Nickel in Hardmetals

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ABSTRACT

Cemented Carbides were first used in Germany in 1925. Although theu are sometimes called hardmetals, they are not metal but complex materials consisting of hard particles (WC) and metals (Co). Hardmetals, and the nickel used in their production, have benefitted industry considerably. The binder phase was tested analytically and it was found that the tungsten content of the binder depends on the carbon content of the alloys, on grain size of the carbide used, on nickel content and on sintering and cooling conditions.

KEY WORDS: CEMENTED CARBIDES, NICKEL BONDED TUNGSTEN-CARBIDE, NICKEL POWDER and CARBIDE GRAIN SIZE.

INTRODUCTION

Cemented carbides have been used since 1925 and are essentially carbide particles of a refractory metal cemented by a metal or alloy of the iron group, cobalt or nickel. There are several reasons why choose a metal as cement for carbides, for instance Nickel:

a) High melting point (nickel 1453ºC);

b) Form a liquid phase with tungsten-carbide at a suitable temperature (nickel does at 1310 ºC. This liquid pulls the sintered parts together by surface tension and eliminates voids;

c) Dissolve WC (nickel forms a eutectic with at ~1310 ºC and dissolves 4% WC at that temperature);

d) On cooling, the binder should reprecipitate WC, leaving a tough matrix with dispersed carbides (nickel can produce particles around 1-2µm).

e) No structural defects (pores,etc), and a good surface roughness showing a mirror appearance.

f) High resistance to corrosion and oxidation;

g) High hardness and strength;

These are the advantages of nickel and explain the paramount importance it has in cemented carbides. Because of these excellent mechanical properties, it is effective in applications requiring a high resistance to corrosion, even under conditions where conventional cemented carbide tools are used. Grade type with moderate resistance to weak acids are indicated for seal rings and with good wear resistance. Because WC+Ni has a microstruture composed of uniformly fine (~3μm max.) carbide grains, it is possible to polish it as a mirror without the surface topology defects found in conventional cemented carbides (WC+Co) because of the hardness difference between the carbide phase and the binder metal phase.

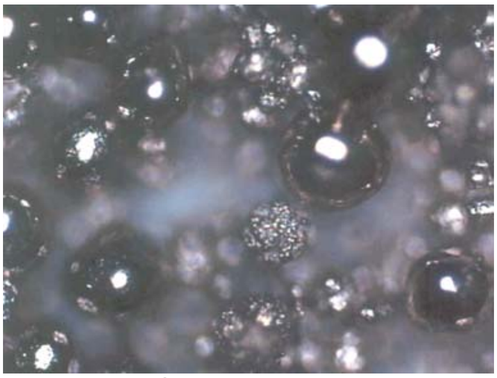


Figure1: Spherical nickel powder.

Spherical nickel powder where all particles larger than 35 μm have been removed, are shown in figure 1. This product is ideal for making PM moulding parts where high sintered density and controlled shrinkage are important. The powder also find application in welding electrodes, thermal spray formulations, sintered magnets and friction materials. Fine sized spherical powders are also available and includes -20 μm, + 10 to 20 μm and - 10 μm.

The properties of tungsten carbide-nickel hard metals are determined by three parameters:

a) Properties of the carbide phase;

b) Properties of the nickel binder phase; and

c) Interaction between carbide and the nickel binder

The present paper is a contribution to the understanding of the binder metal. It is known that nickel is not present in the hard metal in pure form but as a solid solution with tungsten and carbon because of is ability to solve considerable amounts of tungsten carbide at sintering temperature.

Since the solubility if WC in Ni increases substantially with temperature, the composition of the binder phase at the temperature can be expected to be determined by many factors such as sintering temperature and time, rate of cooling, particle size of the carbide used and, consequently, the mean free path in the binder.

For determination of the composition of the binder phase in WC-Ni alloys the carbide was electroytically removed so that the remaining binder could be tested analytically. The chemical analysis can be checked by determining the lattice constants.

Moreover, the work is intended as a contribution to the question of the mecanical properties of nickel-tungsten-carbon alloys. For this purpose, a number of alloys in the range of compositons of interest were prepared and mechanically tested. The results, however, must be examined with care taken into account the conditons of sintered carbides, because the binder in hard metals is present in very thin layers with considerabele internal thermal stress. Nevertheless, they give an idea of the excellent mechanical properties of the binder.

TUNGSTEN CARBIDE-NICKEL ALLOYS

Nickel – bonded tungsten carbide is regarded as the stainless steel of the sintered carbide family. Indeed, its resistance to oxidation and to a wide variety of other corrosive media is superior to that of stainless steel or any other carbide type.

The first commercially available cemented carbides consisted of tungsten carbide particles bonded with nickel. These are commonly referred to as normal grades. A typical commercial product has 92 tungsten carbide and 8 nickel per cent. Abrasion resistance, although rather less than tungsten Carbide-Cobalt – WC-Co, is clearly greatly superior to that of any normal corrosion resistant alloy. These alloy exhibt excellent resistance to simple abrasive wear and thus have many applications in metal cutting. Table 1 lists the representative properties of severval normal WC-Ni alloys.Uses include valve components, plungers and other applications combining both corrosive and abrasive resistance.

The microstructure of WC-Ni alloys should exhibit only two phases: angular WC grains – phase α and Ni binder – phase γ. Representative microstructures of normal WC-Ni alloys are shown in Fig. 2 and Fig 3. The carbon content must be controlled within narrow limits. Too high carbon content results in the presence of free and finely divided graphite, which in small amounts has no adverse effects in machining applications.

STRUCTURAL CHARACTERIZATION

The metallographic structure of polished samples can be revealed using reactants such as: Murakami´s solution, to reveal tungsten carbides, and Nital 2% reagent or aqueous solution of FeCl3, to reveal the metallic phase.

In all samples, diffusion between carbides and the metallic phase during the sintering process, was observed:

a) There are only two phases present: WC - α1 or α2, and γ phase of Ni solid solution;
b) α – phase has simple hexagonal structure with stoichiometric structure 1:1 (W) in all alloys;
c) the highest concentration of W occurs in the centre of α – phase carbides and gradually decreases to the carbide surface;
d) some of W is found inside the metallic phase;

e) Nickel diffuse into the α – phase and is found in the carbide surface; and
f) The structural characterization shows that in all the alloys, the matrix phase has a face centred cubic structure. This give the alloy considerably improved properties compared to the conventional hardmetal (WC+Co) in which a hexagonal structure is found. The fcc structure, which has four slipping compact planes, has the ability to undergo plastic strain and so a high toughness.

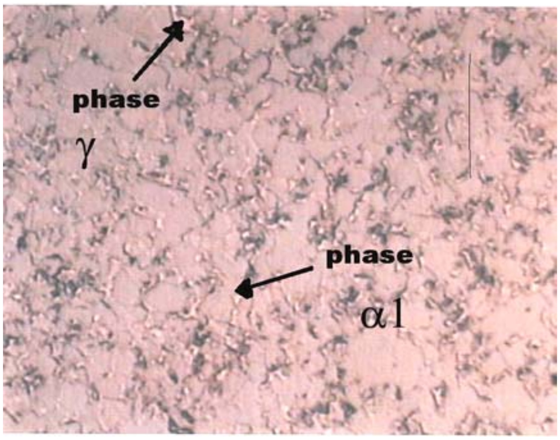


Fig. 2 - 94WC+6Ni alloy, coarse grain. Etched with Murakami's reagent form 10 sec. (5V). Type of sintered carbide was WC+Ni, whose structure is characterise by the irregular of the WC grain – phase α1. (x1500).

PROPERTIES CEMENTED CARBIDE

Many national and ISO standards have been developed for determining the selected properties of cemented carbides (Table 2).

Table 2 Test methods for dtermining the properties of cemented carbides.

PROPERTY	TEST METHOD	
	ASTM	ISO
ABRASIVE WEAR RESISTANCE	B 611	---------
APPARENT GRAIN SIZE	B 390	---------
APPARENT POROSITY	B 276	4505
COERCIVE FORCE	---------	3326
COMPRESSIVE STRENGTH	---------	4506
DENSITY	B 311	3369
FRACTURE TOUGHNESS	---------	---------
HARDNESS, HRA	B 294	3738
HARDNESS, HV	---------	3878
LINEAR THERMAL EXPANSION	B 095	---------

MAGNETIC PERMEABILITY	---------	---------
MICROSTRUCTURE	B 657	4499
POISSON'S RATIO	---------	---------
TRANSVERSE RUPTURE STRENGTH	B 406	3327
YOUNG'S MODULUS	---------	3312

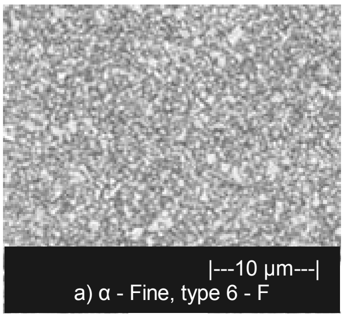
TYPICAL PHYSICAL PROPERTIES CEMENTED CARBIDE

Hardmetals grade G6Ni, G8Ni and G10Ni composite have 3-4µm carbide particle size and 6%,8% and 10% nickel binder. The microstructure shows fine-grained 'pellets' in the coarser matrix. Typical physical properties are shown in table 1.

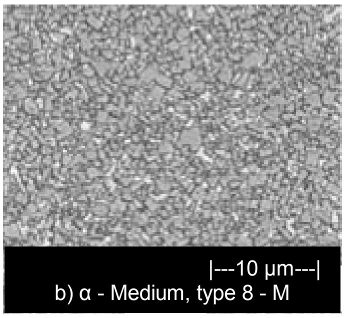
Table 1 properties of representative nickel-bonded cemented carbide.

Nominal composition	Grain Size ASTM B390	Hardness Hra ASTM 294	Density (g/cm^3) ASTM B311	Transverse Strength (N/mm2)	POROSITY ASTM B276
94WC+6Ni	Type 6 F	90,0	14,92	1600	A03
	Type 6 M	88,8	14,85	1760	
	Type 6 C	87,0	14,80	2000	
92WC+8Ni	Type 8 F	89,0	14,85	1950	A02
	Type 8 M	88,0	14,75	2200	
	Type 8 C	87,0	14,69	2500	
90WC+10Ni	Type 10 F	88,5	14,56	2040	A02
	Type 10 M	87,5	14,45	2300	
	Type 10 C	86,5	14,39	2700	

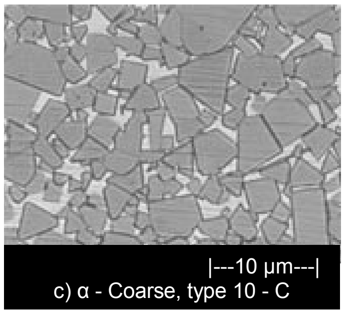
Fig 3- Photomicrographs of various grades of WC+Ni



a) 6% Ni – fine grain



b) 8% Ni – medium grain



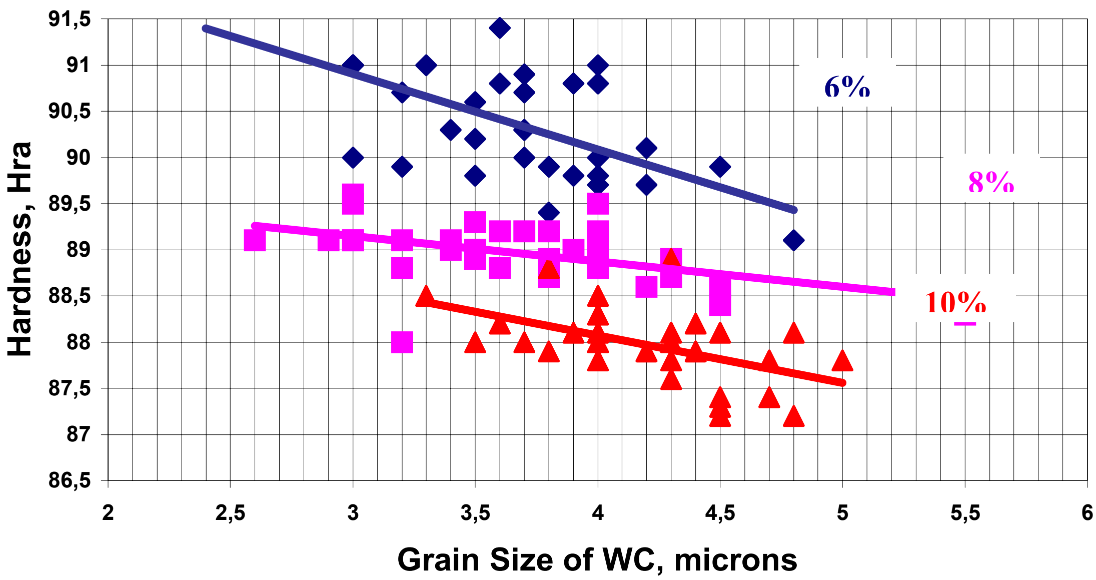
c) 10% Ni – Coarse grain

*Microstructures of normal WC-Ni alloys. a) 94WC+6Ni alloy, fine grain size. b) 92WC+8Ni alloy, medium grain and c) 90WC+10Ni alloy, coarse grain. All etched with Murakami's reagent form 10 sec. (5V). Type of sintered carbide was WC+Ni, whose structure is characterise by the angularity of the WC grain – phase **α2**. (x1500)*

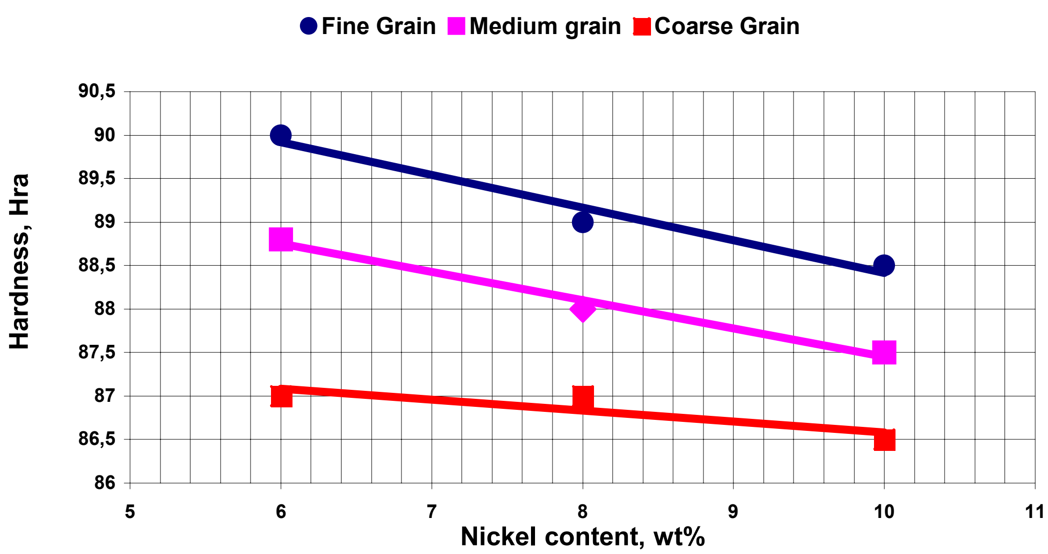
HARDNESS determine the resistance of a material to abrasion and wear. It is affected not only by composition but also by the level of porosity and microstructure. For normal WC-Ni alloys of comparable WC grain size, hardness decreases with increasing nickel content (fig.4). However, because both composition and microstrucure affect hardness, nickel content and grain size must be considered. At a given nickel level, hardness improves with decreasing WC grain size.

In Hardmetal WC+Ni, hardness is measured by the Rockwell A (Hra or Ra), 60 kg, scale diamond cone (∠120º) identation test (Hra) or by the Vickers diamond pyramid indentation test (HV). Hardmetal WC+Ni used in machining applications hardness values range from 86 to 90 Hra.

Fig 4- Variation of Rockwell Hardness of WC-Ni alloys with composition and grain size of WC

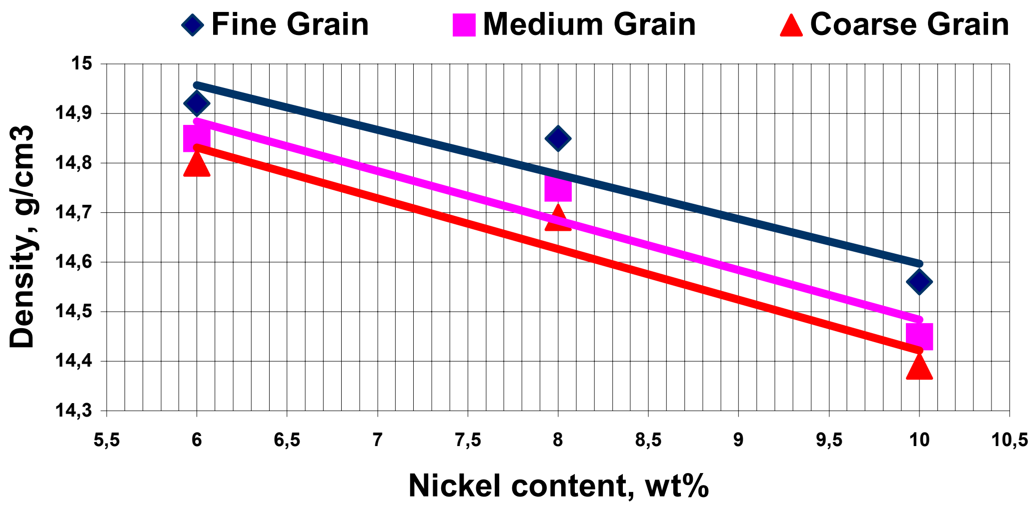


Variation in Hardness



DENSITY, or specify gravity, of WC+Ni, is very sensitive to composition and porosity in the sample and is widely used as a quality control test. Density values of WC+Ni range from 14,97g/cm3 for low-nickel WC-Ni alloy to about 10 or 12 g/m3 for highly alloyed carbide grades (Fig 5).

Fig 5- Variation in Density

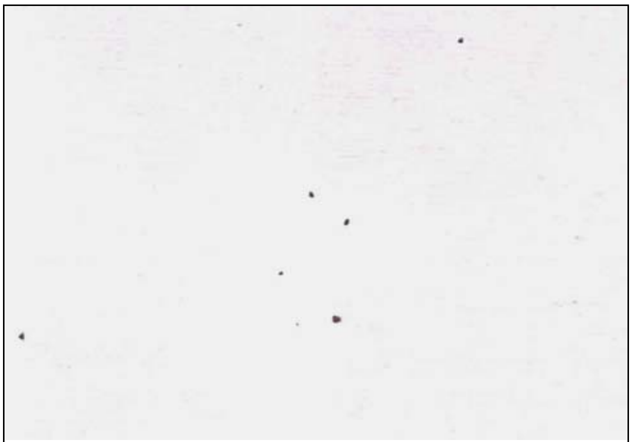


POROSITY - The properties of a WC+Ni, hardmetal, are dependent on its density, which in turn is critically dependent on composition and porosity. Porosity is evaluated on the as polished material. The American Society for testing and materials (ASTM) has established a standard procedure (B276) that rates three types of porosity:

a) type A, covering pore diameters less than 10 µm;
b) type B, covering pore diameters between 10 and 25 µm;

c) type C, covering porosity developed by the presence of free carbon.

Type A porosity is rated at a magnification of 200X, while types B and C porosity are rated at 100X. The degree of porosity is given by four numbers ranging in value from 02 to 08. The number provides a measure of pore volume as a percentage of total volume of the sample. Example is shown ifn Fig 6.



Apparent porosity (200X) - type A03 (0.02 vol%)

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