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M. HUMENIK, JR., ET AL.
DISPERSION STRENGTHENED ALUMINUM OXIDE WITH
TUNGSTEN OR MOLYBDENUM

3,369,877

4 Sheets-Sheet 1

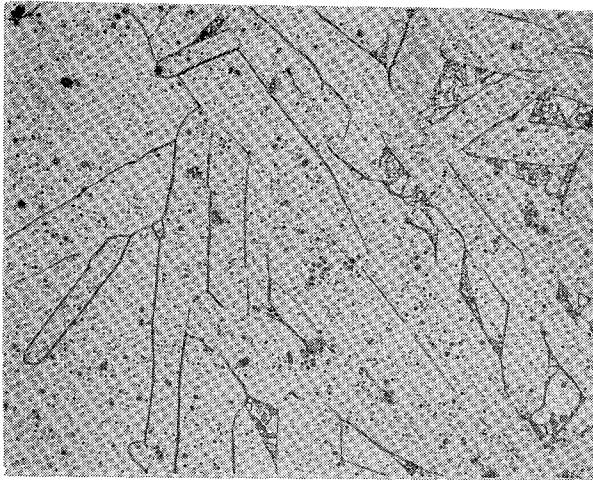


FIG. 1

MICROSTRUCTURE OF SINTERED LINDE A Al_2O_3 SHOWING
SECONDARY RECRYSTALLIZATION (500X) ETCHED WITH H_3PO_4

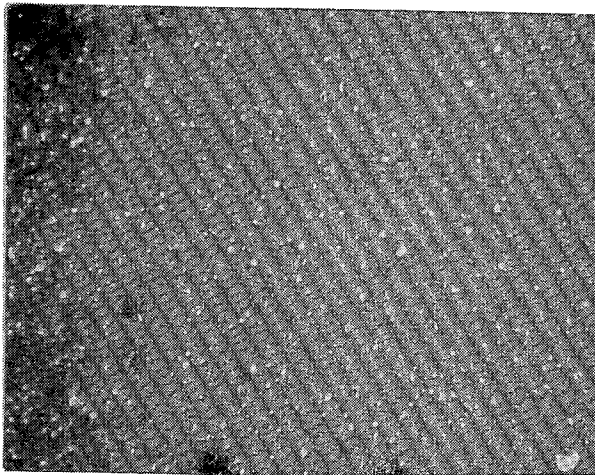


FIG. 2

MICROSTRUCTURE OF Al_2O_3-Mo SPECIMAN PREPARED FROM MIXTURE
OF ALUMINUM OXIDE AND MOLYBDENUM METAL POWDER (1000X) UNETCHED

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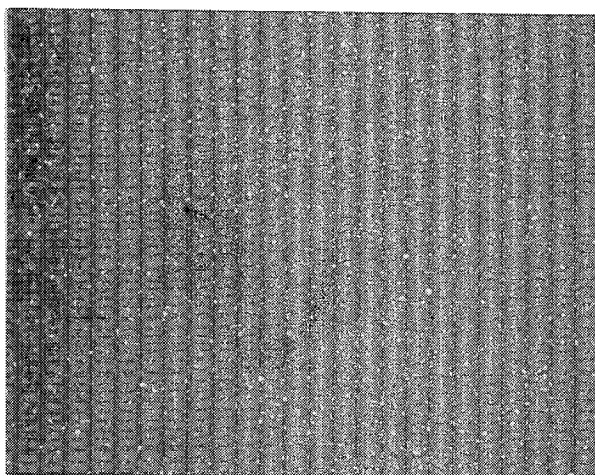


FIG. 3

MICROSTRUCTURE OF Al_2O_3 -Mo MATERIAL PREPARED BY
ISOTHERMAL REDUCTION OF Al_2O_3 - MoO_3 MIXTURE (1000X).
UNETCHED.

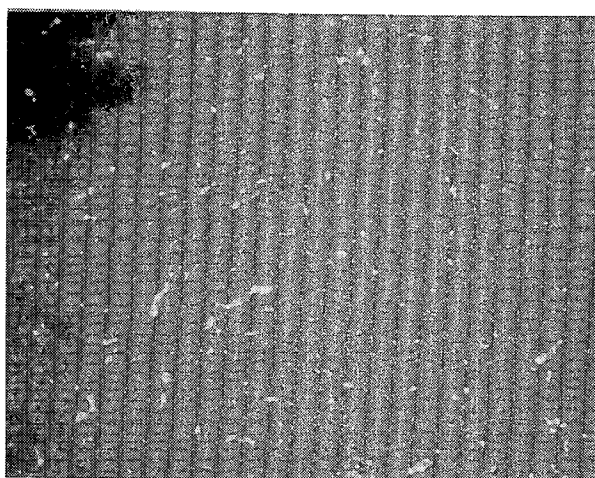


FIG. 4

MICROSTRUCTURE OF Al_2O_3 -Mo MATERIAL PRODUCED BY NON-ISOTHERMAL
REDUCTION OF Al_2O_3 - MoO_3 MIXTURE (1000X). UNETCHED

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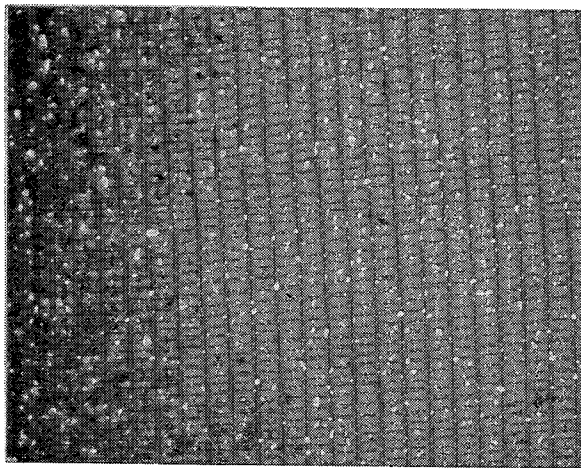
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MICROSTRUCTURE Al_2O_3-Mo MATERIAL OBTAINED BY REDUCTION
OF $Al_2O_3-Al_2(MoO_4)_3$ MIXTURE (1000X). UNETCHED.

FIG.5

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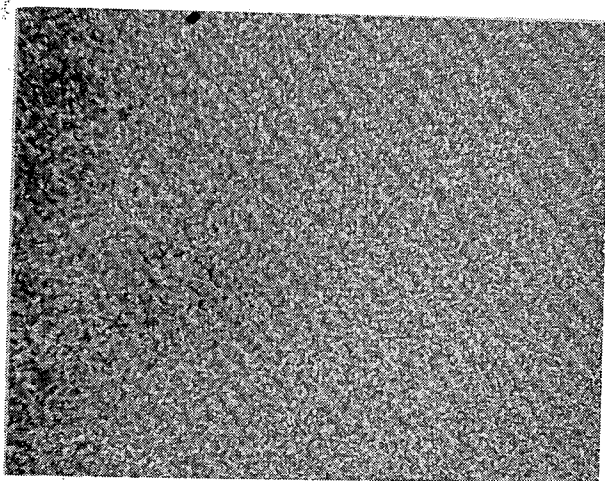


FIG. 6

TYPICAL MICROSTRUCTURE OF SINTERED Al_2O_3 -Mo MATERIAL
(1000X). ETCHED WITH H_3PO_4

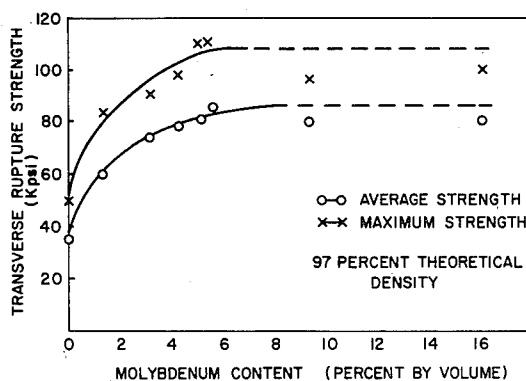


FIG. 7

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DISPERSION STRENGTHENED ALUMINUM OXIDE WITH TUNGSTEN OR MOLYB- DENUM

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6 Claims. (Cl. 29—182.5)

ABSTRACT OF THE DISCLOSURE

This invention relates to a fine grained sintered compact which is essentially aluminum oxide. These compacts have utility as cutting tools for metal working.

The fine grained structure and strength of these compacts is due in part to a small content of dispersed finely divided molybdenum or tungsten.

This invention is concerned with the field of ceramics and is particularly related to a sintered aluminum oxide compact which has been strengthened by the addition of minor amounts of finely divided molybdenum or tungsten in the metallic state.

Theoretical treatises(1) on solid state sintering of Al_2O_3 have divided the process into three stages. The initial and intermediate stages involve neck growth between adjacent particles in the compact and the change in shape of the pores. The final stage of sintering is concerned with the shrinkage of spherical pores and their elimination from the compact. The shrinkage of these pores requires diffusion of vacancies from the pores to sinks in the compact. The most readily available vacancy sinks are grain boundaries. Hence, one immediate advantage of a fine grain size in the material is the large grain boundary area available for the annihilation of vacancies during shrinkage of the pores. It has been shown(2) that pores, not intersected by or very close to grain boundaries, are not removed during sintering.

Normal grain growth(5) proceeds under a driving force which tends to lower the grain boundary energy of the system. The rate of grain growth is inversely proportional to the radius of curvature of the boundary and the direction of growth is toward the center of curvature. These observations are obeyed if inclusions do not interfere with grain boundary migration. Zener(6) has proposed that inclusions inhibit normal grain growth by interaction with the grain boundary and thereby prevent boundary migration. The pores remaining in the compact during the final stage of sintering can act as inclusions to prevent grain growth. As these pores are removed the grain boundaries become free to migrate and normal grain growth can occur.

However, in Al_2O_3 , secondary recrystallization frequently takes place in the latter stages of sintering. Secondary recrystallization or exaggerated grain growth is believed to be nucleated by a many-sided grain which becomes freed from the inclusions or pores restraining its boundary. The small radius of curvature and the high boundary energy are conducive to rapid growth, and the grain boundary moves through the matrix consuming the surrounding grains. This grain ceases to grow only

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when it impinges on another grain which has undergone exaggerated grain growth. FIGURE 1 is a microstructure of an aluminum oxide specimen (Linde A Al_2O_3) which illustrates the phenomenon of secondary recrystallization. The exaggerated grain growth resulted in the entrapment of many pores inside the grain which cannot be removed by further sintering. In order to inhibit secondary recrystallization, special techniques, such as hot pressing, or additions, such as MgO , have been used to control grain size during the latter stages of sintering.

The strength of brittle polycrystalline ionic material⁴ has been shown (3,4) to conform to the general equation:

$$S = K e^{-\beta P} G^{-\alpha}$$

where S is strength in pounds per square inch, G is grain size in microns, P is volume fraction of pores, and K, α , and β are material constants. From this relationship, it is apparent that the strength of sintered aluminum oxide can be enhanced by sintering to a high density and maintaining a fine grain size.

Conventional powder metallurgy techniques are employed in the fabrication of dispersion-strengthened aluminum oxide. Three methods for introduction of the Mo into the Al_2O_3 can be employed. The objective of all methods is the production of an Al_2O_3 -Mo powder mixture in which the Mo is finely divided and uniformly distributed.

A. Al_2O_3 -Mo by metal powder addition

Linde A Al_2O_3 (Metallurgical Grade-Lot 5175-Particle Size, 0.3 micron) and sub-micron Mo metal powder (Union Carbide Lot 1258-73) are mixed in the desired proportions. The mixing is carried out for 24 to 48 hours in a porcelain jar containing Al_2O_3 balls. A benzene medium is employed. The benzene is evaporated and the powder mixture is reduced in dry H_2 at 1200° to 1500° F. for one to two hours. No further processing, other than pressing and sintering, is required. FIGURE 2 illustrates the molybdenum particle size and distribution obtained with this procedure.

B. Al_2O_3 -Mo by isothermal reduction of Al_2O_3 - MoO_3

Linde A Al_2O_3 and MoO_3 (Merck-Reagent Grade) are milled together in the desired proportions in a porcelain jar with Al_2O_3 balls. Benzene is a suitable milling medium since the solubility of MoO_3 in benzene is negligible. The milling is carried out for 72 hours to insure attrition and uniform distribution of the MoO_3 . After evaporation of the benzene, the powder is passed through a 20 mesh screen. Reduction of the MoO_3 to Mo is carried out at 1200° F. to 1500° F. for 1 to 2 hours in a dry H_2 atmosphere. For optimum distribution and particle size, the reduction process is performed isothermally. The Al_2O_3 - MoO_3 powder is placed in an Inconel boat (bed depth 1/2 inch) which is positioned in an Inconel tube in through which flowing H_2 is maintained. The tube is inserted into a furnace which has been pre-heated to the reduction temperature. FIGURE 3 is a photograph which shows the very fine Mo particle size and uniform distribution which results from this procedure. FIGURE 4 illustrates agglomeration of the Mo phase which results from reduction of Al_2O_3 - MoO_3 under non-isothermal conditions (i.e. the powder is heated in a flowing H_2 atmosphere while the furnace temperature was increased gradually

(1),(2),(5),(6) See Bibliography at end of specification.

(3,4) See Bibliography at end of specification.

from room temperature to the reduction temperature).

The isothermal reduction of $\text{Al}_2\text{O}_3\text{-MoO}_3$ is considered important to the minimization of agglomeration of the Mo particles. It is possible that a more refined reduction cycle could be developed to overcome the agglomeration tendencies. However, such investigations have not been made.

C. $\text{Al}_2\text{O}_3\text{-Mo}$ by reduction of $\text{Al}_2(\text{MoO}_4)_3$

The milled mixture of Al_2O_3 and MoO_3 is reacted in air at 1200° to 1500° F. for 1 to 8 hours to form a $\text{Al}_2\text{O}_3\text{-Al}_2(\text{MoO}_4)_3$ material. The reaction between Al_2O_3 and MoO_3 to form $\text{Al}_2(\text{MoO}_4)_3$ has been investigated by Pincus.(7) After formation, the $\text{Al}_2\text{O}_3\text{-Al}_2(\text{MoO}_4)_3$ mixture can be reduced in a dry H_2 atmosphere under non-isothermal conditions without agglomeration of the Mo particles. The reduction is carried out at 1200° F. to 2000° F. for 1 to 2 hours. Al_2O_3 boats are used to contain the powder during reduction and the reduction is performed in an Al_2O_3 combustion tube through which H_2 is flowed. No special precautions as to heating rate are taken in the reduction process except those necessary to minimize thermal shock of the combustion tube. FIGURE 5 is a photograph showing the particle size and distribution of the Mo phase obtained by reduction of $\text{Al}_2\text{O}_3\text{-Al}_2(\text{MoO}_4)_3$.

All of the methods outlined above result in an $\text{Al}_2\text{O}_3\text{-Mo}$ powder mixture which is subsequently processed in the following manner: A pressing lubricant (4 weight percent Carbowax 600) is added, the powder is die pressed at 15,000 pounds per square inch and subsequently isostatically pressed at 90,000 pounds per square inch. The wax is removed at 1200° F. in dry H_2 atmosphere, and the specimens are sintered in vacuum of 0.3 micron (Hg) at temperatures from 2800° F. to 3200° F.

Before mechanical testing, the surfaces of the sintered specimens are wet ground on 350 grit resin-bonded diamond wheels. Approximately 0.003 to 0.004 inch are removed from each surface. The specimens are rectangular shapes which normally measure 0.750" x 0.235" x 0.190". Mechanical testing is carried out on an Instron machine using the three point bending technique.

The sintering procedure outlined above yielded specimens whose densities were consistently 97 to 98 percent of theoretical density. Most of the investigations were made on an $\text{Al}_2\text{O}_3\text{-11}$ weight percent Mo composition which was sintered to these density levels at 3000° F. for 1 hour. The grain size of the specimens is approximately 1 to 2 microns with no evidence of exaggerated grain growth. Higher sintering temperatures (up to 3200° F.) resulted in no increase in relative density, but the cross-section of these specimens indicated normal grain growth with an average grain size of 4 to 5 microns. Lower sintering temperatures resulted in lower relative densities.

In general the average transverse rupture strength of Al_2O_3 containing 11 nominal weight percent Mo is 85,000 pounds per square inch. However, some strength values exceeding 100,000 pounds per square inch have been measured. The possibility for further improvement in the strength of $\text{Al}_2\text{O}_3\text{-Mo}$ material by post-sintering surface treatments and by efforts to minimize internal defects is being investigated.

The effect of a variation in Mo content on the strength of $\text{Al}_2\text{O}_3\text{-Mo}$ material has been investigated. Dispersion strengthened Al_2O_3 specimens containing 7.5, 11.0, and 21.0 weight percent Mo were fabricated and tested. Similar relative densities of 97 to 98 percent could be achieved for these compositions. However, slight modifications in sintering temperature were necessary. For the $\text{Al}_2\text{O}_3\text{-7.5\%}$ Mo material these density levels were obtained at 2950° F. for 1 hour, whereas the $\text{Al}_2\text{O}_3\text{-21\%}$ Mo composition had to be sintered at 3150° F. for 1 hour to achieve this density level. In all compositions considerable refinement of the Al_2O_3 grain size was observed. A study of the

(7) See Bibliography at end of specification.

microstructures of different molybdenum contents indicates that the lower Mo content has a slightly larger grain size. This is consistent with Zener's theory since the lower volume fraction of inclusions would not inhibit grain boundary migration as effectively.

FIGURE 6 is a typical microstructure of sintered aluminum oxide molybdenum material. This figure was produced at $1000\times$ after etching with phosphoric acid.

FIGURE 7 is a further graphical showing of the physical properties attainable in sintered aluminum oxide compacts containing finely divided and uniformly dispersed molybdenum metal.

The attached table is made of record to afford a tabular demonstration of the increase in strength obtained by the addition of molybdenum metal to aluminum oxide compacts.

This disclosure has been thus far concerned only with molybdenum metal additions to aluminum oxide. From ordinary chemical considerations it is apparent that tungsten should also function in a similar manner. Experimental evidence is at hand confirming the prediction that tungsten may be substituted either in whole or part for molybdenum.

TRANSVERSE RUPTURE STRENGTHS OF Al_2O_3 MATERIALS
[Volume percent]

Material	Maximum Strength (K s.i.)	Average Strength (K s.i.)	Number of Specimens
Sintered Al_2O_3	53.3	36.5	44
$\text{Al}_2\text{O}_3\text{-4.3\% Mo}$	98.5	80.0	13
$\text{Al}_2\text{O}_3\text{-5\% Mo}$	116.0	83.9	13
$\text{Al}_2\text{O}_3\text{-5.5\% Mo}$	111.5	84.5	20

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We claim:

1. A fine grained sintered compact consisting essentially of aluminum oxide and an additive selected from the group consisting of finely divided metallic molybdenum and finely divided metallic tungsten, said additive being uniformly dispersed in the compact and being present in an amount to significantly increase the transverse rupture strength of the compact and to limit the size of the aluminum oxide grains product in the sintering operation the metal content of said compact not exceeding 16% by volume of the compact and the average grain size not exceeding five microns.

2. A fine grained sintered compact consisting essentially of aluminum oxide and finely divided metallic molybdenum, said metallic molybdenum being uniformly dispersed in the compact and being present in an amount to significantly increase the transverse rupture strength of the compact and to limit the size of the aluminum oxide grains produced in the sintering operation the metal content of said compact not exceeding 16% by volume of the compact and the average grain size not exceeding five microns.

3. A fine grained sintered compact consisting essentially of aluminum oxide and finely divided metallic tungsten, said metallic tungsten being uniformly dispersed in the compact and being present in an amount to significantly

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increase the transverse rupture strength of the compact and to limit the size of the aluminum oxide grains produced in the sintering operation the metal content of said compact not exceeding 16% by volume of the compact and the average grain size not exceeding five microns.

4. A fine grained sintered compact consisting essentially of aluminum oxide and an additive selected from the group consisting of finely divided metallic molybdenum and finely divided metallic tungsten, said additive being uniformly dispersed in the compact and being present in an amount to significantly increase the transverse rupture strength of the compact and to limit the size of the aluminum oxide grains produced in the sintering operation, said sintered compact exhibiting a density not substantially less than 97% of theoretical density the metal content of said compact not exceeding 16% by volume of the compact and the average grain size not exceeding five microns.

5. A fine grained sintered compact consisting essentially of aluminum oxide and finely divided metallic molybdenum, said metallic molybdenum being uniformly dispersed in the compact and being present in an amount to significantly increase the transverse rupture strength of the compact and to limit the size of the aluminum oxide grains produced in the sintering operation, said sintered compact exhibiting a density not substantially less than 97% of theoretical density the metal content of said com-

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compact not exceeding 16% by volume of the compact and the average grain size not exceeding five microns.

6. A fine grained sintered compact consisting essentially of aluminum oxide and finely divided metallic tungsten, said metallic tungsten being uniformly dispersed in the compact and being present in an amount to significantly increase the transverse rupture strength of the compact and to limit the size of the aluminum oxide grains produced in the sintering operation, said sintered compact exhibiting a density not substantially less than 97% of theoretical density the metal content of said compact not exceeding 16% by volume of the compact and the average grain size not exceeding five microns.

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