Microstructural Evolution of Titanium Carbonitride Based Materials During Oxidation

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Abstract. Ti(C,N) based materials represent a new class of hard and wear resistant structural materials. Nowadays, the main field of applications is focused on metal cutting and finishing operations. For these kinds of applications usually the mentioned materials work in oxidizing environments at high temperatures. The thermophysical stability under these conditions represents therefore a key factor that influences the material’s performance, and consequently the tool life of the component in service.

The present study aimed to investigate the oxidation behaviour of two different Ti(C,N)-WC based materials, the first containing 0.9 wt% of Co and the second 6.2 wt% of Ni and 2.9 wt% of Co. Cycled oxidation tests (20 hours each) were conducted with a muffle furnace in laboratory static air at 1000 °C up to 100 hours. During the initial transitory stage the competition between the mass gain due to the formation of solid TiO₂ (rutile) and the mass loss due to released volatile W oxides controlled the mass change; thereafter the oxidation process obeyed a linear law. Great microstructural modifications occurred on the (sub)surfaces of the oxidized samples: multiphase TiO₂ based scales grew upon the external surfaces of the oxidized specimens. Kinetics and oxidation mechanisms were proposed and discussed.

Key words: Titanium carbonitride; core-rim structure; microstructure; oxidation behaviour.

Ti(C,N) based materials belong to a new interesting class of hard and wear resistant structural materials. Properties such as high flexural strength and thermal conductivity make these materials rather attractive in the field of cutting tools, for example in metal cutting and finishing operations [1–5]. A tailored addition of metallic binders into Ti(C,N) mixtures permits the manufacture of either ceramic type materials (limited binder content) or ceramic-metal composites (i.e. cermets) [6–11]. The introduction of metal carbides and metallic binders into Ti(C,N) based mixtures has become a conventional procedure to design and improve specific properties, for instance sinterability (WC, metals), resistance against thermal stresses or plastic deformation (TaC or NbC), wettability and toughness (metals). The final stoichiometry of the Ti(C,N) phases and of the metallic binder mainly depend on the C/N starting ratio and on the mutual solubility of each element during sintering [1, 2, 6, 7, 10–17]. Considering that in several applications these structural components remain exposed to elevated temperatures in oxidizing environments, the thermophysical stability under these conditions plays a key role influencing the material’s performance. The available literature on the oxidation of Ti(C,N) based materials is rather limited and essentially focused on materials with little content of metallic binders at grain boundaries [18–20]. This study aims to describe the deep microstructural modifications of two different materials after heat treatment at 1000 °C for 100 hours of exposure in ambient air. The first consists of a Ti(C,N)-WC based ceramic type material, whereas the second, besides the same hard phases, contains also a metallic binder in the system Ni–Co–Ti–W. The microstructural evolution was investigated by means of SEM-EDX analyses and X-ray diffraction on polished cross section of the

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oxidized samples. Kinetics and oxidation mechanisms are proposed as well.

**Experimental**

Two dense Ti(C,N) based materials were fabricated with the following compositions (wt%): A (ceramic type): TiC0.5N0.5 + 16.7%(WC-5%Co), hot pressed at 1700°C for 30 minutes under vacuum (0.5 mbar), P = 5 MPa; B (cermet type): TiC0.5N0.5 + 15.3%(WC-5%Co) + 6.2%Ni + 2.1%Co, gas pressure sintered at 1650°C under Argon.

The crystalline phases were analyzed by X-ray diffraction (XRD). Test pieces were cut in the form of bars 2.5 × 2.0 × 10.0 mm³ (surface finish Ra ~0.2). Five interrupted tests (20 hours each, heating rate 10°C/min, free cooling) were performed at 1000°C up to 100 hours under static laboratory air using a muffle furnace. XRD analyses were performed on the exposed surfaces as well as on polished cross sections. Microstructure and microchemistry of polished cross sections from both as-sintered and oxidized specimens were investigated via SEM-EDX. The thickness of the reaction scale (after oxidation) was measured from SEM micrographs.

**Results**

**Microstructure of the as-Sintered Materials**

The microstructure of the two materials (Fig. 1a,b) consists of a core/rim structure, where the core is

![Fig. 1. BSE-SEM micrographs from the polished bulk of the as-sintered material A(a) and B(b): 1 → core, 2 → outer rim, 3 → inner rim, 4 → microporosity, 5 → metallic binder](image)

![Fig. 2. BSE-SEM micrographs from polished section of material A(a) and B(b) after treatment at 1000°C up to 100 hours (RS: reaction scale, UB: unreacted bulk). The numbered boxes 1, 2, 3, 4 identify areas of the reaction scale expanded in Fig. 5, 6a, 6c, 8, respectively](image)