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Amorphous Alloys Containing Cobalt for Orthopaedic Applications

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Abstract: Amorphous metal alloys have properties and structures unlike those of their crystalline counterparts. For example, a multiphase crystalline structure may exhibit poor corrosion resistance while the amorphous structure is corrosion resistant. The high hardnesses of some amorphous alloys may make them useful for wear resistant applications. Cobalt-based, electrodeposited alloys may be particularly compatible for producing desirable surfaces on orthopaedic Co-Cr-Mo alloys. Amorphous Co-20P alloy (A-Co-20P) has an as-deposited Knoop hardness number (HK) of ca 620. The surface of anodized A-Co-20P has been described elsewhere as predominately phosphorus oxide that may react with water to form an adsorbed hypophosphite layer. Others reported corrosion resistance without pitting. Hence, the potential of A-Co-20P for use as an implant coating to induce bony apposition was evaluated. This evaluation consisted of tests of corrosion resistance and solution chemistry. Another alloy, amorphous Co-Cr-C, was found to have an as-deposited HK of ca 690. Heat treatment produced Knoop hardness numbers (HKs) of ca 1350, between the HKs of zirconia and alumina. Wear and corrosion resistance are expected to be good, but adherence needs to be assessed.

Keywords: amorphous metals, glassy alloys, orthopaedic joint surfaces, orthopaedic joint surface coatings, corrosion resistant coatings, wear resistant coatings, wear of ultrahigh molecular weight polyethylene, wear resistant implants, bone conductive, bone induction, implant-bone interface

Numerous approaches are currently being employed in attempts to develop orthopaedic biomaterials that offer improved performance over existing materials. For

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example, numerous approaches for applying calcium-phosphate coatings to orthopaedic implants have been used for the purpose of more rapidly and firmly anchoring them to bone. Also, because wear debris from orthopaedic implants has been implicated as a or cause for the end-of-effective-service of orthopaedic implants [1,2], there is a strong interest in exploring new bearing designs, including new material couples, that may reduce wear debris effects and, hence, help to prolong effective implant service. In this regard, various methods to produce harder, more wear-resistant surfaces on orthopaedic hip implants are being investigated. While modifications of existing materials and mechanical designs must surely be investigated, the potential of new technologies should also be explored for what they may have to offer and for what may be learned toward solving the problem.

This report on work-in-progress is intended to provide results of some tests on the corrosion resistance of amorphous A-Co-20P (atomic fractions are used throughout the paper when specifying particular compositions within an alloy system), and hardness, wear resistance, and adherence of some electrodeposited amorphous Co-Cr-C alloys, Co \ddot{e} (0 to 42) %, Cr \ddot{e} (88 to 14) %, C \ddot{e} (12 to 8) %, respectively {mass fractions, Co \ddot{e} (0 to 50) %, Cr \ddot{e} (97 to 50) %, C \ddot{e} (2 to 3) %}. The Co-Cr-C was electrodeposited onto Co-Cr-Mo alloy meeting the compositional requirements of ASTM Standard F 75 for Co, Cr, & Mo. For the adherence test, a simpler A-Cr-C alloy will be used to obtain an indication of what may be expected from more complex A-Co-Cr-C alloys when they may be used under their own favorable electro-deposited and heat treatment conditions.

Fabrication by Electrodeposition

One way to produce metallic glasses is by electrodeposition, which is a facile method for applying coatings. By this method metallic glasses can be produced that have a variety of structures and properties. They may be produced as alloys of single phase structures or as mixed-phase, layered, structures of which one or all of the layers may be glassy, each with differing, predominate, elemental composition. By control of the electrodeposition times, voltages, voltage waveforms, solutions and other characteristics of processing, the compositions and thicknesses of the layers can be controlled. Brenner et al.[3], Johnson et al.[4], Ratzker et al.[5], and Helfand et al.[6] describe electrochemical processes for fabrication of A-Co-20P alloys; the methods of Ratzker [5] were followed for fabrication of the A-Co-20P alloys evaluated for this paper. The electrodeposition methods reported by Johnson et al.[7,8,] and Soltani [9] were followed for fabrication of the A-Co-Cr-C alloys and A-Cr-C alloys that were tested. There are numerous reports in the patent and other literature that describe the electrodeposition baths and conditions for producing amorphous cobalt-phosphorus alloys, so these will not be reiterated here.

The cobalt-phosphorus and cobalt-chromium-carbon systems are the specific objects of investigation here; carbon is carried into the system from organic components of the electrolyte. Layers in these systems may be homogenized by heat treatments to produce either amorphous materials or materials with noncrystalline structures and/or finely dispersed precipitates. At early stages of treatment, precipitates cannot be detected optically or analyzed by x-ray diffraction; increased hardness indicates their presence.

Composition and Properties

Cobalt-Phosphorus Alloys

In 1993 Ratzker et al.[5] described a method for fabricating dental prosthetic frameworks of metallic glasses, composed of preferred composition Co-20P (mass fractions of ca 88 % cobalt and 12 % phosphorus), for use in resin-retained, fixed-partial dentures. The alloy samples had high hardnesses, ranging from Knoop hardness numbers (HKs) of ca 620 to 1100; the latter was obtained following one hour heat treatment in air at 350 °C. The HK tests were made on film cross sections, supported around the edges by 100 nm nickel deposits, at loads of 0.98 N (0.1 kgf). Based on the method of [10], yield strengths calculated from HKs {(ca 3 MPa)/HK} indicate that these alloys are exceptionally strong, having yield strengths ranging from ca 1,860 MPa to 3,300 MPa (270,000 psi to 478,000 psi). These estimates compare favorably with the minimum yield and tensile strength requirements for cobalt-chromium-molybdenum alloys as given in ASTM specifications F-75 and F-1537, i.e.; 517 MPa and 897 MPa respectively. Such high strength is what was sought for the purpose of fabricating very thin prostheses for conservative tooth preparations. In addition, the corrosion potentials were ca 150 mV versus hydrogen electrode potentials for the as-deposited alloy. In this sense, these are alloys that may be considered noble but their corrosion potentials are lower than those for polished cobalt-chromium-molybdenum dental alloy, which were found to be ca + 700 mV (the dental alloy is virtually the same composition as that required for orthopaedic implant alloys according to ASTM F-75 and ASTM F-1537). The corrosion current of the cobalt-phosphorus alloy was found to be comparable to or less than that for the dental alloy and there was no evidence of pitting in the deposit.

Ratzker et al.[5] described the corrosion current of A-Co-20P as 0.8×10^{-3} cm/year and Co-Cr-Mo as 5.8×10^{-3} cm/year. Ratzker [11] also described the dynamic polarization as exhibiting a passive region. Helfand et al.[6] also reported on an A-Co-20P alloy that they had prepared by electrodeposition. Helfand et al.[6] analyzed the surface of their alloy after it had been subjected to series of anodic polarization treatments, including 10 s at 600 mV, and 1 h at 0 mV (measured against a standard calomel electrode). The latter found evidence for a surface that, after anodic polarization and during immersion in acidic electrolytes, changed to one that was highly enriched in phosphorus, forming a hypophosphite that they speculated inhibits other water molecules from reaching the alloy's surface. Hence, they explain P as inhibiting anodic dissolution by enriching itself on the alloy surface and by the formation of this hypophosphite layer. They termed the anodic polarization as having a region they called "transpassive".

If a stable phosphorus-containing layer of some sort does form on the alloy surface, and if that surface does become truly passive, such a surface may be one to which calcium ions may act as bridges to physiological phosphates in vivo. Under those conditions, it is conceivable that the surface could be osteoconductive and implants could be anchored in bone by use of such amorphous cobalt-phosphorus alloy coating. Therefore, one purpose of investigation was to determine whether the surface layer referred to as passive or "transpassive", formed following anodic polarization of an amorphous Co-20P alloy, would be stable in aqueous solutions.

Cobalt-Phosphorus Alloys, Experimental Procedure

It has been well established that A-Co-20P alloy and the similar Ni-20P [3,6] are enriched in phosphorus following anodic polarization methods treatments. Helfand et al. [6] propose a surface layer that is virtually hypophosphite, $H(H_2PO_2)$. It is further established that the anodic polarization curves display a region that has been interpreted as being passive [11] or “transpassive” [6]. However, implication that this behavior may be passive appears to be questionable in that the anodic current does not fall off as sharply and is not as insensitive to increases in voltage as alloys of the Co-Cr-Mo system that are used for medical and dental purposes. For a binary A-Co-20P alloy to be nontoxic and osteoconductive, the alloy would have to be truly be passive and to have phosphorus incorporated into the surface in a form that is not removed, say by precipitation with calcium ions. Therefore, to investigate whether this capability existed with Co-20P, it was decided to examine the solution behavior of the alloy specimens after several different polarization treatments shown in Table 1.

Specimens were prepared so that portions of the alloy surfaces were masked to prevent surface changes during the polarization treatments. Then tests of the stability of the masked and polarized surfaces were made by monitoring pH changes while the surfaces were in water and in CaP solution (2.1 mmol/L phosphate & 10 mmol/L $CaCl_2$ and at pH = 6.1). The test solutions were also checked afterward for release of cobalt ions. Following this, the specimens were then soaked overnight either in water, 1 mmol/L phosphoric acid or 1 mmol/L sulfuric acid under stirring at a temperature of $\pm 23^\circ C$, to determine whether all cobalt that may exist in the surface could be removed (solutions were in excess volume such that there was ≈ 1 L solution for each 2 cm^2 of Co-20P surface). After the overnight soakings, the specimens were washed with distilled water and they were once again tested in water and in calcium phosphate solution (previously described) to determine whether additional cobalt would be released. In this procedure, one drop of solution, either water or calcium phosphate solution, was put on the surface and a combination pH electrode was used to continuously follow the pH of

Table 1

SOLUTION	<i>Polarization Conditions</i>	
	CURRENT DENSITY	TIME
0.2/3 mol/L H_3PO_4 ,	2.5 mA/cm ²	1 min
0.2/3 mol/L H_3PO_4 ,	6.5 mA/cm ²	2 min
0.2 mol/L HCl.,	6.5 mA/cm ²	2 min

the solution. Afterward, a test for the presence of cobalt ions in the solution was made using cobalt test paper (limit of sensitivity: Co, 25 mg/L; Gallard-Schlesinger Chemical Mfg. Corp. [12]). This method can characterize the solution tendency of the surface. Changes in pH follow the dissolution behavior in water, and the dissolution and precipitation behavior in the calcium phosphate solution. Dissolution of basic cobalt compounds increases the pH of the solutions, conversely, the precipitation of basic apatite from the calcium phosphate solution (metastable with respect to hydroxyapatite) in the absence of release of basic cobalt will decrease the pH of the solution [13].

Cobalt-Phosphorus Alloys, Experimental Results

Figure 1 shows typical increases in pH as function of time in the calcium phosphate solution after polarization (even faster increases in pH of water were observed; typically pH increased from 6.4 to 7.6 in 3 h). These increases in pH indicate the dissolution of the basic cobalt compound into the water and the calcium phosphate solution. While the precipitation may occur in the calcium phosphate solution, it was not observed by the pH measurement because of the dominance of the dissolution process. Within 50 min, cobalt ions were detected both in the water and calcium phosphate solution using the cobalt test paper. Further, after soaking in water, phosphoric acid, or sulfuric acid over night, with stirring, the release of cobalt ions was still observed.

Fig. 1 Typical increase in pH as a function of time in the calcium phosphate solution. The pH is for a drop of solution placed on a previously polarized surface of a Co-20P alloy specimen.

Cobalt-Phosphorus Alloys, Discussion and Conclusions

The continuous dissolution of cobalt from previously anodically polarized amorphous Co-20P alloy, with no apparent cessation of that behavior, is proof that surfaces of that alloy are not passive (this occurred in acids, water, or acidified calcium phosphate solutions). The evidence presented in the literature of a phosphorus enriched surface cannot be discounted, but because the surface does not passivate, amorphous Co-20P is not suitable for use as an implant material. However, there are reports in the literature that amorphous Ni-Cr-P alloys can be passivated and that the presence of phosphorus in the surface layer contributes to this passive behavior. By analogy with the nickel alloys, it is reasonable to expect that similar behavior could be obtained if an amorphous Co-Cr-P alloy could be obtained by adding chromium to the system to make it more corrosion resistant, with both Cr and P contributing to a corrosion resistant surface. If this analogy carries forth, then there remains the possibility of fabricating implantable amorphous Co-Cr-P alloys that would also have the property of osseous

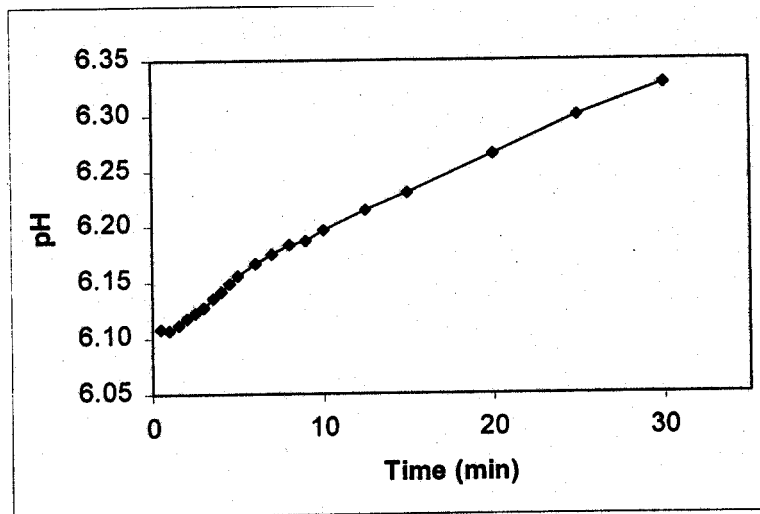


Fig. 1 Typical increase in pH as a function of time in the calcium phosphate solution. The pH is for a drop of solution placed on a previously polarized surface of a Co-20P alloy specimen.

integration by direct bonding to bone, through calcium linkages to phosphorus in the passive layer on the surface of the alloy.

Cobalt-Chromium-Carbon Alloys

Because of the high hardnesses of as-deposited amorphous chromium-carbon (HK \approx 800) [8] the electrodeposited amorphous cobalt-chromium-carbon alloys were chosen for investigation as their hardnesses were expected to be similarly high. The potential advantages of the latter alloys for use as coatings for orthopaedic bearing surfaces and instruments lie in: 1) heat treated condition hardnesses that, based on the hardnesses attainable from heat treated amorphous chromium-carbon, are expected to lie between those of high purity zirconia and high purity alumina and which should, therefore, provide highly wear resistant surfaces, 2) chemical compositions that should impart good corrosion resistance, 3) electrochemical deposition processing that should be a facile method for producing uniform coatings on simple geometry bearing surfaces. Therefore, the objective of this section of this manuscript was to investigate: 1) whether, in fact, high hardnesses, similar to those attainable from heat treated amorphous chromium-carbon, could be attained, 2) and whether the electrodeposited coatings had adherence and wear resistance sufficient to render them potentially useful for service as wear-resistant coatings for orthopaedic implant surfaces and instruments.

Cobalt-Chromium-Carbon Alloys, Experimental Procedure

In essence, the alloys were deposited from electrolytes containing di-valent cobalt and tri-valent chromium ions, with voltages that alternated back and forth between that needed for depositing cobalt to that needed for depositing chromium. This results in a structure composed of amorphous Co-rich and Cr-rich layers (Fig. 2). During such a procedure, the length of time spent at each voltage determines the thickness of a layer. As deposition of each layer proceeds, carbon is known to be carried into the chromium deposits from the organic constituents of the electrolyte [3]. Details of the electrodeposition procedures have been previously described elsewhere [7,8,9]. X-ray diffraction using Cu K α radiation was employed to assess the amorphous nature of the deposits.

The thicknesses of the layers deposited for fabrication of specimens for hardness measurements were *ca* 1 μ m for the chromium-based layer and *ca* 0.4 μ m for the cobalt-based layer. The HKs were taken from film cross sections, supported around the edges by 100 μ m thick nickel deposits, at loads of 0.245 N (.025 kgf), Fig. 3. Prior to indentation the surfaces of the cross sections were polished with 0.05 μ m alumina in distilled water. After hardnesses of as-deposited specimens were obtained, specimens were heat treated

Fig. 2 Layered structure of Co-Cr-C alloy with layers, 0.9 μm for Cr, 0.6 μm for Co, . . . Layers as thin as 10 nm or less can be produced (Magnification = 20000 X).

Fig. 3 As-deposited layered structure of cobalt-chromium-carbon with Knoop hardness indentations (Magnification. = 2000 X)
for 1 h at 600 °C in a vacuum at a pressure of 13.3 Pa (1×10^{-7} Torr). This treatment is known to produce the maximum hardness of ca 1850 from the transformation of the amorphous Cr-C alloys to a crystalline structure that results in clearly visible, dispersed, carbide precipitates in the chromium (in those alloys, treatment at 500 °C for 1 h results in nearly the same hardness, ca 1750 HKs, but precipitation cannot be resolved by either optical nor x-ray diffraction methods). The heat treatment of Co-Cr-C at 600 °C was similarly expected to reveal carbides in the chromium while precipitation in the cobalt

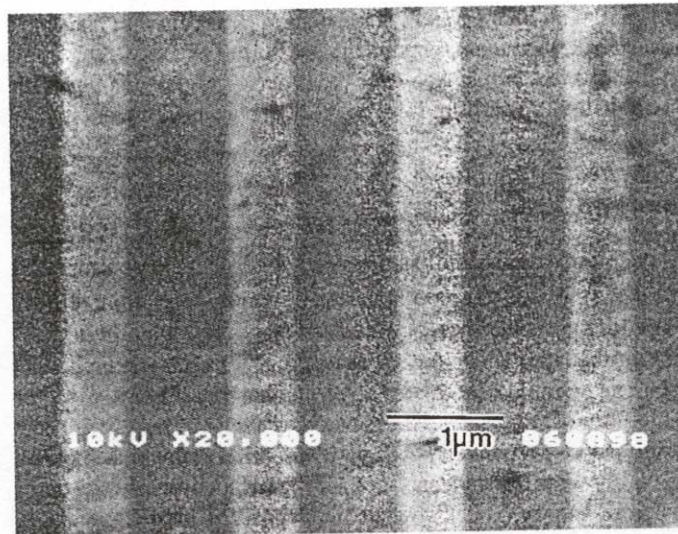


Fig. 2 Layered structure of Co-Cr-C alloy with layers, $0.9 \mu\text{m}$ for Cr, $0.6 \mu\text{m}$ for Co, . Layers as thin as 10 nm or less can be produced (Magnification = $20000 \times$).

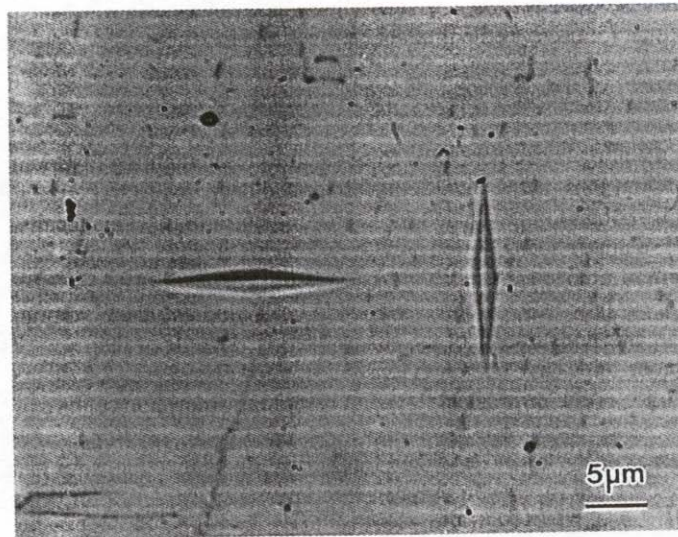


Fig. 3 As-deposited layered structure of cobalt-chromium-carbon with Knoop hardness indentations (Magnification = $2000 \times$)

would be taken as evidence of carbon also having been present in the amorphous cobalt layer. Following the 600 °C treatment, hardness indentations were taken both parallel to and perpendicular to the layer directions (attempts were made to keep the major axes of layer-parallel indents within a single layer and without termination at interfaces but this could not always be done). After the hardness tests, the specimens were etched for 2 min with a solution of 2.67 mol/L $K_3Fe(CN_6)$ and 0.4 mol/L KOH in distilled water, rinsed with distilled water, and dried. They were then observed optically at a magnification of 2000 X to determine whether precipitation had occurred, how uniform precipitation was within the chromium and cobalt layers, and whether there was evidence of diffusion between layers.

Specimen preparations for the wear and adherence tests have not yet been completed as there was an extensive shut-down of the electrodeposition laboratory that

Fig. 4 X-ray diffraction showing the broad pattern from glassy cobalt-chromium-carbon multilayer deposit, mass fraction Cr = 43 %. Counting Rate (s^{-1}), standard uncertainty =

$2 s^{-1}$, vs the diffraction angle, 2θ , (resolution 0.01°).

has inhibited this intended research. At the time of this submission of this manuscript, the laboratory is in the final stages of renovation, after which specimens will be fabricated for these tests.

Cobalt-Chromium-Carbon Alloys, Experimental Results

The X-ray diffraction patterns of as-deposited alloy were characteristic of an amorphous structure (Fig. 4). Distilled water was needed for the polishing procedures

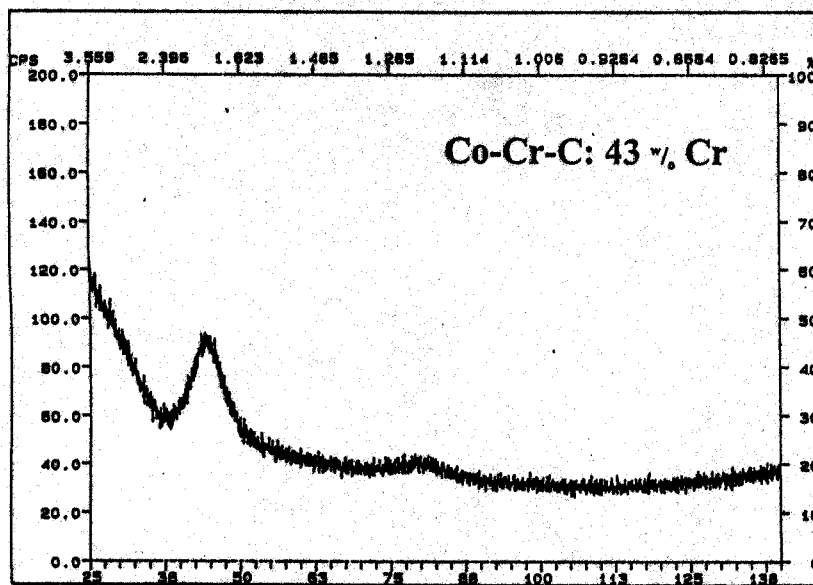


Fig. 4 X-ray diffraction showing the broad pattern from glassy cobalt-chromium-carbon multilayer deposit, mass fraction Cr = 43 %. Counting Rate (s^{-1}), standard uncertainty = $2 s^{-1}$, vs the diffraction angle, 2θ , (resolution 0.01°).

used to prepare surfaces for microscopy and hardness indentations as tap water had an etching effect on the cobalt layer, both before and after the 600 °C heat treatment.

The amorphous Co-Cr-C has an as-deposited HK of (693 Å 7.6), with a value of (692.4 Å 5.4) from measurements along the layer directions, and (694.8 Å 14.4) across the layers (Å is the estimated standard uncertainty of the measurements). Subsequent heat treatment at 600 °C resulted in HKs of ca (1300 to 1400). With the indenter tip in the chromium layer, the HK was (1300 Å 24) when the long axis of the indenter was parallel to the layer; when the long axis of the indenter was perpendicular to the layer the HK was (1407 Å 21). In no instance was delamination between layers found to have been caused by the HK indentations.

After the 600 °C treatment, cracks perpendicular to the layers could be observed in the chromium layers; these cracks were generally blunted by and did not traverse the adjacent cobalt layer. Subsequent etching revealed carbides had precipitated within the chromium layers and carbides appeared to have begun forming within the cobalt. The boundaries between the layers became more diffuse (Fig. 5) than they had been for the

Fig. 5 Co-Cr-C multilayer showing carbides after 600 °C heat treatment. as-deposited structure, indicating that diffusion was also taking place between layers (for an example of layer boundary structure prior to heat treatment see Fig. 2). The extent of the diffuse boundary could be estimated from the Fig. 5 photomicrograph as *ca* 0.2 μm.

Cobalt-Chromium-Carbon Alloys, Discussion and Conclusions

The resistance to delamination under indentation is important because it provides evidence that the layers may be bonded sufficiently to resist delamination during service if the alloys were used for implant coatings. Also, the high HKs appear to be the result of the development of very fine precipitates from transformations from amorphous deposits. Prior experience with amorphous chromium carbon indicates that high HKs

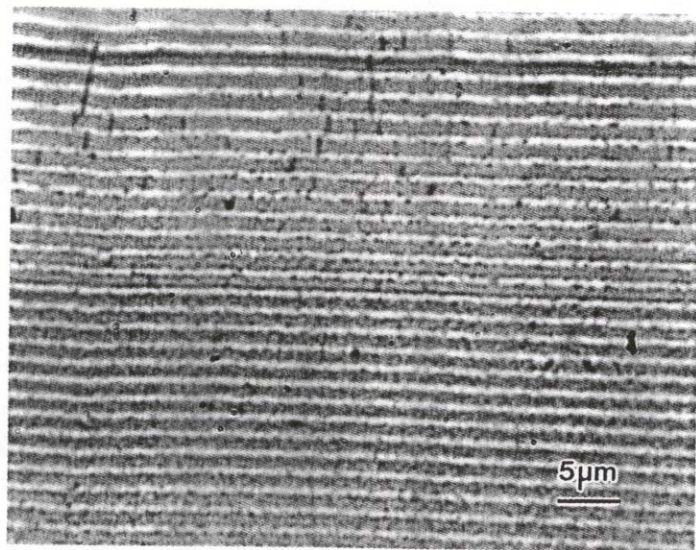


Fig. 5 *Co-Cr-C multilayer showing carbides after 600 °C heat treatment.*

may be achieved before carbides are either visible by optical microscopy at magnifications of 2000 X or detectable by X-ray diffraction. Such deposits are expected to have only small asperities, this could be important for wear couples for which asperities are a source of decreased wear resistance .

Finally, because elements can often be co-electrodeposited as alloys by choosing electrochemical potentials between those of either element, this approach will also be investigated. An amorphous Co-Cr-C alloy deposit may be advantageous for helping to ensure the attainment of corrosion-resistant, heat-treatable, adherent coatings.

While the data have been limited to structure and hardness determinations thus far there are a number of conclusions that may be drawn from the results.

These are:

- 1) X-ray diffraction reveals the as-deposited layers of Cr and Co as both being amorphous.
- 2) Heat treated deposits develop HKs that exceed those of zirconia and significantly approach those of alumina. These high HKs indicate potential usefulness for increasing the wear resistance of orthopaedic joints and instruments.
- 3) The cobalt layer is not corrosion resistant, indicating that chromium is not present in sufficient quantity in the as-deposited Co layer and that the layered deposits used are too thick to have allowed sufficient diffusion of chromium into the cobalt to impart corrosion resistance.
- 4) The cobalt and chromium layers appear to interdiffuse at their interfaces to the extent of ca 0.2 \bar{m} .
- 5) Other experience in this laboratory is that electrodeposition can deposit alternating layers of Co-C and Cr-C, with layer thicknesses controllable from \bar{e} 2 \bar{m} to \bar{e} 10 nm (\bar{e} 40 atoms). Therefore, it is likely that thin, layered structures of cobalt-chromium-carbon can interdiffuse sufficiently to provide good corrosion resistance throughout heat treated deposits.
- 6) Layers are bonded together well enough to resist delamination under indentation.
- 7) Adherence and wear tests are needed to confirm whether or not useful properties can be attained with deposits on orthopaedic bearing alloys.

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