INFLUENCE OF TiC DEPOSITION BY CVD ON *HARTMETAL* TYPE STEEL SUBSTRATE

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The structure and properties (crystallographic phases, hardness) of Hartmetal – type steel were investigated. The modification of the Hartmetal surface as a consequence of a special treatment with the purpose to improve the hardness by deposition of TiC films by chemical vapour deposition (CVD) was carefully analysed.

A continuous interest is paid to hard materials and to surface hardening, in order to increase the lifetime of various devices and tools that are used in material processing and for tribological processes [1-4]. The enhancing of the corrosion resistance of stainless steels by deposition of TiN films is also studied [4]. The hard metal alloys are important for cutting tools and military applications. One of the largely used materials is based on the complex alloy with iron, tungsten, carbon, cobalt and titanium, known as Hartmetal composition. New technologies for the deposition of titanium carbide films (CVD - chemical vapour deposition, PVD – physical vapour deposition) on hard metal tools were developed. These methods are used in the industrial applications due to their efficiency, simplicity and low cost.

The surface hardening technology based on the titanium carbide coverage consists in the treatment of the material in a flux of a gas mixture (titanium chloride, hydrogen and methane) at a temperature of $900 \div 1000$ °C [5-6]. The deposition of the TiC hard film is the result of reactions in gaseous phase and of some reactions at the interface gas-metal. The high temperature treatment of Hartmetal type steel causes, in the same time, the hardening of the alloy through the formation of complex carbides, the so-called η phases.

The Hartmetal samples treated in low and high methane concentration concentration in the mixture with $TiCl_4$ and H_2 have been studied. The conventional concentration for low methane flow is around 1.8% of H_2 and for high methane flux is around 15% of H_2 [7], (reactor pressure is the 100 torr). The samples were prepared by Böhler Company and put at our disposal for investigation.

The samples used in this study are made of steel S705 (Böhler Company): Fe (77.08 %wt) - W(6.2 %wt)-Co(4.8 %wt)-Cr(4.1 %wt)-C(0.92 %wt)-V(1.9 %wt)-Mo(5.0 %wt), (standard DIN 1.3243).

X-ray diffraction and microhardness measurements were performed. In order to get information on the internal structure and properties of the samples, the samples were cut, polished and the sections thus obtained were analysed. The results are reported in this short communication.

We have checked the density of the samples by Arhimede determination. The density is situated in range $7.84 \div 7.91$ g/cm^3 and this corresponds to the usual values for such kind of materials

The X-ray diffraction patterns have been performed on the coated surfaces in comparison with the uncoated surfaces (cut in the core) of the samples treated by CVD. Phase composition was obtained by XRD analysis using an X ray TUR M-62 diffractometer with CuKα radiation. The results are shown in Fig. 1 for the sample treated in low methane flow and in Fig. 2 for those treated in high methane flow.

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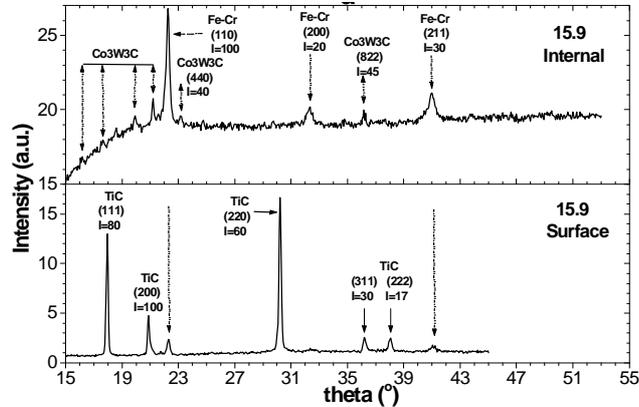
Fig, 1. X-ray diffraction patterns for sample 1, treated in low methane concentration.
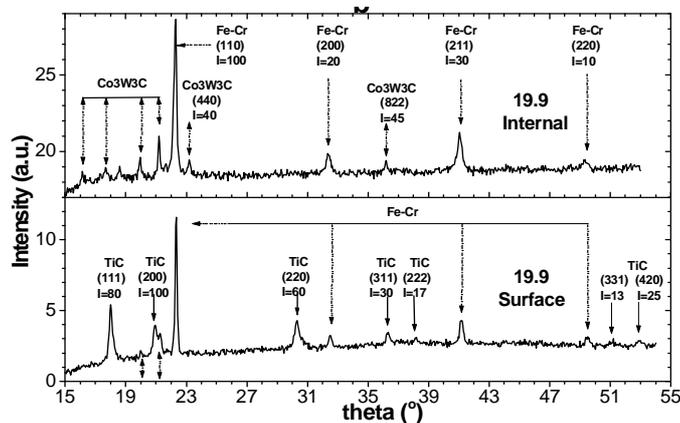
Fig, 2. X-ray diffraction patterns for the sample 2, treated in high methane concentration.

The internal structure in both samples corresponds to two crystallographic phases. The major phase is cubic and corresponds to a possible composition Fe-Cr. The (110) interplanar distance is 20.35 nm, that corresponds perfectly to the (110) distance in the chromium steel (434-L) (fiche no. 34-396, ASTM Powder Diffraction File). The minor phase is the ternary phase of composition Co_3W_3C (fiche no. 27-1125, ASTM Powder Diffraction File).

The phase composition, revealed by recording the X-ray diffraction patterns on the free surfaces of the samples shows the formation of a thick titanium carbide films on the sample 1 (thickness 5.54 ÷0.34 μm, as measured by IPMT Chemnitz) treated in low methane concentration in the gas mixture and of thinner TiC film on the sample treated in high methane concentration in the gas mixture.

It is remarkable that the TiC film formed on the sample 1 is highly oriented (the crystallographic plane (220) of the crystallites is preferentially oriented along the sample surface) while the TiC exhibits a preferentially (111) orientation along the sample surface in sample 2.

The microhardness of the samples has been determined with a PMT-3 hardness tester and calculated in Vickers degrees [7,8]. The load used to perform the measurements was equal to 200 g. Figs. 3 a and b show the results. The basical hardness, as measured on the cross-section of the samples is practical identical for both samples: 550 HV. The hardness raises to the margin of the samples, where the hardening due to CVD treatment is observed. The measurements performed directly on the original surfaces of the samples are denoted by S1 and S2. Remarkable is the strong increase of hardness, especially in sample 2. The microhardness is situated between 1380 and 2240 HV. In sample 2, the growing hardness in spite of the thin layer of TiC can be related to the influence of the substrate that contains the phase Co_3W_3C, a very hard phase.

a   b
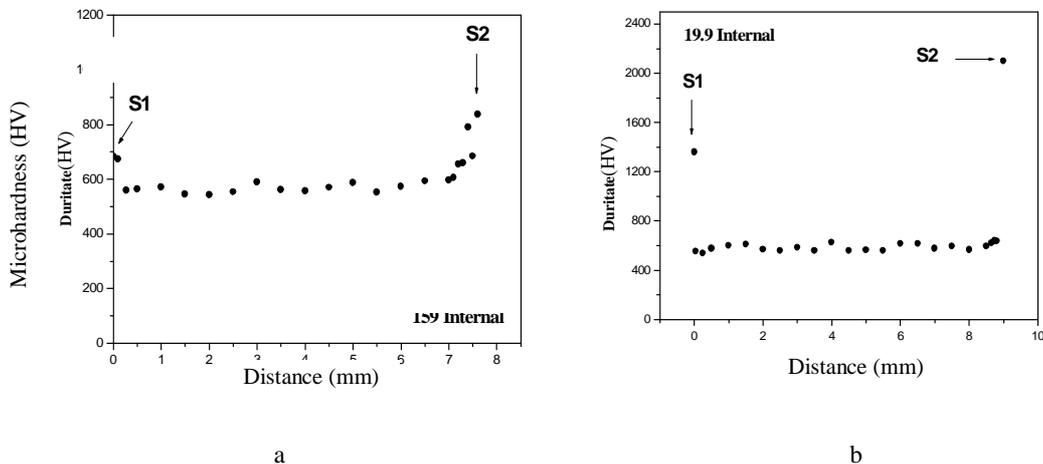
Fig, 3. The microhardness along the cross-section and at the free surface a in sample 1 and in sample 2b.

It is important to remark that the width of the diffraction lines of the phase Fe-Cr measured at the central part of the samples, differs from that measured at the surface. Considering only the effect of the size of crystallites, the calculations (using Scherrer equation) have shown that the average crystallite size of the Fe-Cr phase measured perpendicular to the (110) crystallographic plane, is 20.5 nm in the internal part of the sample, and 63.5 nm near the surface. The effect of narrowing of the diffraction lines near the surface has been observed in many samples of steels. According to our opinion, this effect is related to the influence of the CVD processing that influences also, the size and preferential orientation of the crystallites of the material.

In conclusion, our studies have shown that CVD processing of the Hartmetal steels lead to a higher surface hardness caused not only by the TiC films formed at the surface, but also by the modification of the crystallographic phases during treatment. As a consequence of the CVD treatment, the crystallites near the sample surface becames larger than those from the inner part. It was observed the increase of the surface hardness for high fluency of the methane during the thermal deposition process.

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