A Novel Approach to Micro Alloying and Structure Design of High Performance Coatings

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Abstract

In a constantly growing and developing high precision tools and components market, demands for better coatings are an incentive for coating developers to find unique and customized solutions for their current challenges. Alloying and especially micro-alloying of materials is a technique used to alter materials properties in order to obtain better oxidation and corrosion resistance as well as higher strength and ductility.

Micro-alloying of Cr with Si for instance gives the coatings higher thermal stability and leads to excellent cutting results, especially in dry and high speed cutting applications. It results in high oxidation stability and high hot-hardness combined with low abrasion wear of the coatings. Furthermore, Cr-based micro alloyed coating show advantages in cutting of non-ferrous alloys, including copper alloys.

In the present work, novel high performance micro-alloyed coatings (MAC) are deposited using a multi-purpose deposition system. Hybrid processes, i.e. arc ion plating (AIP) in combination with magnetron sputtering, for the deposition of high performance MACs are demonstrated, and the coating performance is explained in light of the deposition process and the micro-alloying dynamics. All coatings have been prepared in an industrial Metaplas Domino system, which includes both Arc evaporation in the form of APA (Advanced Plasma Assisted) technology and magnetron sputtering in the form of high power pulsed magnetron sputtering, HPPMS.

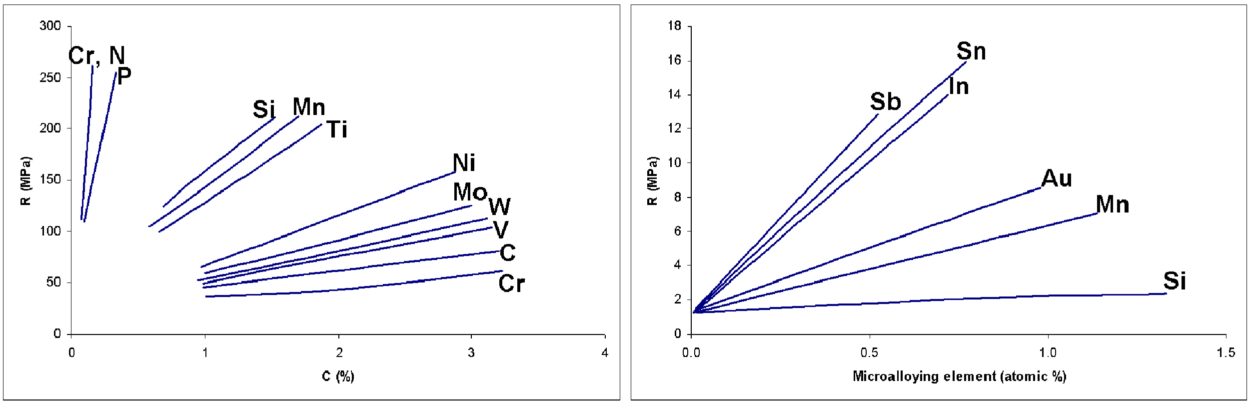
Keywords

Micro-alloying, PVD, silicon, thermal stability, machining

Introduction

Alloying and micro-alloying of steels began approximately half a century ago with the initial drivers being a reduction of material costs and an increase of the steels strength. Soon, new benefits of microalloying were recognized, including better solidification, hydrogen [1], and reheat cracking during fabrication, hardening, and weld metal toughness [2]. For example, in the case of forging steels, full strengthening of the steels was obtained by micro-alloying additions at high soaking temperatures of ~ 1100^{o}C or higher [3]. Nevertheless, it is the choice of the micro-alloying elements that allows a specification of the mechanical properties of the steel material. Other uses of micro-alloynig include employment of vanadium in order to promote intra-granular nucleation, particularly during welding [4]. In the case of C:Mn micro-alloyed steels, use of manganese micro-alloying has been shown to result in an enhancement of the solid solution strength and for enhancement of the solubility of vanadium carbonitrides [5].

In the last decades many coating developers have recognized the benefits of mixing different elements in achieving the enhancement of the properties of coatings [6,7,8,9]. However micro-alloying of coatings has only been used in the last decade, as the coatings composition evolved from binary to ternary and quaternary materials composition. The effect of micro-alloying is not well understood and a number of studies have therefore been initiated by many research groups in order to clarify the processes and mechanisms behind microstructure formation when micro-alloying is used [1-5]. Fig. 1 shows the effect of micro-alloying on the properties of steels (a), where the effect of the different micro-alloying elements on the steel's yield strength R, depends also on its C content, and copper (b).



(a) (b)

Fig. 1: (a) Microalloiyng of steel: the effect of microalloying on the yield strength R of steels depends on the nature and the amount of the microalloying element. (b) The effect of the nature and the quantity of the microalloying elements on Cu yield strength (R)

It is clear that micro-alloying brings not only enhanced properties but also added complexities to the understanding of its effect on materials. Micro-alloying of especially coatings requires therefore deep investigations on the atomistic mechanisms that take place during this process. Furthermore, good control over the coatings material and phase composition is needed. The latter is achieved by adopting different advanced PVD techniques such as arc evaporation and magnetron sputtering. PVD, or Physical vapour deposition, techniques are widely used for the deposition of a large number of compound and metallic coatings with specified mechanical, electrical and optical properties. In general, PVD allows some control over the phase and atomic composition of the coating. Recently, two new approaches have been employed to give added control over the phase composition and the quality of coatings, HPPMS [10] and APA arc evaporation. In HPPMS, high power pulsed magnetron sputtering, high peak power unipolar pulses are applied to the target (cathode) resulting in high peak electron densities (up to 6×10^{19} m^{-3}) in the target's vicinity [11,12]. These densities are three orders of magnitude higher than those achieved by conventional sputtering techniques, such as dc magnetron sputtering (dcMS) and result in high ionization fractions of the sputtered species. Using a negative substrate bias voltage, the ions can easily be manipulated in order to obtain the right energetic bombardment for the growth and for tailoring the film properties. In fact, the high ion-to-neutral ratio in HPPMS has been shown to enable the deposition of ultra-dense and smooth metallic and compound films, allow for phase tailoring [13] and lead to enhancement of film conductivity. APA (Advanced plasma assisted) evaporation is a technique that uses evaporators with a diameter of 100 mm [14]. The evaporator is supplied with a complex adjustable magnetic field that makes sure that the arc spot does not stay in the same spot for too long. The high magnetic field strength results in an increase of plasma activation. As a result the droplet emission is very low and the coatings are much smother when compared to conventional arc evaporation. Both HPPMS and APA techniques are used for the purpose of micro-alloying. In the present paper, the micro-alloying process is discussed and examples of micro-alloyed coatings deposited in a modular and flexible Metaplas DOMINO coating system are presented.

Micro-alloying: theory

The microstructure of a material is controlled by the processing steps chosen for its fabrication. Micro-structural design affects the nature of the phases present, their topology (i.e. geometrical distribution and interconnection) and their dispersion. All other parameters of the microstructure being equal, its size parameters, including grain size, grain boundary width, obstacle spacing, obstacle radius, the equilibrium diameter of a dislocation loop, and the spacing between partial dislocations, exert a strong influence on the materials properties [15]. In fact it is this variability of the property spectrum through micro-structural control that has often led to new materials of metallic and ceramic origin. Most of these size effects come about because of the micro-structural constraint to which a particular physical mechanism is subjected. Consider the classic case of strengthening a metallic matrix by particles or grain boundaries: lattice dislocations are forced, by the micro-structural constraint, to bow out or pile up, which requires an external stress characteristic or a micro-structural parameter. In general it is the competition or coupling between two different size dependencies that determine the properties of a material.

In coating development, the thickness of a coating plays a major role in determining its properties. For example, while a thin coating could be hard, a thicker version of the same coating could show deteriorating properties such as strong brittleness (as a result of the accumulation of the intrinsic stresses) and a weak adhesion to the substrate. Therefore, an important property of thin coatings, which has been studied extensively in recent years, is their plasticity yield stress. This property is of practical importance because it can affect the reliability of thin coating components. In terms of micro-mechanisms, thin coatings plasticity is influence by the dimensional constraint on dislocation movement, which results in pronounced size effect. One elegant way to design the plastic properties of a coating is by micro-alloying.

Micro-alloying is used in order to alter the mechanical properties of a coating, e.g. through employing the micro-alloying element as an obstacle which blocks or retards the motion of lattice dislocations. The interaction of defects with geometrical constraints is less well understood and merit extensive study. Nevertheless, recent microscopy studies have shown that depending on the nature and the amount of the micro-alloying element, different mechanisms could take place: i. e. the micro-alloying element could sit in the lattice of the growing crystal leading to a deformation of the crystalline lattice and a modification of the shear stresses in the coating, ii. The micro-alloying element could sit in the grain boundary and form an obstacle for dislocation. This works in such a way that the dislocation is forced to bend when confronted with the obstacle resulting in an increase of the shear stress of the crystal grains and therefore an increase of the strength. Other effects that could result from such a process are formation of a stress or energy window for formation of a crystalline phase, otherwise not possible. The forces with which the dislocations would bend depend on the size of the obstacle, the distance between the obstacles, and on the nature of the dislocation. Fig. 2 shows a sketch of the different bending mechanism that could take place as a result of micro-alloying for example.

The dislocation bending or curvature versus the obstacle spacing is better known as the “Orowan mechanism” [16], which connects the stress in shear τ with the radius R of the obstacle:

$$\tau \propto \frac{Gb}{R}$$

where G is the shear modulus and b is the magnitude of the Burger vector which characterizes the strength of the lattice distortion caused by the presence of the lattice dislocation.

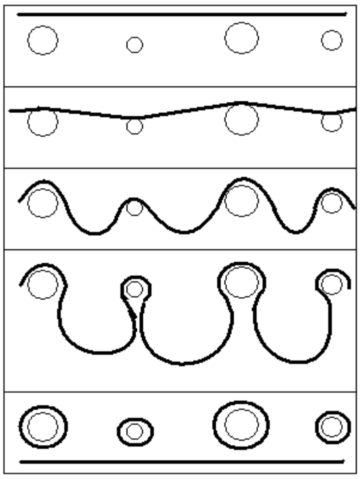


Fig. 2: The presence of foreign elements in a coating can result in a number of different behaviors of the dislocation, depending on the micro-alloying element and on the Orowan mechanism present in the matrix..

Coating development carried out in the last decade has been aimed at improving the properties of binary systems like TiN. For example, C, Al, and Cr are added in order to increase the coating’s hardness. Other approaches focused on the improvement of the thermal stability, the oxidation and the chemical resistance of the coating. For example, ternary AlMeN coatings such as AlTiN and AlCrN show the inherent advantage of in-situ forming of a dense, highly adhesive, protective oxide coating on the surface [17]. Other examples are quaternary materials based on AlTiN; different alloying elements have been tested for their ability to improve selected properties (Si, Y, Hf, Cr) showing grain refinement by Si addition or increased oxidation resistance by Y addition.

One important step in new coating engineering is the development of nano-structured materials. These are in general characterized by special properties in terms of the related process technology and the final product. The nano-structured materials are predominantly marked by the interfaces between the coating forming grains, where different physical and chemical rules are valid. By manipulating atoms, molecules and molecule clusters through micro-alloying, nano-structured materials are changed in a way not characterized by the homogeneous volume as traditionally known. The properties of nano-structured materials are, thus, not anymore material specific but dominated by the structure itself. As a result, better means are provided for tailoring of demands-specific properties and coatings. For example, nano-crystallites (1-10) nm incorporated into a matrix delimit the dislocation mobility, turn around occurring cracks, and limit the crack propagation and increase the hardness [18]. The high ratio of grain boundaries causes a macro-ductility due to shearing strain of the grain boundaries across nano-pores and crack meshes that open up along the grain, and results in coatings with a high toughness.

Examples of micro-alloyed coatings

The discussion above suggests that micro-alloying of coatings necessitates a good understanding of the underlying mechanisms that take place as a result of the addition of one or more micro-alloying elements. In order to achieve this, good control over the deposition process and preferably a deposition setup that allows different deposition techniques, e.g. simultaneous magnetron sputtering and arc evaporation. Magnetron sputtering is a droplet free deposition technique that allows the deposition of more-or-less any material, while arc evaporation is better used when demands are high for adhesion and /or density of the coatings. The examples of micro-alloyed coatings presented in this chapter are prepared in a Domino chamber from Sulzer Metaplas, shown in fig. 3. , where an improved version of the arc evaporation technique known as APA technology is used, while magnetron sputtering is used in the form of high power pulsed magnetron sputtering, HPPMS.

Fig. 3: The Metaplas Domino modular system used for the deposition of micro-alloyed coatings. The system can be configured according to the needs of the process by using different modules.

Tools coated with a double-layered coating consisting of a TiAlN and a micro-alloyed MeSiXN coating top layer has been shown to broaden the range of applications and the life time of tools. This coating which is also known as M_{power} has been shown to have superior qualities in cutting applications as demonstrated by fig. 4. It is seen that the M_{power} performance was more than 50% higher than the state of the art TiSiN coating, which speaks for the positive influence of micro-alloying.

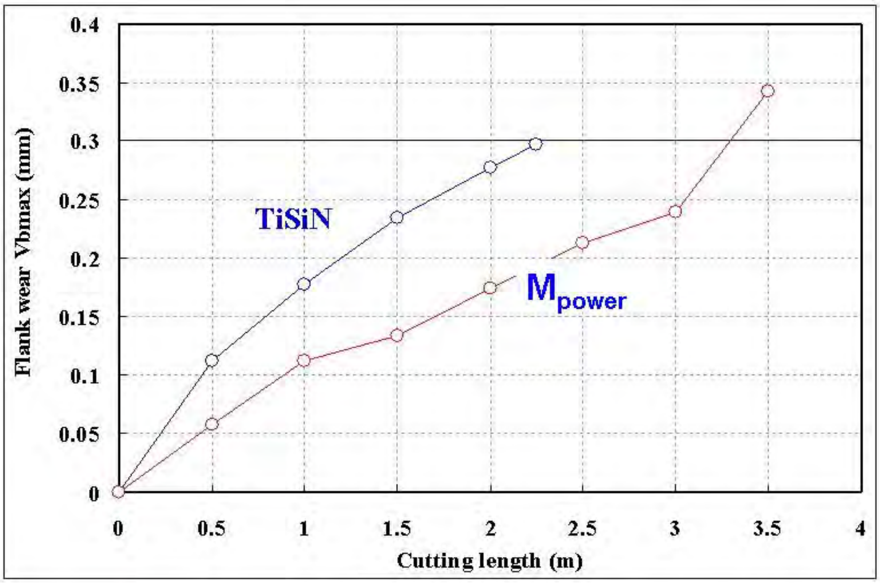
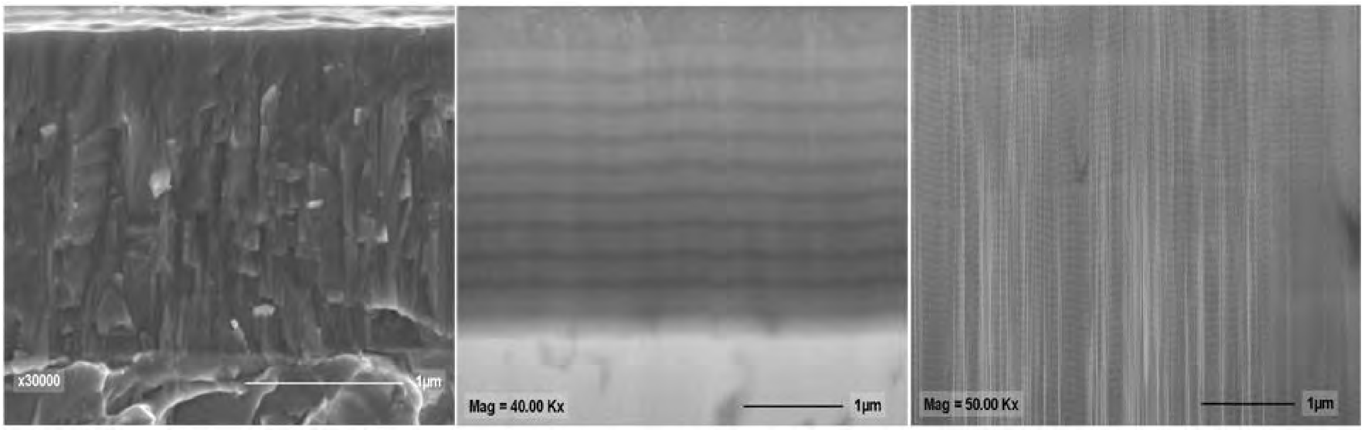


Fig. 4: M_{power} compared to a state-of-the art TiSiN coating showing better performance in dry cutting an annealed X210Cr12 (rough milling: v_c=150m/min, f_z=0,15mm/tooth, a_p=3mm, a_e=10mm)

Furthermore, it is found that the performance of M_{power} could be enhanced for specific applications by controlling the design of the coating. Fig. 5 shows three different M_{power} designs (a) a graded layer design, (b) a multilayer design with relatively thick layers, and (c) a nanolayer design (nano-laminate). Although elementally equal, the different designs have been found to suit best for well defined applications. The multilayered and nano-layered coatings are well suited for applications where the operation can induce high stresses, while the graded coating is best suited for high temperature and high load applications.



(a) (b) (c)

Fig. 5: The M_{power} comes in three different coating designs, depending in the application, (a) a graded layered TiAlN and micro-alloyed MeSiXN, (b) a multilayered and (c) a nano-layered coating design

TiAlN and CrAlN coatings are used in a number of applications where hard and tough coatings are demanded, such as cutting drilling and/or milling applications. By alloying these coatings with Si, better grain refinement is obtained, giving the coated tools a longer life time and a better range of applications. In order to further improve these coatings' oxidation resistance and decrease their intrinsic stresses, micro alloying is utilized. M_{power} and M_{force} are two examples from the M-series (M for machining) coatings which show a much higher oxidation resistance and provide added benefits when used at high temperatures and high load applications. Table 1 shows features of these two coatings where it is seen that the maximum operation temperature is above 1100 °C for both coatings which is much higher than for conventional TiAlN (850-900°C). Further more, when compared to non micro-alloyed coatings, the M_{power} and M_{force} performance was over 100% better during high-speed cutting applications (machining e.g. 1.2767, 1.2312 mold steel). Moreover, when milling 42CrMo4, M_{force} exhibited a much smoother surface than the state-of-the-art AlCrN surpassing the latter's performance by 25%.

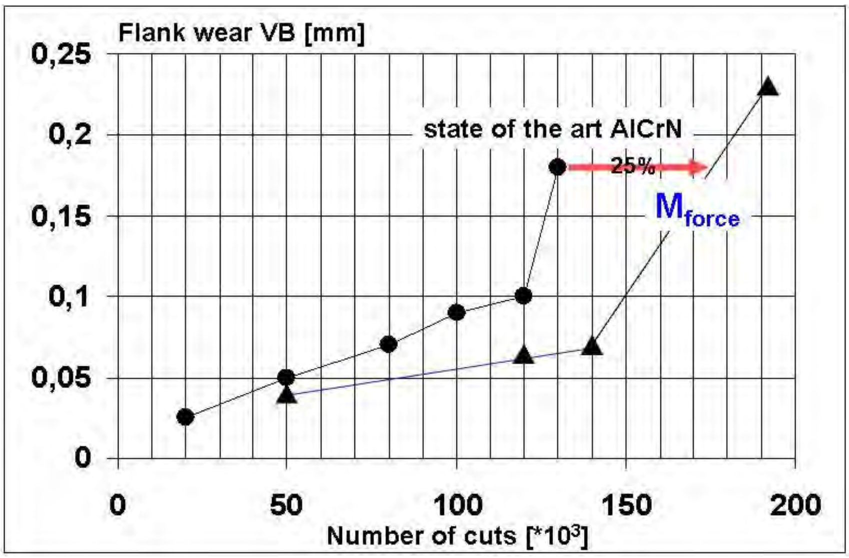


Fig. 6: M_{force} results in 25% better performance than state of the art AlCrN in dry milling on 42CrMo4 (v_c=200m/min, f_z=0,12mm/tooth, a_p=3mm, a_e=3mm)

Table 1: Properties of micro-alloyed TiAl- and CrAl-based coatings.

Overview of features	M_{power}	M_{force}
Micro hardness	3,550 ± 350 HV	3000 +/- 250 HV
Material	maTiSiN	maAlCrN
Typical coating thickness	2 to 7 µm	2 to 6 µm
Maximum operation temperature	1,150 °Celsius	1100
Structure of coating	fine columnar to nanocrystalline Nanolamnate/multilayer	fine columnar to nanocrystalline Nanolaminate/multilayer
Colour	Copper	Dark grey

The addition of small amounts of additional elements to the coatings results in an enhanced oxidation resistance as well as a longer life-time

Summary

In this article, the effect of microalloying on the properties of coatings is discussed. The improvement of coatings mechanical properties through the addition of alloying or microalloying elements was illustrated. Examples of microalloyed coatings deposited by arc evaporation were given showing that by adding small portion of a microalloying element, new and improved properties of a coating could be achieved.

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