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Mechanical and tribological properties of CrTiCu(B,N) glassy-metal coatings deposited by reactive magnetron sputtering

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Abstract

Copper-based bulk nanocrystalline and amorphous alloys offer attractive mechanical properties such as high hardness and fracture toughness—as well as good corrosion resistance. Such materials can potentially be used as thin film tribological coatings to improve the wear resistance of low strength steels and the light alloys. In this paper novel CrTiCu(B,N) glassy-metal coatings have been successfully deposited on Si-wafer, AISI 316 stainless and AISI M2 tool steel substrates, over a wide range of compositions, by hot-filament enhanced reactive magnetron sputtering. The majority of the coatings produced are X-ray amorphous and exhibit Knoop microhardness values above Hk_{25g}=2000 Kgf/mm^2 (i.e. $\geq$20 GPa). The coatings provide a significant improvement, by more than two orders of magnitude, in reciprocating sliding wear rate (compared to the stainless steel substrate) when tested against a 10 mm diameter SAE 52100 hardened steel ball counterface at 10 N normal load. In impact tests for 10^5 cycles against a 10 mm diameter WC–6% Co ball, at a maximum load of 1 kN, the coatings exhibit excellent resilience and ductility—with small impact cavities and little or no peripheral or radial cracking around the impact craters.

Keywords: Glassy-metal coatings; PVD; Sputtering; Hardness; Elastic modulus; Tribological properties

1. Introduction

Metallic coatings such as Cr(N)–Cu 'metal–metal' nanocomposite films [1] or nitrogen doped chromium (CrN$_x$; $x \leq 0.16$) [2] produced by magnetron sputtering can be applied to low strength substrates such as austenitic stainless steel, to improve wear resistance. Since they are predominantly metallic, the elastic moduli of such films are similar to (or somewhat less than) that of chromium metal (i.e. $\leq$280 GPa), providing a reduction in the elastic modulus mismatch between coating and substrate, when compared to many PVD ceramic thin films. The coatings can therefore accommodate substantial deformation of the substrate under loading, without failure. In recent experiments with the (pseudo)binary Cr(N)–Cu metallic system [1,3,4], we found that at around 23 at.% of Cu (and less than 18 at.% of N), the coating microstructure consists of a mixture of amorphous and quasi-amorphous phases (i.e. regions $\leq$2 nm wide, which are largely X-ray amorphous, yet appear crystalline in TEM studies), exhibiting relatively high hardness (15 GPa) and a reduction by more than 2 orders of magnitude in sliding wear rate when deposited on stainless steel.

Due to low equilibrium solid-state mutual solubility between Cr and Cu (which is retained to high temperatures), and an apparently wide miscibility gap on solidification, there is a strong tendency for the system to be driven thermodynamically into a segregation of phases by (at least in the early stages) processes exhibiting some of the characteristics of spinodal decomposition, resulting in a nanocomposite crystalline/amorphous structure. Therefore, a mixture of solely amorphous phases was not anticipated to occur in the 320–350 °C deposition temperature range employed in this work. However, Cu-containing early transition-metal binary

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and ternary alloy systems are known also to be bulk metallic glass formers under certain conditions. Zr–Cu and Hf–Cu (both of which are low-miscibility binary alloy systems) can exhibit amorphous phases within certain composition ranges between 30 and 70 at.% Zr or Hf [5–7]. Similarly, a strong glass forming ability is exhibited by the ternary Zr–Cu–Ti and Hf–Cu–Ti systems [8], where associated high tensile strength (above 2000 MPa), and elasticity can be seen—particularly since the Young's moduli of both Zr and Hf are low (i.e. the *H*/*E* ratio tends to be large for such alloys).

In bulk metallic glasses the formation of a glassy phase occurs by frustrating the process of recrystallisation through chemical disorder [9,10]. When mixing several elements, factors such as different atomic sizes [12] and contrasting valence electron configurations [13,14] can promote a metallic glass to be formed-even at mild quench rates of ~1 K/s or less. It is often found when mixing elements of different atom size, or which prefer differing crystallographic configurations – either in melt solidification, or in vapour deposition (PVD/CVD) processes – that films with disordered or amorphous structure can easily be formed. In particular, this tends to occur at a lower substrate temperature (and/or electrical negative bias)—and therefore a faster effective condensation/solidification rate.

According to Egami's topological criterion [11] amorphisation can be induced by local atomic strain (generated by atom size and valence electron configuration differences) of the constituent solute and solvent elements, which changes the local atomic coordination number. In fact Hume-Rothery and Coles [12] was the first to propose that alloying elements with a 14% (or higher) difference in atomic radii will most likely create an alloy with restricted mutual solubility. Due to the above-mentioned atom size differences, when one element is substituted for another in a crystalline structure, high lattice strain (and consequently increased 'lattice friction') will result, which affects considerably the yield strength (and therefore measured hardness). Thus substitutional additions of very large (e.g. atomic radii 0.09 nm or above) atoms and/or interstitial additions of very small (e.g. atomic radii 0.06 nm or below) atoms within the crystalline lattice of 'averaged sized' (i.e. 0.075±0.005 nm radius) metal atoms will tend to promote immiscibility or metallic glass formation. The bcc-Cr/fcc-Cu binary system, despite similar atom sizes, appears to exhibit a low mutual solubility and wide miscibility gap, due to contrasting valence electron configurations.

Holleck's proposed PVD phase field schematic for the Cu–Cr system [15] is displayed in Fig. 1. It shows that a Cr–Cu amorphous phase can exist around a 30/70 Cr/Cu mixture—even at relatively high deposition temperatures. Low-miscibility binary systems such as Cr–Cu can potentially be strong glass formers—particularly at higher Cu content. Binary mixtures however show limitations to their glass forming abilities compared to more complex ternary, quaternary, quinary, etc. systems. In the binary Ti–Cu (and similarly for Zr–Cu) phase diagram (see Fig. 2) at around 55 at.% Cu there is a competing point between body-centred-cubic (bcc) and face-centred-cubic (fcc) solid solution phases. These competing crystalline phases limit the glass forming ability of the system to the centre of the phase diagram (30–70 at.% Cu). In ternary systems such as Zr–Ti–Cu the ability to form a glass is greater since the competing phases (i.e. cph and fcc) have very little mutual solubility, frustrating the system more. Similarly it is likely that, at a certain (metastable) supersaturated content, nitrogen incorporated interstitially in the Cr–Cu binary system further promotes metallic glass formation.

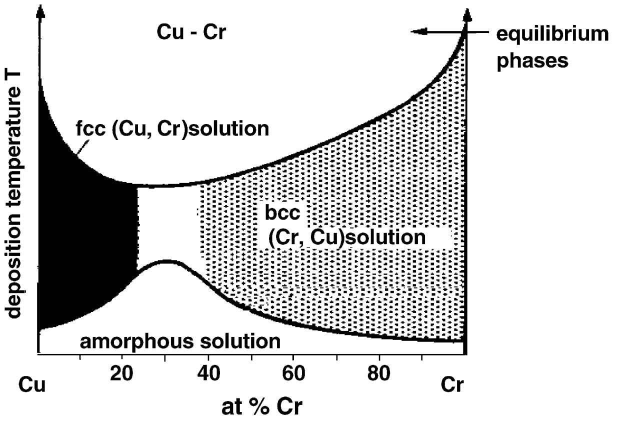

Fig. 1. Schematic of proposed PVD phase fields for the Cu–Cr system [15].

At the moment there is no unified theory to predict with complete accuracy the ease of formation of a glass—although models have recently been proposed [11,16–20]. Senkov and Miracle [17] proposed a topological model where a glassy phase is formed through the destabilisation of the host crystallite lattice by substitutional and/or interstitial alloying elements. It is quite possible that, in the Cr(N)–Cu binary system, at nitrogen contents below ~15–17 at.% N (which appears to be the approximate metastable solubility limit of nitrogen in Cr over the typical range of temperatures employed in PVD coating deposition), the result of nitrogen occupying interstitial sites is partial frustration of crystallisation—leading to a mixture of amorphous phases. Above that limit, metal nitride precipitation tends to result in the formation of a metal–ceramic nanocomposite crystalline structure.

Sanchette et al. [21] reported that nitrogen additions of less than 10% (by volume) in metastable Al–Ti and Al–Cr alloy coatings can lead to complete amorphisation at high substitutional element compositions. In fact, Musil's XRD data published previously for the Cr–Cu–N system [22] revealed an apparently amorphous structure for films deposited at low deposition temperatures (≤300 °C) for a $Cr_{30}Cu_{50}N_{20}$ composition—and amorphous Cr–Cu binary alloy films when deposited on unheated substrates. Unfortunately, the composition of these coatings appeared to vary non-systematically with substrate bias and temperature, therefore little can be concluded without further experimentation under closely controlled conditions. However the