-asperities on the coating surface, only minimal plastic deformation occurs under normal load, resulting in slight plowing marks. At large cycling periods, thin TiN layers reduce coating hardness, and severe surface plastic deformation occurs during sliding against the counterface ball. The shear stress at the TiN/Ti interface easily causes delamination and spalling of the outermost TiN layer, exposing the inner Ti layer to the corrosive solution where it rapidly oxidizes to TiO_2. The thinner TiO_2 layer is then crushed and detached under repeated normal and frictional forces, creating a cycle of three-body abrasive wear and adhesive wear. This mechanism explains why the 3-cycle multilayer film exhibits optimal wear resistance while the 9-cycle multilayer film shows the highest friction coefficient and most severe wear surface. Thus, optimizing the cycling period and controlling the Ti/TiN thickness ratio are critical for improving the adhesion and corrosion-wear performance of Ti/TiN multilayer films.

Conclusions

(1) Alternating soft/hard Ti/TiN multilayer films deposited on Ti6Al4V alloy by magnetron sputtering show a transformation of TiN columnar crystal orientation from (111) to (200) preferred orientation compared with monolithic TiN films. The columnar crystal size is significantly refined, surface roughness is reduced, hardness is increased, and substrate adhesion strength is enhanced.

(2) With increasing cycling periods, the reduced TiN layer thickness leads to gradually decreasing coating hardness, but substrate adhesion strength progressively increases.

(3) In Hank's solution, multilayer films demonstrate superior wear resistance compared with monolithic films. However, in 6-12 cycle Ti/TiN multilayer films, the reduced TiN layer thickness makes the surface TiN layer prone to fracture and delamination during friction and wear, generating oxidative and adhesive wear that gradually increases the friction coefficient over time. The 3-cycle Ti/TiN multilayer film, with moderate TiN/Ti thickness ratio and high hardness, exhibits only slight abrasive wear, with friction coefficient and volumetric wear rate significantly lower than those of monolithic TiN and other multilayer films, demonstrating optimal corrosive-wear resistance.

References

[1] Huang H H, Hsua C H, Pana S J, Heb J L, Chen C C, Lee T L. Appl Surf Sci, 2005; 244: 252
[2] Cheng Y, Zheng Y F. Surf Coat Technol, 2007; 201: 6869
[3] Jeong Y H, Lee C H, Chung C H, Son M K, Choe H C. Surf Coat Technol, 2014; 243: 71
[4] Zalnezhad E, Sarhan A A D, Hamdi M. Mater Sci Eng, 2013; A559: 436
[5] Zhang X H, Liu D X. Trans Nonferrous Met Soc China, 2009; 19: 97
[6] Yu X, Wang C B, Liu Y, Yu D Y. Acta Metall Sin, 2006; 42: 662
[7] Liu C L, Lin G Q, Yang D Z, Qi M. Surf Coat Technol, 2006; 200: 6673
[8] Cheng Y, Zheng Y F. Mater Lett, 2006; 60: 2243
[9] Shao A L, Cheng Y, Zhou Y, Li M, Xi T F, Zheng Y F, Wei S C, Zhang D Y. Surf Coat Technol, 2013; 228: S257
[10] Liu T W, Dong C, Wu S, Tang K, Wang J Y, Jia J P. Surf Coat Technol, 2007; 201: 6737
[11] Shao H H, Peng Y T, Jiang X Y, Liu X L, Chen C, Zhu Z H. Funct Mater, 2014; 45: 14145
[12] Gong H F, Shao T M, Zhang C H, Xu J. J Inorg Mater, 2008; 23: 758
[13] Serro A P, Completo C, Colaço R, Santos F D, Lobato da Silva C, Cabral

J M S, Araújo H, Pires E, Saramago B. Surf Coat Technol, 2009; 203: 3701
[14] Lin N M, Huang X B, Zhang X Y, Fan A L, Qin L, Tang B. Appl Surf Sci, 2012; 258: 7047
[15] Liu C L, Chu P K, Lin G Q, Yang D Z. Corros Sci, 2007; 49: 3783
[16] Wang L, Su J F, Nie X. Surf Coat Technol, 2010; 205: 1599
[17] Zhang S, Sun D, Fu, Y, Du H. Surf Coat Technol, 2003; 167: 113
[18] Zhang G J, Wang T, Chen H L. Surf Coat Technol, 2015; 261: 156
[19] Zhang S, Fu Y, Du H, Zeng X T, Liu Y C. Surf Coat Technol, 2002; 162: 42
[20] Rebholz C, Monclus M A, Baker M A, Mayrhofer P H, Gibson P N, Leyland A, Matthews A. Surf Coat Technol, 2007; 201: 6078
[21] Xu X M, Wang J, Zhao Y, Zhang Q Y. Acta Phys Sin, 2006; 55: 5380
[22] Zheng J Y, Hao J Y, Liu X Q, Gong Q Y, Liu W M. Surf Coat Technol, 2012; 209: 110
[23] Yip S. Nature, 1998; 391: 532
[24] Zhou D P, Peng H, Zhu L, Guo H B, Gong S K. Surf Coat Technol, 2014; 258: 102
[25] Naghibi S A, Raeissi K, Fathi M H. Mater Chem Phys, 2014; 148: 1039
[26] Park J J, Choe H C, Ko Y M. Mater Sci Forum, 2007; 539-543: 1039

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