removal rate due to their rough surface while maintaining the same defectuosity thanks to equivalent size distributions compared to dispersions of smooth surface cerium oxide particles having no shell in accordance with the present invention.

The dispersions of cerium based core-shell particles of the invention can be used to prepare powders of cerium based core-shell particles, as well as polishing compositions, as it will be detailed hereafter in the specification.

Additionally, one advantage of the core-shell particles of the invention is that the nanoparticles from the shell are well attached to the core particle. It has notably been observed that they remain attached to the core during the whole chemical mechanical polishing process in which they are implemented. It is all the more important since the particles shells withstand the mechanical stress during the chemical mechanical polishing process. If the nanoparticles of the shell came off during the polishing, these small cerium oxide particles could remain attached to the substrate even after a washing step, which is not acceptable by the end users. It would result in unacceptable costs due to the substrate loss and the recurrent polishing composition replacement.

Another advantage of the core-shell particles of the invention lies in the fact they have the adapted size range for the CMP application and are monodisperse.

In one aspect, the present disclosure provides a process for producing a dispersion of cerium based core-shell particles in a liquid, comprising the following steps:
(a) providing an aqueous dispersion comprising particles of cerium oxide and/ or particles of cerium oxide doped with at least one metal (M); providing an aqueous solution comprising a cerium (III) salt; providing an aqueous peroxygen solution; and optionally providing an aqueous solution comprising at least one metal (M') salt;
(b) contacting the aqueous dispersion with the aqueous solutions provided in step (a), while maintaining the temperature comprised between 0°C and 80°C and the pH lower or equal to 11, to produce the dispersion of cerium based core-shell particles; at least one of the steps (a) and (b) being carried out in the presence of nitrate ions.

In one aspect, there is provided a polishing composition comprising a dispersion of cerium based core-shell particles as described herein or a cerium based core-shell particles powder as described herein.

In another aspect, there is provided a method of removing a portion of a substrate, the method comprising polishing the substrate with a polishing composition prepared from a dispersion as described herein or from a dispersion prepared from a core-shell cerium oxide particles powder as described herein.

FIGURES

Figures 1 is a TEM picture of a dispersion of the core-shell particles of the invention obtained by the process illustrated in example 1, having a cerium oxide core and a cerium oxide shell.

Figures 2 is a SEM picture of a dispersion of the cerium oxide particles intended to be used as core particles in the process illustrated in example 1.

Figures 3 is a TEM picture of a dispersion of the core-shell particles of the invention obtained by the process illustrated in example 2, having a lanthanum doped cerium oxide core and a cerium oxide shell.

Figures 4 is a TEM picture of a dispersion of the core-shell particles of the invention obtained by the process illustrated in example 3, having a cerium oxide core and a lanthanum doped cerium oxide shell.

Comparative example 1:

Example 1 is repeated except for the temperature applied which is of 85°C instead of 35°C.

The dispersion is observed by TEM. It is noted that the starting particles are uncovered by small crystallites (no core-shell structure).

Comparative example 2:

Example 1 is repeated except for the pH which is of 12 instead of 8.

The dispersion is observed by TEM. It is noted that the starting particles are agglomerated and uncovered by small crystallites (no core-shell structure).

Comparative example 3: hydrothermal synthesis

A dispersion of cerium oxide particles in water at 5% in weight is prepared by adding 41.6 g of cerium oxide aqueous dispersion Zenus® commercially available from Solvay (average primary particles size = 60 nm calculated from BET measurements) at 30% in weight in 208.4 g of deionized water. A 1N ammonia solution is prepared by adding 28 g of 28% aqueous ammonia in 771 g of deionized water. A solution of trivalent cerium nitrate solution is prepared by adding 0.75 g of trivalent cerium nitrate solution at 2,87 M in 249.25 g of deionized water.

The cerium oxide suspension at 5% in weight and the trivalent cerium nitrate solution are introduced in a 2L jacketed reactor semi closed and then stirred (agitator with four blades inclined at 300 rpm). The pH of the mixture is adjusted at 11 by the addition of the proper amount of 1N ammonia solution and stirred for two hours. The solution is then transferred to a Teflon bottle and placed in a stainless steel autoclave at 170°C for 12 h.

The dispersion is observed by TEM. It is noted that the starting particles are uncovered by small crystallites (no core-shell structure).

Evaluation of the polishing performance

The polishing machine used is a Struers Tegramin. The surface to be polished is made of amorphous silica. The dispersions of the core-shell particles in water were tested under the following conditions:

- pressure applied on the head: 50N;
- rotation speed: 150 rpm;

CLAIMS

1. A process for producing a dispersion of cerium based core-shell particles in a liquid, comprising the following steps:
   (a) providing an aqueous dispersion comprising particles of cerium oxide and/ or particles of cerium oxide doped with at least one metal (M); providing an aqueous solution comprising a cerium (III) salt; providing an aqueous peroxygen solution; and optionally providing an aqueous solution comprising at least one metal (M') salt;
   (b) contacting the aqueous dispersion with the aqueous solutions provided in step (a), while maintaining the temperature comprised between 0°C and 80°C and the pH lower or equal to 11, to produce the dispersion of cerium based core-shell particles;

   at least one of the steps (a) and (b) being carried out in the presence of nitrate ions.

2. Process according to claim 1, wherein the aqueous dispersion in step (a) comprises at least 3 wt%, in particular at least 5 wt%, in particular at least 10 wt %, in particular at least 15 wt%, more particularly at least 20 wt% of particles of cerium oxide optionally doped with at least one metal (M) relative to the total weight of the aqueous dispersion.

3. Process according to claim 1 or 2, wherein the particles provided in the aqueous dispersion in step (a) are particles of cerium oxide.

4. Process according to claim 1 or 2, wherein the particles provided in the aqueous dispersion in step (a) are particles of cerium oxide doped with at least one metal (M) chosen from the group consisting of alkali metal elements, alkaline earth metal elements, rare earth elements, actinide elements, transition metal elements and post transition metal elements, from the Periodic Table.

5. Process according to claim 4, wherein the metal (M) is chosen from the group consisting of Zr, Al, La, Pr, Nd, Y, and Sr.

6. Process according to claim 4 or 5 wherein the molar ratio M / (M+Ce) in the particles provided in the aqueous dispersion in step (a) is comprised between 0.01 and 0.15, preferably between 0.01 and 0.12.

7. Process according to any one of claims 1 to 6, wherein the aqueous peroxygen solution provided in step (a) is a solution of hydrogen peroxide.

8. Process according to any one of claims 1 to 7, wherein the aqueous solution comprising the at least one metal (M') salt is provided in step (a) and wherein the metal (M') is chosen from the group consisting of alkali metal elements, alkaline earth metal elements, rare earth elements, actinide elements, transition metal elements and post transition metal elements, from the Periodic Table.

9. Process according to claim 8, wherein the metal (M') is chosen from the group consisting of Zr, Al, La, Pr, Nd, Y, and Sr.

10. Process according to claim 8 or 9 wherein the molar ratio M'/(M'+ Ce) in the shell of the core-shell particles produced is comprised between 0.01 and 0.15, preferably between 0.01 and 0.12.

11. Process according to any one of claims 1 to 10 wherein the temperature in step (b) is maintained between 10°C and 60°C, more preferably between 15°C and 45°C, in particular between 20°C and 40°C, more particularly between 25°C and 35°C, even more particularly between 30°C and 35°C.

12. Process according to any one of claims 1 to 11, wherein the pH in step (b) is maintained between 3 and 11, in particular between 4 and 11, in particular between 8 and 11, in particular between 8 and 10, more particularly between 8 and 9.

13. Process according to any one of claims 1 to 12, wherein the molar ratio cerium oxide/cerium (III) before starting step (b) is comprised between 1/1 and 100/1, preferably between 3/1 and 30/1, preferably between 5/1 and 15/1.

14. Process according to any one of claims 1 to 13, further comprising, in any order, a step (c) of acidifying and/or a step (d) of washing the dispersion of cerium based core-shell particles.

15. Process according to any one of claims 1 to 14, further comprising a step (e) of deagglomeration of the cerium based core-shell particles.

16. Process according to any one of claims 1 to 15, further comprising a step (f) of drying the cerium based core-shell particles.

17. Dispersion of cerium based core-shell particles in a liquid obtainable by the process according to any one of claims 1 to 15, wherein each cerium based core-shell particle has a core particle made of cerium oxide optionally doped with at least one metal (M) and a shell consisting of a plurality of nanoparticles of cerium oxide optionally doped with at least one metal (M'), said nanoparticles being formed on the surface of the core particle, wherein the ratio of the average size of the core-shell particles measured by TEM to the average size of the core-shell particles measured by BET is of at least 1.5.

18. Cerium based core-shell particles powder obtainable by the process according to claim 16, wherein each cerium based core-shell particle has a core particle made of cerium oxide optionally doped with at least one metal (M) and a shell consisting of a plurality of nanoparticles of cerium oxide optionally doped with at least one metal (M'), said nanoparticles being formed on the surface of the core particle, wherein the ratio of the average size of the core-shell particles measured by TEM to the average size of the core-shell particles measured by BET is of at least 1.5.

19. Polishing composition comprising a dispersion of cerium based core-shell particles according to claim 17 or a cerium based core-shell particles powder according to claim 18.

20. Use of the dispersion of cerium based core-shell particles of claims 17 or of the cerium based core-shell particles powder of claim 18 for the preparation of a

polishing composition, more particularly a chemical mechanical polishing composition.

21. Method of removing a portion of a substrate, the method comprising polishing the substrate with a polishing composition prepared from a dispersion according to claim 16 or from a dispersion prepared from a core-shell cerium oxide particles powder according to claim 18.