

COMPOSITE OXIDE TARGET AND MANUFACTURING METHOD THEREOF

The present invention relates to a composite oxide target and a manufacturing method thereof, more particularly to a composite oxide target for a barrier layer of a heat-assisted magnetic recording (HAMR) medium and a manufacturing method thereof.

All data in a computer are recorded magnetically in tracks of disk platters. In the past, data were stored parallel to the surface of the platters by using longitudinal magnetic recording media; but in recent years, perpendicular magnetic recording media—aligning data vertically to the disk—have been employed to achieve higher storage capability of hard disks. However, under limitations in thermal stability, writability, and signal-to-noise ratio, the perpendicular magnetic recording media have approached the maximum limit of the theoretical storage capacity. In order to keep increasing the storage capacity of hard disks so as to fulfill the demand for storing a vast quantity of data, Heat-Assisted Magnetic Recording (HAMR) has been developed to resolve the above key issues.

For writing in HAMR media, the magnetic recording area is heated by a focused laser beam, and the magnetic composite materials thereof are heated to above the Curie temperature so as to temporarily reduce the coercivity of the magnetic composite materials. After the data writing, the laser beam does not focus on the magnetic recording layer anymore, so the magnetic recording layer would be cooled to stabilize the recorded data.

The layered structure of the HAMR media includes a substrate, an

under layer, a soft magnetic layer, a crystal orientation control layer, a heat dissipation layer, a barrier layer, a magnetic recording layer, a lubricating layer, and an overcoat layer from bottom to top. The magnetic recording layer requires a highly stable magnetic composite material such as FePt alloys to endure the heat from a focused laser beam. Since the FePt alloys are prone to diffuse into layers under the magnetic recording layer under high temperature, it is essential to arrange the barrier layer under the magnetic recording layer so as to mitigate or inhibit the diffusion of the FePt alloys.

The barrier layer of the HAMR media is usually made from a heat-resistant material such as magnesium oxide (MgO). Since MgO is not electrically conductive, MgO targets are usually sputtered by radio frequency (RF) magnetron sputtering to form a film. However, the RF magnetron sputtering has drawbacks of low film formation rate and low production yield. Currently, it is known that titanium (II) oxide (TiO) can be added to the MgO target to improve conductivity, so the barrier layer can be produced by direct current (DC) magnetron sputtering. Nevertheless, a current composite oxide target made of MgO powders and TiO powders inevitably contains MgO aggregates after sintering, so properties of the composite oxide target are deteriorated. Besides, lots of particles are produced during sputtering, and thus characteristics and yields of the resulting films manufactured from the current composite oxide target are affected.

To overcome the shortcomings of the prior arts, one of the objectives of the present invention is to inhibit and/or mitigate MgO aggregation in a composite oxide target.

Another objective of the present invention is to effectively inhibit particle production and/or decrease the number of falling particles produced during sputtering the composite oxide target.

Another objective of the present invention is to improve the bending strength and the thermal conductivity of the composite oxide target.

To achieve the aforementioned objectives, the present invention provides a composite oxide target, which comprises magnesium oxide (MgO) and titanium (II) oxide (TiO). Based on a total atom number of the composite oxide target, a total atom number of the magnesium oxide may be more than or equal to 5 atomic percent (at%) and less than or equal to 90 at%, and a total atom number of the titanium (II) oxide may be more than or equal to 10 at% and less than or equal to 95 at%. The composite oxide target includes multiple black phases including the magnesium oxide, the average grain size of the black phases may be less than or equal to 2 micrometers (μm), and the variance of the grain size of the black phases may be less than 0.2.

By controlling the composition of the composite oxide target, and the average grain size and the variance of the grain size of the black phases of metallographic microstructures of the composite oxide target, MgO aggregation in the composite oxide target of the present invention may be inhibited and/or mitigated, so as to effectively inhibit particle production and/or decrease the number of falling particles produced during sputtering the composite oxide target. Also, the bending strength and the thermal conductivity of the composite oxide target are enhanced.

In one embodiment, the average grain size of the black phases of the

composite oxide target may be more than or equal to 0.05 μm and less than or equal to 2 μm . In another embodiment, the average grain size of the black phases of the composite oxide target may be more than or equal to 0.3 μm and less than or equal to 2 μm .

In one embodiment, the variance of the grain size of the black phases of the composite oxide target may be more than or equal to 1.00×10^{-5} and less than 0.2. In another embodiment, the variance of the grain size of the black phases of the composite oxide target may be more than or equal to 5.00×10^{-5} and less than 0.2.

In one embodiment, the composite oxide target may further comprise an additive, wherein the additive may be a first additive, a second additive, or a combination thereof. Specifically, the first additive may be selected from the group consisting of aluminum oxide (Al_2O_3), zirconium dioxide (ZrO_2), chromium(III) oxide (Cr_2O_3), silicon dioxide (SiO_2), and any combination thereof. The second additive may be selected from the group consisting of aluminum (Al), zirconium (Zr), chromium (Cr), silicon (Si), and any combination thereof. According to the present invention, by adding the first additive and/or the second additive, the growth of the black phases of the composite oxide target can be inhibited and the variance of the grain size of the black phases of the composite oxide target can be controlled.

In the present specification, the total amount of the additive refers to the total amount of the first additive(s), the total amount of the second additive(s), or the sum of the total amounts of the first additive(s) and the second additive(s).

When the first additives include Al_2O_3 , ZrO_2 , Cr_2O_3 , and SiO_2 , the term “the total amounts of the first additives” refers to the sum of the respective amounts of Al_2O_3 , ZrO_2 , Cr_2O_3 , and SiO_2 ; and when the first additive is Al_2O_3 , ZrO_2 , Cr_2O_3 , or SiO_2 , the term “the total amount of the first additive” refers to the respective amount of Al_2O_3 , the respective amount of ZrO_2 , the respective amount of Cr_2O_3 , or the respective amount of SiO_2 .

When the second additives include Al, Zr, Cr, and Si, the term “the total amounts of the second additives” refers to the sum of the respective amounts of Al, Zr, Cr, and Si; and when the second additive is Al, Zr, Cr, or Si, the term “the total amount of the second additive” refers to the respective amount of Al, the respective amount of Zr, the respective amount of Cr, or the respective amount of Si.

In one embodiment, based on the total atom number of the composite oxide target, a total atom number of the additive may be more than or equal to 1 at% and less than or equal to 6 at%. In another embodiment, based on the total atom number of the composite oxide target, the total atom number of the additive may be more than or equal to 3 at% and less than or equal to 6 at%. Herein, the average grain size and the variance of the grain size of the black phases of the composite oxide target of the present invention may be further decreased.

According to the present invention, the composite oxide target may be suitable for a magnetron sputtering process such as the RF magnetron sputtering process and the DC magnetron sputtering process. By inhibiting and/or mitigating MgO aggregation in the composite oxide target, the number

of falling particles during sputtering of the composite oxide target may be less than 50. Preferably, the number of falling particles during the DC magnetron sputtering of the composite oxide target may be less than 40, less than 30, less than 20, and even less than 10. Therefore, films which are sputtered from the composite oxide target have improved characteristics and yield, and thus are suitable for the barrier layer of the HAMR media.

In the present specification, the term “bending strength” refers to the stress upon rupture that a target experiences when a bending load per unit area is applied on the target, and the unit thereof is million pascals (MPa).

According to the present invention, the bending strength of the composite oxide target may be more than or equal to 100 MPa. Specifically, the bending strength of the composite oxide target may be more than or equal to 100 MPa and less than or equal to 200 MPa; preferably, the bending strength of the composite oxide target may be more than or equal to 110 MPa and less than or equal to 180 MPa; more preferably, the bending strength of the composite oxide target may be more than or equal to 120 MPa and less than or equal to 170 MPa; even more preferably, the bending strength of the composite oxide target may be more than or equal to 130 MPa and less than or equal to 170 MPa.

According to the present invention, the thermal conductivity of the composite oxide target may be more than or equal to 10 watts per meter per kelvin ($\text{W/m}\cdot\text{K}$). Specifically, the thermal conductivity of the composite oxide target may be more than or equal to 10 $\text{W/m}\cdot\text{K}$ and less than or equal to 30 $\text{W/m}\cdot\text{K}$; preferably, the thermal conductivity of the composite oxide target may

be more than or equal to 15 W/m·K and less than or equal to 30 W/m·K; more preferably, the thermal conductivity of the composite oxide target may be more than or equal to 20 W/m·K and less than or equal to 25 W/m·K.

In addition, the present invention further provides a method of manufacturing a composite oxide target, which comprises the following steps:

preparing magnesium oxide powders (MgO powders) and titanium (II) oxide powders (TiO powders), wherein particle sizes of the MgO powders may be less than or equal to 5 μm , and particle sizes of the TiO powders may be less than or equal to 10 μm ;

mixing the MgO powders and the TiO powders to obtain a powdered mixture, wherein based on a total atom number of the powdered mixture, a total atom number of the MgO powder may be more than or equal to 5 at% and less than or equal to 90 at%, and a total atom number of the TiO powder may be more than or equal to 10 at% and less than or equal to 95 at%;

grinding the powdered mixture for more than or equal to 48 hours to obtain a fine powdered mixture;

preforming the fine powdered mixture into a green compact; and

sintering the green compact at a temperature ranging from 900°C to 1400°C to obtain the composite oxide target.

According to the present invention, by controlling the particle sizes and the mixing ratio of the raw material powders, the grinding time, and the sintering temperature, the composite oxide target manufactured by the method of the present invention can have decreased average grain size of the black phases and reduced variance of the grain size of the black phases in its

metallographic microstructure. That is, the method of the present invention can inhibit and/or mitigate MgO aggregation in the composite oxide target, so as to effectively inhibit particle production and/or decrease the number of falling particles produced during sputtering of the composite oxide target. Also, the bending strength and the thermal conductivity of the composite oxide target can be enhanced.

In one embodiment of the aforesaid method, the particle sizes of the MgO powders may be more than or equal to 0.5 μm and less than or equal to 5.0 μm , and the particle sizes of the TiO powders may be more than or equal to 0.5 μm and less than or equal to 10.0 μm ; preferably, the particle sizes of the MgO powders may be more than or equal to 1.0 μm and less than or equal to 5.0 μm , and the particle sizes of the TiO powders may be more than or equal to 1.0 μm and less than or equal to 10.0 μm ; more preferably, the particle sizes of the MgO powders may be more than or equal to 2.0 μm and less than or equal to 5.0 μm , and the particle sizes of the TiO powders may be more than or equal to 2.0 μm and less than or equal to 10.0 μm .

Alternatively, the aforesaid method further comprises providing a powdered additive and mixing the MgO powders, the TiO powders, and the powdered additive to obtain the powdered mixture. The powdered additive comprises a first powdered additive, a second powdered additive, or a combination thereof. The first powdered additive may be selected from the group consisting of Al_2O_3 powders, ZrO_2 powders, Cr_2O_3 powders, SiO_2 powders, and any combination thereof, and the particle size of the first powdered additive may be less than or equal to 3 μm . The second powdered

additive may be selected from the group consisting of Al powders, Zr powders, Cr powders, Si powders, and any combination thereof, and the particle size of the second powdered additive may be less than or equal to 50 μm . Based on the total atom number of the powdered mixture, a total atom number of the powdered additive may be more than or equal to 1 at% and less than or equal to 6 at%. Specifically, the particle size of the first powdered additive may be more than or equal to 0.1 μm and less than or equal to 3 μm , and the particle size of the second powdered additive may be more than or equal to 1 μm and less than or equal to 50 μm ; preferably, the particle size of the first powdered additive may be more than or equal to 0.1 μm and less than or equal to 1 μm , and the particle size of the second powdered additive may be more than or equal to 10 μm and less than or equal to 50 μm .

In one embodiment of the aforesaid method, the particle sizes of the MgO powders may be more than or equal to 0.5 μm and less than or equal to 5.0 μm , the particle sizes of the TiO powders may be more than or equal to 0.5 μm and less than or equal to 10.0 μm , and the particle sizes of the ZrO₂ powders may be more than or equal to 0.1 μm and less than or equal to 1.0 μm . Preferably, the particle sizes of the MgO powders may be more than or equal to 1.0 μm and less than or equal to 5.0 μm , the particle sizes of the TiO powders may be more than or equal to 1.0 μm and less than or equal to 10.0 μm , and the particle sizes of the ZrO₂ powders may be more than or equal to 0.2 μm and less than or equal to 0.8 μm . More preferably, the particle sizes of the MgO powders may be more than or equal to 2.0 μm and less than or equal to 5.0 μm , the particle sizes of the TiO powders may be more than or equal to 2.0 μm and

less than or equal to 10.0 μm , and the particle sizes of the ZrO_2 powders may be more than or equal to 0.3 μm and less than or equal to 0.6 μm .

In one embodiment of the aforesaid method, the particle sizes of the MgO powders may be more than or equal to 0.5 μm and less than or equal to 5.0 μm , the particle sizes of the TiO powders may be more than or equal to 0.5 μm and less than or equal to 10.0 μm , and the particle sizes of the Al powders may be more than or equal to 10 μm and less than or equal to 70 μm . Preferably, the particle sizes of the MgO powders may be more than or equal to 1.0 μm and less than or equal to 5.0 μm , the particle sizes of the TiO powders may be more than or equal to 1.0 μm and less than or equal to 10.0 μm , and the particle sizes of the Al powders may be more than or equal to 20 μm and less than or equal to 60 μm . More preferably, the particle sizes of the MgO powders may be more than or equal to 2.0 μm and less than or equal to 5.0 μm , the particle sizes of the TiO powders may be more than or equal to 2.0 μm and less than or equal to 10.0 μm , and the particle sizes of the Al powders may be more than or equal to 30 μm and less than or equal to 50 μm .

Preferably, in the aforesaid method, the grinding time may be more than or equal to 48 hours and less than or equal to 120 hours. In some embodiments of the aforesaid method, the grinding time may be more than or equal to 60 hours and less than or equal to 120 hours.

Alternatively, in the aforesaid method, the powdered mixture may be ground for more than or equal to 48 hours and further screened with a sieve to obtain the fine powdered mixture, wherein the mesh size of the sieve may be from 400 mesh to 600 mesh.

It is understood that the fine powdered mixture may be preformed under various conditions as long as it can be preformed into the green compact. In one embodiment, the fine powdered mixture may be uniformly filled into a mold and then preformed into the green compact under a pressure from 50 kilograms per square centimeter (kg/cm^2) to 100 kg/cm^2 .

Preferably, in the aforesaid method, the sintering temperature may be from 1000°C to 1300°C .

According to the present invention, in the aforesaid method, the sintering time may be from 1.5 hours to 5 hours; preferably, the sintering time may be from 1.5 hours to 4 hours; more preferably, the sintering time may be from 1.5 hours to 3 hours.

According to the present invention, in the aforesaid method, the sintering pressure may be from 300 kg/cm^2 to 510 kg/cm^2 ; preferably, the sintering pressure may be from 300 kg/cm^2 to 400 kg/cm^2 .

According to the present invention, the green compact may be sintered by hot pressing (HP), spark plasma sintering (SPS), hot isostatic pressing (HIP), or any combination thereof. In one embodiment, the sintering temperature of HP process may be from 1000°C to 1300°C , and the sintering pressure of HP process may be from 300 kg/cm^2 to 450 kg/cm^2 . In another embodiment, the sintering temperature of SPS process may be from 950°C to 1150°C , and the sintering pressure of SPS process may be from 400 kg/cm^2 to 510 kg/cm^2 . In yet another embodiment, the sintering temperature of HIP process may be from 1050°C to 1150°C , and the sintering pressure of HIP process may be from 350 kg/cm^2 to 510 kg/cm^2 .

Other objectives, advantages, and novel features of the invention will become more apparent from the following detailed description when taken in conjunction with the accompanying drawings.

IN THE DRAWINGS:

FIG. 1 shows two selected spots that are analyzed by an energy dispersive X-ray spectrometer (EDS or EDX) to identify the composition of the white and the black phases of the composite oxide target of Example 1, wherein these two selected spots are indicated on a metallographic image taken by a scanning electron microscope (SEM).

FIG. 2A is the SEM image showing the metallographic structure of the composite oxide target of Example 1.

FIG. 2B is a high-resolution image of FIG. 2A, which is processed by an image analysis software ImageJ.

FIG. 3A is an SEM image showing the metallographic structure of the composite oxide target of Example 8.

FIG. 3B is a high-resolution image of FIG. 3A, which is processed by the image analysis software ImageJ.

FIG. 4A is an SEM image showing the metallographic structure of the composite oxide target of Example 10.

FIG. 4B is a high-resolution image of FIG. 4A, which is processed by the image analysis software ImageJ.

FIG. 5A is an SEM image showing the metallographic structure of the composite oxide target of Example 17.

FIG. 5B is a high-resolution image of FIG. 5A, which is processed by

the image analysis software ImageJ.

FIG. 6A is an SEM image showing the metallographic structure of the composite oxide target of Comparative Example 1.

FIG. 6B is a high-resolution image of FIG. 6A, which is processed by the image analysis software ImageJ.

FIG. 7A is an SEM image showing the metallographic structure of the composite oxide target of Comparative Example 9.

FIG. 7B is a high-resolution image of FIG. 7A, which is processed by the image analysis software ImageJ.

Several composite oxide targets are exemplified below to demonstrate that the technical means of the present invention can inhibit and/or mitigate the aggregation of the black phases in composite oxide targets and decrease the grain size of the black phases and reduce the variance of the grain size of the black phases so as to improve properties of composite oxide targets and effectively inhibit particle production and/or decrease the number of falling particles produced during sputtering the composite oxide target. A person skilled in the art can easily realize the advantages and effects of the present invention in accordance with the contents of the specification. Various modifications and variations could be made in order to practice or apply the present invention without departing from the spirit and scope of the invention.

Examples 1 to 23 (E1 to E23): composite oxide targets

To simplify the description of the experiment, E1 is taken as an example to illustrate the steps. The composite oxide targets of E2 to E23 were produced by the similar method as stated below.

First, MgO powders with a purity of 99.99% and particle sizes of 3.0 μm to 4.5 μm , TiO powders with a purity of 99.9% and particle sizes of 7.0 μm to 9.5 μm , ZrO₂ powders with a purity of 99.9% and particle sizes of 0.5 μm , and Al powders with a purity of 99.5% and particle sizes of 45 μm in appropriate amounts were provided as raw materials for the preparation of the composite oxide targets of E1 to E23, wherein the ZrO₂ powders were used as a first powdered additive while the Al powders were used as a second powdered additive. The amounts of all raw material powders and the particle sizes thereof for each of E1 to E23 are shown in Table 1 below.

Subsequently, the raw material powders used for E1, including MgO powders, TiO powders, and the first and second powdered additive, were mixed to obtain a powdered mixture. In Table 1, the amount of each of the raw material powders is decided based on a total atom number of the powdered mixture, and the unit thereof is at%.

The powdered mixture was ground for at least 48 hours according to the grinding time in Table 1 and then screened with a 400 mesh sieve in order to obtain a fine powdered mixture. In other embodiments, the screening could be omitted based on practical needs; *i.e.*, the fine powdered mixture was obtained simply by grinding the powdered mixture.

Afterward, the fine powdered mixture was filled into a selected mold uniformly, and then preformed by an oil hydraulic press under a pressure of 70.31 kg/cm² to obtain a green compact.

At last, the green compact was sintered at a sintering temperature from 1000°C to 1300°C under a sintering pressure of 400 kg/cm² for two hours to

obtain the composite oxide target of E1 by HP, SPS, or HIP.

The composite oxide targets of E2 to E23 were produced in accordance with Table 1 and the above similar method.

It is understood that the amounts of the raw material powders shown in Table 1 are substantially the same or similar to the amounts of the composition of the composite oxide targets produced by the method mentioned above.

Taking E1 as an example, according to the amounts of the raw material powders thereof, based on a total atom number of the composite oxide target of E1, the total atom number of MgO of the composite oxide target of E1 is 50 at% and the total atom number of TiO of the composite oxide target of E1 is 50 at%.

Comparative Examples 1 to 9 (CE1 to CE9): composite oxide targets

To simplify the description of the experiment, CE1 is taken as an example to illustrate the steps. The composite oxide targets of CE2 to CE9 were produced by the similar method as stated below.

First, MgO powders with a purity of 99.99% and particle sizes of 12.5 μm to 14.0 μm , TiO powders with a purity of 99.9% and particle sizes of 29.5 μm to 38.5 μm , ZrO₂ powders with a purity of 99.9% and particle sizes of 1.2 μm , and Al powders with a purity of 99.5% and particle sizes of 60 μm in appropriate amounts were provided as raw materials for the preparation of the composite oxide targets of CE1 to CE9, wherein the ZrO₂ powders were used as a first powdered additive while the Al powders were used as a second powdered additive. The amounts of all raw material powders and the particle

sizes thereof for each of CE1 to CE9 are shown in Table 1 below.

Subsequently, the raw material powders used for CE1 were mixed to obtain a powdered mixture. In Table 1, the amount of each of the raw material powders is decided based on a total atom number of the powdered mixture, and the unit thereof is at%.

The powdered mixture was ground from 24 hours to 36 hours according to the grinding time in Table 1 in order to obtain a fine powdered mixture.

Afterward, the fine powdered mixture was filled into a selected mold uniformly, and preformed by the oil hydraulic press under a pressure of 70.31 kg/cm² to obtain a green compact.

At last, the green compact was sintered at a sintering temperature from 1000°C to 1300°C under a sintering pressure of 400 kg/cm² for two hours to obtain the composite oxide target of CE1 by HP, SPS, or HIP.

The composite oxide targets of CE2 to CE9 were produced in accordance with Table 1 and the above similar method.

Table 1: Amounts of raw material powders and particle sizes thereof for composite oxide targets of E1 to E23 and CE1 to CE9, process parameters, characteristics of the composite oxide targets, and number of falling particles during sputtering of E1 to E23 and CE1 to CE9.

No.	amounts of raw material powders (at%)				particle sizes of raw material powders (μm)				grinding time (h)	sintering method	sintering temp. ($^{\circ}\text{C}$)	avg. grain size of black phases (μm)	variance of grain size of black phases	bending strength (MPa)	thermal conductivity ($\text{W/m}\cdot\text{K}$)	number of falling particles
	MgO	TiO	ZrO ₂	Al	MgO	TiO	ZrO ₂	Al								
E1	50	50	0	0	3.5	7.5	-	-	72	HP	1100	1.28	5.35×10^{-2}	145	15.06	25
E2	54	46	0	0	3.0	7.5	-	-	72	HP	1100	1.45	3.04×10^{-3}	135	17.25	23
E3	60	40	0	0	4.0	9.0	-	-	60	HP	1100	1.61	7.25×10^{-2}	139	18.58	21
E4	55	45	0	0	4.0	7.5	-	-	60	HP	1100	1.39	5.44×10^{-2}	140	17.39	21
E5	70	30	0	0	4.0	9.5	-	-	60	HP	1150	1.68	7.73×10^{-2}	131	20.51	41
E6	90	10	0	0	3.5	8.5	-	-	48	HP	1200	1.86	7.35×10^{-2}	128	21.23	46
E7	65	35	0	0	4.0	9.0	-	-	60	HP	1150	1.75	6.57×10^{-2}	129	19.34	38
E8	40	60	0	0	3.5	7.0	-	-	72	HP	1100	0.96	8.73×10^{-3}	131	14.87	30
E9	35	65	0	0	3.5	8.0	-	-	84	HP	1100	1.22	8.26×10^{-3}	139	14.84	27
E10	20	80	0	0	4.5	9.0	-	-	96	HP	1300	1.81	8.66×10^{-4}	152	13.21	22
E11	5	95	0	0	4.0	7.0	-	-	120	HP	1000	0.76	9.74×10^{-5}	149	10.65	12
E12	20	80	0	0	4.0	9.0	-	-	96	HP	1100	0.91	9.25×10^{-5}	141	14.38	9
E13	10	90	0	0	4.0	9.5	-	-	120	HP	1100	0.89	7.52×10^{-5}	168	13.91	13
E14	50	50	0	0	4.0	7.0	-	-	72	HP	1000	1.09	4.02×10^{-3}	131	16.65	19
E15	48.5	48.5	3	0	4.0	8.0	0.5	-	84	HP	1200	1.09	3.05×10^{-3}	129	12.22	30
E16	47	47	6	0	4.5	9.5	0.5	-	96	HP	1200	0.98	2.18×10^{-3}	125	11.84	34
E17	50	49	1	0	4.0	9.5	0.5	-	72	HP	1100	1.22	4.74×10^{-3}	132	12.89	26
E18	48.5	48.5	0	3	4.0	9.0	-	45	96	HP	1100	1.11	1.46×10^{-3}	128	18.07	24

E19	47	47	0	6	4.5	9.5	-	45	120	HP	1100	1.01	6.71×10^{-4}	115	19.98	28
E20	50	49	0	1	4.0	9.5	-	45	84	HP	1100	1.26	2.94×10^{-3}	141	16.12	23
E21	75	25	0	0	4.0	7.0	-	-	60	SPS	1100	1.58	6.36×10^{-2}	128	20.15	38
E22	50	50	0	0	4.0	7.0	-	-	72	SPS	1000	0.97	3.00×10^{-2}	143	16.20	42
E23	30	70	0	0	3.0	7.0	-	-	72	HIP	1100	1.06	5.09×10^{-4}	155	14.71	18
CE1	50	50	0	0	13.5	33.0	-	-	36	HP	1000	4.85	5.01×10^{-1}	80	8.07	127
CE2	45	55	0	0	13.5	38.5	-	-	36	HP	1000	4.75	3.41×10^{-1}	79	7.69	105
CE3	95	5	0	0	14.0	29.5	-	-	24	HP	1200	6.41	9.84×10^{-1}	81	9.27	151
CE4	50	50	0	0	14.0	29.5	-	-	24	HP	1300	6.08	7.67×10^{-1}	88	9.01	96
CE5	3	97	0	0	13.5	31.0	-	-	24	HP	1100	5.11	2.93×10^{-1}	97	7.91	78
CE6	46	46	8	0	12.5	35.5	1.2	-	36	HP	1150	3.15	8.57×10^{-1}	99	8.91	83
CE7	46	46	0	8	12.5	33.0	-	60	36	HP	1100	3.67	7.26×10^{-1}	89	9.11	91
CE8	30	70	0	0	12.5	31.0	-	-	36	SPS	1000	4.27	2.19×10^{-1}	87	8.31	84
CE9	50	50	0	0	14.0	38.5	-	-	24	HIP	1100	5.81	5.52×10^{-1}	91	8.48	70

Test Example 1: average grain size and variance of grain size of black phases

In this test example, metallographic microstructures of the composite oxide targets of E1 to E23 and CE1 to CE9 were first observed under SEM. The composition of black and white phases of the metallographic microstructures was analyzed by EDX, and the grain size of the black phases was analyzed by an image analysis software.

The composite oxide targets of E1 to E23 and CE1 to CE9 were machined into disc-shaped composite oxide targets with a diameter of 152 millimeters (mm) and a thickness of 6 mm by waterjet cutting and grinding. Then, a 10 mm*10 mm sample was taken out from each of the disc-shaped composite oxide targets at its half-radius ($r/2$) by wire cutting.

Herein, the 10 mm*10 mm sample of E1 was taken as an example to illustrate the composition of the black phases of the composite oxide target of E1 and the calculation of the average grain size and the variance of the grain size of the black phases of E1. The average grain size and the variance of grain size of the black phases of the composite oxide targets of E2 to E23 and CE1 to CE9 were calculated by the same method.

First, the metallographic microstructure of the sample of E1 was observed under SEM (manufacturer: HITACHI; model: S-3400N) at 2000x magnification. Subsequently, the composition of the white and black phases of the metallographic microstructure was analyzed by EDX. As shown in FIG. 1, one spot marked with “A” was in the black phase and the other spot marked with “B” was in the white phase, and both of the spots in the metallographic

microstructure were analyzed by EDX to identify their compositions. The results are shown in Table 2 below.

Table 2: Amount of the composition of the white and black phases of composite oxide target of E1; unit: at%.

	selected spots	phases	Mg	Ti	O
E1	A	black	37.61	0	62.39
	B	white	0	37.06	62.94

As shown in Table 2, in the composite oxide target of E1, the composition of the black phase is MgO while that of the white phase is TiO. Based on the EDX results, the average grain size and the variance of the grain size of the black phase were analyzed by an image analysis software to assess MgO aggregation in the composite oxide target of E1.

Specifically, the 10 mm*10 mm sample of E1 was observed under SEM, and five metallographic images were randomly taken at five different regions of the sample. The five metallographic images were processed into five high-resolution images by the built-in function “Color Threshold” on an image analysis software ImageJ. FIGs. 2A and 2B, FIGs. 3A and 3B, FIGs. 4A and 4B, FIGs. 5A and 5B, FIGs. 6A and 6B, and FIGs. 7A and 7B are SEM metallographic images and the corresponding high-resolution images of the composite oxide targets of E1, E8, E10, E17, CE1, and CE9. When the high-resolution images of FIGs. 2B, 3B, 4B, and 5B are compared with those of FIGs. 6B and 7B, it is understood that the grain size is smaller and the black phases are more uniform in the composite oxide targets of E1, E8, E10, and E17.

In order to objectively assess MgO aggregation in the composite oxide target of E1, the average of grain sizes of black phases in each of the five SEM metallographic images was analyzed by the built-in function “Analyze Particles” on ImageJ, and five average values—1.16 μm , 1.10 μm , 1.61 μm , 1.02 μm , and 1.49 μm —were obtained. The above five average values were averaged, *i.e.* dividing the sum of the five averaged values by 5, to obtain 1.28 μm , the mean (*i.e.*, the average grain size) of the black phases of the composite oxide target of E1. The result is shown in Table 1 above.

Subsequently, the variance of the grain size of the black phases of the composite oxide target of E1 was calculated using the following formula:

$$\frac{\Sigma(\text{average of grain size of each of the five metallographic images} - \text{mean})^2}{5}.$$

Specifically, the detailed calculation was as follows:

$$\frac{(1.16-1.28)^2 + (1.10-1.28)^2 + (1.61-1.28)^2 + (1.02-1.28)^2 + (1.49-1.28)^2}{5} = 5.35 \times 10^{-2}.$$

The result of the variance of the grain size of the black phases of the composite oxide target of E1 is shown in Table 1. Similarly, the results of E2 to E23 and CE1 to CE9 were obtained by the same method and shown in Table 1.

As shown in Table 1, since the composite oxide targets of E1 to E23 were produced by mixing appropriate amounts of raw material powders with specific grain size and controlling suitable grinding time as well as sintering temperature, they possess specific compositions, the average grain size of the black phases thereof is less than or equal to 2 μm , and the variance of the grain size of the black phases is less than 0.2.

In contrast, the grinding time taken in the production of the composite

oxide targets of CE1 to CE9 was not properly controlled, and the particle size of the raw material powders used by CE1 to CE9 were larger; therefore, for the composite oxide targets of CE1 to CE9, the average grain size of the black phases is more than 3 μm , and the variance of the grain size of the black phases is more than 0.2.

From the above experimental results, the average grain size of the black phases of the composite oxide targets produced by the method of the present invention is smaller and the variance of the grain size of the black phases is relatively low.

Further, from examples to which the first additive or the second additive was added as needed (for example, E15 to E17 and E18 to E20), it is observed that as the total amount of the additive increases, the average grain size of the black phases of the composite oxide targets decreases and the variance of the grain size of the black phases also decreases.

Test Example 2: bending strength

The composite oxide targets of E1 to E23 and CE1 to CE9 were machined into disc-shaped composite oxide targets with a diameter of 152 mm and a thickness of 6 mm by waterjet cutting and grinding. Then, three samples, each with a length of 50 mm, a width of 3 mm, and a height of 4 mm, were taken out from each of the disc-shaped composite oxide targets at its half-radius ($r/2$) by wire cutting.

Herein, the three samples of E1 were used to illustrate how the bending strength of the composite oxide target of E1 was analyzed. The bending strength of the composite oxide targets of E2 to E23 and CE1 to CE9 was

obtained by the same method.

The bending strength of the three samples of E1 was measured by a universal testing machine (manufacturer: Instron; model: 3365 Series; pressurizing speed: 0.008 millimeters per second (mm/s)), and three values were obtained. The mean of the three values was used to evaluate the mechanical strength of the composite oxide target of E1. The result of the bending strength of the composite oxide target of E1 is shown in Table 1, and the unit thereof is MPa. Similarly, the results of E2 to E23 and CE1 to CE9 were obtained by the same method and shown in Table 1.

As shown in Table 1, the bending strength of the composite oxide targets of E1 to E23 is more than 110 MPa; preferably, the bending strength of the composite oxide targets of E1 to E5, E8 to E14, E17, E20, E22, and E23 is more than 130 MPa; more preferably, the bending strength of the composite oxide targets of E10, E13, and E23 is more than 150 MPa.

In contrast, the bending strength of the composite oxide targets of CE1 to CE9 is less than 100 MPa; particularly, the bending strength of the composite oxide targets of CE1 to CE4, CE7, and CE8 is less than 90 MPa; more particularly, the bending strength of the composite oxide target of CE2 is even less than 80 MPa.

From the above experimental results, the bending strength of the composite oxide targets produced by the method of the present invention is excellent.

Test Example 3: thermal conductivity

The composite oxide targets of E1 to E23 and CE1 to CE9 were

machined into disc-shaped composite oxide targets with a diameter of 152 mm and a thickness of 6 mm by waterjet cutting and grinding. Herein, the disc-shaped composite oxide target of E1 was used as an example to illustrate how the thermal conductivity of the composite oxide target of E1 was calculated. The thermal conductivity of the composite oxide targets of E2 to E23 and CE1 to CE9 was obtained by the same method.

First, a sample with a length of 15 mm, a width of 15 mm, and a height of 5 mm was taken out from the disc-shaped composite oxide target of E1 at its half-radius ($r/2$) by wire cutting. The weight of the sample in the air and that in a liquid were measured based on Archimedes principle. Then, the actual density (symbol: ρ ; unit: kilogram per cubic meter (kg/m^3)) of the composite oxide target of E1 was calculated using the following formula:

$$\rho = \frac{\text{sample weight}_{\text{air}} \times \text{liquid density}}{\text{sample weight}_{\text{air}} - \text{sample weight}_{\text{liquid}}}.$$

Subsequently, a pie-shaped sample with a diameter of 12.7 mm and a height of 2 mm was taken out from the disc-shaped composite oxide target of E1 at its half-radius ($r/2$) by wire cutting. Then, the thermal diffusivity (symbol: α ; unit: square meter per second (m^2/s)) was obtained by the laser flash method; the specific heat capacity (symbol: c_p ; unit: joule per kilogram per kelvin ($\text{J/kg} \cdot \text{K}$)) was obtained by the differential scanning calorimetry (DSC).

At last, the thermal conductivity (symbol: k ; unit: $\text{W/m} \cdot \text{K}$) of the composite oxide target of E1 was calculated by substituting the values of the thermal diffusivity (α), the actual density (ρ), and the specific heat capacity (c_p)

into the following formula:

$$\alpha = \frac{k}{\rho \cdot c_p},$$

and the result are shown in Table 1.

The thermal conductivity of the composite oxide targets of E2 to E23 and CE1 to CE9 was obtained by the same method and shown in Table 1.

As shown in Table 1, the thermal conductivity of the composite oxide targets of E1 to E23 is more than 10 W/m·K; preferably, the thermal conductivity of the composite oxide targets of E1 to E7, E14, and E18 to E22 is more than 15 W/m·K; more preferably, the thermal conductivity of the composite oxide targets of E5, E6, and E21 is more than 20 W/m·K.

In contrast, the thermal conductivity of the composite oxide targets of CE1 to CE9 is less than 10 W/m·K; particularly, the thermal conductivity of the composite oxide targets of CE1, CE2, CE5, CE6, CE8, and CE9 is less than 9 W/m·K; more particularly, the thermal conductivity of the composite oxide targets of CE2 and CE5 is even less than 8 W/m·K.

As shown in the above results, the thermal conductivity of the composite oxide targets produced by the method of the present invention is excellent.

Further, from examples which only contain MgO and TiO (such as E1 to E14 and E21 to E23), it is observed that as the total amount of MgO increases, the thermal conductivity of the composite oxide targets also increases. In addition, from E18 to E20 to which the second additive was added as needed, it is observed that as the total amount of the second additive

increases, the thermal conductivity of the composite oxide targets also increases.

Test Example 4: number of falling particles produced during sputtering

The composite oxide targets of E1 to E23 and CE1 to CE9 were machined into disc-shaped composite oxide targets with a diameter of 5.08 centimeters (cm) and a thickness of 4 mm by waterjet cutting and grinding. The disc-shaped composite oxide targets of E1 to E23 and CE1 to CE 9 were respectively put into a magnetron sputtering machine, and dirt on the surface of each disc was removed by a pre-sputtering process. A composite oxide film was deposited on a 2 cm*2 cm wafer by DC sputtering, wherein the working pressure was set as 10^{-3} torr to 10^{-7} torr, the sputtering power was set as 250 watts per square centimeter (W/cm^2), and the sputtering time was set as 300 seconds. The numbers of falling particles produced, also called “particle yield”, during the DC sputtering of the disc-shaped composite oxide targets of E1 to E23 and CE1 to CE 9 were respectively recorded and shown in Table 1.

As shown in Table 1, the numbers of falling particles during the DC sputtering of the composite oxide targets of E1 to E23 are each less than 50; preferably, the numbers of falling particles during the DC sputtering of the composite oxide targets of E1 to E4, E9 to E14, E17 to E20, and E23 are each less than 30; more preferably, the numbers of falling particles during the DC sputtering of the composite oxide targets of E11 to E14 and E23 are each less than 20; even more preferably, the number of falling particles during the DC sputtering of the composite oxide target of E12 is less than 10.

In contrast, the numbers of falling particles during the DC sputtering of the composite oxide targets of CE1 to CE9 are each more than or equal to 70; particularly, the numbers of falling particles during the DC sputtering of the composite oxide targets of CE1 to CE4 and CE7 are each more than 90; more particularly, the numbers of falling particles during the DC sputtering of the composite oxide targets of CE1 to CE3 are each more than 100. It is noted that the number of falling particles by CE3 is even more than 150, which is at least three times each of that produced by E1 to E23.

From the above results, the number of falling particles during the DC sputtering of the composite oxide target of the present invention is significantly decreased, and thus, properties of the films sputtered from the composite oxide target of the present invention are improved and the yield of the film is also increased.

Based on the foresaid results, by controlling the grain size and the mixing ratio of the raw material powders as well as the grinding time and the sintering temperature, the average grain size of the black phases of the metallographic microstructures of the composite oxide target is less than or equal to 2 μm and the variance of the grain size of the black phases is less than 0.2. Therefore, particle production during sputtering is effectively inhibited and/or the number of falling particles during sputtering is decreased to less than 50. Moreover, the bending strength of the composite oxide target is more than 100 MPa, and the thermal conductivity of the composite oxide target is more than or equal to 10 W/m·K.

Even though numerous characteristics and advantages of the present

invention have been set forth in the foregoing description, together with details of the structure and features of the present invention, the disclosure is illustrative only. Changes may be made in the details, especially in matters of size within the principles of the present invention to the full extent indicated by the broad general meaning of the terms in which the appended claims are expressed.

CLAIMS:

1. A composite oxide target, comprising magnesium oxide and titanium (II) oxide,

wherein a total atom number of the magnesium oxide is more than or equal to 5 atomic percent and less than or equal to 90 atomic percent and a total atom number of the titanium (II) oxide is more than or equal to 10 atomic percent and less than or equal to 95 atomic percent based on a total atom number of the composite oxide target; and

wherein the composite oxide target includes multiple black phases including the magnesium oxide, the average grain size of the black phases is less than or equal to 2 micrometers, and the variance of the grain size of the black phases is less than 0.2.
2. The composite oxide target as claimed in claim 1, comprising an additive, wherein the additive is a first additive, a second additive, or a combination thereof, the first additive is selected from the group consisting of aluminum oxide, zirconium dioxide, chromium(III) oxide, silicon dioxide, and any combination thereof, and the second additive is selected from the group consisting of aluminum, zirconium, chromium, silicon, and any combination thereof.
3. The composite oxide target as claimed in claim 2, wherein a total atom number of the additive is more than or equal to 1 atomic percent and less than or equal to 6 atomic percent based on the total atom number of the composite oxide target.
4. The composite oxide target as claimed in any one of claims 1 to

3, wherein the bending strength of the composite oxide target is more than 100 million pascals.

5. The composite oxide target as claimed in any one of claims 1 to 4, wherein the thermal conductivity of the composite oxide target is more than 10 watts per meter per kelvin.

6. A method of manufacturing a composite oxide target, comprising the following steps:

preparing magnesium oxide powders and titanium (II) oxide powders, wherein particle sizes of the magnesium oxide powders are more than or equal to 2 micrometers and less than or equal to 5 micrometers, and particle sizes of the titanium (II) oxide powders are more than or equal to 2 micrometers and less than or equal to 10 micrometers;

mixing the magnesium oxide powders and the titanium (II) oxide powders to obtain a powdered mixture, wherein a total atom number of the magnesium oxide powders is more than or equal to 5 atomic percent and less than or equal to 90 atomic percent and a total atom number of the titanium (II) oxide powders is more than or equal to 10 atomic percent and less than or equal to 95 atomic percent based on a total atom number of the powdered mixture;

grinding the powdered mixture for more than or equal to 48 hours to obtain a fine powdered mixture;

preforming the fine powdered mixture into a green compact; and

sintering the green compact at a temperature ranging from 900°C to 1400°C to obtain the composite oxide target.

7. The method as claimed in claim 6, wherein the method comprises

a step of screening the powdered mixture with a sieve after the step of grinding the powdered mixture for more than or equal to 48 hours to obtain the fine powdered mixture, and the mesh size of the sieve is from 400 mesh to 600 mesh.

8. The method as claimed in claim 6 or 7, wherein the green compact is sintered for 1.5 hours to 5 hours under a pressure ranging from 300 kilograms per square centimeter to 510 kilograms per square centimeter.

9. The method as claimed in any one of claims 6 to 8, wherein the method comprises a step of providing a powdered additive and mixing the magnesium oxide powders, the titanium (II) oxide powders, and the powdered additive to obtain the powdered mixture; wherein the powdered additive comprises a first powdered additive, a second powdered additive, or a combination thereof; the first powdered additive selected from the group consisting of aluminum oxide powders, zirconium dioxide powders, chromium(III) oxide powders, silicon dioxide powders, and any combination thereof; the particle size of the first powdered additive being less than or equal to 3 micrometers; the second powdered additive selected from the group consisting of aluminum powders, zirconium powders, chromium powders, silicon powders, and any combination thereof; the particle size of the second powdered additive being less than or equal to 50 micrometers; and wherein, based on the total atom number of the powdered mixture, a total atom number of the powdered additive is more than or equal to 1 atomic percent and less than or equal to 6 atomic percent.

10. The method as claimed in any one of claims 6 to 9, wherein the

powdered mixture is ground for more than or equal to 48 hours and less than or equal to 120 hours.