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Cathodic arc deposited $(Cr,Si_x)N$ coatings: From solid solution to nanocomposite structure

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ABSTRACT

This paper aims to investigate the effect of silicon addition on the microstructure and mechanical properties of CrN coatings with an emphasis on their stability at high temperature. Thin films were deposited onto M2 tool steels using a cathodic arc deposition process. Silicon was introduced using duplex $Cr–Cr_3Si$ targets, allowing Si enrichment within the 0.6–10.8 at.% range.

The microstructure of the films was characterized by SEM and TEM, while their crystalline structure at room temperature and after high temperature annealing treatments (up to 1000 °C) was determined by XRD analyses. Mechanical properties were deduced from nanoindentation measurements and from residual stress experiments.

A minimum content of 2 at.% was evidenced as the solubility limit of Si in CrN. Below this value, Si substituted Cr in the CrN lattice to form a solid solution. Above 2 at.% Si, a nanocomposite bi-phased structure appeared, composed of Si-poor CrN nanograins surrounded by an amorphous Si-rich CrN matrix. Si addition induced significant grain shrinkage, without a significant effect on hardness at room temperature. For $(Cr,Si_x)N$ films annealed at high temperatures, the nanocomposite structure allowed a delay in structural transformations linked to nitrogen losses, preserving better and more stable mechanical properties.

1. Introduction

The machining industry is a major consumer of oils for different purposes such as cooling, lubricating or chip removing [1]. Reducing or eliminating oil in machining processes requires the development of new materials that will thus present a high thermal stability combined with a high wear resistance [2,3]. Over the last twenty years, there have been considerable efforts to develop new sustainable coating techniques and advanced materials in order to reduce the environmental impact of machining [4–10].

One limitation of lubricant-free machining is the impact of high temperature on the structure and properties of cutting materials. For example, high-speed steel hardness shows a critical decrease at around 500 °C [7], whereas it is well established that rubbing can induce heating able to exceed 900 °C [11]. Moreover, the development of ultra high speed machining tends to increase this critical temperature. These considerations highlight the need for a stable material operating at elevated temperature.

Nanocomposite coatings could provide a good solution for tool protection [11,12] as they exhibit improved durability in severe conditions. Various combinations of Me(X)N, where Me is a transition metal and X a doping element, have been studied in the literature, such as TiSiN [13–15], TiAlN [16–18], ZrSiN [19] or CrAlN [20]. While conventional titanium nitride based coatings show attractive mechanical properties, their relatively poor oxidation resistance hinders their use at very high temperatures. Chromium nitride based coatings present an interesting alternative thanks to their better intrinsic refractory characteristics, but are characterized by lower mechanical properties than Ti-based nitride coatings. Alloying CrN with a nanocomposite-former element such as Si might be a solution capable of combining both physico-chemical and mechanical properties. Many authors have studied such Si-containing CrN coatings over the last ten years [21–25].

It is indeed established in the literature that outstanding properties can be observed when a dual-phased (crystallized-amorphous) nanodistributed structure is achieved [26–30]. However, little information is available regarding the evolution of microstructure for a wide silicon concentration range. Moreover, once the desired nanocomposite structure is obtained, its thermal stability is often neglected, whereas such films are specially developed for extreme temperature conditions.

This paper is first focused on how silicon enrichment may influence the microstructure of $(Cr,Si_x)N$ coatings. Then, thermal stability of films in inert atmosphere is studied in terms of phase's transformation on the

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Table 1
Chemical composition of M2 steel substrates.

Element	C	Si	Mn	P	S	Cr	Mo	Ni	V	W
Composition (wt.%)	0.86–0.94	0.45	0.4	0.03	0.03	3.80–4.50	4.70–5.20	–	1.70–2.10	5.90–6.70

one hand, and through the preservation of mechanical properties on the other hand. Results are then discussed in light of the composition and microstructure of studied films.

2. Experimental

2.1. Deposition parameters

CrN and $(Cr,Si_x)N$ ($0<x<10.8$ at.%) coatings were deposited on M2 steel samples in an industrial Plassys cathodic arc physical vapor deposition (PVD) system. Cr and CrSi targets (100 mm in diameter), manufactured by Plansee with a purity rate ranging from 99.73% to 99.83%, were respectively used as cathodes for the deposition of the CrN reference coating and the different $(Cr,Si_x)N$ coatings. The silicon concentration of the CrSi targets was adjusted by sintering different amounts of Cr and Cr_3Si phases in a duplex target. With such dilution operations, the material manufacturer Plansee obtained a target's silicon concentration ranging from 3 to 20 at.%.

M2 steel substrates ($15*8*3\ mm^3$) were mirror polished down to a 1 μm diamond paste, cleaned with ethanol in an ultrasonic bath, and then rinsed in acetone. The chemical composition of the M2 substrates is given in Table 1. Prior to deposition, the chamber was pumped down to a pressure lower than 3.10^{-3} Pa. Two ion bombardments were performed in the vacuum chamber before the coating stage; first with argon ions in a gas mixture of argon–hydrogen and then with Cr ions (metallic cleaning). The target–substrate distance was kept constant at 60 mm. Nitrogen pressure, substrate bias and substrate temperature were 1 Pa, −100 V and 350 °C, respectively. The power level of arc discharges was kept constant at 1.6 kW for the Cr target and 2.0 kW for the CrSi ones. A substrate holder was animated with a planetary motion at a rotation speed of 3 rpm. For all coatings, a thickness of 3 μm was targeted.

2.2. Chemical and structural characterizations

The chemical composition of the coatings was checked over the whole thickness by glow discharge optical emission spectrometry (GDOES). The concentration of the different elements is calculated from the average of the concentration profile. Elemental composition has been measured by using silicon and chromium standard. The

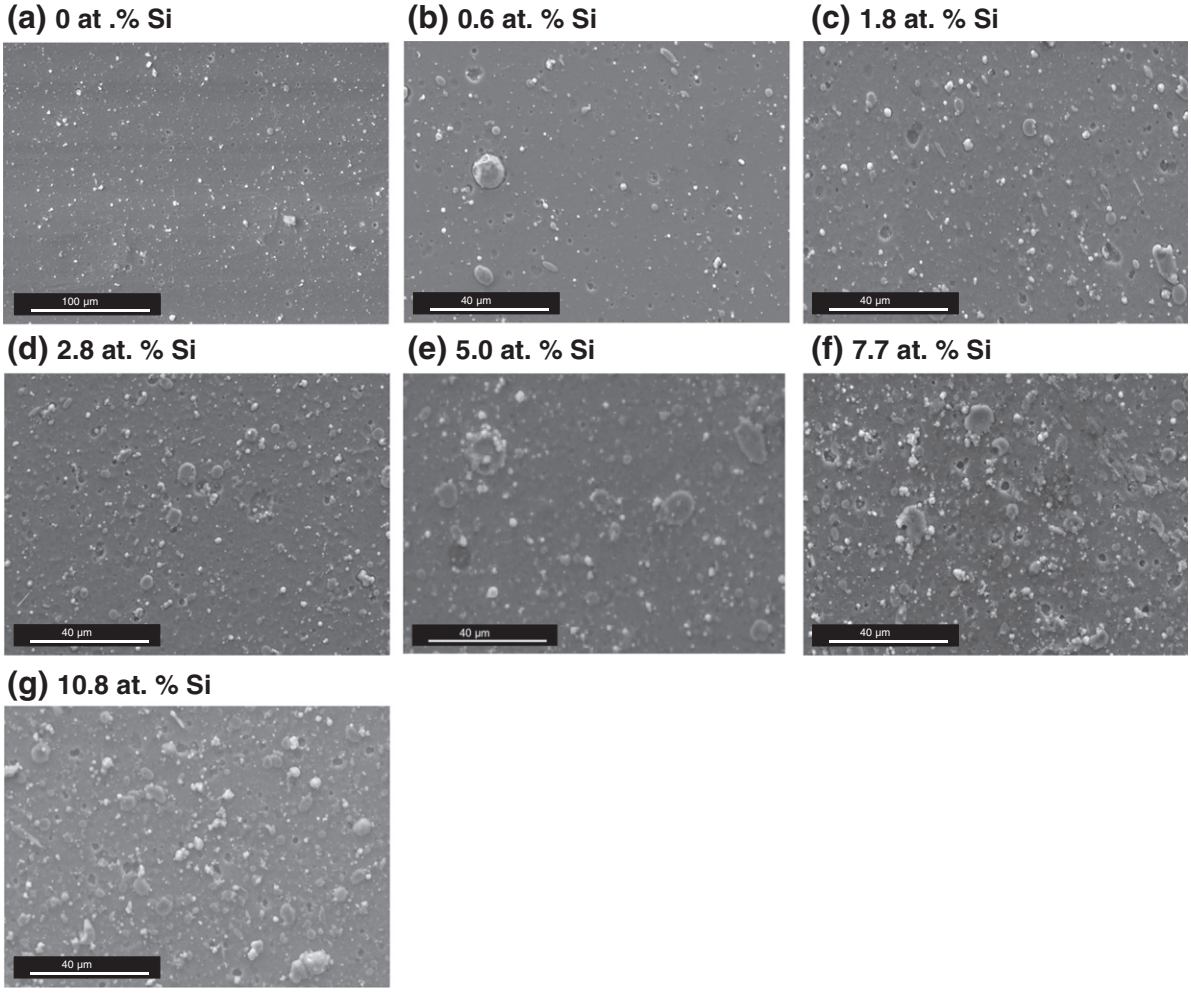

Fig. 1. SEM micrographs on the surface of $(Cr,Si_x)N$ coatings for the different silicon concentrations.