METHOD OF PREPARATION OF A METAL / CEMENTED CARBIDE FUNCTIONALLY GRADED MATERIAL

Technical field

[0001] The present invention relates generally to a method of preparation of a metal / cemented carbide, such as a steel / cemented tungsten carbide, functionally graded material shape by sintering, preferably by spark plasma sintering (SPS).

Background art

[0002] Previous attempts have been made to consolidate a steel / cemented tungsten carbide gradient component (as a complete tool without brazing) which can be used as a carbide tool in areas where components are exposed to excessive wear and shocks, such as cutting picks used in the mining industry, and wear graders in the road maintenance applications e.g. snow plows and road cleaning, etc. Preferred materials to combine are for example steel and cemented tungsten carbide to offer a tough steel base with a hard and wear resistant carbide surface.

[0003] The common cemented carbide graded tools are usually fabricated by making tungsten carbide (WC, often referred to as hard metal) bi-layers with different content of binder phase, such as cobalt (Co), and/or various tungsten carbide grain sizes and sinter-bonding them with steel. This process is metastable and the graded microstructure is very sensitive to the sintering conditions such as sintering temperature, holding time and other factors. It is usually difficult to make a final material with a cobalt gradient because of the flow of liquid phase cobalt and its homogenization during sintering at high temperature.

[0004] An alternative is to make a gradient composition which changes from the steel base to the cemented carbide surface, i.e. a functionally graded material (FGM).

[0005] A functionally graded material (FGM) is a material design concept which provides a joining solution to relieve the residual thermal stresses and to incorporate incompatible properties of two dissimilar materials, such as the heat, the wear, and the oxidation resistance of a refractory ceramic, such as for example cemented carbide, with the high toughness, the high strength, and the machinability of a metal, such as steel, by placing graded composite interlayers of the two materials between the pure end layers.

[0006] Generally, in a metal / ceramic FGM system with a graded region consisting of several composite layers, there is a gradual variation of the microstructure with the composition change. The matrix is replaced gradually from metal to ceramic, and the microstructure profile varies concurrently from (i) a pure metal, (ii) a metal-rich region (the ceramic particles are dispersed in metal matrices), (iii) intertwined composites (networks of metal and ceramic phases with comparable volume fractions), (iv) a ceramic-rich region (the metal matrix diminishes and turns into discrete phases or particles in ceramic matrices), to finally (v) a pure ceramic.

[0007] FGMs can be prepared through different techniques such as conventional powder metallurgy processing, vapour deposition and sintering techniques. The spark plasma sintering method (SPS), also referred to as for example field assisted sintering technique (FAST), is a powerful sintering technique which allows very rapid heating under high mechanical pressures. This process, hereafter referred to as SPS, has proved to be very well suited for the production of functionally graded materials. Other sintering techniques could possibly also be used for preparing FGMs, such as for example direct hot-pressing, hot-pressing or hot isostatic pressing.

[0008] For materials such as steel / tungsten carbide, there is a difference in the materials' sintering temperatures. In this case tungsten carbide has the higher sintering temperature, approximately 200°C higher than steel. It is necessary to sinter the FGM component at a proper temperature at which the whole component can be fully sintered. When sintering, especially when using spark plasma sintering, it is critical not to sinter steel or stainless steel alloys above around 1000°C otherwise melting occurs due to local overheating spots, which can reach a temperature close to the melting point of steel, i.e. ≈1500°C. On the other hand, the appropriate sintering temperature of tungsten carbide by SPS is generally 100-200°C higher than this limit. The sintering temperature is influenced by the tungsten carbide grain size and the content of binder material.

[0009] One method of preparing a cemented carbide / steel FGM is described in paper J Jpn Soc Powder Powder Metall. Vol 47, No 5, pp. 564-568, 2000, wherein a Japanese group reported the preparation of cemented carbide / steel FGM using SPS by sinter bonding WC-Co bi-layers with a steel substrate. The FGM had a gradient in WC grain size and cobalt composition. It consisted of 3 layers: steel/WC-40Co/WC-25Co. The particle size of WC in the surface layer is coarser than that in the middle layer and the end product was not fully dense. They have used the material in oil well drilling tools.

[0010] At the 2002 International Conference on Functionally Graded Materials, NJ, D. K. Agrawal et al. presented a method of producing compositionally gradient steel / tungsten carbide-cobalt-diamond FGM systems (steel / WC-25Co-dia FGM) by microwave heating. In-situ hot pressing was needed to prevent mushrooming of sintered samples. The outcome of the production process was fairly dense product depending on the steel composition, the sintering temperature and the diamond coating type. When using microwave heating, a special and expensive equipment has to be used.

[0011] In US2007/0214913 A1, the formation of various bi-layers WC-Co FGM by liquid phase sintering (LPS) is described. Because the liquid phase cobalt normally homogenizes during sintering, a complex process of enriching/deficienting each layer with an element of for example carbon is used. The exact gradient composition will be a function of the sintering time and temperature and the dimension of the part to be made.

[0012] Another way of preparing a tungsten carbide / stainless steel FGM (stainless steel / WC-25Co) by SPS is presented by Y. Kawakami et al. in Solid State Phenomena Vol 127, pp. 179-184, 2007. Here they tried to prepare the compositionally gradient material by using a special shape graphite mold set (with upper thinner part and lower thicker part) to overcome the difference between the two sintering temperatures of stainless steel and tungsten carbide. Even so, it was hard to obtain a properly sintered body and the process is sensitive to the sintering temperature and the number of graded layers.

[0013] Therefore, there is a need for a simple yet effective production method for the fabrication of a metal / cemented carbide functionally graded material (preferably a steel/tungsten carbide FGM) that is highly dense and has no cracking.

Summary of invention

[0014] An object of the present invention is to prepare a metal / cemented carbide functionally graded material by sintering, preferably by spark plasma sintering (SPS), in order to combine a tough metal base with a hard carbide surface in an economical way. The functionally graded material can be a steel/cemented tungsten carbide (steel / WC-Co FGM). The end product is a fully dense compositionally gradient shape with pure metal and pure cemented carbide alloy as two end surfaces (pure metal layer / x number of composite layers / pure cemented carbide layer).

[0015] The term "cemented" means that the carbide alloy powder includes an amount of metallic binder, such as for example cobalt, nickel, iron, or their alloys. During the sintering process, the tungsten carbide particles are captured in the metallic binder and cemented together by forming a metallurgical bond.

[0016] The base layer can be a steel alloy, a stainless steel alloy or other metallic material.

[0017] Thus, the invention relates to a method of preparation of a FGM shape with a first surface comprising up to 100% of a first material and a second surface comprising up to 100% of a second material. The method is characterized in that it comprises the steps of:

selecting the first material with a first sintering temperature and a first melting temperature and the second material with a second sintering temperature and a second melting temperature , wherein the first melting temperature is higher than the second melting temperature,

loading a first layer of the first material in a sintering mold referred to as die,

adding at least one intermediate layer on the first layer, the intermediate layer comprising a mix of the first and second material creating an intermediate graded composite region,

loading a second layer of the second material on the at least one intermediate layer,

adding an electrically insulating layer on the second layer of the second material,

adding a pressure on the layers creating a FGM shape, and

sintering the whole shape under a predetermined time, pressure and temperature.

[0018] The layers are preferably added as powders, but solid blocks of the pure materials and composites can also be used.

[0019] When using this method for creating a FGM-shape, the electrically insulating layer added on the second material enforces the current from the sintering process to flow only through the die and not through the second layer of the FGM-shape. Thus, the temperature increase in the second layer becomes limited. The temperature in the first layer is high enough to sinter the first material but it does not exceed the melting temperature of the second material. The resulting end product from the process is a near fully dense FGM without any melted material.

[0020] In embodiments of the invention said first material is a cemented carbide and said second material is a metal, preferably said first material is cemented tungsten carbide and said second material is steel.

[0021] When using a cemented carbide, such as for example cemented tungsten carbide, and combining it with a metal, preferably steel, it is possible to combine the high wear resistance of the carbide with the high toughness, the high strength, and the machinability of the metal. Due to the different sintering and melting temperatures of the respective materials, these materials are especially suitable to sinter using the above described inventive method.

[0022] In another embodiment, the first material includes a metallic binder. The metallic binder may be cobalt and the amount of cobalt can be between 5 and 25wt%.

[0023] During the sintering process, the carbide particles are captured in the metallic binder and cemented together by forming a metallurgical bond. The result is a more dense FGM.

[0024] In another embodiment, said electrically insulating layer is chosen from any of the materials boron nitride, alumina, zirconia, silicon nitride, aluminum nitride, silica, magnesia.

[0025] All above mentioned materials are electrically insulating. When steel/cemented tungsten carbide FGM is sintered, the most preferred insulating material is boron nitride. The insulating layer can either be a powder or a solid disc.

[0026] In one embodiment of the method, the sintering takes place under a sintering temperature of between 1000 °C and 1200 °C, preferably between 1050°C and 1150°C, more preferably between 1070 °C and 1120°C and most preferably 1100 °C, a pressure of between 20 and 120 MPa, preferably between 50 and 90 MPa, more preferably between 65 and 80 MPa and most preferably 75 MPa, and a sintering time of between 5 and 30 min, preferably between 10 and 20 min, more preferably 15 min.

[0027] In one embodiment the shape is sintered using one of the following sintering techniques; spark plasma sintering (SPS) or direct hot pressing (DHP). Possible sintering techniques are also hot pressing (HP) or hot isostatic pressing (HIP). But preferably, spark plasma sintering (SPS) is used.

[0028] In another embodiment, the sintering pressure is applied through two punches arranged on opposite sides of the loaded material in the die.

[0029] In one embodiment, the dies are lined with a graphite foil and this is also inserted between the first and second surface of the FGM shape and the two punches. In another embodiment, the dies are graphite dies surrounded by graphite felt.

[0030] The graphite foil ensures good electric and thermal contacts between the die and the punches and also facilitates removal of the sintered compact without damaging the die or punch surfaces.

[0031] In one embodiment of the method, the method further comprises the step:

removing the electrically insulating layer after the sintering process has been performed.

[0032] Removal of the remains of the insulating layer after sintering can be performed through sand blasting or similar. The end product is a pure FGM ready to be manufactured into a cemented carbide tool.

[0033] All individual features of the above methods may be combined or exchanged unless such combination or exchange is clearly contradictory.

[0034] The sintering conditions, such as holding time and pressure, depend on the size of the FGM shape and the die dimension.

Brief description of drawings

[0035] The invention is now described, by way of example, with reference to the accompanying drawings, in which:

Fig. 1 shows a longitudinal cross-section of a FGM die setup

Table 1 lists the relative densities and the sintering conditions during sintering of individual steel and cemented carbide powders by SPS

Table 2 lists the relative densities and the sintering conditions during sintering of steel / WC-Co FGM compacts by SPS at 1100°C/75MPa/15min/50°C/min.

Description of embodiments

[0036] The invention will now be described in more detail in respect of embodiments and in reference to the accompanying drawings. All examples herein should be seen as part of the general description and therefore possible to combine in any way in general terms. Again, individual features of the various embodiments and methods may be combined or exchanged unless such combination or exchange is clearly contradictory to the overall method of production of the functionally graded material shape.

[0037] FIG. 1 shows a longitudinal cross-section of the die setup for producing a FGM-shape 4 according to the invention. Powders of at least a first and a second material M1, M2 are sintered under a pressure created by punches 3a, 3b in a die 1, preferably a graphite die. The sintering process creates samples of the FGM shape 4, for example cylindrical-shaped discs. Other shapes including any polygonal-shaped discs can also be sintered. The sintering process is performed by spark plasma sintering under a high temperature and pressure on the closed die to create a dense/near fully dense FGM-shape. The powder layers to be sintered can be cold-pressed prior to the sintering. The sintering takes preferably place at a sintering temperature of between 1000 °C and 1200 °C, preferably between 1050°C and 1150°C, more preferably between 1070 °C and 1120°C and most preferably 1100 °C, a pressure of between 20 and 120 MPa, preferably between 50 and 90 MPa, more preferably between 65 and 80 MPa and most preferably 75 MPa, and a sintering time of between 5 and 30 min, preferably between 10 and 20 min, more preferably 15 min. Different sintering techniques can be used, such as for example spark plasma sintering (SPS) or direct hot pressing (DHP). Preferably spark plasma sintering (SPS) is used. Other sintering techniques are also hot pressing (HP) or hot isostatic pressing (HIP).

[0038] The FGM shape has a first layer l1 with a first surface 4a comprising up to 100% of the first material M1 and a second layer l2 with a second surface 4b comprising up to 100% of the second material M2. Between the first layer l1 of the first material M1 and the second layer l2 of the second material M2 at least one third layer l3 comprising a mix of the first and second material M1, M2 is added. The at least one third layer is creating an intermediate graded composite region 1c. Preferably the numbers of graded layers are between two and ten, with a 50-10vol% gradient change. However, other numbers of layers are of course also possible, as is a non-linear gradient change in composition.

[0039] The first material M1 has a first sintering temperature Ts1 and a first melting temperature Tm1 and the second material M2 has a second sintering temperature Ts2 and a second melting temperature Tm2. The first melting temperature Tm1 is higher than the second melting temperature Tm2. Thus, in order to achieve a fully dense FGM-shape, the sintering temperature during the SPS-process needs to reach the first sintering temperature Ts1 of the first material but not exceed the second melting temperature Tm2 of the second material. Otherwise, this can lead to melting of the second material M2.

[0040] In order to decrease the temperature increase locally in the second material M2, an electrically insulating layer 5 of an electrically insulating powder is placed on the second surface 4b of the FGM-shape 4, between the second layer l2 of the second material M2 and the graphite punch 3b. The function of the electrically insulating powder is to enforce the current to flow only through the die and not through the second layer l2 of the FGM-shape.

[0041] The first material M1 is preferably a cemented carbide and the second material M2 a metal. More preferably, the first material M1 is cemented tungsten carbide and the second material M2 is steel. The first material M1 includes a metallic binder such as for example cobalt Co or an iron-nickel alloy Fe-Ni.

[0042] The electrically insulating layer can be chosen from any of the electrically insulating materials of boron nitride, alumina, zirconia, silicon nitride, aluminum nitride, silica, magnesia, but preferably boron nitride BN is used. This material can either be a powder or a solid disc.

[0043] The inner walls of the dies 1 can be lined with thin graphite foil 2 inserted between the shape 4 and the two punches 3a, 3b. A graphite foil can also be inserted between the first and second surface 1a, 1b of the FGM shape 1 and the two punches (3a, 3b). The graphite foil 2 ensures good electric and thermal contacts between the die 1 and the punches 3a, 3b, and also facilitates removal of the sintered compact without damaging the die 1 or punch surfaces 3a, 3b.

[0044] The graphite dies 1 can be surrounded by graphite felt 6 to reduce the heat loss by radiation from the outer die surface. The temperature can for example be measured at a hole 7 in the graphite die 6.

Examples

[0045] The present invention is further illustrated by the following experimental results, which should not limit the claims in any way. For example, other metals and cemented carbide powders than steel/cemented tungsten carbide can be used. Other sintering techniques than SPS can also be used.

[0046] At the beginning, basic SPS experiments for single steel and tungsten carbide powders were carried out to find an optimum sintering condition at which both materials become highly dense. Fabrication of steel / cemented tungsten carbide FGM compacts was thereafter performed. Steel powders with low carbon content and cemented tungsten powders of about 10wt% cobalt composition were used in the experiment.

[0047] For the FGM gradient layers, the steel and tungsten carbide composite powder mixtures were dry mixed at room temperature for one hour in plastic containers with tungsten carbide milling rods on a jar rolling mill.

[0048] The steel / WC-Co FGMs were designed to comprise four composite interlayers between the pure steel and tungsten carbide layers at the two ends. The composites consisted of steel - cemented carbide mixtures with a 20vol% gradient change (i.e. 80/20, 60/40, 40/60, 20/80 vol%). The total six layers were loaded in order, layer by layer, in a graphite die and a BN insulating layer was interposed between the punch and the steel layer.

[0049] A steel / cemented tungsten carbide FGM disc (ø20×6 mm) was successfully sintered according to the above conditions. It was fully dense and no cracks could be observed. Experiments have also successfully been performed with discs of the sizes ø20x8.25 mm and ø12x7.25 mm.

[0050] The sintering was done in ordinary cylindrical graphite molds.

[0051] During the sintering of single steel powders, the samples 4 were sintered with and without an electrically insulating layer 5 of boron nitride powder BN placed between the steel powder to be sintered and the graphite punches 3a, 3b.

[0052] The powders inside the closed dies were first cold-pressed. Then, the samples were sintered in vacuum in a spark plasma sintering unit (SPS-5.40 MK-VI system from SPS Syntex Inc, Japan). Once the pre-determined SPS-pressure was applied, the dies were heated to 600 °C in 3 minutes and then heated further at a rate of 50-100 °C/min to the desired holding temperature. The holding time was between 5 and 15 minutes. The temperature was measured with an optical pyrometer focused on a hole 7 at the half height of the outer surface of the die.

[0053] After sintering, the resulting sintered discs were blasted to remove the residues of graphite foil and BN layer, and then polished with #120 silicon carbide grinding paper. The relative densities were measured by Archimedes method (European Standard EN 993-1) using deionized water as the immersion medium. The possible existence of surface cracks in the sintered pellets was examined visually and through optical microscopy (Olympus SZx12 model, Olympus Optical Co. Ltd, Japan).

[0054] The relative densities and the sintering conditions are listed in Tables 1 and 2, wherein Table 1 lists sintering of individual steel and cemented carbide powders by SPS and Table 2 lists sintering of steel / WC-Co FGM compacts by SPS at 1100°C/75MPa/15min/50°C/min.

[0055] From the results, it can be seen that when no BN insulation was used the melting of steel occurred when the SPS temperature was 1100°C which implies that the temperature was locally at the powder particle surfaces much higher than that measured on the die surface and very close to the melting point of the steel alloy (1516°C). When BN was used, the current flow through the steel powder was inhibited, which prevented the local overheating and thus no melting was observed. The tungsten carbide alloy was well densified at this sintering temperature of 1100 °C when a holding time of 15 minutes was applied under a pressure of 75 MPa.

[0056] The steel / WC-Co FGM compacts were properly sintered with high densities by the sintering process described above and no cracks were observed.