Isothermal Oxidation Behavior of CrSiN Coating Deposited by Magnetron Sputtering at 700°C

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Abstract. CrSiN coatings have been successfully deposited on the surface of GH169 alloy by closed field unbalanced magnetron sputtering (CFUBMS). The microstructure, chemical and phase composition of the coatings were characterized by SEM, EDS and XRD, respectively. The mechanical properties of the coatings such as microhardness and adhesion strength were measured by indentation method and scratch method, respectively. The isothermal oxidation behavior of CrSiN coating at 700°C was investigated using thermogravimetric analysis. Results show that Cr, Cr2N and CrN coexisted in the dense as-deposited CrSiN coating without Si-containing phases; the coating surface was rough and a small amount of oxide (Cr2O3 and SiO2) was formed on the surface after oxidation at 700°C for 24 hours. The isothermal oxidation result suggested that CrSiN coating possesses excellent oxidation resistance at 700°C. It is considered that the good oxidation resistance of CrSiN coating itself and the formation of dense protective Cr2O3 and SiO2 films are primarily responsible for the good service performance during the oxidation process at 700°C.

1. Introduction
The premature failure of cutting tools will occur under harsh working environment due to high-temperature oxidation, wear and friction, etc., resulting in a large amount of material waste and huge economic losses. It has been proved that preparing a hard coating with high strength, high toughness, and wear and corrosion resistance on the tool surface is an effective and feasible way to improve working efficiency and reduce economic losses [1–6]. In recent years, CrN coating has attracted much attention because of its good ductility, good adhesion, low friction coefficient, corrosion resistance and thermal stability and other advantages [7–9]. However, CrN coating has disadvantages such as low hardness, poor oxidation resistance, which restrict its wide application. Doping Si in CrN coating can refine the grain size to improve the coating hardness by fine grain strengthening effect, and it is likely that Si will react with N to form amorphous structure of Si3N4 to further improve the hardness and high temperature stability of the coating; besides, the dense oxide films of SiO2 and Cr2O3 may be formed on the coating surface to prevent the high temperature corrosion. Therefore, CrSiN coatings have caused the interest of the researchers [10–14].
Presently, the commonly used coating preparation technologies are multi-arc ion plating, magnetron sputtering, etc. Among them, magnetron sputtering technology has been widely used in industrial field because of its unique advantages of "low working temperature and high deposition speed" and the preparation of uniform, compact and smooth coating. In order to further improve the overall performance of CrN coating, Si was added to CrN coating produced by magnetron sputtering in our previous study [12]. The effects of Si content on the microstructure and the microhardness of the CrSiN coatings have been studied in detail. In this work, the oxidation behavior of CrSiN coating at 700°C for 24 hours was investigated to clarify its oxidation resistance mechanism.

2. Experimental

GH169 alloy (15mm × 10mm × 2mm) was selected as the substrate. Prior to the coating deposition, the substrate surface was ground with water-abrasive paper to 2000 mesh first and then polished with metallographic abrasive paste to 2.5 micron followed by ultrasonically cleaned in acetone and alcohol. Subsequently, the cleaned substrates were air-dried for further use. CrSiN coatings were prepared by using the FDJ 700 CFUMSIP system (SKY Technology Development Co. Ltd, Shenyang, China) from a mosaic target (cylindrical Si particles were placed in the erosion track of the Cr target) in N2/Ar atmosphere. The deposition parameters were listed in table 1. Details of deposition process can be found in our previous work[12].

| Parameter                          | Value                  |
|------------------------------------|------------------------|
| Based pressure (Pa)                | 2×10⁻³                 |
| Working pressure (Pa)              | 0.5                    |
| Substrate temperature (°C)         | 200                    |
| Bias voltage (V)                   | -50                    |
| N2/Ar flow ratio (mL·min⁻¹)        | 18:12                  |
| Deposition Time (min)              | 90                     |
| Target power (W)                   | 500 (Cr bonding layer) |
|                                    | 600 (CrSiN coating)    |

After the coating deposition, the coating samples were taken out of the vacuum chamber for various tests. The isothermal oxidation behavior of CrSiN coating was conducted at 700°C with a thermal analyzer (Setaram, France) in oxygen atmosphere. The samples were heated with a rate of 5°C/min to the target temperatures. Once the temperature reached the desired value, the mass change was recorded as a function of time. The phase composition of the coatings before and after oxidation was identified by an X-ray diffraction (XRD, Cu-Kα radiation, λ=0.15406 nm; XRD-6100, Shimadzu, Japan) over 20 values of 25°–80° with a scanning rate of 5°/min by a step width of 0.02°. The microstructure, chemical composition and thickness of the coatings before and after oxidation were examined by a field emission scanning electron microscopy (FE-SEM, Sigma, Zeiss, Germany) coupled with an energy disperse spectroscopy (EDS, Inca, Oxford, UK). The coating hardness was determined by the microhardness indentations performed onto the polished cross-section of the as-deposited coating with a digital micro-hardness tester (MH-50, EVERONE Precision Instruments Co. Ltd, Shanghai, China). At least 9 valid indentations were taken and then the average value was identified as the coating hardness. The bonding strength of the as-deposited coating to the GH169 substrate was measured by scratch method with a multi-functional tester for material surface properties (MFT-4000, Huahui Instruments technology Co. Ltd, Lanzhou, China).

3. Results and discussions

It can be found from our previous studies [12] that CrSiN coatings change from crystalline to amorphous structure with the increased Si content, and CrSiN coating with Si content of 1.13%
possessed the best comprehensive performance (hardness: 42 GPa; adhesion: 30 N). In this work, the CrSiN coating with Si content of 1.13% was selected as the research object to reveal its oxidation resistance at 700°C.

![Figure 1](image1.png)

**Figure 1.** XRD patterns of CrSiN coating before and after oxidation.

The XRD pattern of CrSiN coating after oxidation is shown in figure 1, and the XRD pattern of as-deposited CrSiN coating is also presented in figure 1 for comparison. It is clear that there are three phases in the as-deposited CrSiN coating, namely the main phase CrN and tiny Cr₂N and Cr phases. No Si-containing phase was detected, probably because Si reacted with N to form amorphous phase of Si₃N₄ [15, 16]. After oxidation at 700°C for 24 hours, apart from the original phases, a small number of two new phases (Cr₂O₃ and SiO₂) were found in the pattern, indicating that CrSiN coating was only slightly oxidized at 700°C, but it does not significantly affect the service lifetime of the coating. In addition, the preferred orientation of CrN (111) crystal plane was also found after oxidation and the characteristics peak is sharper, showing that the coating after oxidation has better crystallinity with increased crystal size. With the growth of CrN grain size at high temperature for a long period, the coating structure becomes loose and the loose structure will become the oxygen channel, which is detrimental to the oxidation resistance of the coating. On the other hand, at high temperature, the Cr₂O₃ and SiO₂ films are denser and denser with time, which is beneficial to the oxidation resistance of the coating. Therefore, the growth rate of CrN grain and Cr₂O₃ and SiO₂ films is a competitive relationship.

![Figure 2](image2.png)

**Figure 2.** Surface morphologies of CrSiN coating before (a) and after oxidation (b).
Surface morphologies of CrSiN coating before and after oxidation at 700°C are shown in figure 2. From the figure 2, we can see that the as-deposited CrSiN coating is uniform and dense while the coating after oxidation has larger grains size and loose structure, which is consistent with XRD results. According to the EDS result (not shown here), O element was also detected at a low atomic percentage, indicating that CrSiN coating has a relatively good oxidation resistance at 700°C. But beyond that, no other differences were observed.

After oxidation at 700°C for 24 hours, the SEM cross-sectional morphology and composition analysis along the cross section of CrSiN coating by EDS is shown in figure 3. It can be clearly seen from the figure 3(a) that there is no obvious defects such as micro-cracks observed in the cross section of the coating, and the interface between the coating and the matrix is smooth and clear, implying the excellent bonding strength between substrate and coating, which can supply a longer service lifetime to the coating. Figure 3(b) gives the EDS line scanning results based on the figure 3(a). According to the six curves (O, N, Si, Cr, Ni, Fe element distribution, respectively) from the figure 3(b), it can be seen that only slight oxidation occurred on the coating surface and the coating is still mainly nitride, and thus the coating can continue to protect the substrate from damage, which is in good agreement with the above results.

![Figure 3](image1.png)

**Figure 3.** Cross-sectional micrograph and EDS line scanning of CrSiN coating after oxidation.

![Figure 4](image2.png)

**Figure 4.** Oxidation kinetics curves of CrSiN coating at 700°C.

In order to better understand the oxidation resistance of CrSiN coating, the isothermal oxidation kinetics curve of CrSiN coating at 700°C is depicted in Fig.4. The result shows the oxidation process curve can be divided into three sections: the first part from 0 h to 6 h, the second part from 6 h to 18 h
and the third part from 18 h to 24 h. As can be seen from the curve, the weight gain rate of CrSiN coating is very large at the beginning of oxidation and slowly drop with the time increases. This may be caused by the competition of the growth rate between CrN crystal and Cr₂O₃ and SiO₂films. Combined with the analysis from XRD, SEM and EDS results, it can be concluded that although the coating was slightly oxidized, the oxidized CrSiN coating can still play the good protective role on the substrate. This is mainly attributed to the better oxidation resistance of CrSiN coating at 700°C, and also to the dense Cr₂O₃ and SiO₂films formed on the coating surface.

4. Conclusion
CrSiN coatings with Si content of 1.13% were successfully prepared on the surface of GH169 alloy by magnetron sputtering. The oxidation behavior of CrSiN coating at 700°C and corresponding oxidation resistance mechanism were studied in detail. The followings are the main conclusions: the phases in as-deposited CrSiN coating are mostly CrN and a small amount of Cr and Cr₂N, and the coating surface is compact and smooth; after oxidation at 700°C for 24 hours, the coating surface became loose resulted from the growth of CrN grains and a small amount of oxide films (Cr₂O₃ and SiO₂) is formed on the surface, but the coating still has good protection ability.

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