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SYNTHESIS OF NEW SUPERHARD MATERIALS AND THEIR APPLICATION TO CUTTING TOOLS

R.F. BUNSHAH
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ABSTRACT

Two major areas of effort are encompassed:

I. Synthesis of Superhard Materials: The process of Activated Reactive Evaporation is used to synthesize superhard materials like carbides, oxides, nitrides and ultrafine grain cermets. The deposits are characterized by hardness, microstructure, microprobe analysis for chemistry and lattice parameter measurements. The synthesis and characterization of TiC-Ni cermets, Al_2O_3, and VC-TiC alloy carbides is given.

II. Study and the Effect of Superhard Coatings on the Performance of High Speed Steel Tools: High speed steel tools coated with TiC, TiC-Ni and TaC are tested for machining performance at different speeds and feeds. The machining evaluation and the selection of coatings is based on the rate of deterioration of the coating, tool temperature, and cutting forces. Tool life tests show coated high speed steel tools having 150 to 300% improvement in tool life compared to uncoated tools.

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I. OBJECTIVE

The objectives of this research are two-fold: Firstly, the synthesis of new superhard materials. Secondly, to examine the effect of superhard coatings on the performance of high speed steel cutting tools. Such applications as well as others, e.g., grinding tools, hard coatings for abrasion and wear resistance in engines, aircraft, tanks, metal forming machinery, dies, punches, etc., could be of great interest to the DOD.

There are several reasons for concentrating the application effort on cutting tools in general and high speed steel tools in particular. Firstly, very little work has been carried out in the application of hard carbide coatings to improve the life of high speed steel tools (single point tools, end mills, cutters, etc.) even though they form the largest single item in the tool production of cutting tools; the present mill shipments of high speed steel tools is estimated at $600 million. Secondly, the Activated Reactive Evaporation (ARE) process, recently developed at UCLA under ARPA sponsorship,[1] is uniquely suited for this purpose since the hard coating can be applied even at low substrate temperatures, i.e., about 500°C, which would still retain the substrate (high speed steel tools) in its hardened and tempered condition without softening. Competing processes such as chemical vapor deposition require that the substrate be at temperatures of 1000°C or higher for the deposition of hard compounds such as TiC which would, of course, ruin the strength and toughness of the high speed steel. Such CVD processes are commercially used today to coat TiC onto a WC-Co type carbide machining inserts which can withstand high deposition temperatures (1000°C). Hard coating can also be laid down by sputtering; however, the deposition rates from sputtering are very low.

In the Activated Reactive Evaporation process, Bunshah and his co-workers[1,2] have developed a new high rate physical vapor deposition process for the synthesis of oxides, nitrides and carbides. Furthermore, they found that by controlling the deposition temperature or by heat-treatment,[3] it was possible to change the microstructure and consequently increase the hardness of TiC from 3000 to 5400 kg/mm, a value second only to diamond (see Table I) and comparable to or better than the second hardest material known, borazon (cubic boron nitride). Moreover, TiC should cost 100 times less than borazon or diamond, which is a considerable economic incentive. Finally, high speed steel (a strong and tough material) coated with a superhard layer such as TiC or other materials, would be an ideal system to study for improved tool performance since the necessary requirements of hardness for cutting and toughness to absorb the impact loads are fulfilled by this composite system.

TABLE I

Hardness of Various Materials

Material	Knoop Hardness (kg/mm^2) Room Temperature	Knoop Hardness (kg/mm^2) 900°C	Wooddell Scale (relative) Room Temperature
Diamond	7000		43
Borazon (cubic/boron nitride)	4700		19
Samarium Borides (Sm $B_{\sim 2}$)	3610		
(Sm $B_{\sim 70}$)			
Rare Earth Borides (REB $_{70}$)	3500-4000		
Titanium Carbide*	3000	400	
Hafnium Carbide	2400	800	
Vanadium Carbide	2400	400	
Silicon Carbide	2480		14
Niobium Carbide	2200	500	
Aluminum Oxide	2100		9
Tungsten Carbide	1850	1200	
Tantalum Carbide	1700	400	
Chromium Carbide (Cr_7C_3)	1500	600	
Chromium Carbide ($Cr_{23}C_6$)	950	700	
Quartz	820		7

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*The hardness of TiC produced by Activated Reactive Evaporation can be as high as 5400 kg/mm^2.

II. RESEARCH PROGRAM

The proposed research program is divided into the following two parts:

A. Synthesis of New Superhard Materials

The Activated Reactive Evaporation (ARE) process will be used to synthesize new superhard materials such as carbides, nitrides, oxides and two-phase alloys. The ARE is a versatile process that is capable of the following:

1) Synthesizing oxides, carbides, nitrides and possibly borides and silicides.

2) Synthesizing mixed carbides (i.e., carbides of more than one metal) of controlled composition, e.g., (TiZr)C.

3) Synthesizing mixed compounds (i.e., carbo-nitrides, oxy-carbides, etc.)

4) Changing the microstructure and mechanical properties by variation of process parameters, e.g., (deposition temperature).

5) Producing material ranging from full density coatings all the way to powder.

6) Producing very fine grain sizes.

7) Varying and controlling the stoichiometry of carbides and other compounds.

8) Laying down a deposit which is strongly adherent to the substrate due to a diffusion bond produced between the two.

9) Producing graded microstructures, e.g., from metal to carbide.

10) Obtaining high deposition rates for coatings (5 to 25 μ per minute) which make it an economical process.

This part of the research program will be concentrated on the synthesis and characterization of the following superhard materials:

1. Carbides

a) Carbides of tungsten since they have the highest hot hardness of all carbides.

b) HfC since it has the second highest hot hardness and has been reported to be a good cutting tool coating for machining titanium.

c) Boron carbide since it is a very hard material in current usage.

d) Mixed carbides in the system VC-TiC. Jangg et al[4] report a maximum in hardness at TiC - 30% VC.

e) Mixed carbides in the system TaC-HfC. The TaC-20% HfC alloy has the highest reported melting point of all alloys.

f) Mixed carbides in the system TiC-ZrC. "Alloys" in this system are reported to be harder than TiC. It is also an experimentally easy alloy to evaporate and will serve as a model system for studying mixed carbides.

2. Nitrides

The synthesis of cubic boron nitride will be attempted since past work has shown that it is possible to synthesize β-SiC[5] which is also cubic. Success would provide an alternate and possible cheaper method of producing a proven hard material.

3. Oxides

a) $A\ell_2O_3$ since this is a commercially used grinding material, and will be used as a model system.

b) Mixed oxides in the system $A\ell_2O_3$-ZrO_2 to produce fine grained two-phase structures of different morphology[6] harder than the pure oxides.

4. Two-Phase Alloys

a) TiC + B and VC + B - a tenfold increase in strength has been reported due to precipitation hardening.

b) Ultrafine grained cermets-carbides in a matrix of metal or alloy in an effort to improve the toughness of the carbides. The present-day cermets have a lower limit of 3 μ in carbide particle size. The toughness increases very rapidly as the size of the carbide becomes smaller. Such a very fine grained cermet coating would be expected to retain the cutting ability of the hard carbide while improving its resistance to fracture. Preliminary work at UCLA has shown the ability to synthesize TiC-Ni cermet coating using the ARE process. As a further step, resistance to degradation at high tool tip temperatures would be improved by substituting a more refractory metal for the ductile matrix in the cermet.

c) High temperature ultrafine grained cermets-carbides in a matrix of refractory metal to improve the hot hardness of the composite structure.

The important <u>process variables</u> that will be studied are:

1. Substrate temperature which affects grain size, density, particle size in two-phase alloys and residual stresses. The range of substrate temperatures to be explored is 500-1500°C.

2. Heat treatment - to study annealing effects in single phase material and to study precipitation effects where applicable.

Substrate materials will be a metal and/or ceramic. Deposit thickness will be about .001-.005" so as to assure bulk properties.

<u>Characterization</u> of the synthesized materials will be carried out by the following:

1. Microhardness at room and elevated temperature.

2. Chemical analysis using the microprobe, the non-dispersive detector and other analytical techniques as required.

3. Microstructure using optical, scanning and transmission electron microscopy.

4. X-ray diffraction to measure precision lattice parameters, "particle size" and residual stresses. Computer programs have been developed at UCLA to handle the X-ray data.

5. Density.

At the start of the project, a preliminary study will be run to explore the synthesis of the various materials followed by limited characterization (lattice parameter, microhardness and structure as a function of C/M ratio) to aid material selection for detailed studies.

B. Effect of Superhard Coatings on Cutting Tool Performance

During metal cutting, tool damage can be due to tool wear (flank and crater wear), and/or cracking along the tool face. The tool must support the cutting forces at the high temperatures attained during cutting, and it must also endure the cyclic thermal stresses induced by the cutting, non-cutting cycle. Such conditions call for a tool material that is both hard and tough and resistant to wear.

During this phase of the research program, high speed steel tools will be coated initially with TiC and subsequently with other superhard materials developed in the first part of this program. The coating will provide the necessary hardness and wear resistance while the core, which is the high speed steel tool in this case, will provide the toughness and the resistance to impact loading. Machining tests will be carried out on the coated tools at different conditions of cutting speeds, feed, and depth of cut. Intermittant as well as non-intermittant tests will be employed. The cutting forces will be measured in each case using a tool dynamometer. The tool work interface temperature and friction coefficient along the tool face will be determined. Tool damage and surface finish of the machined part will be examined. Tool life will be determined. The wear process and mechanism of the different coatings will be investigated using tool-maker's microscope, scanning electron microscope techniques, and electron microprobe analyses. The crater and flank wear heights will be measured at different locations. The scanning electron microscope brings out topographical details of tool wear, cracks, and failure with more clarity and detail than one can observe with an optical microscope. While a SEM photograph provides fine details of tool surfaces, it is still necessary to have the electron microprobe analysis for identification of specific elements in the worn tool surfaces which then helps to understand the contact interactions between workpiece and tool. Correlation between microstructure and mechanical properties of the coating and the core material to their cutting performance will also be examined. Comparison of the cutting forces, temperature, friction coefficient, surface finish of the machined part, and tool wear will be examined and correlation to the physical and mechanical properties of the different coatings will be carried out.

Tool damage vs. cutting speed for a given feed and depth of cut will be compared for different tool coatings. Wear measurements will be obtained from direct comparison of the tool contours before and after test. Correlation of tool wear results to parameters characterizing the coating (coating composition, grain size, density, lattice parameter, coating thickness, microhardness and C/M ratio) will be investigated. Such correlation will constitute the feedback information for the synthesis of the superhard coating materials.

III. PROGRESS TO DATE

Work during this period was interrupted for 6 weeks during July and August 1975 for a major overhaul of the high vacuum deposition apparatus whose performance had gradually deteriorated over a period of 3 years since the last overhaul. It is now fully operational.

Work during this period was concentrated in four areas:

1. Synthesis of Fine Grained TiC-Ni Cermets

This work was described in the prior report UCLA-ENG-7559, dated April 1975 and was completed in the early part of the current reporting period. A paper was written and presented at the American Vacuum Society meeting in October 1974 and is included as Appendix 1. At that time, the microstructure was too fine to be resolved by the techniques used.

Further work was carried out in cooperation with Dr. Vinod Sarin of Sandvik, Sweden to resolve the microstructure. The results of this investigation showed fine Ni precipitate in a TiC fine grained matrix. It is being written up for presentation at the International Conference on Metallurgical Coatings to be held in San Francisco, April 5-9, 1976.

2. Synthesis of $A\ell_2O_3$ Deposits by the Activated Reactive Evaporation Process

a) Introduction and Objective

Prior work in the literature has reported the production of $A\ell_2O_3$ deposits by direct evaporation of $A\ell_2O_3$ billets using electron beam heating.[7,8] In the first reference, bulk deposits were obtained. In the second reference, thin films were deposited and the stoichiometry of the deposit (i.e. O/Aℓ ratio) was aided by bleeding in a low partial pressure of O_2 into the vacuum chamber.

In this investigation, the Activated Reactive Evaporation process[1,2] was used to produce $A\ell_2O_3$ deposits by the evaporation of Aluminum metal in the presence of a partial pressure of oxygen. Such synthesis work has not been reported previously. This work is similar to the synthesis of Y_2O_3 deposits by evaporation of Y in the presence of O_2.[9]

b) Experimental Procedure

A one inch diameter billet of 1100 S grade aluminum was evaporated from a rod fed electron beam source in the presence of a partial pressure of 99.5% pure oxygen gas from 2×10^{-5} torr to 2×10^{-4} torr. The substrates were stainless steel, tantalum and alumina at 700°C and 800°C deposition temperatures using radiant heating. For higher deposition temperatures of 1100°C and 1200°C, a Ta foil substrate was used and heated by direct resistance.

The deposits were characterized by x-ray diffraction analysis, adherence to substrate and appearance.

c. Results and Discussion

The results of this investigation are shown in Table II. The specimens deposited at 700°C and 800°C yielded only broad peaks characteristic of amorphous (or microcrystalline) material. The deposit appeared to be porous and of white color on the stainless steel substrate and a medium gray color on the alumina substrate. The high temperature deposits (at 1100°C and 1200°C deposition temperature showed α-$A\ell_2O_3$ diffraction peaks as well as those corresponding to $A\ell TaO_4$ which is the reaction product between the Ta substrate and the $A\ell_2O_3$ deposit. The $A\ell TaO_4$ is probably present as a layer at the Ta-$A\ell_2O_3$ interface. The lattice parameters of α-$A\ell_2O_3$ are shown in Table III. The high temperature deposits appeared to be very dense and adhered strongly to the substrate.

TABLE II

Deposition Parameters for $A\ell_2O_3$

Run No.	Substrate Temperature °C	Structure by X-Ray Diffraction	Deposit Thickness (Mils)	Condensation Time (Min)	O_2 Gas Pressure (Torr)	Evap. Rate (g/min)	Probe Voltage (Volts)	Electron Beam Current A
Aℓ-D-2	700	Amorphous	4	11	3×10^{-4}	0.37	60	0.7
Aℓ-D-3	700	Amorphous	> 12	20	3×10^{-4}	0.30	60	0.6
Aℓ-D-4	800	Amorphous	8	8	7×10^{-5}	0.46	50	0.5
Aℓ-D-5	1200	α-$A\ell_2O_3$+$A\ell TaO_4$	1	10	2×10^{-4}	0.33	45	0.5
Aℓ-D-6	1100	α-$A\ell_2O_3$+$A\ell TaO_4$	1	15	3×10^{-4}	0.24	45	0.5
Aℓ-D-7	1100	α-$A\ell_2O_3$+$A\ell TaO_4$	1	~15	2×10^{-5}	0.30	55	0.5
Aℓ-D-8	1100	α-$A\ell_2O_3$ (trace) +$A\ell TaO_4$	1	15	2×10^{-5}	0.15	0	0.3

TABLE III

Lattice Parameter of $\alpha\text{-A}\ell_2\text{0}_3$ Deposits

Run No.	a(A°)	C(A°)	c/a
Aℓ-D-5	4.750	13.001	2.74
Aℓ-D-6	4.750	12.89	2.71
Aℓ-D-7	4.748	12.97	2.73
ASTM Card File	4.758	12.991	2.730

In one experiment by Reactive Evaporation without activation, only traces of $A\ell_2O_3$ were obtained; compare run Aℓ-D-7 to Aℓ-D-8.

d. Conclusions

α-$A\ell_2O_3$ deposits can be obtained by evaporation of Aℓ in the presence of a partial pressure of oxygen gas along with activation of both the metal atoms and the gas molecules using the ARE process. At low deposition temperatures, the deposit was porous, flaky, and gave an amorphous diffraction pattern, whereas at high deposition temperatures, the deposit was dense, strongly adherent to the Ta substrate and gave an α-$A\ell_2O_3$ diffraction pattern.

3. Synthesis of VC-TiC alloy Carbides

a. Objective:

To synthesize VC-TiC alloy carbides by Activated Reactive Evaporation (ARE) process and characterize them by microhardness, lattice parameter and chemical analysis by electron microprobe analyzer.

b. Experimental Procedure

In the synthesis of VC-TiC alloy carbides, a V-Ti alloy rod is evaporated in the presence of the reactive gas C_2H_2. Both V and Ti form carbides and VC-TiC alloy carbide will be formed since VC and TiC have been found to form complete series of solid solutions in all proportions.[10] Two experiments were made at the conditions given in Table IV. In A-1 run, first V-Ti alloy was deposited in the absence of C_2H_2 and then the reactive gas was introduced to form VC-TiC alloy carbide.

X-ray diffraction of the deposits showed peaks corresponding to VC with TiC in solid solution. Lattice parameters of the deposits were determined. Microhardnesses of the samples were measured using knoop indentor and 50 g load on micromet microhardness tester. The results are also given in Table IV.

TABLE IV

Synthesis of VC-TiC Alloy Carbides

Run No.	Evaporation Rate g/min.	Deposition rate mil/min.	Reactive gas Pressure Torr	Temperature of Deposition °C	Hardness KHN Kg/mm^2	Lattice Parameter A°
V-Ti-A-1	0.62	0.11	$4\text{-}5\times10^{-4}$	700	2064	4.197 ± 0.001
V-Ti-A-2	0.28	0.036	$8\text{-}10\times10^{-4}$	700	1385	4.208 ± 0.002

A sample from A-1 deposit was electroplated with copper and was mounted in cross-section along with a piece of V-Ti evaporant rod as a standard for chemical analysis. The mount was given a metallographic polish and the deposit and the standard were analyzed on a Kevex unit attached to a Scanning electron. microscope (electron microprobe analysis). The electron beam was moved across the thickness of the deposit while tracing each element intensity at the same time. Electron micrograph of the deposit and the traces of intensities of elements in the deposit cross-section are shown in Figures 1 and 2. Intensities of V and Ti in the standard rod are also shown in Figure 2.

c. Results and Discussion

Figure 1 shows the V-Ti alloy deposit and VC-TiC alloy carbide deposit of the A-1 run. From Figure 2, we see that after the deposition of V-Ti alloy was started, initially the deposit was V rich. There is steep decrease of V and increase of Ti up to 13.3 μ thickness corresponding to 4.6 min. of deposition. Ti decreases and V increases gradually until the reactive gas was started being introduced, which corresponds to 56.5 μ thickness and 18 mins. of deposition. During introduction of the gas, both V and Ti intensities decrease (due to carbon) and during the deposition of VC-TiC alloy carbide, their intensities remain more or less constant with some fluctuations. The drop of the intensities of V and Ti in the last 20.5 μ corresponds to the step formed due to the polishing off of the soft copper coating as can be seen in Fig. 1.

The intensity ratio of V/Ti in the standard rod varies from 1.0 to 1.34 and the atomic ratio is 2.98. Intensity ratios of V/Ti in the alloy carbide region of the deposit were calculated at points A, B, C, D, E and F as marked in Figure 2. They are found to vary from 1.23 to 1.42 which correspond to atomic ratio of 3.15 to 3.66. The analysis of the standard rod was accurate

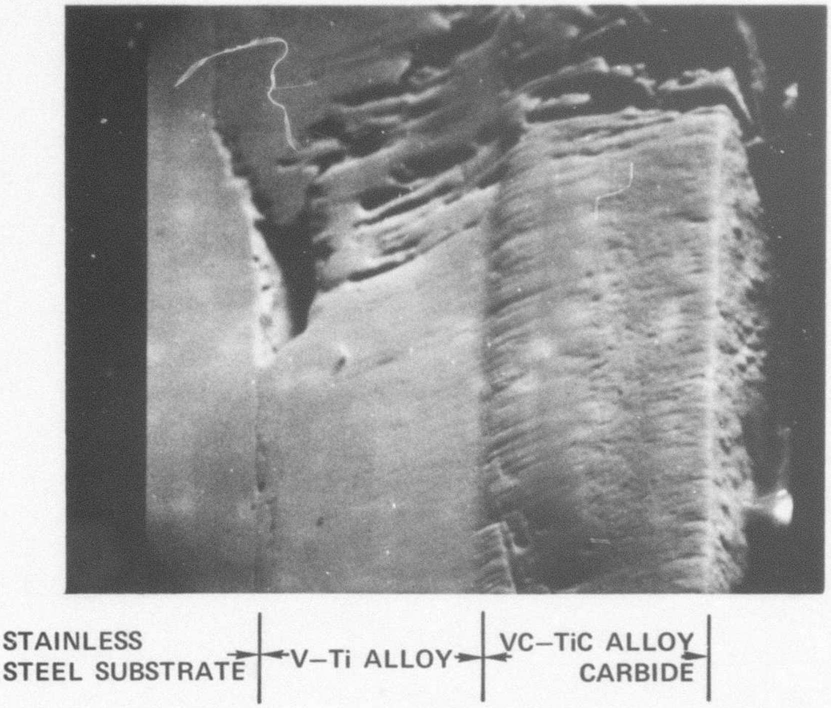

Figure 1. Electron Micrograph of A-1 Deposit in Cross-Section Showing V–Ti Alloy and VC–TiC Alloy Carbide Layers. 585X.

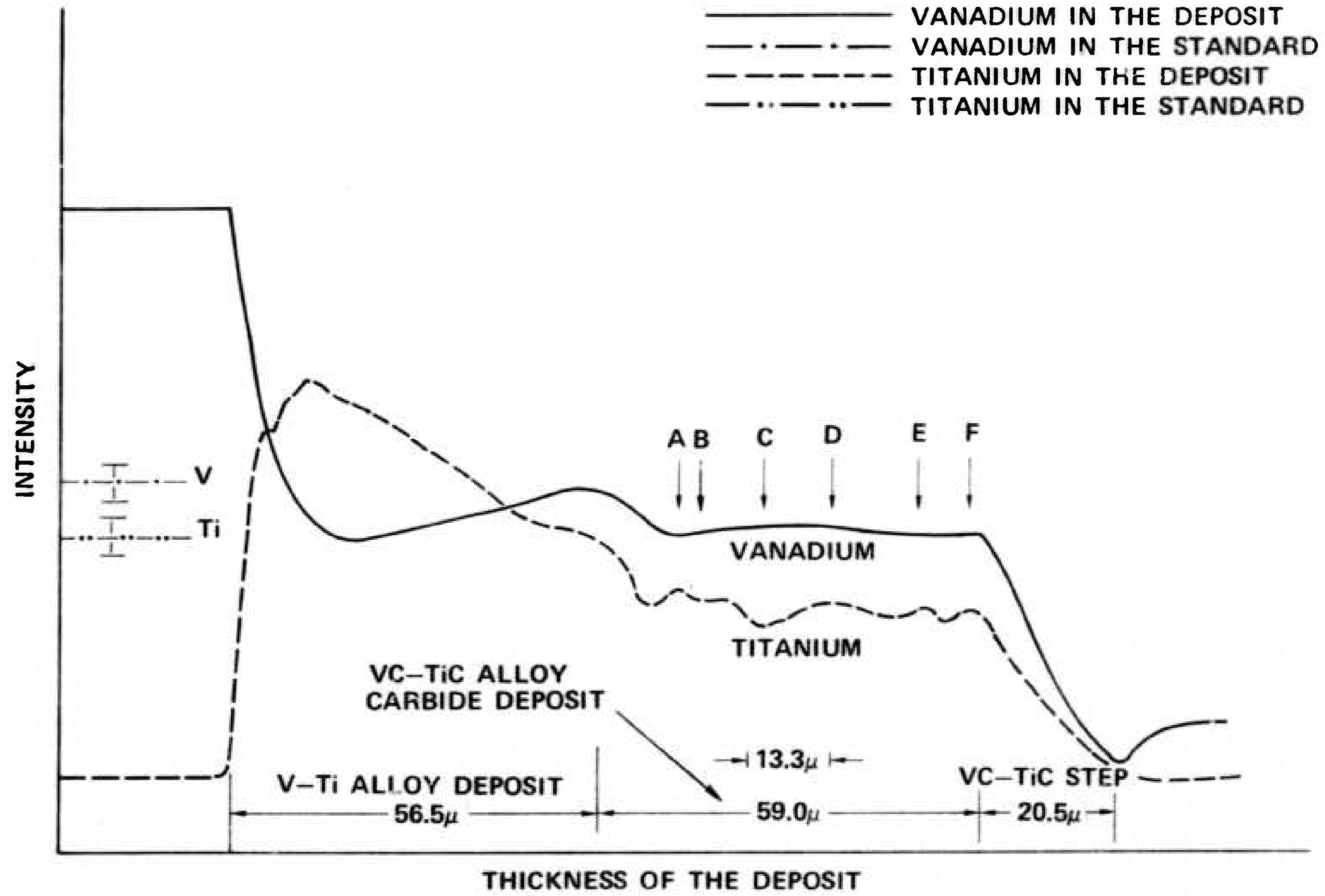

Figure 2. Microprobe Traces of the Elements V and Ti Across the Thickness of the A-1 Deposit and the Standard V–Ti Evaporant Rod.

to ± 10% and the atomic ratio of V/Ti could vary from 2.62 to 3.41. Thus we see that the V/Ti ratio in the alloy carbide is very close to the V/Ti ratio in the evaporant rod.

The hardness of the A-1 deposit is 2064 Kg/mm^2 (Table IV). This is in close agreement with the published data of hardness variation with composition of VC-TiC alloy carbides.[11] The A-2 deposit is very soft (1385 Kg/mm^2). This is probably due to the lower evaporation rate and higher gas pressure in the A-2 run. Under these conditions there will be some free carbon present in the deposit which will make it softer.

d. Conclusions

These results show that VC-TiC alloy carbides can be synthesized by activated reactive evaporation. Further experiments will be carried out changing the experimental parameters such as deposition temperature, alloy evaporation rate and reactive gas pressure to synthesize and characterize the VC-TiC alloy carbides.

4. Machining Evaluation of Coated High Speed Steel Tools

Turning operations of a 5" dia. workpiece of 4340 steel using high speed steel inserts (M43) with and without coatings were carried out.

A summary of the data is shown in Table V. It is seen that TiC, TiC-10Ni and TaC coatings all improve the life of high speed steel tools substantially. Examination of the uncoated M-43 inserts on the microscope showed a considerable variability in the preparation of the insert surface by the supplier.

TABLE V

Machining Evaluation of Coated High Speed Steel Tools

Test No.	Specimen No.	Coating	Thickness Microns	Tool Life	Increase in Tool Life (%)	Cutting Conditions	Mode of Failure
1.	M43	Uncoated		3 min. 40 sec.		rpm=150 f=0.003 d=.050	Fracture of tool edge
2.	M43-1	TiC-10Ni	5	>12 min. 40 sec	>300	" "	NO FAILURE (Test was stopped at end of workpiece)
3.	M43-2	TiC-10Ni	12	11 min. 30 sec	300	" "	Fracture of tool edge
4.	M43-3	TiC	12	12 min.	300	" "	Fracture of tool edge
		Uncoated		45 sec.		rpm=280 f=.003 d=.050	Fracture of tool edge
5.	M43-4	TiC-10Ni	7.5	3 min.	300	" "	Fracture of tool edge
		Uncoated		1 min. 58 sec.		rpm=480 f=.003 d=.018	Fracture of tool edge
6.	M43-5	TaC	7	>3 min. 35 sec.	>150	" "	Fracture of tool edge

f = feed in in/rev.

d = depth of cut in inches

IV. FUTURE RESEARCH EFFORTS

The research effort in the next period will consist of:

1. Further development of the BARE process and its effect on structure and properties of carbides.

2. Continuation of the synthesis and evaluation of VC-TiC alloy carbides.

3. Examination of the coated tools after machining.

4. Coating of high speed steel tool inserts and evaluating their machining performance.

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APPENDIX

SYNTHESIS OF TiC-Ni CERMETS BY THE ACTIVATED REACTIVE EVAPORATION (ARE) PROCESS

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ABSTRACT

This investigation is concerned with the deposition of TiC-Ni cermets using the ARE process.(10) A Ti-10Ni alloy rod was evaporated from an EB source in the presence of acetylene (C_2H_2), the vapor species being activated or partially ionized using the ARE process. The deposits were characterized by X-ray diffraction, microhardness, X-ray fluorescence, X-ray imaging for different elements on an electron microprobe analyzer, optical microscopy and electron microscopy. It has been shown that TiC-Ni cermets can be deposited by the ARE technique and they are quite hard. When the deposition was made on tantalum substrates at high temperatures, it was observed that Ni diffuses into Ta and forms an intermetallic phase near the interface between the substrate and the deposit.

INTRODUCTION

"Cermet" is a term applied to materials which combine a ceramic phase and a metallic phase so that the resulting material has a combination of properties superior to those attained from ceramics or metals separately. They are expected to provide high temperature materials that would combine the desirable property of high temperature strength of ceramic with the toughness and thermal shock resistance of the metallic phase. Gas-turbine blades and machining tools are two major applications of cermets. Considerable progress was made in the development of TiC base cermets with Ni-alloy matrix because of their superior oxidation resistance and lower density resulting in a higher strength to weight ratio which is desirable for turbine blade applications, as compared to WC base cermets. TiC base cermet cutting tools were also shown to be markedly superior to the WC base cermet(1,2) tools in tool life, flank wear resistance, crater wear resistance and surface finish of the work piece. Compositions of TiC based cermets were developed which had superior thermal shock resistance and stress-rupture resistance compared to many super-alloys as well as good oxidation resistance. However, their low impact strength prohibited their use in high temperature applications.(3,4)

Cermets are normally produced by conventional powder metallurgy techniques in which the sintering is accomplished in the presence of a liquid phase. The grain size of the sintered products has been shown to depend on the interfacial energies of different phases present in the system.(5) The interfacial energies between phases determine the degree to which the liquid phase wets the ceramic. Complete wetting leads to fine grain size and low wetting produces very coarse grain structure of the cermet. The liquid phase in TiC base cermets with Ni or Co does not wet the ceramic phase completely and this results in coalescence of the carbide phase leading to an apparent increase in the carbide particle size.

improvement in the wettability of the Ni-TiC systems by the addition of Mo was found to promote the dispersion of the carbide phase and to lead to improved hardness and impact resistance,(5) but not enough for the desired high temperature applications. It is well known that the hardness and toughness of cermets increase with decreasing grain size and spacing of the ceramic phase.(6) It has also been shown that in cermets having fine grain size, fracture is intergranular leading to high strengths, whereas coarse grain cermets fail with transgranular fracture resulting in low strengths.(7,8,9) Therefore, it is essential to synthesize very fine grain cermets in order for them to have high strength and toughness.

This research was undertaken to make a feasibility study of synthesizing fine grain TiC-Ni cermets by the activated reactive evaporation (ARE) process.(10) They were characterized by X-ray diffraction, microhardness measurements, electron microprobe analysis, optical microscopy and electron microscopy.

EXPERIMENTAL PROCEDURE

A Ti-10Ni alloy rod was evaporated by electron beam heating in the ARE process experimental arrangement described by Bunshah and Raghuram.(10) The reactive gas, C_2H_2, was introduced into the system after steady state conditions of evaporation were attained,(11) i.e., the vapor composition was same as that of the evaporant rod. Temperature of deposition, evaporation rate of alloy and pressure of the reactive gas are the experimental variables. The deposition conditions are given in Table I. The reaction is as follows:

$$\mathrm{Ti(vapor) + Ni(vapor) + 1/2\ C_2H_2(gas) \rightarrow TiC\text{-}Ni(solid) + 1/2\ H_2}$$

Ti reacts with C_2H_2 to form titanium carbide and Ni remains as metal because the free energy of formation for nickel carbide (Ni_3C) is unfavorable ($\Delta G^\circ_{900} = + 8.2$ Kcal/mol).(12) The occurrance of free Ni in TiC deposits has been previously observed by Nimmagadda and Bunshah in the syntehsis of Ni-TiC dispersion strengthened alloys.(13)

The deposits were analyzed by X-ray diffraction to ascertain the phases present. The microhardnesses of the deposits were measured using a Micromet microhardness tester with a Knoop indentor and 50 g load. Deposits C-8 and C-9 were mounted in cross-section and were given a metallographic polish. Composition profiles and X-ray image pictures of the elements Ti, Ni and Ta were taken across the thickness of the deposit and the substrate using an electron microprobe analyzer. The polished samples of the surface and in cross-section were etched with a solution of 10 g potassium hydroxide, 10 g potassium ferricyanide and 100 ml water, and examined with an optical microscope. Carbon replicas of these samples were made and observed in a transmission electron microscope.

RESULTS AND DISCUSSION

X-ray diffraction patterns show that the deposits C-1 and C-2 are made up of TiC and Ti_2Ni and the deposits C-8 and C-9 consist of TiC and Ni (Table I). The probable explanation for this difference is the evaporation rate of the alloy. In the deposits C-1 and C-2 the evaporation rates were much higher than for deposits C-8 and C-9 resulting in a greater amount of Ti in the vapor phase than could react with C_2H_2 to form TiC. This is in agreement with previous work on the synthesis of TiC by the ARE process where a high evaporation rate produced free Ti in the TiC deposit.(14) In this case the excess Ti in the vapor phase reacts with Ni to form Ti_2Ni. The deposits C-8 and C-9 are the TiC-Ni cermets. The lattice parameters of TiC in C-8 and C-9 deposits were determined and given in Table I and correspond to titanium carbide of the composition(15) $TiC_{0.8-0.95}$. The cermets C-8 and C-9 are quite hard as can be seen from the microhardness values given in Table I.

Table I

Synthesis of TiC-Ni Cermets

Run	Emission Current A	Evap. Rate g/min.	Reactive gas C_2H_2, press. torr	Dep. Temp. °C	Substrate Material	Micro-hardness KHN Kg/mm^2	X-ray diffraction showed peaks of	Lattice Parameter of TiC Å
C-1	0.30	0.66	$7\text{-}8\times10^{-4}$	700	Stainless Steel	1830	TiC & Ti_2Ni	Not Determined
C-2	0.30	0.79	$8\text{-}9\times10^{-4}$	550	Stainless Steel	1760	TiC & Ti_2Ni	Not Determined
C-8	0.20	0.32	$1.2\text{-}1.3\times10^{-3}$	1000	Tantalum	2810	TiC & Ni	4.328 ± 0.002
C-9	0.20	0.21	$1.1\text{-}1.2\times10^{-3}$	700	Tantalum	2050	TiC & Ni	4.327 ± 0.002

The compositional variations of the three elements Ti, Ta and Ni across the thickness of the C-8 and C-9 deposits mounted in cross-section were obtained by an electron microprobe analyzer and are shown in Figs. 1 and 2. They show the fluctuations in composition of the elements in the deposit. These fluctuations could be due to the variation in composition of the evaporation rod and also small changes in evaporation conditions, such as electron beam current, reactive gas pressure and the level of the liquid pool.(11) In the high temperature deposit (C-8) there is a region in tantalum substrate near the interface to which Ni has diffused and formed an intermetallic Ni Ta_2 as can be seen from the amounts of Ni and Ta in that region in Fig. 1 (approximately 1 Ni: 2Ta). In the low temperature deposit C-9, a small peak of Ni can be seen in tantalum near the interface, but not as prounounced as the C-8 deposit, indicating a smaller amount of diffusion.

The X-ray elemental image pictures for Ti, Ta and Ni near the interface between the deposit and the substrate are shown in Figs. 3 and 4. The pictures are aligned along the interface so that the distribution of the elements in that area can be seen. The presence of 4 μ thick Ni-rich band in Ta near the interface in the high temperature deposit C-8 in Fig. 3 agrees with the results shown in Fig. 1. The fine distribution of Ni in TiC-Ni cermets can also be seen in Figs. 3 and 4.

The optical micrograph of the high temperature (C-8) etched deposit in cross-section is shown in Fig. 5. The white region at the interface between the deposit and the substrate is the diffusion zone where Ni diffused into Ta and formed an intermetallic phase. The deposit shows a fine grain columnar morphology. The surface of the C-8 deposit, and surface and cross-section of C-9 deposit did not reveal any grain structure in the optical microscope. Carbon replicas of C-8

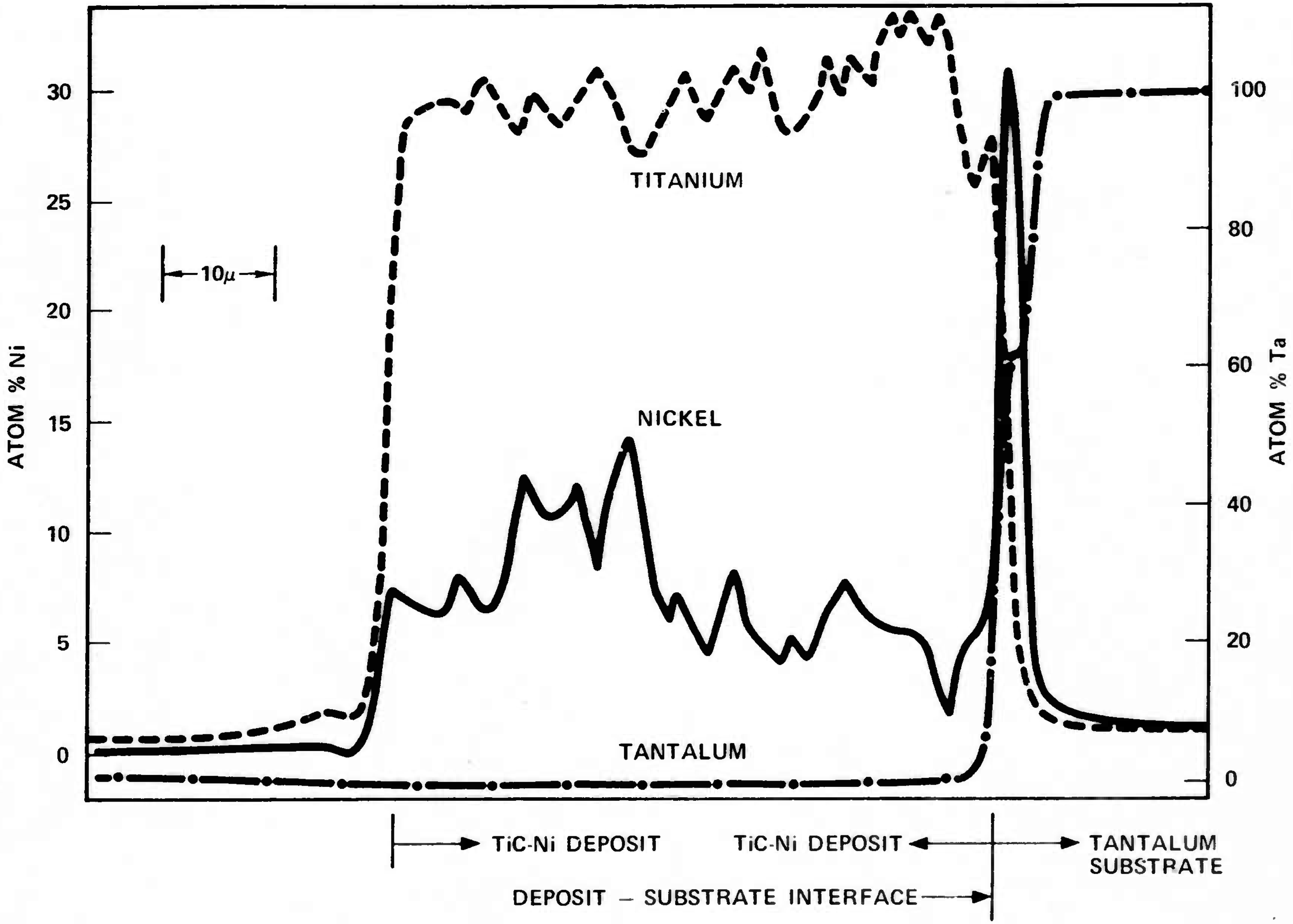

Figure 1. Microprobes Traces of the Elements Ti, Ni and Ta across the Thickness of the High Temperature Deposit (C-8) and Tantalum Substrate.

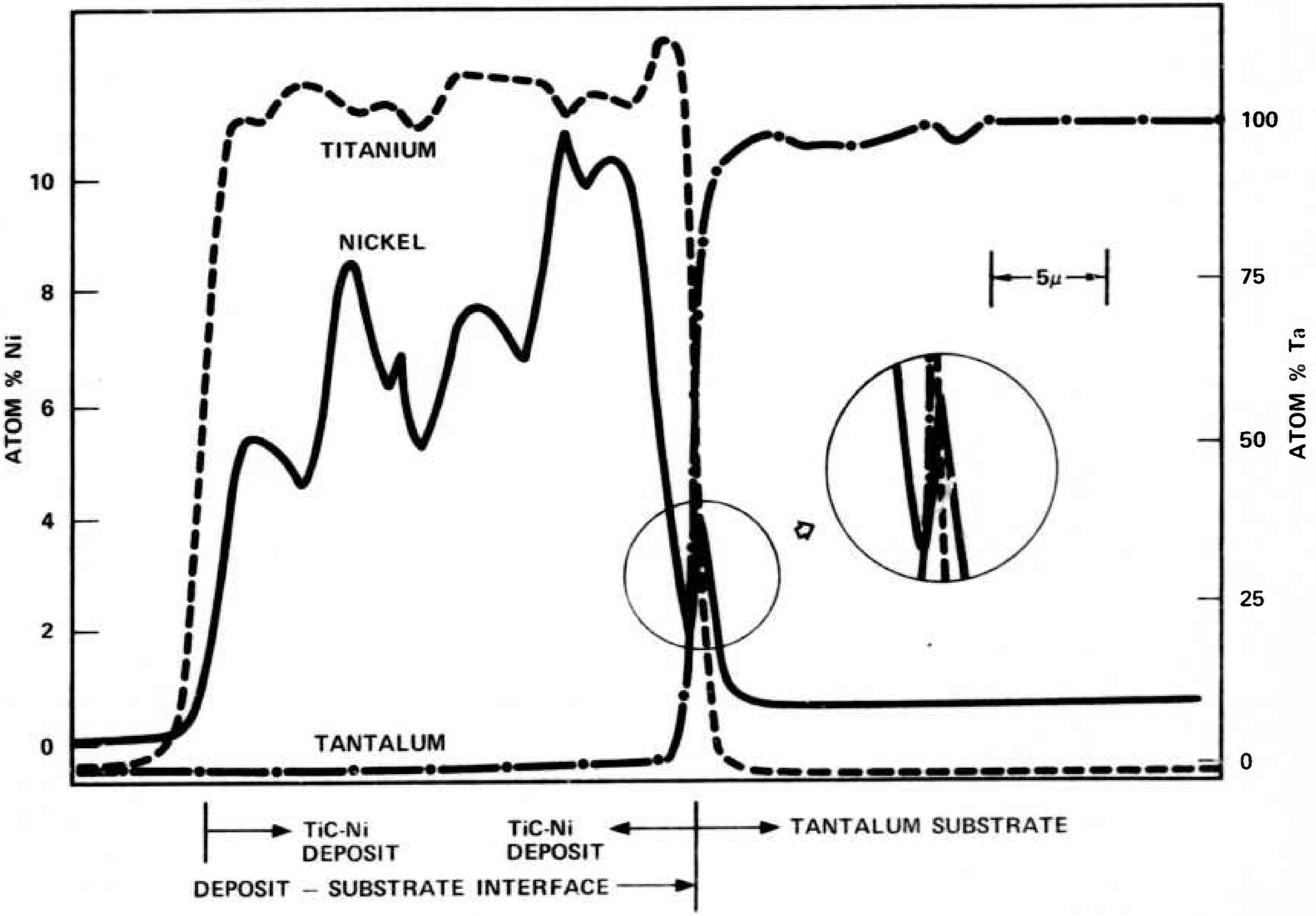

Figure 2. Microprobe Traces of the Elements Ti, Ni and Ta across the Thickness of the Low Temperature Deposit (C-9) and Tantalum Substrate.

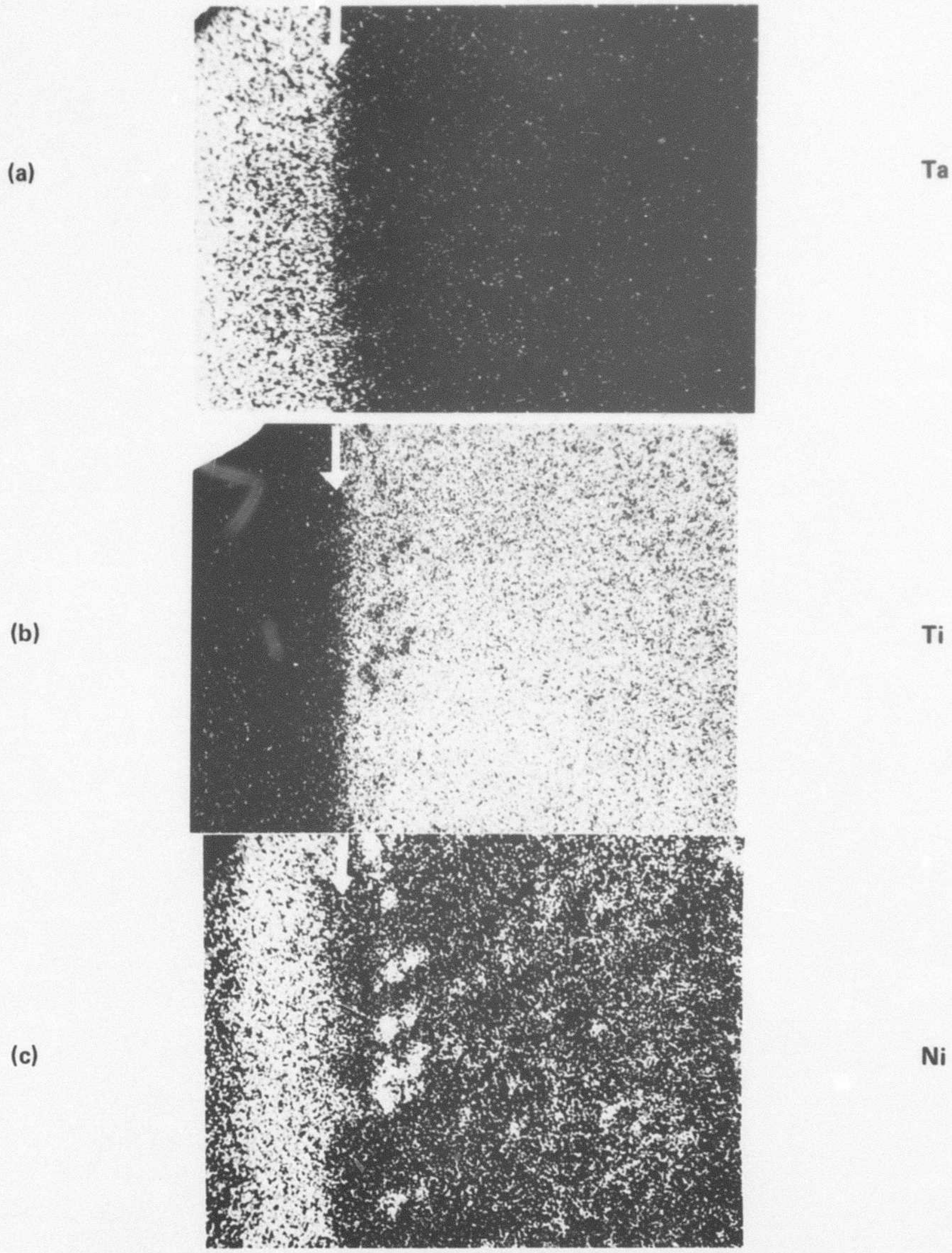

Figure 3. X-Ray Maps of Sample C-8 for Ta, Ti and Ni Near the Interface Between Ta Substrate and TiC-Ni Deposit. There is a concentration of Ni at the interface on the Ta side. White arrow indicates the deposit-substrate interface. (5000X)

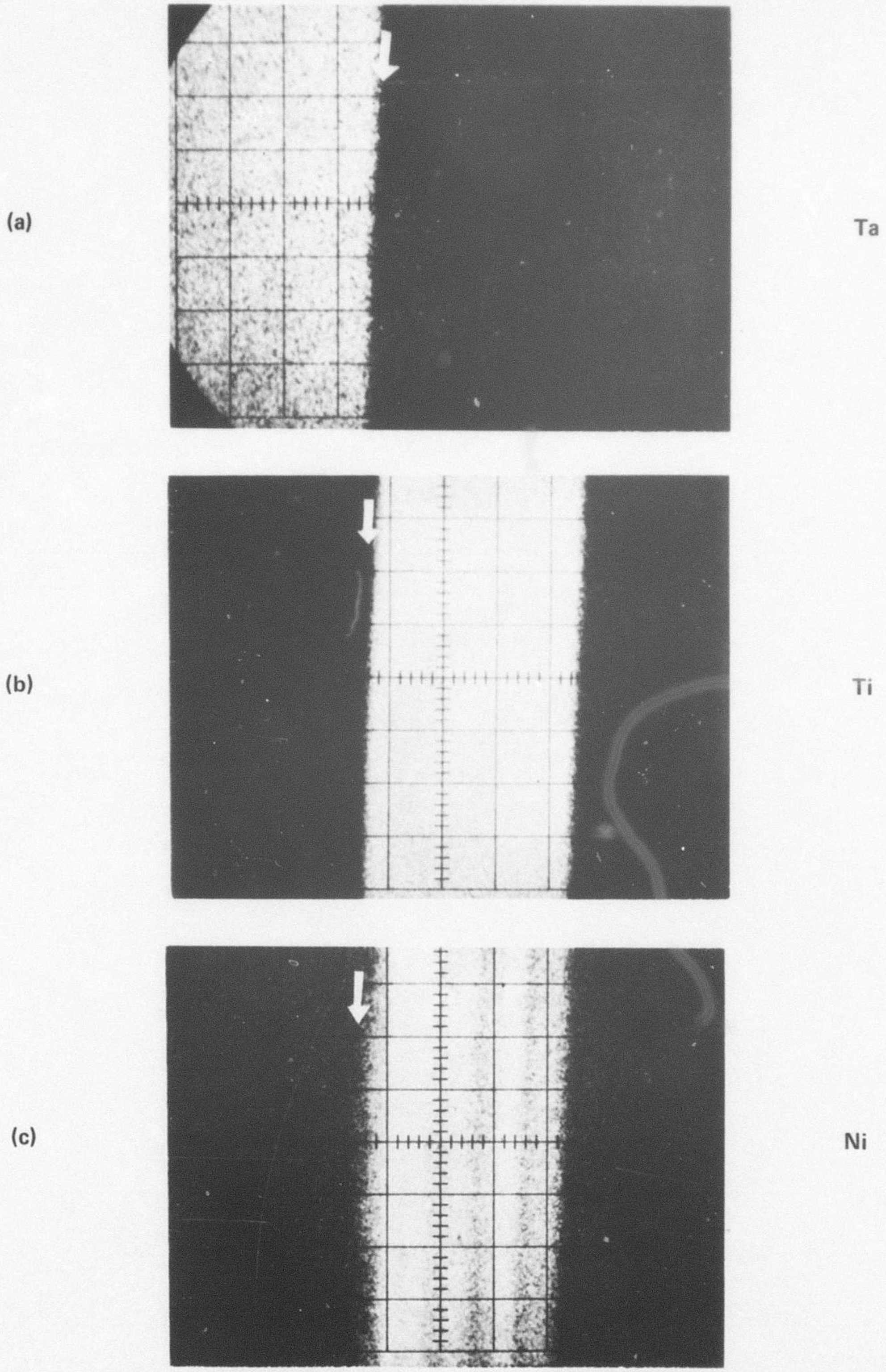

Figure 4. X-Ray Maps of Sample C-9 for Ta, Ti and Ni Near the Interface Between Ta Substrate and TiC-Ni Deposit. White arrow indicates the deposit-substrate interface. (1000X)

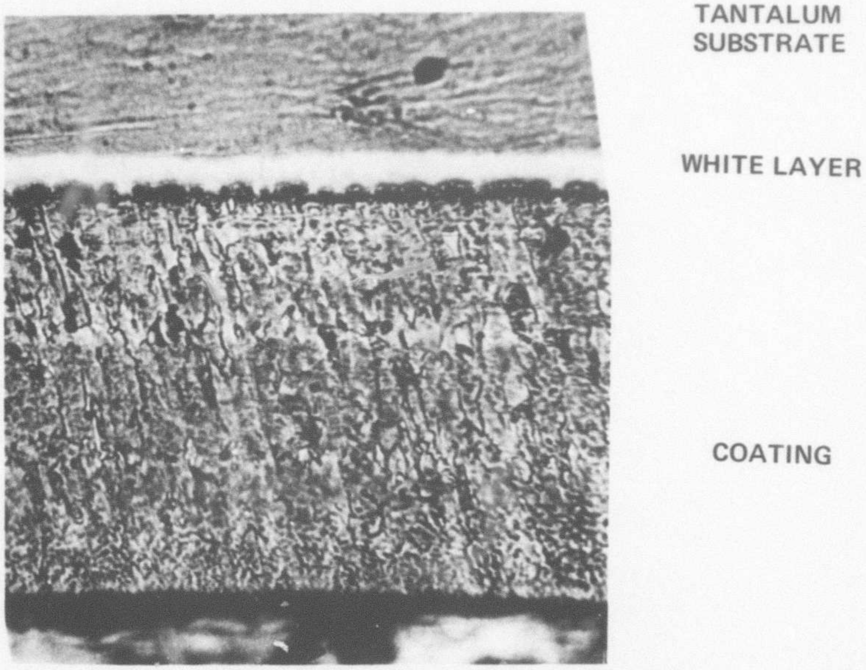

Figure 5. Optical Micrograph of C-8 Deposit Showing a Fine Grain TiC-Ni Deposit, a Diffusion Zone (White) and Ta Substrate. (1000X)

surface, and cross-section and surface of C-9 observed in a transmission electron microscope (35000 m) also did not reveal the grain size. Thin films of these samples are being made for examination in transmission electron microscope to determine the actual grain size and Ni distribution in these TiC-Ni cermets with respect to the grains and grain boundaries.

CONCLUSIONS

This study shows that TiC-Ni cermets can be synthesized by activated reactive evaporation process. The cermets have fine grain size and high hardness. Ni is very finely distributed in TiC-Ni cermets. The grain size and actual distribution of Ni in the cermets with respect to the grain and grain boundaries could probably be determined after transmission electron microscopy of thin foils is completed. When Ta is used as substrate, Ni diffuses into Ta and forms an intermetallic phase near the interface. This is more pronounced at high temperatures.

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The process of Activated Reactive Evaporation is used to synthesize superhard materials like carbides, oxides, nitrides, ultrafine grain cermets. The deposits are characterized by hardness microstructure and lattice parameter measurements. The synthesis and characterization of TiC-Ni cermets, Al_2O_3 and VC-TiC alloy carbides is given. Tools of different coating characteristics are tested for machining performance at different speeds and feeds. The machining evaluation and the selection of coatings is based on the rate of deterioration of the coating, tool temperature, and cutting forces. Tool life tests show coated high speed steel tools show a 300% improvement in tool life.

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