EROSION-CORROSION RESISTANT NITRIDE CERMETS

FIELD OF INVENTION

[0001] The present invention is broadly concerned with cermets, particularly cermet compositions comprising a metal nitride. These cermets are suitable for high temperature applications wherein materials with superior erosion and corrosion resistance are required.

BACKGROUND OF INVENTION

[0002] Erosion resistant materials find use in many applications wherein surfaces are subject to eroding forces. For example, refinery process vessel walls and internals exposed to aggressive fluids containing hard, solid particles such as catalyst particles in various chemical and petroleum environments are subject to both erosion and corrosion. The protection of these vessels and internals against erosion and corrosion induced material degradation especially at high temperatures is a technological challenge. Refractory liners are used currently for components requiring protection against the most severe erosion and corrosion such as the inside walls of internal cyclones used to separate solid particles from fluid streams, for instance, the internal cyclones in fluid catalytic cracking units (FCCU) for separating catalyst particles from the process fluid. The state-of-the-art in erosion resistant materials is chemically bonded castable alumina refractories. These castable alumina refractories are applied to the surfaces in need of protection and upon heat curing hardens and adheres to the surface via metal-anchors or metal-reinforcements. It also readily bonds to other refractory surfaces. The typical chemical composition of one commercially available refractory is 80.0% Al_2O_3, 7.2% SiO_2, 1.0% Fe_2O_3, 4.8% MgO/CaO, 4.5% P_2O_5 in wt%. The life span of the state-of-the-art refractory liners is significantly limited by excessive mechanical attrition of the liner from the high

velocity solid particle impingement, mechanical cracking and spallation. Therefore there is a need for materials with superior erosion and corrosion resistance properties for high temperature applications. The cermet compositions of the instant invention satisfy this need.

[0003] Ceramic-metal composites are called cermets. Cermets of adequate chemical stability suitably designed for high hardness and fracture toughness can provide an order of magnitude higher erosion resistance over refractory materials known in the art. Cermets generally comprise a ceramic phase and a binder phase and are commonly produced using powder metallurgy techniques where metal and ceramic powders are mixed, pressed and sintered at high temperatures to form dense compacts.

[0004] The present invention includes new and improved cermet compositions.

[0005] The present invention also includes cermet compositions suitable for use at high temperatures.

[0006] Furthermore, the present invention includes an improved method for protecting metal surfaces against erosion and corrosion under high temperature conditions.

[0007] These and other objects will become apparent from the detailed description which follows.

SUMMARY OF INVENTION

[0008] The invention includes a cermet composition represented by the formula $(PQ)(RS)$ comprising: a ceramic phase (PQ) and a binder phase (RS) wherein,

P is a metal selected from the group consisting of Si, Mn, Fe, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W and mixtures thereof,

Q is nitride,

R is a metal selected from the group consisting of Fe, Ni, Co, Mn and mixtures thereof,

S consists essentially of at least one element selected from Cr, Al, Si, and Y, and at least one reactive wetting aliovalent element selected from the group consisting of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W and mixtures thereof.

BRIEF DESCRIPTION OF THE FIGURES

[0009] Figure 1 is a scanning electron microscope (SEM) image of TiN cermet made using 30 vol% 304 stainless steel (SS) binder illustrating the TiN ceramic phase particles dispersed in binder and reprecipitation of new phase M_2N where M is mainly Cr, Fe, and Ti.

[0010] Figure 2 is a SEM image of CrN cermet made using 30 vol% 304SS binder illustrating CrN ceramic phase particles dispersed in binder and the reprecipitation of new phase M_2N where M is mainly Cr and Fe.

DETAILED DESCRIPTION OF THE INVENTION

[0011] One component of the cermet composition represented by the formula (***PQ***)(***RS***) is the ceramic phase denoted as (***PQ***). In the ceramic phase (***PQ***), ***P*** is a metal selected from the group consisting of Si, Mn, Fe, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W and mixtures thereof. Thus the ceramic phase (***PQ***) in the nitride cermet composition is a metal nitride. The molar ratio of ***P*** to ***Q*** in (***PQ***) can vary in the range of 1:3 to 3:1. Preferably in the range of 1:2 to 2:1. As non limiting illustrative examples, when ***P*** = Ti, (***PQ***) can be TiN wherein ***P***:***Q*** is about 1:1. When ***P*** = Cr then (***PQ***) can be Cr_2N wherein ***P***:***Q*** is 2:1. The

ceramic phase imparts hardness to the nitride cermet and erosion resistance at temperatures up to about 1000°C.

[0012] The ceramic phase (***PQ***) of the cermet is preferably dispersed in the binder phase (***RS***). It is preferred that the size of the dispersed ceramic particles is in the range 0.5 to 3000 microns in diameter. More preferably in the range 0.5 to 100 microns in diameter. The dispersed ceramic particles can be any shape. Some non-limiting examples include spherical, ellipsoidal, polyhedral, distorted spherical, distorted ellipsoidal and distorted polyhedral shaped. By particle size diameter is meant the measure of longest axis of the 3-D shaped particle. Microscopy methods such as optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) can be used to determine the particle sizes. In another embodiment of this invention, the ceramic phase (***PQ***) is dispersed as platelets with a given aspect ratio, i.e., the ratio of length to thickness of the platelet. The ratio of length:thickness can vary in the range of 5:1 to 20:1. Platelet microstructure imparts superior mechanical properties through efficient transfer of load from the binder phase (***RS***) to the ceramic phase (***PQ***) during erosion processes.

[0013] Another component of the nitride cermet composition represented by the formula (***PQ***)(***RS***) is the binder phase denoted as (***RS***). In the binder phase (***RS***), ***R*** is the base metal selected from the group consisting of Fe, Ni, Co, Mn and mixtures thereof. ***S*** is an alloying metal consisting essentially of at least one element selected from Cr, Al, Si, and Y, and, at least one reactive wetting aliovalent element selected form the group consisting of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W and mixtures thereof. The combined weight of Cr, Al ,Si, Y and mixtures thereof are at least about 12 wt% based on the weight of the binder (***RS***). The reactive wetting aliovalent element is about 0.01 wt% to about 5 wt%, preferably about 0.01 wt% to about 2 wt% of based on the weight of the binder. The elements Ti, Zr, Hf, Ta provide enhanced wetting by reducing the

contact angle between the ceramic (***PQ***) and binder phases (***RS***) in the temperature range of 1300°C to 1750°C. These elements can be added as a pure element during mixing of the nitride and metal powder in processing or can be part of the metal powder prior to mixing with nitride powder. The elements Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W are aliovalent elements characterized by multivalent states when in an oxidized state. These elements decrease defect transport in the oxide scale thereby providing enhanced corrosion resistance.

[0014] In the nitride cermet composition the binder phase (***RS***) is in the range of 5 to 70 vol%, preferably 5 to 45 vol%, and more preferably 5 to 30 vol%, based on the volume of the cermet. The mass ratio of ***R*** to ***S*** can vary in the range from 50/50 to 90/10. In one preferred embodiment the chromium content in the binder phase (***RS***) is at least 12 wt% based on the weight of the binder (***RS***). In another preferred embodiment the combined zirconium and hafnium content in the binder phase (***RS***) is about 0.01 wt% to about 2.0 wt% based on the total weight of the binder phase (***RS***).

[0015] The cermet composition can further comprise secondary nitrides (***P'Q***) wherein ***P'*** is selected from the group consisting of Si, Mn, Fe, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Ni, Co, Al, Y, and mixtures thereof. Stated differently, the secondary nitrides are derived from the metal elements from ***P***, ***R***, ***S*** and combinations thereof of the cermet composition (***PQ***)(***RS***). The ratio of ***P'*** to ***Q*** in (***P'Q***) can vary in the range of 1:3 to 3:1. The total ceramic phase volume in the cermet of the instant invention includes both (***PQ***) and the secondary nitrides (***P'Q***). In the nitride cermet composition (***PQ***) + (***P'Q***) ranges from of about 30 to 95 vol% based on the volume of the cermet. Preferably from about 55 to 95 vol% based on the volume of the cermet. More preferably from 70 to 90 vol% based on the volume of the cermet.

[0016] The volume percent of cermet phase (and cermet components) excludes pore volume due to porosity. The cermet can be characterized by a porosity in the range of 0.1 to 15 vol%. Preferably, the volume of porosity is 0.1 to less than 10% of the volume of the cermet. The pores comprising the porosity is preferably not connected but distributed in the cermet body as discrete pores. The mean pore size is preferably the same or less than the mean particle size of the ceramic phase (*PQ*).

[0017] One aspect of the invention is the micro-morphology of the cermet. The ceramic phase can be dispersed as spherical, ellipsoidal, polyhedral, distorted spherical, distorted ellipsoidal and distorted polyhedral shaped particles or platelets. Preferably, at least 50% of the dispersed particles is such that the particle-particle spacing between the individual nitride ceramic particles is at least about 1 nm. The particle-particle spacing may be determined for example by microscopy methods such as SEM and TEM.

[0018] The cermet compositions of the instant invention possess enhanced erosion and corrosion properties. The erosion rates were determined by the Hot Erosion and Attrition Test (HEAT) as described in the examples section of the disclosure. The erosion rate of the nitride cermets of the instant invention is less than 1.0×10^{-6}cc/gram of SiC erodant. The corrosion rates were determined by thermogravimetric (TGA) analyses as described in the examples section of the disclosure. The corrosion rate of the nitride cermets of the instant invention is less than $1 \times 10^{-10} gm^2/cm^4 sec$.

[0019] The cermets of the instant invention possess fracture toughness of greater than about 3 $MPa \cdot m^{1/2}$, preferably greater than about 5 $MPa \cdot m^{1/2}$, and more preferably greater than about 10 $MPa \cdot m^{1/2}$. Fracture toughness is the ability to resist crack propagation in a material under monotonic loading conditions. Fracture toughness is defined as the critical stress intensity factor at which

a crack propagates in an unstable manner in the material. Loading in three-point bend geometry with the pre-crack in the tension side of the bend sample is preferably used to measure the fracture toughness with fracture mechanics theory. (*RS*) phase of the cermet of the instant invention as described in the earlier paragraphs is primarily responsible for imparting this attribute.

[0020] Another aspect of the invention is the avoidance of embrittling intermetallic precipitates such as sigma phase known to one of ordinary skill in the art of metallurgy. The nitride cermet of the instant invention has preferably less than about 5 vol% of such embrittling phases. The cermet of the instant invention with (*PQ*) and (*RS*) phases as described in the earlier paragraphs is responsible for imparting this attribute.

[0021] The cermet compositions are made by general powder metallurgical technique such as mixing, milling, pressing, sintering and cooling, employing as starting materials a suitable ceramic powder and a binder powder in the required volume ratio. These powders are milled in a ball mill in the presence of an organic liquid such as ethanol for a time sufficient to substantially disperse the powders in each other. The liquid is removed and the milled powder is dried, placed in a die and pressed into a green body. The resulting green body is then sintered at temperatures above about 1200°C up to about 1750°C for times ranging from about 10 minutes to about 4 hours. The sintering operation is preferably performed in an inert atmosphere or a reducing atmosphere or under vacuum. For example, the inert atmosphere can be argon and the reducing atmosphere can be hydrogen. Thereafter the sintered body is allowed to cool, typically to ambient conditions. The cermet prepared according to the process of the invention allows fabrication of the cermet exceeding 5 mm in thickness.

[0022] One feature of the cermets of the invention is their microstructural stability, even at elevated temperatures, making them particularly suitable for

use in protecting metal surfaces against erosion at temperatures in the range of up to about 1000°C. It is believed this stability permits their use for time periods greater than 2 years, for example for about 2 years to about 10 years. In contrast many known cermets undergo transformations at elevated temperatures which results in the formation of phases which have a deleterious effect on the properties of the cermet.

[0023] The high temperature stability of the cermets of the invention makes them suitable for applications where refractories are currently employed. A non-limiting list of suitable uses include liners for process vessels, transfer lines, cyclones, for example, fluid-solids separation cyclones as in the cyclone of Fluid Catalytic Cracking Unit used in refining industry, grid inserts, thermo wells, valve bodies, slide valve gates and guides, catalyst regenerators, and the like. Thus, metal surfaces exposed to erosive or corrosive environments, especially at about 300°C to about 1000°C are protected by providing the surface with a layer of the cermet compositions of the invention. The cermets of the instant invention can be affixed to metal surfaces by mechanical means or by welding.

EXAMPLES

Determination of Volume Percent:

[0024] The volume percent of each phase, component and the pore volume (or porosity) were determined from the 2-dimensional area fractions by the Scanning Electron Microscopy method. Scanning Electron Microscopy (SEM) was conducted on the sintered cermet samples to obtain a secondary electron image preferably at 1000x magnification. For the area scanned by SEM, X-ray dot image was obtained using Energy Dispersive X-ray Spectroscopy (EDXS). The SEM and EDXS analyses were conducted on five adjacent areas of the sample. The 2-dimensional area fractions of each phase was then determined using the image analysis software: EDX Imaging/Mapping Version 3.2 (EDAX

Inc, Mahwah, New Jersey 07430, USA) for each area. The arithmetic average of the area fraction was determined from the five measurements. The volume percent (vol%) is then determined by multiplying the average area fraction by 100. The vol% expressed in the examples have an accuracy of +/-50% for phase amounts measured to be less than 2 vol% and have an accuracy of +/-20% for phase amounts measured to be 2 vol% or greater.

Determination of weight percent:

[0025] The weight percent of elements in the cermet phases was determined by standard EDXS analyses.

[0026] The following non-limiting examples are included to further illustrate the invention.

EXAMPLE 1

[0027] 70 vol% of 2-5 μm average diameter of TiN powder (99.8% purity, from Alfa Aesar) and 30 vol% of 6.7 μm average diameter 304SS powder (Osprey Metals, 95.9% screened below -16 μm) were dispersed with ethanol in HDPE milling jar. The powders in ethanol were mixed for 24 hours with Yttria Toughened Zirconia (YTZ) balls (10 mm diameter, from Tosoh Ceramics) in a ball mill at 100 rpm. The ethanol was removed from the mixed powders by heating at 130°C for 24 hours in a vacuum oven. The dried powder was compacted in a 40 mm diameter die in a hydraulic uniaxial press (SPEX 3630 Automated X-press) at 5,000 psi. The resulting green disc pellet was ramped up to 400°C at 25°C/min in argon and held at 400°C for 30 min for residual solvent removal. The disc was then heated to 1500°C and held at 1500°C for 2 hours at 15°C/min in argon. The temperature was then reduced to below 100°C at -15°C/min.

[0028] The resultant cermet comprised:

i) 70 vol% TiN with average grain size of about 4 μm

ii) 2 vol% secondary nitride M_2N with average grain size of about 1 μm, where M=68Cr:20Fe:12Ti in wt%

iii) 28 vol% Cr-depleted alloy binder (71Fe:11Ni:15Cr:3Ti in wt%).

[0029] Figure 1 is a SEM image of TiN cermet processed according to this example, wherein the bar represents 5 μm. In this image the TiN phase appears dark and the binder phase appears light. The Cr-rich secondary M_2N phase is also shown in the binder phase. By Cr-rich is meant that the metal Cr is of higher proportion than the other constituent metals (M) of the secondary nitride M_2N.

EXAMPLE 2

[0030] 70 vol% of CrN powder (99.8% purity, from Alfa Aesar, 99% screened below 325 mesh) and 30 vol% of 6.7 μm average diameter 304SS powder (Osprey Metals, 95.9% screened below -16 μm) were used to process the cermet disc as described in Example 1. The cermet disc was then heated to 1450°C and held at 1450°C for 1 hour at 15°C/min in argon. The temperature was then reduced to below 100°C at -15°C/min.

[0031] The resultant cermet comprised:

i) 20 vol% CrN with average grain size of about 25 μm

ii) 50 vol% secondary nitride M_2N with average grain size of about 1 μm, where M = Cr, Fe, Ni

iii) 30 vol% Cr-depleted alloy binder.

[0032] Figure 2 is a SEM image of CrN cermet processed according to this example, wherein the bar represents 50 μm. In this image the CrN phase appears dark and the binder phase appears light. The Cr-rich secondary M_2N phase is also shown in the binder phase.

EXAMPLE 3

[0033] Each of the cermets of Examples 1 and 2 was subjected to a hot erosion and attrition test (HEAT). The procedure employed was as follows:

1) A specimen cermet disk of about 35 mm diameter and about 5 mm thick was weighed.

2) The center of one side of the disk was then subjected to 1200g/min of SiC particles (220 grit, #1 Grade Black Silicon Carbide, UK abrasives, Northbrook, IL) entrained in heated air exiting from a tube with a 0.5 inch diameter ending at 1 inch from the target at an angle of 45°. The velocity of the SiC was 45.7 m/sec.

3) Step (2) was conducted for 7 hours at 732°C.

4) After 7 hours the specimen was allowed to cool to ambient temperature and weighed to determine the weight loss.

5) The erosion of a specimen of a commercially available castable refractory was determined and used as a Reference Standard. The Reference Standard erosion was given a value of 1 and the results for the cermet specimens are compared in Table 1 to the Reference Standard. In Table 1 any value greater than 1 represents an improvement over the Reference Standard.

TABLE 1

Cermet {Example}	Starting Weight (g)	Finish Weight (g)	Weight Loss (g)	Bulk Density (g/cc)	Erodant (g)	Erosion (cc/g)	Improvement [(Normalized erosion)$^{-1}$]
TiN/304SS {1}	17.9379	15.8724	2.0655	6.200	5.04E+5	6.6100E-7	1.6
CrN/304SS {2}	19.8637	17.7033	2.1604	6.520	5.04E+5	4.9576E-7	2.1

EXAMPLE 4

[0034] Each of the cermets of Examples 1 and 2 was subjected to an oxidation test. The procedure employed was as follows:

1) A specimen cermet of about 10 mm square and about 1 mm thick was polished to 600 grit diamond finish and cleaned in acetone.

2) The specimen was then exposed to 100 cc/min air at 800°C in thermogravimetric analyzer (TGA).

3) Step (2) was conducted for 65 hours at 800°C.

4) After 65 hours the specimen was allowed to cool to ambient temperature.

5) Thickness of oxide scale was determined by cross sectional microscopy examination of the corrosion surface.

6) In Table 2 any value less than 150 μm represents acceptable corrosion resistance.

TABLE 2

Cermet {Example}	Thickness of Oxide Scale (μm)
TiN-30 304SS {1}	110.0
CrN-25 304SS {2}	1.5

CLAIMS

1. A method for protecting a metal surface subject to erosion at temperatures up to 1000°C, the method comprising providing the metal surface with a cermet composition represented by the formula (***PQ***)(***RS***) comprising: a ceramic phase (***PQ***) and a binder phase (***RS***) wherein,

P is a metal selected from the group consisting of Si, Mn, Fe, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W and mixtures thereof,

Q is nitride,

R is a metal selected from the group consisting of Fe, Ni, Co, Mn and mixtures thereof,

S consists essentially of at least one element selected from Cr, Si, Y and mixtures thereof, and at least one reactive wetting aliovalent element selected from the group consisting of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W and mixtures thereof, wherein the combined weights of said Cr, Si, and Y and mixtures thereof is at least 12 wt% based on the weight of the binder phase (***RS***) and

wherein the ceramic phase (***PQ***) ranges from about 30 to 95 vol% based on the volume of the cermet.

2. The method of claim 1 wherein said surface is subjected to erosion at temperatures in the range of 300°C to 1000°C.

3. The method of claim 1 wherein said surface comprises the inner surface of a fluid-solids separation cyclone.

4. The method of claim 1 wherein the molar ratio of ***P***:***Q*** in the ceramic phase (***PQ***) can vary in the range of 1:3 to 3:1.

5. The method of claim 1 wherein (***PQ***) ranges from of about 55 to 95 vol% based on the volume of the cermet.

6. The method of claim 1 wherein said ceramic phase (***PQ***) is dispersed in the binder phase (***RS***) as spherical particles in the size range of 0.5 microns to 3000 microns diameter.

7. The method of claim 1 wherein the binder phase (***RS***) is in the range of 5 to 70 vol% based on the volume of the cermet and the mass ratio of ***R*** to ***S*** ranges from 50/50 to 90/10.

8. The method of claim 1 wherein said at least one reactive wetting aliovalent element selected from the group consisting of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W and mixtures thereof is in the range of 0.01 to 5 wt% based on the total weight of the binder phase (***RS***).

9. The method of claim 1 further comprising a secondary nitride (***P'Q***) wherein ***P'*** is selected from the group consisting of Si, Mn, Fe, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Ni, Co, Al, Y, and mixtures thereof.

10. The method of claim 1 having a fracture toughness of greater than about 3 MPa $m^{1/2}$.

11. The method of claim 1 having an erosion rate less than about $1x10^{-6}$ cc/gram loss when subject to 1200 g/min of 10 μm to 100 μm SiC particles in air with an impact velocity of at least about 45.7 m/sec (150 ft/sec) and at an impact angle of about 45 degrees and a temperature of at least about 732°C (1350°F) for at least 7 hours.

12. The method of claim 1 having corrosion rate less than about $1x10^{-10}$ $g^2/cm^4 \cdot s$ or an average oxide scale of less than 150 μm thickness when subject to 100 cc/min air at 800°C for at least 65 hours.

13. The method of claim 1 having an erosion rate less than about $1x10^{-6}$ cc/gram when subject to 1200 g/min of 10 μm to 100 μm SiC particles in air with an impact velocity of at least about 45.7 m/sec (150 ft/sec) and at an impact angle of about 45 degrees and a temperature of at least about 732°C (1350°F) for at least 7 hours and a corrosion rate less than about $1x10^{-10}$ $g^2/cm^4 \cdot s$ or an average oxide scale of less than 150 μm thickness when subject to 100 cc/min air at 800°C for at least 65 hours.

14. The method of claim 1 having embrittling phases less than about 5 vol% based on the volume of the cermet.

15. The method of claim 1 wherein the overall thickness of the cermet composition is greater than 5 millimeters.