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**EROSION-CORROSION RESISTANT CARBIDE
CERMETS FOR LONG TERM HIGH TEMPERATURE SERVICE**

FIELD OF INVENTION

[0001] The present invention relates to cermet compositions. More particularly the invention relates to chromium carbide containing cermet compositions and their use in high temperature erosion and corrosion applications.

BACKGROUND OF INVENTION

[0002] Abrasive and chemically resistant materials find use in many applications where metal surfaces are subjected to substances which would otherwise promote erosion or corrosion of the metal surfaces.

[0003] Reactor vessels and transfer lines used in various chemical and petroleum processes are examples of equipment having metal surfaces that often are provided with materials to protect the surfaces against material degradation. Because these vessels and transfer lines are typically used at high temperatures protecting them against degradation is a technological challenge. Currently refractory liners are used to protect metal surfaces exposed at high temperature to erosive or corrosive environments. The lifespan of these refractory liners, however, is significantly limited by mechanical attrition of the liner, especially when exposed to high velocity particulates, often encountered in petroleum and petrochemical processing. Refractory liners also commonly exhibit cracking and spallation. Thus, there is a need for liner material that is more resistant to erosion and corrosion at high temperatures.

[0004] Ceramic metal composites or cermets are known to possess the attributes of the hardness of ceramics and the fracture toughness of metal but

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only when used at relatively moderate temperatures, for example, from 25°C to no more than about 300°C. Tungsten carbide (WC) based cermets, for example, have both hardness and fracture toughness making them useful in high wear applications such as in cutting tools and drill bits cooled with fluids. WC based cermets, however, degrade at sustained high temperatures, greater than about 600°F (315°C).

[0005] Chromium carbide has been a potentially suitable ceramic phase for use in cermets because its three crystallographic forms: the cubic (Cr_{23}C_6) the hexagonal (Cr_7C_3) and the orthorhombic (Cr_3C_2) have excellent oxidation resistance at elevated temperatures; yet cermets formed from these carbides typically undergo transformations at elevated temperatures which result in the formation of microstructural phases which have a deleterious effect on the properties of such cermets.

[0006] The object of the present invention is to provide new and improved cermet compositions.

[0007] Another object of the invention is to provide chromium carbide containing cermet compositions suitable for use at high temperatures.

[0008] Another object of the invention is to provide chromium carbide containing cermet compositions with long term microstructural stability suitable for long term service at high temperatures.

[0009] Yet another object of the invention is to provide an improved method for protecting metal surfaces against erosion and corrosion under high temperature conditions.

[0010] These and other objects will become apparent from the detailed description which follows.

SUMMARY OF INVENTION

[0011] Broadly stated, the present invention is a cermet composition comprising a chromium carbide ceramic phase dispersed in a binder phase. The ceramic phase which constitutes about 50 vol% to about 95 vol% of the total volume of the cermet composition is a chromium carbide selected from the group consisting of Cr_{23}C_6 , Cr_7C_3 , Cr_3C_2 and mixtures thereof.

[0012] The binder phase is selected from the group consisting of (i) alloys containing about 60 wt% to about 98 wt% Ni; about 2 wt% to about 35 wt% Cr; and up to 5 wt% of an element selected from the group consisting of Al, Si, Mn, Ti and mixtures thereof; and (ii) alloys containing about 0.01 wt% to about 35 wt% Fe; about 25 wt% to about 97.99 wt% Ni, about 2 wt% to about 35 wt% Cr; and up to about 5 wt% of an element selected from the group consisting of Al, Si, Mn, Ti and mixtures thereof, the wt% in each instance based on the total weight of the alloy.

[0013] This and other embodiments of the invention, including where applicable those preferred, will be elucidated in the detailed description which follows.

BRIEF DESCRIPTION OF THE FIGURES

[0014] Figure 1 is a scanning electron microscopy (SEM) image of the surface of a cermet made with an initial Cr_3C_2 in 30 vol% Ni-20 Cr binder. Ni-20 Cr indicates 80 wt% Ni and 20 wt% Cr.

[0015] Figure 2 is a SEM image of the surface of a cermet made with an initial Cr_7C_3 in 30 vol% Ni-20 Cr binder.

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[0016] Figure 3 is a SEM image of the surface of a cermet made with an initial Cr_{23}C_6 in a 30 vol% Ni-20 Cr binder.

[0017] Figure 4 is a SEM image of the surface of a cermet made with an initial Cr_3C_2 in a 30vol% 304 stainless steel (304SS) binder after exposure to 800°C for 1000 hours.

DETAILED DESCRIPTION OF THE INVENTION

[0018] In one embodiment the invention is a cermet composition comprising a chromium carbide ceramic phase dispersed in a continuous binder phase.

[0019] The ceramic phase constitutes about 50 vol% to about 95 vol% of the total volume of the cermet composition, the ceramic phase being a chromium carbide selected from the group consisting of Cr_{23}C_6 , Cr_7C_3 , Cr_3C_2 , where this group is intended to include sub and super stoichiometric variances thereof.

[0020] The particle size diameter of the ceramic phase typically is below about 3 mm, preferably below about 100 μm and more preferably below about 50 μm . 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.

[0021] The binder phase is selected from the group consisting of (i) alloys containing about 60 wt% to about 98 wt% Ni; about 2 wt% to about 35 wt% Cr; and up to about 5 wt% of an element selected from the group consisting of Al, Si, Mn, Ti and mixtures thereof; and (ii) alloys containing about 0.01 wt% to

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about 35 wt% Fe; about 25 wt% to about 97.99 wt% Ni, about 2 wt% to about 35 wt% Cr; and up to about 5 wt% of an element selected from the group consisting of Al, Si, Mn, Ti and mixtures thereof, the wt% in each instance based on the total weight of the alloy.

[0022] Illustration of cermet compositions suitable for use at elevated temperatures include:

(1) about 50 vol% Cr_7C_3 in a binder comprising 78 wt% Ni, about 4 wt% Fe and 18 wt% Cr;

(2) about 70 vol% Cr_7C_3 in a binder comprising 78 wt% Ni, about 4 wt% Fe and 18 wt% Cr;

(3) about 94 vol% Cr_7C_3 in a binder comprising 75 wt% Ni, about 7 wt% Fe, and about 18 wt% Cr;

(4) about 50 vol% Cr_{23}C_6 in a binder comprising 72 wt% Ni, about 10 wt% Fe, and 18 wt% Cr;

(5) about 50 vol% Cr_{23}C_6 in a binder comprising 67 wt% Ni, 15 wt% Fe and 18 wt% Cr; and

(6) about 90 vol% Cr_{23}C_6 in a binder comprising 77 wt% Ni, 5 wt% Fe and 18 wt% Cr.

[0023] Preferred cermet compositions are the follows:

- (1) 50 vol% to 90 vol% Cr_{23}C_6 in binder (i);
- (2) 50 vol% to 90 vol% Cr_7C_3 in binder (i);
- (3) 65 vol% to 95 vol% of a mixture of Cr_3C_2 and Cr_7C_3 where the latter is about 1 vol% to about 18 vol% of the mixture and binder (i).
- (4) 50 vol% to 95 vol% of Cr_3C_2 in binder (i).

[0024] The cermet compositions are made by general powder metallurgical techniques such as mixing, milling, pressing, sintering and cooling, employing as starting materials a chromium carbide ceramic powder and a binder powder in

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the volume ratio of 50:50 to 95:5 respectively. Preferably the chromium carbide powder is one of Cr_{23}C_6 , Cr_7C_3 and Cr_3C_2 although mixtures of these may be used. Preferably the binder is one of the alloy compositions set forth in Table 1.

Table 1

Alloy Type	Composition (wt%)
NiCr	Bal Ni:20 Cr
NiCrSi	Bal Ni:20.1 Cr:2.0 Si:0.4 Mn:0.09 Fe
FeNiCr	Bal Fe:> 12 Cr > 36 Ni

Bal = Balance

[0025] These powders are milled in a ball mill in the presence of a sufficient amount 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 green body is then sintered at temperatures above about 1200°C up to about 1600°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 instance, 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 production according to the process described herein allows fabrication of bulk cermet bodies exceeding 5 mm in thickness.

[0026] These processing conditions result in the dispersion of the carbide or carbides in the binder. Additionally, the processing results in some compositional changes in the ceramic and binder. For example when the carbide ceramic employed is Cr_3C_2 and the binder is a Ni-20Cr alloy, the resultant cermet contained both Cr_3C_2 and Cr_7C_3 phases with some depletion of Cr in the binder

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phase. On the other hand, when the ceramic employed is Cr_{23}C_6 in the same binder there is substantially no change in the composition of the ceramic.

[0027] 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 chromium carbide ceramic phase.

[0028] One feature of the cermets of the invention is their long term microstructural stability, even at elevated temperatures, making them particularly suitable for use in protecting metal surfaces against erosion at temperatures in the range of about 300°C to about 1000°C. This stability permits their use for prolonged time periods, for example greater than 2 years. In contrast many known cermets undergo transformations at elevated temperatures which result in the formation of phases which have a deleterious effect on the properties of the cermet.

[0029] The long term microstructural stability of the cermets of the instant invention was confirmed by computational thermodynamics using calculation of phase diagram (CALPHAD) methods known to one of ordinary skill in the art of computational thermodynamic calculation methods. These calculations confirmed that the various carbide phases, their amounts, the binder amount and the respective chemistries lead to cermet compositions with long term microstructural stability. Further, lab experiments were conducted in which the cermet compositions of the instant invention were exposed at 800°C for 1000 hours in air. Analysis of the bulk microstructure of the resultant cermet after this

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1000h high temperature exposure showed that the starting microstructure was substantially preserved as determined by SEM.

[0030] The cermet compositions of the instant invention can exhibit long term microstructural stability lasting at least 25 years when exposed to temperatures up to 1000°C.

[0031] Another feature of the cermets of this invention is that they have fracture toughness of greater than about $3 \text{ MPa}\cdot\text{m}^{1/2}$, preferably greater than about $5 \text{ MPa}\cdot\text{m}^{1/2}$, and most preferably greater than about $10 \text{ MPa}\cdot\text{m}^{1/2}$. 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. The binder phase of the cermet of the instant invention as described in the earlier paragraphs is primarily responsible for imparting this attribute.

[0032] 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, side 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 ceramic 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:

[0033] 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:

[0034] The weight percent of elements in the cermet phases was determined by standard EDXS analyses.

[0035] The following non-limiting examples are included to further illustrate the invention.

EXAMPLE 1

[0036] 70 vol% of 14.0 μ m average diameter of Cr₃C₂ powder (99.5% purity, from Alfa Aesar) and 30 vol% of Ni-20Cr alloy binder powder (Alfa Aesar,

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screened below 325 mesh) were dispersed with ethanol in high density polyethylene milling jar. The powders in ethanol were mixed for 24 hours with yttria toughened zirconia 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 for 30 min for residual solvent removal. The disc was then heated to 1450°C at 15°C/min in argon and held at 1450°C for 1 hour. The temperature was then reduced to below 100°C at -15°C/min.

[0037] The resulting cermet comprises:

- i) 63 vol% Cr_3C_2 with average grain size of 20 μm
- ii) 12 vol% Cr_7C_3 with average grain size of 20 μm
- iii) 25 vol% Cr-depleted alloy binder (87Ni:13Cr in wt%).

[0038] Figure 1 is a SEM image of the cermet processed according to this example, wherein the bar represents 20 μm . In this image the chromium carbide phase appears light and the binder phase appears dark.

EXAMPLE 2

[0039] The mixing and pressing procedures of Example 1 was followed using 70 vol% of 14.0 μm average diameter of Cr_7C_3 powder (99.5% purity, from Alfa Aesar) and 30 vol% of Ni-20Cr alloy binder powder (Alfa Aesar, screened below 325 mesh). The disc was then heated to 1400°C for 1 hour at 15°C/min in hydrogen. The temperature was then reduced to below 100°C at -15°C/min.

[0040] The resulting cermet comprised:

- i) 67 vol% Cr_7C_3 with average grain size of 20 μm

ii) 33 vol% Cr-enriched alloy binder (76Ni:24Cr in wt%).

[0041] Figure 2 is a SEM image of the cermet processed according to this example, wherein the bar represents 20 μ m. In this image the chromium carbide phase appears light and the binder phase appears dark.

EXAMPLE 3

[0042] The procedure of Example 2 was followed using 70 vol% of 14.0 μ m average diameter of Cr₂₃C₆ powder (99.5% purity, from Alfa Aesar) and 30 vol% of Ni-20Cr alloy binder powder (Alfa Aesar, screened below 325 mesh).

[0043] The result cermet comprised of:

- i) 67 vol% Cr₂₃C₆ with average grain size of 20 μ m
- ii) 33 vol% Cr-enriched alloy binder (69Ni:31Cr in wt%).

[0044] Figure 3 is a SEM image of the cermet processed according to this example, wherein the bar represents 20 μ m. In this image the chromium carbide phase appears light and the binder phase appears dark.

EXAMPLE 4

[0045] The procedure of Example 2 was followed using 85 vol% of 14.0 μ m average diameter of Cr₃C₂ powder (99.5% purity, from Alfa Aesar) and 15 vol% of Ni-20Cr alloy binder powder (Alfa Aesar, screened below 325 mesh).

[0046] During heating, some Cr₃C₂ phase is replaced by Cr₇C₃ phase. As result, carbide volume fraction increases and Cr content is depleted in the binder. The result cermet comprised of:

- i) 80 vol% Cr₃C₂ with average grain size of 20 μ m
- ii) 7 vol% Cr₇C₃ with average grain size of 20 μ m

iii) 13 vol% Cr-depleted alloy binder (85Ni:15Cr in wt%).

EXAMPLE 5

[0047] The cermet compositions of examples 1, 2 and 3 were exposed in air at 800°C for 1000 hours in a Lindberg box furnace. After exposure the samples were analyzed using SEM. No significant precipitation of new phases, change in the proportion of the original phase composition or change in the respective chemistry was observed in any of the 3 aforesaid samples. Thus the cermet composition of example 1, 2 and 3 were determined to possess long term microstructural stability.

EXAMPLE 6 (COMPARATIVE EXAMPLE)

[0048] A comparative example of a system that does not form a preferred thermodynamically stable cermet is prepared using the procedure of Example 1 and 70 vol% of 14.0µm average diameter of Cr₃C₂ powder (99.5% purity, from Alfa Aesar) and 30 vol% of 6.7µm average diameter 304SS alloy binder powder (Osprey Metals, Fe(balance):18.5Cr:9.6Ni:1.4Mn:0.63Si, 95.9% screened below -16µm). The disc was then heated to 1400°C at 15°C/min in argon and held at 1400°C for 1 hour. During heating, a significant vol% of Cr₃C₂ phase is replaced by Cr₇C₃ phase. As net result, carbide volume fraction increases and Cr content is depleted in the binder.

[0049] The result cermet comprised of the non-equilibrium microstructure:

- i) 8 vol% Cr₃C₂ with average grain size of 20µm
- ii) 72 vol% Cr₇C₃ with average grain size of 20µm
- iii) 20 vol% Cr-depleted alloy binder

[0050] Next, the sintered disc was heated in air at 800°C for 1000 hours. After exposure to 800°C in air for 1000 hours this cermet comprises:

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- i) >9.5 vol% Cr_3C_2
- ii) >85.5 vol% Cr_7C_3
- iii) <5 vol% Cr-depleted alloy binder (13.2Si:9.4Cr:8.9Fe:68.5Ni in wt%).

[0051] Figure 4 is a SEM image of the cermet after heating in air according to this example, wherein the bar represents 10 μm . In this image the chromium carbide phase appears light and the binder phase appears dark. This figure shows < 5 vol% 304SS and > 95 vol% chrome carbides after this relative short-term exposure to high temperature. The metal composition has become depleted in chromium content thereby decreasing the fracture toughness of the cermet.

EXAMPLE 7

[0052] Each of the cermets of Examples 1 to 4 was subjected to a hot erosion and attrition test (HEAT) and was found to have an erosion rate of less than 1.0×10^{-6} cc/gram SiC erodant. 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 hrs at 732°C.
- 4) After 7 hrs 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 2 to the Reference Standard. In Table 2 any value greater than 1 represents an improvement over the Reference Standard.

Table 2

Cermet {Example}	Starting Weight (g)	Finish Weight (g)	Weight Loss (g)	Bulk Density (g/cc)	Erodant (g)	Erosion (cc/g)	Improvement [(Normalized erosion) ⁻¹]
Cr3C2 L 30 NiCr {1}	18.6737	15.0660	3.6077	7.350	5.04E+5	7.3766E-7	1.4
Cr7C3 L 30 NiCr {2}	23.6681	21.0301	2.6380	7.360	5.34E+5	6.7121E-7	1.6
Cr23C6 L 30 NiCr {3}	23.5976	21.6016	1.9960	7.350	5.04E+5	5.3882E-7	1.9
Cr3C2 L 15 NiCr {4}	19.6071	17.6609	1.9462	7.090	5.04E+5	5.4464E-7	1.9

EXAMPLE 8

[0053] Each of the cermets of Examples 1 to 4 was subjected to a corrosion test and found to have a corrosion rate less than about $1.0 \times 10^{-11} \text{ g}^2/\text{cm}^4\text{s}$. 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) All the thickness of oxide scale formed on specimen surface was less than 1 μm , representing superior corrosion resistance.

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CLAIMS:

1. A cermet composition comprising:

(a) about 50 vol% to about 95 vol%, based on the total volume of the cermet composition, of a ceramic phase, wherein the ceramic phase being a chromium carbide selected from the group consisting of Cr_{23}C_6 , Cr_7C_3 , Cr_3C_2 and mixtures thereof; and

(b) a binder phase selected from the group consisting of

(i) alloys containing, based on the total weight of the alloy, about 60 wt% to about 98 wt% Ni; about 2 wt% to about 35 wt% Cr; and up to about 5 wt% of an element selected from the group consisting Al, Si, Mn, Ti and mixtures thereof; and

(ii) alloys containing about 0.01 wt% to about 35 wt% Fe; about 25 wt% to about 97.99 wt% Ni, about 2wt% to about 35 wt% Cr; and up to about 5 wt% of an element selected from the group consisting of Al, Si, Mn, Ti and mixtures thereof,

2. The composition of claim 1 wherein the binder is (i).

3. The composition of claim 2 wherein the chromium carbide is Cr_{23}C_6 .

4. The composition of claim 2 wherein the chromium carbide is Cr_7C_3 .

5. The composition of claim 2 wherein the chromium carbide is a mixture of Cr_3C_2 and Cr_7C_3 .

6. The composition of claim 2 wherein the chromium carbide is Cr_3C_2 .

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7. The composition of claim 1 wherein the binder is (ii).
8. The cermet compositions as in any one of the preceding claims having a long term microstructural stability lasting at least 25 years when exposed at temperatures up to 1000°C.
9. A method for protecting a metal surface exposed to an erosive material at temperatures in the range of 300°C to 850°C, the method comprising providing the metal surface with a cermet composition according to claims 1-7.
10. The method of claim 9 wherein said surface comprises the inner surface of a fluid-solids separation cyclone.