AN ELECTRON MICROSCOPICAL INVESTIGATION OF HARD
ALLOYS BASED ON CHROMIUM CARBIDE

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Nickel-bonded hard alloys based on chromium carbide (generically designated as KKhN alloys) are comparatively easy to produce and possess high hardness and good wear, oxidation, and corrosion resistance. Thanks to these qualities today they successfully compete with the tungsten carbide VK (WC + Co) hard alloys and are widely used in tools for the plastic working of metals, in particular, forging dies [1].

One factor severely limiting the range of application of these alloys is their relatively low strength, which is due, inter alia, to substantial growth of their carbide phase grains [2]. The alloying of the nickel binder with phosphorus (KKhNF alloys) not only still further simplifies the manufacture of these alloys, by lowering their sintering temperature, but also appreciably increases their transverse rupture strength (by ~15–60%) [3–5]. In this connection, the present work was undertaken with the aim of studying the effect of phosphorus content and sintering temperature upon the microstructure and fracture structure of nickel-bonded hard alloys based on chromium carbide (Cr₃C₂).

Chromium carbide alloys with 15 wt.% of nickel and nickel–phosphorus binders were chosen for investigation. The amounts of phosphorus in the binder were 0.1, 0.6, and 1.65 wt.% relative to the weight of the alloy as a whole. Alloy specimens were prepared by sintering compacts in a vacuum corresponding to 1·10⁻⁴ mm Hg at temperatures varying, in 50°C steps, from 1020 to 1320°C. Examination was performed by optical and electron microscopy, using an MIM-8M metallographic microscope and a JEM-6A electron microscope, respectively. Electron microscopical examination was made by the two-stage chromium-shadowed plastics–carbon replica technique. As far as is known, this was the first systematic electron microscopical investigation of alloys of this class.

A comparison of the microstructures of KKhN-15 alloy and KKhNF-15 alloy with 0.1% of phosphorus (sintered at 1270°C), as revealed by the traditional metallographic and electron microscopical methods, shows that, while being virtually identical when examined under the optical microscope (Fig. 1a and b), they differ substantially when studied by electron microscopy (Fig. 1c and d). Thus, in the microstructure of KKhNF-15 alloy with 0.1 wt.% of phosphorus (Fig. 1f) there are areas in which the Cr₃C₂ grains are almost totally separated from one another by interlayers of the binder phase, whereas in the phosphorus-free KKhN-15 alloy the cementing phase appears in the microsection plane in the form of individual, irregular-shaped inclusions (Fig. 1e). This difference is due to the nickel–phosphorus binder being more fluid than the nickel binder, which enables it to penetrate more readily into the zones of contact between the chromium carbide particles.

Experiments showed that, over the whole range of phosphorus contents investigated, the angle of contact of a nickel–phosphorus binder on chromium carbide is the same as that of pure nickel on chromium carbide. The fields of microstructure in which the cementing phase almost completely separates the Cr₃C₂ grains is characterized by a slightly more rounded carbide grain shape. The mean grain size of the carbide constituent in the two cases is virtually identical, ~4 μ. The formation of fields of microstructure in which the carbide grains are almost completely surrounded by cementing phase interlayers is observed also in alloys containing 0.6 wt.% of phosphorus (Fig. 1g). Raising the amount of phosphorus to 1.65 wt.% has no significant effect upon the character of distribution of the structural constituents in the alloy. However, as such an alloy is sintered at a lower temperature (1180°C), a structure is obtained in which the mean grain size of the carbide phase does not exceed 2 μ (Fig. 1d).

At the interfaces between the carbide and binder phases phosphorus is precipitated in the form of the nickel phosphide Ni$_3$P, which constitutes one of the components of the nickel–phosphorus eutectic Ni–Ni$_3$P (Fig. 1h). This is in accord both with the constitution diagram of the Ni–P system [6] and with results of x-ray phase analyses and electron probe microanalyses published in [7].

An electron microscopical investigation was made also of fractures obtained in transverse rupture tests on specimens of chromium carbide alloys with a pure nickel binder (KKhN-15) and nickel binders containing...