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Nitrogen implantation in tungsten carbides

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In order to investigate some properties of nitrogen implantation in tungsten carbides, massive carbides WC and W_2C were prepared by bulk diffusion of carbon in pure tungsten. Isothermal analysis of W–C diffusion couples was performed to determine the optimal conditions for their preparation. Nitrogen implantation was executed with an isotope separator. The samples were analysed by using the $^{15}N\,(p, \alpha\gamma)^{12}C$ nuclear reaction and were wear tested. The increase of wear resistance was shown to be effective and the importance of parameters such as fluence or loading conditions was underlined. Nitrogen migration during abrasive wear occurred on a very small scale and was dependent on the nature of the carbide.

1. Introduction

Nitrogen implantation has been reported [1, 2] to result in an increase of wear resistance of cemented carbides. But mechanisms for this improvement are not well known. Nevertheless, the cobalt-binder phase is thought to play an important role [3, 4]. The problem of mobility of implanted nitrogen, in particular, underlined as a possible mechanism, may depend on the presence of the binder phase and on the carbide structure. In order to examine these differences, nitrogen implantation has been compared between cemented carbide WC–Co, and massive carbides WC and W_2C.

2. Preparation of massive tungsten carbides WC and W_2C

Tungsten forms two hexagonal carbides: the monocarbide WC and the subcarbide W_2C. The phase relations in the tungsten–carbon system have been studied by numerous authors [5–10], but the proposed diagrams differ. Indeed, a complete and accurate study is difficult at the very high temperatures at which the carbides are formed.

To prepare the massive carbides, it was necessary to perform an additional examination of the diagrams by isothermal analysis of W–C diffusion couples. The resulting calculations of the kinetics of formation of the different phases thus allowed the optimal conditions for preparation of WC and W_2C to be defined.

2.1. Experimental procedure

Diffusion couples were made from tungsten samples (8 mm × 6 mm × 0.5 mm) compacted in extremely pure carbon powder ("graphite qualite 207 Carbone Lorraine" impurities 20 p.p.m.). Samples were put in graphite melting-pots and heated to the required temperature in an induction furnace under an argon atmosphere. An electronic pyrometer was used to measure and regulate the temperatures which were calibrated by direct measurement of the melting temperatures of molybdenum ($T_m = 2625 \pm 10^\circ$ C) and niobium ($T_m = 2468 \pm 10^\circ$ C). Carburized samples were characterized by micrography, microanalysis and X-ray diffraction.

2.2. Results

For temperatures below 2530° C, carburization led to the preferential formation of W_2C: the amount of subcarbide increased notably above 1600° C. The monocarbide also grew at these temperatures but appeared only as superficial traces provided the tungsten was not completely carburized (Fig. 1). After 2 h at 1800° C, tungsten was entirely transformed to W_2C with a small superficial WC layer (Fig. 2). At 1900° C, the transformation took place after only 1 h. A treatment at 1900° C for 8 h resulted in a 25 μm WC layer (Fig. 3), the bulk was entirely W_2C. At 2500° C, the morphology was the same, but the WC formation was more rapid (35 μm in 25 min). The relatively slow growth of WC required an increase in temperature above that of the isothermal reaction $\alpha WC_{1-x} \rightleftarrows W_2C + WC$ fixed by Rudy at 2530° C [11]. It appears that the growth kinetics of the layers are drastically modified. The accuracy and position of the isothermal reaction are confirmed by our experiments: above 2530° C, a superficial layer of WC was still present and a dual phase structure W_2C + WC appeared in the bulk (Fig. 4), resulting from the eutectoid decomposition of WC during cooling. Nevertheless, the growth of the superficial WC layer was always very slow and significant porosity appeared when the temperature was higher. Therefore, treatments were performed below 2500° C to obtain WC layers of about 30 μm, which were large enough for the implantation studies. The subcarbide W_2C was prepared at 1800° C in order to minimize the size of the WC layer which was then eliminated by polishing.

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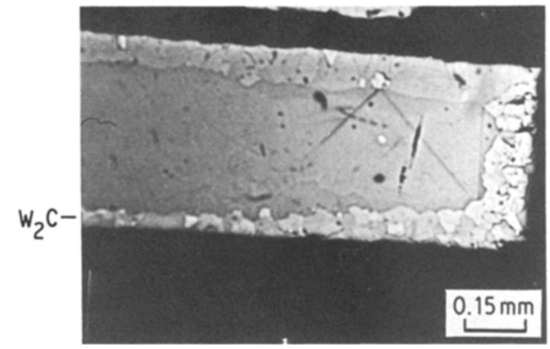

Figure 1 Superficial layers of W_2C (1680° C, 2 h).

3. Nitrogen implantation in carbides

The use of ion implantation for non-semiconductor applications has been widely applied for several years, particularly for steels [12–15]. Chosen atomic species are first ionized and then accelerated with energies usually varying from 10 to 200 keV in a vacuum. Ions penetrate the surface layers of the substrate where they accumulate in a close approximation to a gaussian profile [16, 17].

Nitrogen ions have been primary source for most implantation studies and results from friction and wear experiments were often promising when carbides have been used as substrates for industrial tools such as dies for wire drawing and rolling cylinders [2]. Mechanisms which result in the improved wear resistance are not well known and a surprising corollary is the persistance of this resistance over a distance deeper than the initial implanted layer. Some authors have observed that nitrogen is present in steels in considerable quantities within wear tracks that are more than 10 times deeper than the original implant depth [18–20]. However, these results are complicated by the non-uniform removal of material during friction and wear tests. Using a purely erosion test that does not modify the surface state, Bolster and Singer [21] found a very small nitrogen migration in 304 stainless steel. In previous papers, we have determined the evolution of nitrogen profiles during such a test in chromium steel [22] and the evolution of the chemical state of nitrogen in low-alloyed steel [23]. In every case, the nitrogen migration is very short (< 200 nm). In this paper, the friction behaviour of WC–Co is presented. In order to understand the possible role of the cobalt-binder phase, the nitrogen migration is compared between the three kinds of carbides.

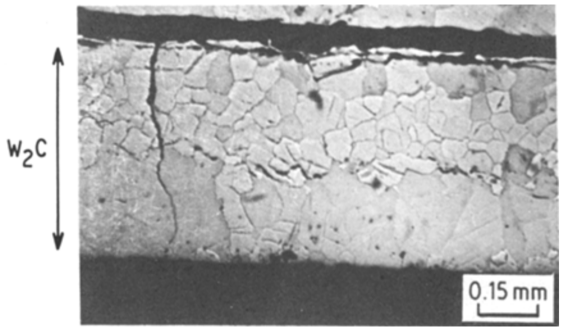

Figure 2 Completely carburized tungsten: formation of W_2C and very superficial layer of WC (1900° C, 2 h).

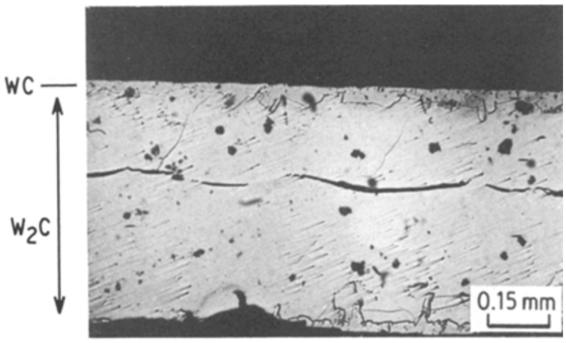

Figure 3 25 μm layer of WC after an 8 h treatment at 1900° C.

3.1. Experimental procedure

Samples of cemented carbide WC–8 wt % Co and massive carbides WC and W_2C prepared as previously described, were implanted with 40 keV $^{15}N^+$ ions on one side after polishing with 0.25 μm diamond paste. The isotope separator of the Institut de Physique Nucleaire de Lyon was used to perform the implantations. The samples were implanted at room temperature (25° C) maintained by water circulation. The nitrogen concentration profiles were obtained without erosion using the $^{15}N(p, \alpha\gamma)^{12}C$ reaction which presents an isolated resonance at 429 keV. The width of this peak (< 0.9 keV) allowed a spatial analytical resolution of 5 nm to be obtained in a direction perpendicular to the specimen surface. The protons were accelerated with a 2.5 MV Van de Graaff generator and the γ-rays were detected with a NaI(Tl) crystal.

After implantation, samples were worn for a given time on a fabricated non-woven synthetic textile charged with 0.25 μm diamond powder. They were then cleaned ultrasonically in trichloroethylene and rinsed. The weight losses were measured with an uncertainty of 10^{-6} g and were proportional to the worn depth due to the uniform removal of the surface [23]. As the analytical technique was non-destructive, we could follow the evolution of the nitrogen profiles after different stages of wear on the same sample.

Tribological tests were made with a tribometer allowing a cylinder-flat pin contact (Fig. 5). Friction coefficient and weight losses of samples (with an uncertainty of 10^{-4} g) were measured.

3.2. Results

3.2.1. Nitrogen profiles

Samples of cemented WC and massive WC and W_2C were implanted with fluence of 10^{17} ion cm^{-2}. The

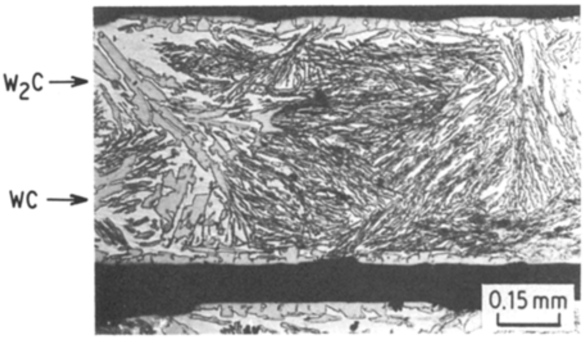

Figure 4 Dual phase structure WC + W_2C.

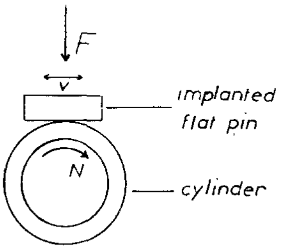

Figure 5 Schematic diagram of the cylinder-flat pin tribometer.

experimental profiles are given in Fig. 6. Projected range R_p and range straggling ΔR_p (Fig. 6) can be inferred from these curves and then compared to theoretical values expected from the Lindhard, Scharff, Schiøtt theory and extracted from Winterbon's tables [24]. These results are given in Table I. The comparison between theory and experiment for R_p is rather good. For ΔR_p the experimental results showed a larger broadening of the distribution than expected from theory. This fact has previously been observed on steels [16].

The distribution of nitrogen implanted as a function of fluence was analysed on the cemented carbide WC–Co (Fig. 7a). This study indicated a saturation at 2.5×10^{17} ion cm^{-2} (nitrogen amount remaining in WC–Co after implantation of fluences superior to 2.5×10^{17} ion cm^{-2}) (Fig. 7b). This value was close to that obtained on steels (2×10^{17} ion cm^{-2}).

3.2.2. *Tribological tests*

Implanted cemented carbide WC–Co flat samples were tested against a HSS steel cylinder (18% W, 4% Cr, 4% Co, 1% V, austenitised at 1120 and 1500 K, quenched and tempered at 820 K, hardness = 62 HRC). Friction tests were made in water with normal loads of 200 and 500 N at a sliding speed of 0.36 m sec^{-1}. No significant changes of friction coefficient were detected between implanted and non-implanted samples. Results of wear are given in Fig. 8. No difference appeared between implanted and non-implanted samples when the normal load was 500 N. With a normal load of 200 N, wear was a function of the fluence. At the beginning of the test (under 4 h) all the fluences appeared to reduce the amount of wear. After 4 h, only the implantation of 10^{17} ion cm^{-2} improved the tribological properties of the carbide. Finally, after 8 h, the curves became parallel: implantation had no more effect. This appeared after a removal of 1 mg which corresponded for uniform wear to about 0.5 μm depth.

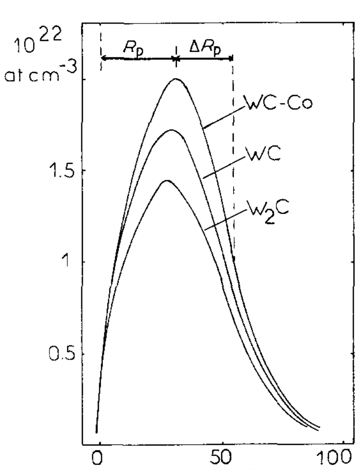

Figure 6 ^{15}N distribution profiles in tungsten carbides (40 keV, 10^{17} ion cm^{-2}).

TABLE I Theoretical and experimental parameters of nitrogen distribution in carbides

		WC–Co	WC	W_2C
R_p (μg cm^{-2})	Theoretical	43	41.8	47.2
	Experimental	43	41.5	46
ΔR_p (μg cm^{-2})	Theoretical	30.7	30.4	38.9
	Experimental	34	36	40

3.2.3. *Nitrogen migration during abrasive wear*

The carbides tested in abrasive wear were implanted with a fluence of 10^{17} ion cm^{-2}. The changes in the nitrogen profiles after wear are given in Fig. 9 and the quantities of nitrogen remaining in the materials after each part of the wear test are given in Fig. 10. The migration of nitrogen was about 400 nm in the cemented carbide but noticeably less in the massive carbides: 280 nm in WC and 250 nm in W_2C.

4. Discussion

The effectiveness of nitrogen implantation in improving the wear resistance of cemented carbide depends on several parameters: the conditions of implantation; and the conditions of the friction test. If the loading conditions are too high, superficial layers are removed too quickly and no effects are seen. With lower conditions, the role of the fluence appears and it is possible to obtain an improvement of the wear resistance. This result seems to be different from that obtained by Dearnaley *et al.* [25] who conclude that nitrogen implantation (at 100 keV) produces softening of carbide if the implantation temperature is below 200° C. But the results of our work are achieved with lower energy for which the increase of hardness is not measurable (because of a smaller implanted depth) using conventional methods of microhardness. Actually, our results are similar to those of Dearnaley in a fundamental conclusion: for given conditions of implantation (temperature and energy), an optimum implantation fluence exists: in our case, this is 10^{17} ion cm^{-2}, 40 keV, 25° C.

The wear tests show that nitrogen remains in the samples beyond the initial implanted layer. The nitrogen profiles after wear were asymmetrical. The maximum concentration was nearer the surface and the profiles were broader. This behaviour was similar in each of the carbides but it was different to results obtained on steels under the same conditions [21–23] where nitrogen was more quickly eliminated (less than 200 nm).

Mechanisms which govern the improvement of the wear resistance and the migration of the nitrogen are difficult to understand, partly because the chemical state of nitrogen in carbide is not well known. Pethica

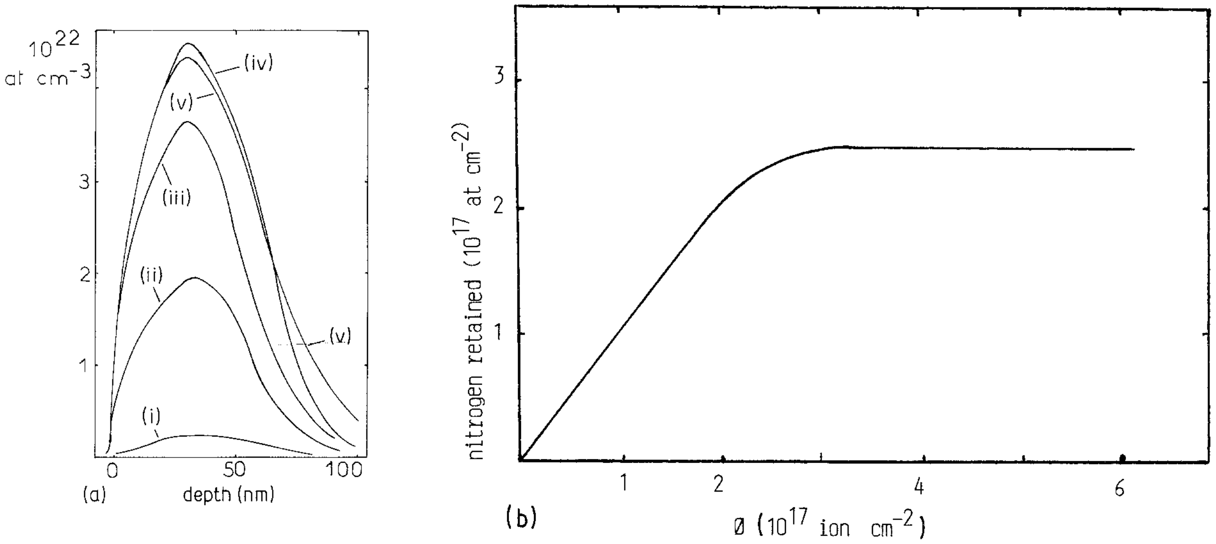

Figure 7 (a) ^{15}N distribution profiles in WC–Co as a function of fluence (ion cm^{-2}): (i) 10^{16}; (ii) 10^{17}; (iii) 2×10^{17}; (iv) 4×10^{17}; (v) 6×10^{17}. (b) Experimental collection curve for 40 keV N implanted in WC–Co.

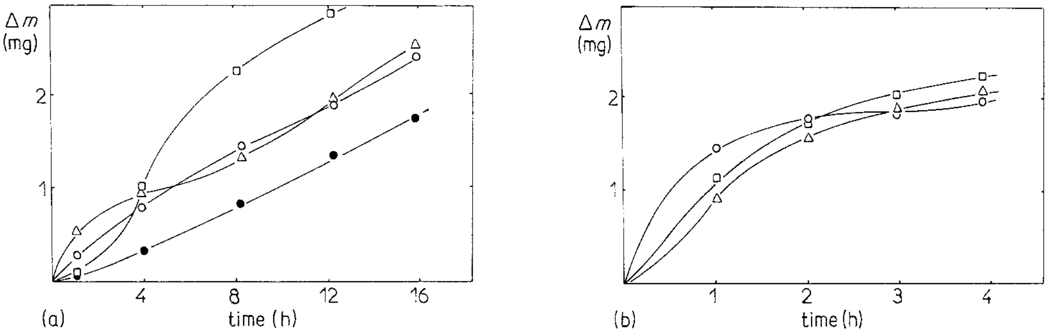

Figure 8 Weight losses of WC–Co as a function of wear time (a) F = 200 N, (b) F = 500 N. (△) non implanted, (●) 10^{17}, (○) 2×10^{17}, (□) 4×10^{17}.

[26] has observed that implantation in cemented carbide produces an important drop in yield stress in the near surface zone. By transmission electron microscopy, Greggi and co-workers [27, 28] have not detected nitrogen compounds. They have shown that implantation induces changes in the binder phase and alters the defect structure of the WC grains at a fluence of 10^{17} ion cm^{-2}, 75 keV. These defects consisted mainly of planar features or faults or dislocation tangles with a high density. These microstructures are similar to those observed in compressively deformed WC–Co and are in favour of an increased mobility of nitrogen since all these defects multiply during wear.

The comparison between the behaviour of the three carbides in our work allows the following remarks to be made.

1. The difference between penetration depths cannot be explained by the difference of retained nitrogen amount. In steels [23], migration is greater after a 10^{16} ion cm^{-2} implantation than after one of 10^{17} ion cm^{-2}. The reasons must be sought in the nitrogen chemical state and in the migration mechanisms.

2. The binder phase of the cemented carbide probably plays an important role. It is possible that the

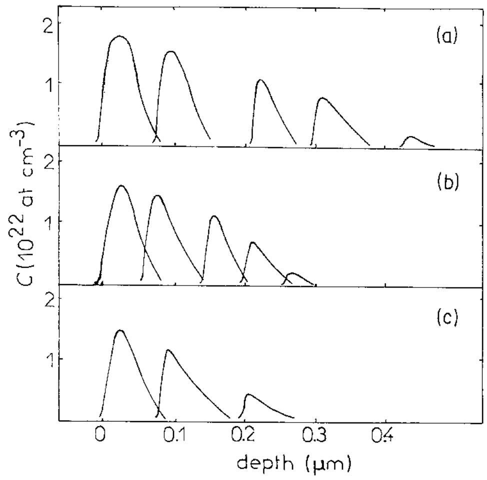

Figure 9 ^{15}N profile evolutions during abrasive wear. (a) WC–Co, (b) WC, (c) W_2C.

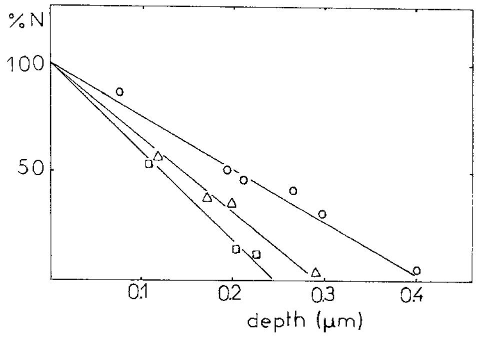

Figure 10 Retained nitrogen after wear in tungsten carbides. (○) WC–Co, (△) WC, (□) W_2C.

areas between the carbide grains act as a short circuit for nitrogen diffusion, particularly as the result of the numerous phase and inter-phase boundaries.

3. The more important migration of nitrogen in WC–Co in comparison with steels can be explained by this boundary-enhanced diffusion and probably also by the fact that there are no nitrogen compounds in WC–Co, contrary to the nitrides formed in steels [29].

4. The W_2C structure, which has many vacancies [30] is not favourable to the easy mobility of nitrogen. The nitrogen atoms possibly end up in the non-occupied interstitial sites of the hexagonal structure and are more bound than in WC.

The depth of nitrogen ingress in the erosion wear test and the depth at which there is no longer wear resistance improvement are nearly the same ($\sim 0.5\,\mu$m). But the wear mechanisms are different. So, in a tribological test when wear of the surface is not uniform, migration phenomena probably occur too, but they concern only the outermost layers of the less quickly worn areas (between scratches). Other mechanisms resulting directly from friction (hardening of the binder phase, plastic deformation and work hardening of WC [31]) are more likely to be dominant after the first stage of low wear resulting from nitrogen implantation.

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