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Substitution Effects of Nickel and Cobalt in WC Based Hard Metal

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In the present work, the effects of partial and complete substitution of cobalt by nickel in some WC-10% binder phase hard metals have been investigated.

Key Words: Cobalt, Nickel, Substitution, WC, Hard, Metal.

INTRODUCTION

High world price of cobalt metal and its strategic importance have prompted investigation into its possible replacement in hard metals by a cheaper, more readily available substitute binder material. Iron and nickel are the most promising substitutes for cobalt, in terms of their physical, chemical and metallurgical properties and from economic considerations.

In the present work the effects of partial and complete substitution of cobalt by nickel in some WC-10% binder phase hard metals have been investigated.

By control of carbon balance the binder composition and hence the magnetic saturation of the materials was optimized. Microstructural effects were minimized by standardizing the grain size and relative density of the grades.

A major effect noticed in the nickel bonded hard metals was a greatly increased solubility of tungsten and carbon in the binder phase relative to cobalt bonded grades. This resulted in a much wider compositional range of the two-phase field without precipitation of eta phase of graphite. It was associated with a wide range of magnetic properties within the two-phase field.

The following mechanical properties were measured:

(i) Vickers hardness, (ii) transverse rupture strength,
(iii) Palmqvist fracture toughness[1], (iv) compressive strength.

These have been related to the changes in binder phase composition from 100% Co to 100% Ni. It was found that certain WC-Co-Ni material exhibited superior mechanical properties in comparison with WC-Co grade material. This may be due to the $\beta \rightarrow \varepsilon$ transformation occurring in the binder phase when less than 32% Ni is present.

EXPERIMENTAL

Preliminary Sintering Trials

Preliminary sintering trials were carried out in high vacuum, to determine suitable sintering temperatures for the different grades, on the basis of density and microstructure. It was found that Grade A (cobalt binder) sintered satisfactory at 1400°C. Grades B and C required a temperature of 1420°C and a slightly higher temperature (1440°C) was necessary to achieve satisfactory sintering in the high nickel grades D and E.[2]

The sintering trials revealed a marked loss of carbon during processing, in all the grades. The origin of this carbon loss was traced by chemical analysis at each stage of manufacture and was found to occur predominantly during the presintering operation. There was no significant difference in the extent of carbon loss among the WC-Co, WC-Co-Ni and WC-Ni compositions. It was noticed, however, that the decarburizsed WC-Co hardmetals contained substantial amounts of eta phase, whilst the nickel-containing compositions showed the normal two-phase microstructure.

It was also noticed that the decarburized WC-Ni hard metals showed variable magnetic properties and in some cases the material was completely non-ferromagnetic.

Sintering in Gas atmospheres

In view of the extensive carbon loss in presintering, causing highly variable magnetic properties, it was decided to control the carbon balance of the hard metal by sintering in a carburising atmosphere. In order to isolate the specific effects of nickel substitution, the carbon balance for each grade was standardized at that level resulting in a magnetic saturation value equal to the theoretical maximum value obtainable.

The appropriate carburizing cycle for each grade was determined by a series of trial experiments. The carburizing potential (carbon activity) was varied by adjusting the relative ratios of methane and hydrogen, the total furnace pressure being maintained at 430 torr.

Because of the highly decarburizing conditions of presintering, it was found necessary to use methane/hydrogen ratios considerably in excess of those theoretically indicated. This explains why carbon "activities" greater than unity were required.

The effects of increasing the carburizing potential and carburizing time during the sinter cycle, on some properties of the experimental grades, are shown in Table-1.

Appropriate carburizing cycles for each grade were selected, as indicated in Table-1. These were used for subsequent sintering of test pieces for mechanical properties determination.

TABLE-1
EFFECTS OF VARIOUS CARBURIZING TREATMENTS
ON HARD METAL PROPERTIES

Grade	Gas treatment (Activity/time)	Sinter temperature (°C)	Magnetic saturation $(T.m^3/kg) \times 10^{-7}$	Hardness Hv 30
A_1	nil	1400	155	1222
A_2	1, 5/1 h	1400	184	1257
A_3*	1, 5/2 h	1400	187	1203
B_1	nil	1420	126	1246
B_2	1, 5/1 h	1420	148	1189
B_3	1, 5/2 h	1420	155	1203
B_4	1, 8/1 h	1420	171	1183
B_5*	1, 8/3 h	1420	180	1190
C_1	nil	1420	76	—
C_2	1, 5/2 h	1420	148	1149
C_3*	1, 8/3 h	1420	157	1150
D_1	1, 8/1 h	1420	90	1088
D_2	1, 8/3 h	1440	100	1083
E_1	nil	1440	Nil	—
E_2	1, 8/1 h	1440	23	1016
E_3*	1, 8/3 h	1440	44	1066

*Conditions selected for subsequent sinter cycles.

Mechanical properties

Tensile properties were assessed by means of the transverse rupture test, carried out on as-sintered rectangular beams, with chamfered edges. The mean transverse rupture strength values are given in Table-2, together with statistical data and Vickers hardness values.

TABLE-2
TRANSVERSE RUPTURE STRENGTH DATA

Grade	Transverse rupture strength		Harness Hv 30
	Mpa	Coeff. of variation (%)	
A	1615	9	1200
B	1773	8	1190
C	1720	9	1150
D	1285	10	1080
E	1601	13	1060

The hardness decreased continuously with increasing nickel content, the pure nickel grade being about 10% lower in hardness than WC-Co hardmetal.

The transverse rupture strength increased with nickel additions up to 30% and then decreased slowly, but exhibited a sharp drop around the 70% Ni–30% Co composition. The WC-Ni hardmetal showed similar strength to the WC-Co grade.

The fracture toughness was assessed by means of the palmqvist indentation cracking test using an indenting load of 60 kg. The experimental results are given in Table-3. The palmqvist toughness increased with nickel additions up to about 30% and then decreased again. The toughness of the WC-Ni grade was slightly higher than that of the WC-Co hardmetal.

TABLE-3
PALMQVIST TOUGHNESS DATA

Grade	Palmqvist Toughness $\times 10^6$ Nm^{-1}
A	3.88
B	6.69
C	11.02
D	6.61
E	5.20

The results of compressive strength determinations are given in Table-4. The compressive strength decreased continuously with increasing nickel content, the pure nickel grade having a strength value approximately 18% lower than the pure cobalt grade.

TABLE-4
COMPRESSIVE STRENGTH DATA

Grade	Compressive strength	
	Mpa	Coeff. of variation (%)
A	3969	3
B	3859	7
C	3741	4
D	3426	7
E	3252	7

Microstructure

With appropriate sintering conditions, all the hardmetal grades showed a normal two-phase microstructure (Figs. 1–5). The presence of nickel did not appear to cause any change in the WC grain morphology. There was no significant variation in the WC grain size among the experimental compositions, the average grain size, measured by the mean linear intercept method, being 1.65 ± 0.1 μm for all grades.

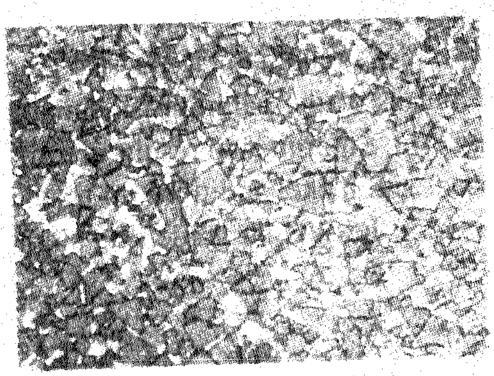

Fig. 1. Microstructure of grade A × 2000

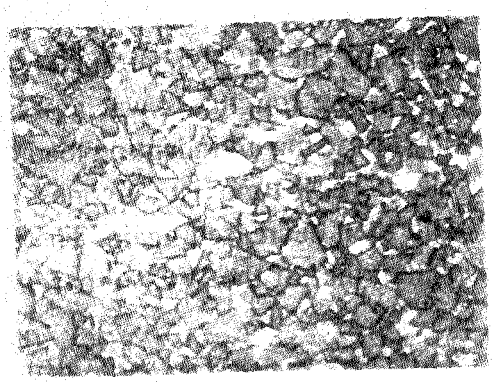

Fig. 2. Microstructure of grade B × 2000

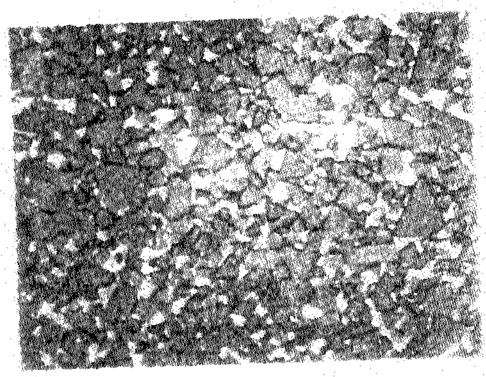

Fig. 3. Microstructure of grade C × 2000

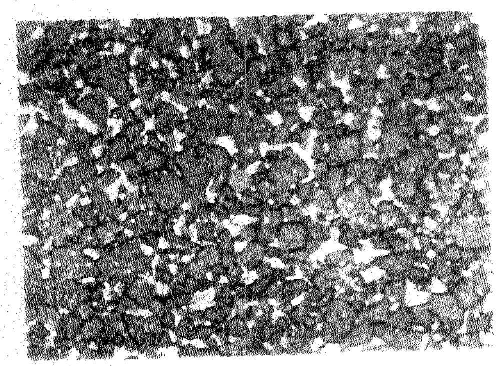

Fig. 4. Microstructure of grade D × 2000

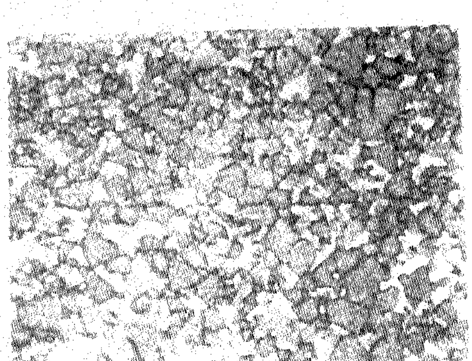

Fig. 5. Microstructure of grade E × 2000

RESULTS AND DISCUSSION

The experimental results have shown that controlled gas carburizing is an effective method for controlling the binder phase composition, as evidenced by the experimental values of magnetic saturation. However, anomalous behaviour was shown by the pure nickel hard metal, in which only *ca.* 70% of the theoretical magnetic saturation could be achieved, even after extended carburizing times. This confirms the earlier findings of Suzuki and Yamamoto[3] and of Roebuck[4]. Roebuck[3] proposed that this anomaly was attributable to the significant effect of dissolved carbon on the magnetic properties of nickel, compared with its almost negligible effect on the magnetic properties of cobalt. An alternative explanation is that dissolved carbon does not displace dissolved tungsten in nickel to the same extent as it does in cobalt, *i.e.*, the apparent "solubility product" relationship between dissolved carbon and tungsten is not exhibited by pure nickel.

The mechanical properties of the hard metals exhibited some interesting trends as nickel was added to the binder. The hardness decreased continuously with increasing nickel content. This indicates that the flow stress of the binder was decreased by nickel additions. It is thought that this explains the observed trends in compressive strength, which also decreased continuously with increasing nickel content. The reduced flow stress relative to pure cobalt can account for the reduced stress at failure, assuming that binder ductility is exhausted at approximately similar levels of total plastic strain for all the grades. The effects of binder composition on hardness and compressive strength are shown in Fig. 6.

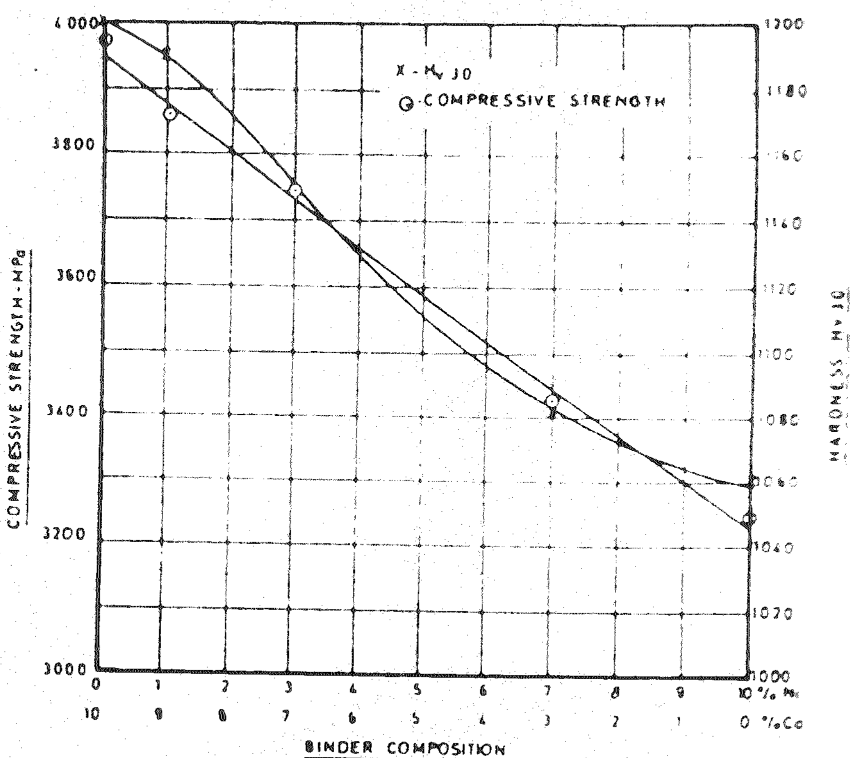

Fig. 6

The fracture toughness and transverse rupture strength are mechanical properties which measure tensile strength in relation to the presence of stress-intensifying flaws or microcracks in the material. Both tests provide a measure of the resistance of the material to crack propagation under tensile stress components. The crack propagation resistance is thought to be controlled by the contiguity of the carbide grains and the mechanical properties of the binder phase. In the present series of hard metal grades, the binder content and WC grain size are essentially constant. It is therefore assumed that the degree of contiguity is also constant. In this case, the crack propagation resistance should be controlled by the tensile deformation properties of the binder.

Both the palmqvist toughness and transverse rupture strength values increased with increasing nickel content up to about 30% Ni, after which the values decreased again. The values of these parameters were approximately the same for the pure cobalt and pure nickel binders.

In the case of WC-Co hardmetals, it is known that the stable hcp (ε) structure is not preseent to a significant degree after sintering. It is thought that the metastable fcc (β) phase is retained at room temperature owing to the stabilizing effects of dissolved tungsten and carbon. Considerable amounts of ε-cobalt are detected after deformation. The deformation process can therefore occur *via* two major mechanisms, *viz.*,

(a) Normal slip and

(b) The formation of stacking faults (ε-phase).

The formation of stacking faults leads to a very high work hardening rate during deformation. This has been confirmed by studies of Co-W-C synthetic binder phases by Roebuck[4]. It can be postulated therefore that the tensile properties and toughness of WC-Co hardmetals are dominated by the influence of the deformation-induced $\beta \rightarrow \varepsilon$ transformation *via.* its effect on work hardening charcteristics at the sites of concentration of plastic flow (*i.e.*, at stress-intensifiers).

Dannefaer[2] showd that addition of nickel to cobalt depresses the normal $\beta \rightarrow \varepsilon$ transformation temperature. At the Co-32% Ni composition the β (fcc) phase is stable at room temperature. Beyond this composition the ε (hcp) phase cannot be obtained by deformation of β phase. This is reflected in the values of stacking fault energy (SFE) which reach a minimum around the Co-32% Ni composition. In a similar manner, the stacking fault width reaches a maximum at this composition.

It is known that increased stacking fault width leads to higher work hardening rates. It is suggested that the increased toughness and transverse rupture strength observed in the present work as the nickel content was increased up to 30% Ni, can be attributed to the increased rate of work hardening, as a function of stacking fault width. The relationships among toughness, transverse rupture strength and stacking fault width as a function of binder composition are shown in Fig. 7.

When nickel contents greater than 32% Ni, the ability of the binder phase to deform *via* the $\beta \rightarrow \varepsilon$ transformation is removed, and hence the β phase becomes stable. In this case only normal slip processes are possible. This is expected to result in a sharp drop in toughness and tensile properties, since the capacity for high work hardening rates at stress raisers is also removed. This behaviour was, in fact, demonstrated by the experimental data.

The anomalously low transverse rupture strength value exhibited at the 70% Ni + 30% Co composition cannot be explained by this model. Since no anomalies were found at this composition in the other test data, it is possible that this particular batch of specimens contained excessive porosity, which can greatly reduce the transverse rupture strength, without noticeable effects on other mechanical properties. This could not be confirmed by metallography. Further experimental work is required to confirm these findings.

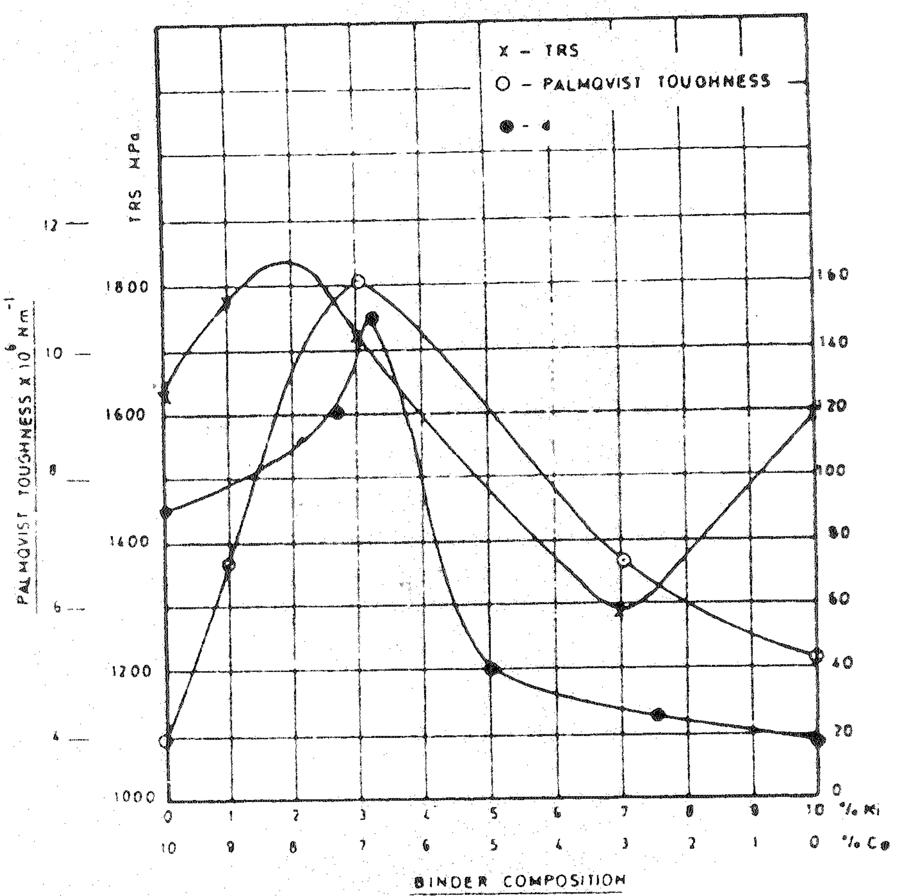

Fig. 7

Conclusions

- Hard metals containing Co-Ni alloy binders and pure Ni binders can be processed satisfactorily using the conventional powder metallurgy techniques.
- In high nickel grades, the width of the two-phase (WC + β) field with respect to carbon content is considerably greater than in WC-Co hardmetals.
- By means of a carburizing gas treatment prior to sintering, full density material with saturation magnetization close to theoretical values can be obtained.
- Full saturation magnetization cannot be achieved in hardmetal with a pure nickel binder. This is thought to be an effect of dissolved carbon and tungsten levels in nickel.
- The hardness and compressive strength decrease continually with increasing nickel additions. It is proposed that this is due to the reduced flow stress of nickel-containing binders, assuming the capacity for compressive ductility to be approximately constant for all grades.
- The toughness and transverse rupture strength exhibit a maximum value around the WC-70% Co-30% Ni composition. It is suggested that this is due to the enhanced work hardening characteristics of the low nickel binder phases owing to the formation of wide stacking faults as a result of the deformation-induced fcc (β) → hcp (ε) transformation. Beyond the 32% Ni

composition, the $\beta \rightarrow \varepsilon$ transformation is not possible, and reduced toughness and strength are observed.

- A very low transverse rupture strength was observed at the WC-70% Ni-30% Co composition. Since no other anomalous properties were found in this region, it is possible that processing defects were responsible.
- On the basis of these results it is concluded that superior combinations of properties may be available from certain WC-Co-Ni hardmetal compositions, compared with conventional WC-Co grades.
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- Beyond the 32% Ni composition, the $\beta \rightarrow \varepsilon$ transformation is not possible, and reduced toughness and strength are observed.
- A very low transverse rupture strength was observed at the WC-70% Ni-30% composition. Since no other anomalous properties were found in this region, it is possible that processing defects were responsible.
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