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Publication number:

**0 085 125  
A1**

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## EUROPEAN PATENT APPLICATION

Application number: 82100684.8

Int. Cl.<sup>3</sup>: **C 22 C 29/00  
E 21 B 10/46**

Date of filing: 01.02.82

Date of publication of application:  
10.08.83 Bulletin 83/32

Designated Contracting States:  
AT BE CH DE FR GB IT LI NL SE

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**54** Cemented carbide compositions and process for making such compositions.

**57** The compositions comprise about 80 to about 97% by weight of the refractory particles of, for example, tungsten carbide. The particles are bonded within an alloy matrix of between about 5 and about 50% nickel, sufficient carbon to avoid the formation of detrimental carbon deficient or excess carbon phases and a balance of about 95 to about 50% iron by weight. In a preferred embodiment, the alloy matrix additionally contains from about 5 to about 20% by weight of manganese.

These compositions are useful for rock drilling.

**EP 0 085 125 A1**

## CEMENTED CARBIDE COMPOSITIONS AND PROCESS FOR MAKING SUCH COMPOSITIONS

This invention is concerned with cemented compositions and, more particularly, with cemented carbide compositions having unique characteristics and physical properties particularly suited for drilling and mining operations.

Similar compositions are well known for their combinations of hardness, compressive strength and abrasion resistance. Because of these properties, as well as others, cemented carbide compositions are used extensively in industrial applications. Representative are cutting tools, drawing dies, wear parts, drills and other applications where hardness, compressive strength and abrasion resistance are of paramount importance.

A representative and wide variety of these compositions, different physical forms in which they may be utilized and means of production are described in U.S. Patent No 3,384,465 and U.S. Patent No. 3,450,511. These compositions are primarily composed of refractory particles of, for example, tungsten carbide bound within a metallic matrix. Although cobalt is the most common metal for such matrix binders, many others have also been employed.

It is known, for example, that various advantages may flow from the use of nickel and/or iron in these matrix binders. These metals have been substituted for some or all of the cobalt in selected compositions. Such substitutions are described in U.S. Patents No. 3,816,081, 3,372,066 and 3,746,519. There, alloys containing both nickel and iron are disclosed as being useful in matrix binders for tungsten and other such carbide particles.

An important quality of a cemented carbide composition is its ability to resist the propagation of small cracks which form in the composition surface. It is of particular importance in, for example, a rock drill where such cracks may form soon after it is put into service. The resistance to propagation of surface cracks is referred to as fracture toughness or, in more exact terms, critical stress intensity parameter, i.e.,  $K_{IC}$ . This property is best measured in a test where a natural crack can be started and stopped several times, in such manner that the energy required to propagate the crack can be accurately determined.

Another quality of particular importance is resistance to high applied stress; a circumstance again encountered in rock drilling. The involved property of hardness directly affects wear resistance and therefore the longevity of use of articles made from these cemented  
5 compositions.

Despite the wide spread use and investigation of such cemented compositions, substantial improvement in compositions useful in rock drilling has not been achieved. Where increases in one such property have been obtained, other important ones often including abrasion resistance  
10 and hardness have suffered. Thus compositions having the composite properties desired for this purpose have remained unavailable.

Figure 1 is a graph reflecting the surface hardening as a result of simulated rock drilling of representative compositions of the prior art and present invention as a function of distance from the composition  
15 surface. Figure 2 is a graph of fracture toughness versus abrasion resistance for some compositions of this invention as compared to prior art cobalt tungsten carbide compositions.

The present invention is directed to improved cemented compositions and, more particularly, to cemented tungsten carbide compositions  
20 having particular utility for rock drilling and/or mining operations. These compositions solve many of the drawbacks of the prior art, including those already discussed above.

The present compositions are composed generally of from about 80 to about 97% by weight of refractory particles of, for example, tungsten  
25 carbide. These particles are bound within from about 3 to about 20% by weight of a metallic matrix comprising an alloy of between about 5 and about 50% nickel, sufficient carbon to avoid the formation of detrimental carbon deficient or excess carbon phases and a balance of from about 95 to about 50% iron by weight. In a further improved embodiment these alloys  
30 additionally contain manganese.

The major component of the present cemented compositions is its refractory particles. It is this component, generally present in about 80 to about 97% by total weight, which is primarily responsible for the abrasion resistance necessary for these compositions' utilities.

35 Tungsten carbide generally constitutes at least 50%, and preferably from 70 to 100%, of these refractory particles. Its well known physical properties make it particularly suitable for this purpose. In

addition, various other materials may be employed in conjunction with it. For specific applications, particles of titanium carbide, tantalum carbide and/or various other known refractories may be admixed with the particles of tungsten carbide. Most commonly, these secondary refractories are  
5 utilized in an amount less than 50%, preferably less than 20%, by total weight of particles.

As known in the art, the carbide grain size may range widely. To provide the most desired combination of abrasion resistance and toughness, the carbide grain size may be from about one-half ( $\frac{1}{2}$ ) to about 15  $\mu$ m or  
10 mixtures thereof.

The matrix binder for the refractory particles of the present invention is a metallic alloy. It is this alloy which is responsible for maintaining the physical integrity of the composition. Because of the unique properties of the present alloys, a superior combination of  
15 fracture toughness and abrasion resistance can be achieved as compared to many of those of the prior art.

The metallic alloy comprises and may consist essentially of from about 5 to about 50% by weight nickel with the remainder or balance being from about 95 to about 50% by weight iron. Other metals such as cobalt,  
20 molybdenum, copper, chromium and others may be present also. Within the foregoing proportions, such alloys may provide substantial improvement of, in particular, the critical property of fracture toughness.

In addition to the foregoing metallic components, the alloy should contain a sufficient amount of carbon to avoid the formation of  
25 carbon deficient phases. Generally, no more than about 2% carbon by alloy weight will be present. An excess of carbon, sufficient to produce a C-2 or above rating per ASTM specification B-276 should be avoided also. Such an excess may reduce the desirable performance characteristic of the composition.

This carbon performs several functions in the alloy. Most  
30 importantly, it may be utilized to avoid the formation of harmful double carbides of, for example, iron with the tungsten. Such double carbides are generally quite brittle and therefore also detract from important properties of the composition.

In a further embodiment of the present invention, the alloy of  
35 the binder matrix additionally contains manganese, desirably from

about 5 to about 20% by weight. This metal component has been discovered to be especially advantageous in the foregoing alloys where they contain about 5 to about 30% by weight nickel.

5 The present cemented carbide compositions may be employed in any necessary shape and prepared by standard cemented carbide manufacturing techniques. For convenience, the separate alloy components (generally in finely powdered form) are first mixed together, for example in a ball mill. The admixture may then simply be pressed or molded into the desired shape. These steps are usually performed in the presence of a lubricant  
10 such as paraffin or polyethylene glycol which can subsequently be substantially removed.

Once in (or simultaneous with formation of) the desired shape, the molded components can be sintered by any standard carbide sintering technique known to one skilled in the art. Upon cooling, this yields an  
15 integral compact suitable for initial use.

For those compositions containing manganese, it is preferred to heat them in hydrogen or other reducing gas to the liquidus temperature of the binder and then complete the sintering in an inert or reducing gas. This is done to keep the loss of manganese from the composition to a  
20 minimum.

Many of the unique and desirable properties of the present invention are believed to arise from a strain-induced partial transformation of the austenitic matrix alloy to martensite. This occurs under a variety of circumstances, including high applied stress. In the case of  
25 Hertzian contact (similar to that experienced by compacts in rock drilling) the surface layer will partially transform to martensite while the interior portion will remain austenite.

In accordance with the present invention, strain-induced transformation is believed to cause the present composition to exhibit a  
30 hardened surface, which enhances the wear resistance, while retaining a tough core of austenitic alloy matrix to resist breaking. The requisite cold working (or strain hardening) for the partial alloy transformation will take place under the conditions of use of the cemented carbide composition in, for example, rock drilling.

35 The presence of manganese in the subject alloys has an especially significant effect on this phenomenon. The manganese provides a highly desirable hardening transformation when the matrix binder is

subjected to plastic deformation, such as that resulting from high applied stress. Work hardening is localized at the outer surface region of the composition, where the stress is applied. Consequently, the overall toughness of the product is maintained.

The invention of this application will be more fully described and better understood from the following examples and comparative results.

EXAMPLE I

Various tungsten carbide sample compositions were prepared containing from 84 to 85% by weight of tungsten carbide and 15 to 16% by weight of binder matrix. These samples contained differing alloy constituents. Their physical properties were determined and were compared with the standard commercial grades of tungsten carbide - cobalt binder (WC-Co). as follows :

TABLEAU I

Composition Désignation UNITS	BINDER MATRIX WT PERCENT	HARDNESS ROCKWELL A	ABRASION RESISTANCE l/VOLUME LOSS cm <sup>3</sup>	TRANSVERSE RUPTURE daN/mm <sup>2</sup>	FRACTURE TOUGHNESS (K <sub>IC</sub> ) daN.mm <sup>-3/2</sup>
X7503-86	20% Ni; 1,2% C; Fe*	87.5	5.0	275.76	45.14
X7503-86A	20% Ni; 0.9% C; Fe*	87.5	4.0	275.76	52.08
X7503-86B	30% Ni; 0.9% C; Fe*	87.0	3.5	258.52	58.34
X7503-86E	30% Ni; 0.5% C; Fe*	85.4	2.1	289.54	60.07
X7503-86F	40% Ni; 0.5% C; Fe*	85.4	2.1	296.44	63.20
X7503-86G	50% Ni; Fe*	85.0	1.8	303.33	59.03
X7503-86H	40% Ni; Fe*	86.2	1.9	248.18	55.56
X7503-86J**	30% Ni; 0.5% C ; Fe*	87.0	3.3	289.54	61.11
Grade 55B	100% Co	86.7	2.5	289.54	54.86
Grade 268	100% Co	87.3	2.8	337.80	50.35

\* balance to 100%

\*\* X7503-86J uses a finer WC particle size than its otherwise identical composition (X7503-86E).

Compositions X7503-86 and X7503-86A had relatively low nickel additions and relatively high carbon additions. These compositions had a fracture toughness ( $K_{IC}$ ) which was inferior to that of comparable commercial grade WC-Co. i.e., Grade 55B and Grade 268.

5 Compositions X7503-86B, X7503-86E, X7503-86F and X7503-86J, in which the nickel addition was from 30 to 40% and the carbon addition was 0.5%, showed a substantial increase in fracture toughness without significant decrease in abrasion resistance.

10 Compositions X7503-86G and X7503-86H, in which the nickel addition was in excess of 40% and the carbon was eliminated showed fracture toughness and abrasion resistance which were lower. Because abrasion resistance is equally as important as is fracture toughness to suitability of compositions for rock drilling, these compositions, even though equal or superior to commercial Grades 55B and 268 in fracture  
15 toughness, were inferior.

#### EXAMPLE II

Tungsten carbide sample compositions, all consisting of 88% by weight of tungsten carbide and 12% by weight of binder matrix were prepared. Their physical properties were determined and were compared with  
20 designated standard commercial grades of WC-Co compositions, as follows:

TABLEAU II

Compositions Désignation	BINDER MATRIX COMPONENTS		HARDNESS ROCKWELL A	ABRASION RESISTANCE 1/VOL. LOSS ( $\text{cm}^3$ )	FRACTURE TOUGHNESS ( $K_{IC}$ ) $\text{daN}\cdot\text{mm}^{-3/2}$
	Units	Amount wt. percent			
25 X7801-301	12%	20% Ni; 10% Mn; 1.5% C; Fe*	85.7	5.5	59.03
X7800-302	12%	25% Ni; 10% Mn; 1.5% C; Fe*	85.5	4.3	62.50
30 Grade 231	10%	100 % Co	87.7	3.6	52.08
Grade 55B	16%	100 % Co	86.7	2.5	54.86

\* balance

All compositions of this invention showed significant improvement in abrasive resistance and fraction toughness. Thus the combination of properties exhibited by those compositions having iron/nickel/manganese/ carbon alloy binders were particularly desirable are shown in Figure 2.

EXAMPLE III

A hardness profile was determined on inserts used for drilling rock for each of the following:

DESIGNATION	BINDER MATRIX	
	AMOUNT	COMPONENTS
X7800-302G	12 %	25% Ni; 10% Mn ; 1.5% C, Balance Fe
X7800-301Aa	12 %	20% Ni; 10% Mn ; 1.5% C, Balance Fe
Grade 231	10 %	100% Co
Grade 55B	16 %	100% Co
Grade 241	10 %	100% Co

These profiles were obtained by Tukon Microhardness tester using a knoop indenter and a 500 gram load. They are plotted as the graph of Figure 1.

As depicted in Figure 1, both samples of the present invention show bases for their substantial improvement over standard grades of cobalt-bound compositions. At the composition surfaces, samples X7800-302G and X7800-301Aa exhibited the highest degree of work hardening. This localized surface superiority translated directly into improved wear resistance, particularly under high applied stress.

That surface superiority was combined with a rapid and substantial decrease in hardness with distance from the compositions surface. Thus, they also displayed higher degrees of localization of hardness superiority. This in turn permits the retention of internal toughness. Consequently, the compositions of the present invention exhibited relatively higher overall toughness than ones bound with a conventional cobalt matrix.

Figure 2 also shows the superiority of various of the present compositions. There the relative fracture toughness and abrasion resistance for the sample and commercial compositions of Example II are depicted. It may be seen from FIG.2 that the properties of the present compositions are superior to those of conventional tungsten carbide-cobalt ones.

C L A I M S

1. A cemented composition comprising refractory particles of tungsten carbide within a metallic matrix binder, characterized in that said matrix represents between 3 and 20% by weight of said composition and  
5 comprises an alloy of between 5 and 50% nickel, an amount of up to 2% carbon sufficient to avoid formation of detrimental carbon deficient or excess phases and the balance of from .95 to 50% by weight comprising iron.

2. The compositions of Claim 1, characterized in that the refractory particles additionally comprise titanium or tantalum carbide.

10 3. The composition of Claim 2, characterized in that the composition has an austenitic matrix which partially transforms to martensite at the surface under applied stress.

4. The composition of Claim 1, characterized in that the alloy additionally contains manganese.

15 5. The composition of Claim 1, characterized in that the alloy is between 5 and 20 % manganese and 5 and 30% nickel.

6. The composition of Claim 5, characterized in that the refractory particles additionally comprise titanium or tantalum carbide.

20 7. The composition of Claim 5, characterized in that the composition has an austenitic matrix core which partially transforms to martensite at the surface under applied stress.

8. A process for drilling through rock with a cemented carbide tool, characterized in that said tool is composed of the cemented carbide composition of any of Claims 1-7.

25 9. A process for producing the composition of any of Claims 1-7 characterized in that it comprises :

(a) preparing a powdered admixture of the refractory particles and metallic alloy;

30 (b) subjecting said admixture to sufficient heat and pressure to produce an integral, sintered compact;

(c) cooling said compact; and

(d) subjecting said compact to high applied stress to induce formation of martensite in the surface layer of said composition.

35 10. The process of Claim 9, characterized in that the alloy contains manganese and the admixture is heated first under reducing gas to the alloy liquidus temperature and then sintered under inert or reducing gas.

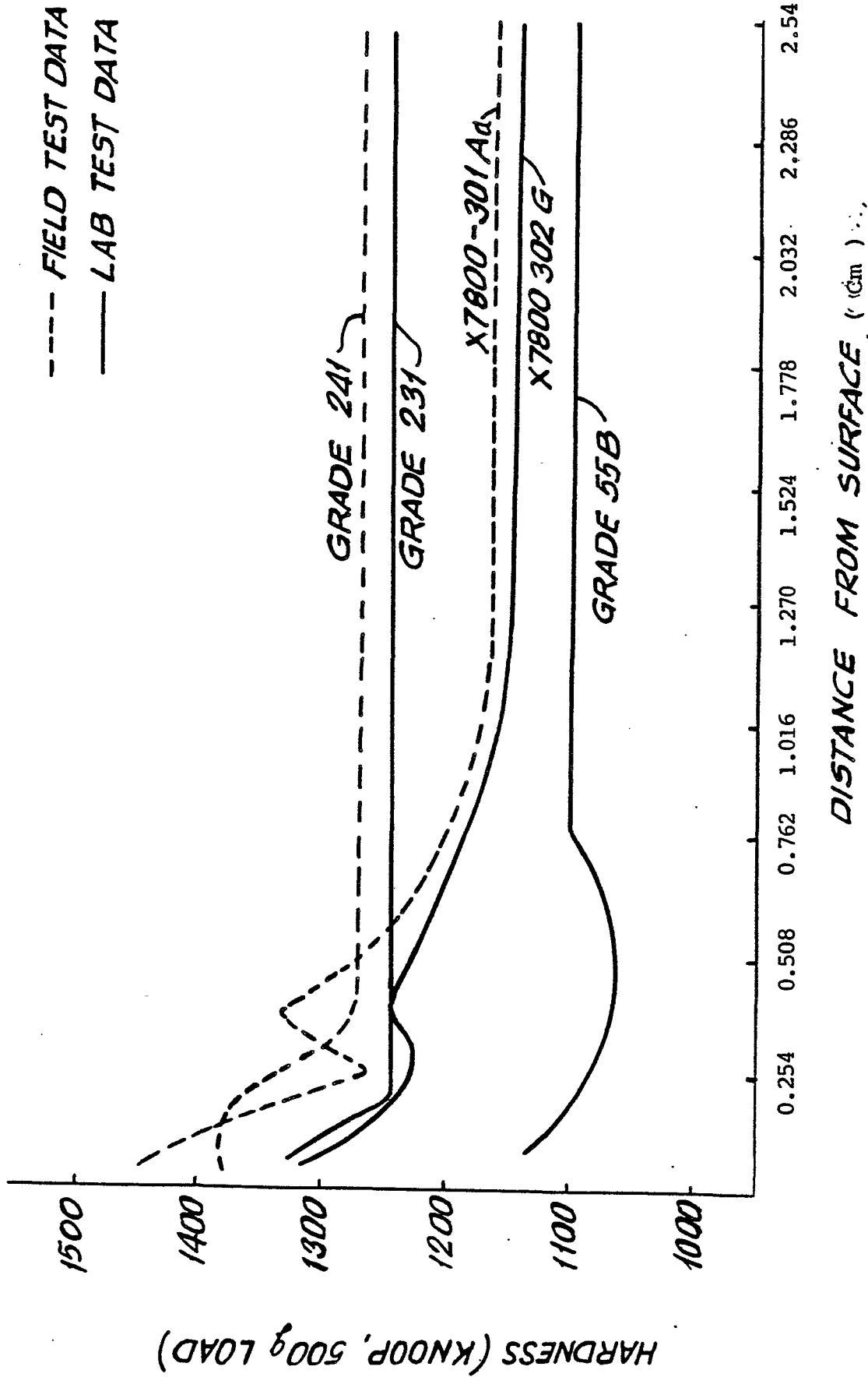


FIG. 1

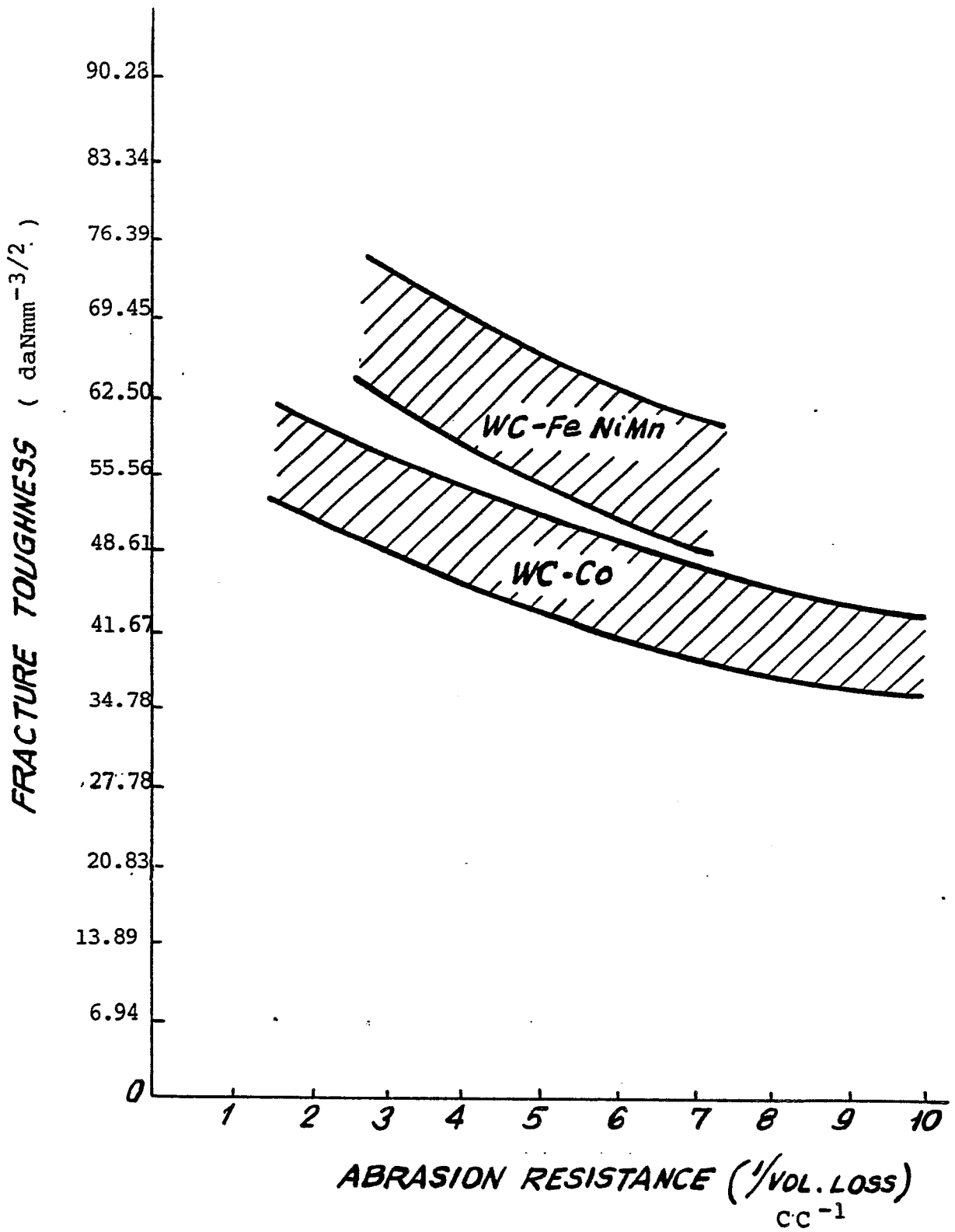


FIG. 2



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. <sup>3</sup> )
X	DE-A-2 718 594 (FORD-WERKE) *Claims 1,9*	1,9	C 22 C 29/00 E 21 B 10/46
Y	EP-A-0 023 095 (R.K.GROVER et al.) *Claims 1-5,7; page 1, line 29 - page 2, line 23*	1-6,9-10	
Y	DE-B-1 813 533 (CHROMALLOY AMERICAN CO.) *Claims 1,3; column 3, lines 25-68; column 6, lines 7-22*	1-8	
Y	FR-A-2 215 482 (GENERAL ELECTRIC CO.) *Claims 1,2* & US - A - 3 816 081 (Cat. D)	1-2	
Y	US-A-3 698 878 (T.E.HALE) *Claim 1*	1	TECHNICAL FIELDS SEARCHED (Int. Cl. <sup>3</sup> )  C 22 C 29/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 01-10-1982	Examiner SCHRUERS H.J.
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			