Production of CERMET mixture and use in Composite Materials - A review

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Abstract

Metal matrix composites are formed by combination of two or more materials having dissimilar characteristics. Among MMCs large interest is being given to improve aluminium based MMCs and to develop high temperature ceramics. The present paper review, discusses the processing and properties of Al7075 reinforced with (WC-Co) cermets particulates. The (WC-Co) cermets are usually prepared at high temperature, The present work demonstrate powerful and simple process- using high energy milling for WC-Co base cermets. Cermets like WC-Co (Tungsten carbide and Cobalt) have been widely used and studied because of their good corrosion resistance and unique combination of high hardness and toughness, which results from the mixture of brittle (hard) and ductile(soft) phase. Tungsten carbide has been well known for its exceptional hardness and wear resistance.

Key words— *WC-Co, Cermets, MMCs.*

1. Introduction

Many of our modern technologies require materials with unusual contribution of properties that cannot be met by the conventional metal alloys, ceramics and polymeric materials. To satisfy the material property combinations and ranges have been and are yet being extended by the development of composite materials. Metal matrix composites (MMCs) being used to replace conventional materials in many applications especially in automobiles, aerospace industry and machine industries [1]. For engineering applications MMC plays a major role and aluminium is an excellent material in non ferrous family because of its excellent properties like low density, high strength to weight ratio, high thermal and electrical conductivity and fluidity [2]. The major advantages of aluminium matrix composites include high specific strength, stiffness, electrical and thermal conductivity, low coefficient of thermal expansion and wear resistance [3]. The introduction of ceramic material into a metal matrix produces composite materials which gives an attractive combination of mechanical properties which cannot be obtained with monolithic alloys [4]. There is a need for knowledge about the processing techniques and mechanical behavior of particulate MMCs is view of their rising production volume and their wider commercial applications. There is an increase in the interest on the particulate reinforced MMCs mainly due to their easy availability of particles and economic techniques adopted for producing the particulate reinforced MMCs [5]. Interest in reinforcing Al alloy matrices with ceramic particles is mainly due to its low density, low coefficient of thermal expansion and high strength of the reinforcements and also due to wide availability [6]. Cermets are a combination of ceramic and metallic phases. Cermets like WC-Co (Tungsten carbide and Cobalt) have been widely used and studied because of their good corrosion resistance and unique combination of high hardness and toughness, which results from the mixture of brittle (hard) and ductile(soft) phases. Tungsten carbide has been well known for its exceptional hardness and wear resistance. Ductile metals such as cobalt greatly improve its toughness so that brittle fracture can be avoided [7]. In recent years considerable work has been done on the cermets (WC-Co) reinforced MMCs which exhibit low wear resistance, corrosion resistance and high temperature applications. The objective of this study is to investigate the synthesis and evaluate the mechanical properties.

Cermet materials combine opposite properties from metals and ceramics, being the key components to drive new applications in several engineering areas. Cermet materials, which contain light metal alloys, have very good mechanical properties and therefore they are applied as construction materials in defence, aircraft and cars technology [8]. The mechanical properties of composite materials reinforced with ceramic particles depend on the matrix properties, mutual wettability of interphase and the amount of reinforcing particles. Currently copper-based composite materials are produced by using several routes such as mixing of Cu and alumina powders, internal oxidation of Cu-Al alloy in powdered form or by mechanical blending of copper with dispersed Al2O3 powder and subsequently cold pressed. The mechanochemical approach to the MMCs synthesis is likely to be the most promising because it allows obtaining materials characterized with nanocrystalline structure. This technique allows incorporating the metallic and ceramic phases into particles. It causes that material is more homogenous in microstructure and therefore has high strength and better interfacial contacts between reinforcements and the matrices [9]. Copper–based composites have relatively good mechanical properties and electrical conductivity. However, it is worth to mention, that even small amount of alumina additions into Cu matrix, increases its mechanical properties, simultaneously lowering considerably electrical conductivity [10-11].

2. PREPARATION OF CERMETS

Ball milling is an efficient and simple method for the fabrication of sub-micron or micro structured powder materials, especially for manufacturing of various composite powders [2]. The high energy ball milling process produces strong mechanical energy transfer which results in formation of extremely fine powder [4]. The homogeneous distribution of hard phases in ductile metallic matrices is due to counteract breaking and cold welding process during milling, breaking of particle's is mainly caused by shear load transferred by grinding balls colliding under a low angle, while cold welding is dominate for perpendicular impact of grinding balls and the crystallite size decreases with proceeding milling time [4]. There are different types of ball milling methods based on the movement of milling balls such as planetary ball milling, vibration mill, planetary mill and attriator [2]. The most commonly used milling devices are compared concerning their processing features.

Table 1: Features of the typical milling devices [5]

MILL DESIGN	SHAKER MILL	SIMOLOYER®	PLANETARY BALL MILL	VERTICAL ATTRITOR®	DRUM/BALL-MILL
processing kinetic	very fast	fast	medium	medium	slow
influence of gravity	low	very low	low	difficult	necessary
max. charge [kg]	0.2	500	2	250	12,000
max. total volume [l]	0.2	400	8	1,000	20,000
specific energy [kW/l]		0.55 - 3		0.1 - 0.75	0.01 - 0.03
max. relative velocity [m/s]	12	14	5	5	> 5
up-scaling	impossible	possible	impossible	possible	impossible
contamination	low	low - high	low	low - high	low
vacuum	possible	> 10^{-2} Pa	possible	hardly possible	hardly possible
discharging	very demanding	easy	very demanding	demanding	easy
temperature control	hardly possible	possible	difficult	possible	possible
investment costs	low	very high	low	high	low
operating costs	very high	high	low	high	very low

Among the comparative observation of different types of milling devices, shaker mills with horizontally operating rotor shows the highest achievable relative velocity of grinding balls with respective units. Shaker mill type permits even shorter processing times in comparative to the Simoloyer type of device. The major disadvantages of the shaker mill are the very demanding discharge and the resulting high operating costs. Planetary ball mill features low investment and operating costs. Due to the moderate maximum relative velocity of grinding balls longer processing is required in comparison to the Simoloyer and Shaker mills. Planetary mills are designed only for processing of laboratory scale amounts and also up scaling of processing parameters to systems with large dimensions would not be possible. Attritors, which have vertical operating rotors, work at conditions with lower specific energy in comparison to the Simoloyer with horizontally arranged rotor. Therefore the processing is longer and also an activation energy required for reactive milling might not be provided. Drum mills are the most commonly used milling devices these days because of the comparatively low investment and operating costs due to the large amounts of materials, which can be processed in a batch. However, the very low specific energy of this process generally requires long processing.

2.1. DRY MILLING

Ball milling is an effective and simple method for the fabrication of sub-micron powder materials especially for manufacturing of composite powders. By looking into several research works it appears that the mostly accepted routes for developing WC-CO hard metals could be by direct milling WC with Co powders or by milling elemental powders of tungsten, carbon and cobalt to desired composition. Many parameters are to be taken care while milling which includes milling time, milling atmosphere, milling temperature, milling speed and milling medium. The effect of ball milling time on the production of cermets (WC-Co) studied and it was found that milling conclude to fine grain sizes but with higher elemental contamination from the milling medium. To reduce the contamination of milling medium and vial are made by ceramic material for milling WC-Co cermets. Inert atmosphere argon is used as a milling atmosphere to reduce the contamination. Increase in milling temperature and time will lead to more impact and higher energy transfer to the milled powder which ultimately lead to more damage to the milled powder [6]. Most popularly ball mills are used for powdering the materials to micro size.

2.2. WET MILLING

WC powder is mixed with cobalt powder, polymeric pressing additives in the form of Polyethylene glycol (PEG) and grinding liquid , mixture of ethanol and water, in a cylindrical ball mill and milled to a homogenous slurry using spherical milling balls, as show in fig.1 .

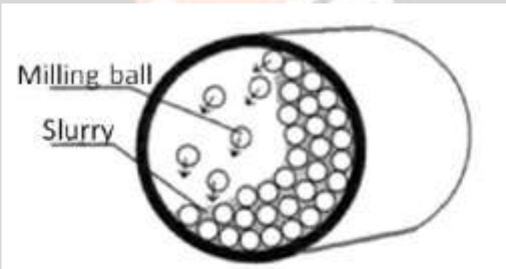

Fig.1. General set up of ball mill [5]

The milling balls are made from sintered hard metal to avoid contamination of the powder during milling. The pressing additive helps to form granules in the spray drying process and lowers the friction in the pressing. Water is added to the grinding liquid which helps dissolve the Poly ethylene glycol (PEG). Ethanol will reduce oxidation of the powder as new surfaces are constantly formed and exposed during milling. Another advantage with ethanol additives is that it will lower the energy consumption when drying the slurry, compared to using only water, due to its lower boiling point. Cobalt is normally used as the metal binder due to its extraordinary wetting capability. The wetting capability will enable the cobalt to distribute itself evenly around the WC grains and completely fill the pores in the sintering process, thereby generating a microscopically homogenous powder. In wet milling both speed of rotation and the milling time will affect the result. Crushing has the advantages of having a higher milling efficiency, the rate with which the grains are reduced in size. Ideally, crushing will lead to one particle being divided in to many like sized particles. The milling efficiency decreases with increased milling time as the particles become smaller. It is assumed to subside completely when the grain size reaches a critical value. This is a consequence of the force applied to the slurry as two milling balls approach one another, causing a slurry flow away from the balls prior to collision , the smaller particles, the more likely it is to be caught in the slurry flow.

SPRAY DRYING AND SIEVING - After milling, the homogenous slurry is dried to spherical granules, consisting of hundreds of carbide and metal particles, using a spray drier. The slurry is pumped through a nozzle at the bottom of a drying chamber and is encountered by a flow of hot inert N_2 gas, as shown in Fig.2.

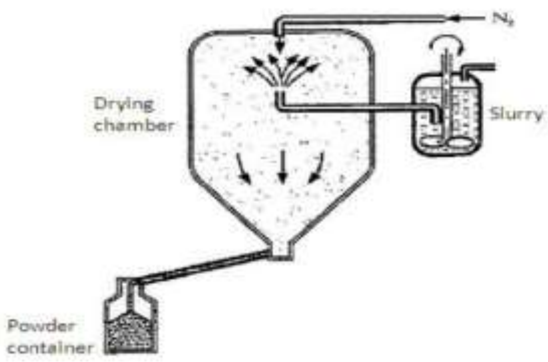

Fig.2. Schematic picture of air drier [5]

The gas flow serves both to dry the droplets, i.e. to evaporate the milling liquid, and to scatter the upcoming droplets towards the sides of the drying chamber in order to prevent collision and fusion of liquid or semidried droplets. Sieves with well-defined mesh sizes are used to narrow the granule size span of the dried powder. Both the too large and the too small granules are separated from the approved powder and recycled.

2.3. SYNTHESIS TECHNIQUES OF NANOSIZED WC-CO POWDER

Spray conversion process developed by Mccandlish and Kear at Rutgers university is one of the most commercially used method to produce Nano-structured material which involves building up the Nano scale structure form at molecular level. In this an aqueous solution of ammonium metatungstate [$(NH_4)6(H_2W_{12}O_{40})4H_2O$] and cobalt chloride [$COCL_2$] or cobalt nitrate [CO $(NO_3)_2$] or CO $(CH_3COO)_2$ is spray dried to get a precursor powder which is reduced and carbonized in a fluidic bed reactor to yield Nano structured WC and CO. Chemical vapour synthesis, vapour phase precursor of tungsten hexachloride (WCl_6) is reduced and then subsequently carburized using CH_4 as carburizing agent to produce Nano-structured WC powder. Recently a thermochemical single step displacement reaction processing route was used to produce finer grains of <10nm was developed, in which carburization of ammonium metatungstate is done in a single operation via slow heating to ensure balance between reduction and carburization.

3. COMPOSITE PROCESSING ROUTES

The processes classified according to whether the matrix is in the liquid, solid or vapour phase while it is combined with the reinforcements.

3.1 Liquid metallurgy route

Liquid metallurgy route has been adopted to fabricate composites. Liquid metallurgy technique is the most economical of all the available routes for MMCs production and generally classified into two categories.

1. Liquid matrix and ceramic reinforcement- stir casting (Particulate) and compo or rheo casting (Dispersoids)

2. Pre-forms and in filtering liquid matrix

- Squeeze casting (short fibre or Whiskers)
- Melt infiltration (continuous fibre)

3.1.1. Stir casting

In manufacturing particulate reinforced MMCs stir casting techniques is one of the popular liquid metallurgy route (LMR) and known as a very promising route for manufacturing near net shape metal matrix composite components at a normal cost. Stir casting is a primary process of composite production where by the reinforcement ingredient material incorporated into molten metal by stirring. This involves stirring the metal with ceramic particles and thus allowing the mixture to solidify. The principle used in this method is matrix is melted generating the vortex by stirring adding ceramic reinforcement for homogeneous mixing and solidified. Heating coils are used Canthol < 1000°C and SiC up to 1300°C. Crucible is made of alloy graphite and SiC.

Magnate (MgO) / dolomite (MgOCuO) fused as neutral refractory lining to reduce interfacial reduction between matrix and mould cavity. Stirrer is coated with zirconium dioxide (ZrO_2) to prevent entrapment of other particles. Difficulties can occur from the increase in viscosity while adding to a melt. Viscosity should be sufficiently low to allow carried out casting operation. Microstructure in homogeneities may arise, due to agglomeration and sedimentation in the melt.

Stir casting often involves prolonged liquid ceramic contact, which can cause extensive interfacial reaction. Stir casting is characterized by following features.

1. This method is simple and low cost.
2. Homogeneous mixture can be obtained by proper stirring.
3. In-homogeneities may occur due to clusters of dispersed particles.
4. Suitable for particulate reinforcement.

3.1.2. Rheocasting

In this method reinforcements used are dispersoids with 12 Wt% is restricted and upto 20 Wt% is possible. Here, reinforcement is in semi liquid state. Induction furnace is used for melting. With respect to stirring external and internal stirring is possible. External stirring by stirring rod and for internal induction stirring due to magnetic flux is used because of induction furnace. This method is suitable for alloys with wide mushy zone and it can be subjected to heat treatment.

3.1.3. Squeeze casting

Squeeze casting or pressure casting is the most common manufacturing variants for MMCs. Molten metal is injected into a form with fibers or particles preplaced inside it. A two-stage process is often used. In the first stage the melt is pressed into the form at low pressure and then at high pressure for the solidification phase. This prevents damage to the perform by too fast infiltration. The squeeze casting permits the use of relatively reactive materials, since the duration of the infiltration and thus the response time, are relatively short. One advantage is the possibility to manufacture difficultly shaped construction units. [2]

3.2. Solid state processing

3.2.1. Powder metallurgy

The main popularity of powder metallurgy process lies in the ability of this process to produce complex metal shapes with exact dimensions, economical price and with high quality. Powder metallurgy process was chosen for preparing MMCs because of the following reasons

1. Due to wide gap difference in their density and thermal co-efficient it is difficult to synthesise Al and WC.
2. Wettability of molten Al and WC is very poor in stir casting technique.
3. Possibility of undesirable reaction between the constituents may occur.

Using powder metallurgy process composite can be prepared at room temperature by using cold compaction. Processing of MMCs, stirring materials includes matrix (Al), light alloy in the form of powder with binders are reinforced with particulates, whiskers, short fibers etc.. Blending and mixing is carried out to ensure uniform distribution of constituents and additives. Blending is carried out to achieve particle of same composite with different sized particle and mixing the powders of different chemistry.

Different types of additives used are,

1. Lubricants – to reduce friction between die and particle (wax, graphite).
2. Binders – Adhesion between matrix and reinforcement (sodium silicate).
3. Deflocculates – to increase the flow characteristics (sodium silicate).
4. Compacting – consolidation of particles with pressure without heat. Compacting stage gives required given shape, green density and green strength.

Sintering is most critical part when it comes to Al composite processing, as Al readily oxidizes forming Al oxide and prevent sintering. It is a heating process during which densification and adhesion between particles take place. Sintering temperature is equal to 0.8Tm. During sintering grain boundary, void size is decreased and moisture is expelled.

4. Experimental

The paper highlighted on tungsten carbide properties (in connection with mechanical characteristics) of some particulate reinforced composites, based on a commercial aluminium alloy. Several techniques followed by researchers for the processing of particulates reinforced MMCs. The composites meant for improving the mechanical properties of the base and made by vortex casting in laboratory conditions. Most of test for tensile strength, hardness and elastic modules of the prepared cast matrix and their composition carried out as per ASTM standards.

5. DISCUSSION AND CONCLUSION

This paper is to review the development of metal matrix composite and wide range of materials, which includes cermets. The mostly accepted routes for developing WC-Co cermets hard metals would be done by directly milling WC with Co powders. To reduce the contamination from the ball milling, milling balls are coated by ceramic coating or ceramic balls are used. Milling time and milling atmosphere also affects the size and production. Techniques employed for production of metal matrix composites material and components depend on the type of matrix and reinforcements. These have been classified according to whether the matrix is in the liquid, solid or vapour state, when it is combined with the reinforcements each process has their own advantages and disadvantages. In particular, some are more expensive than others. The cast routes are generally those in which particle reinforcement with aluminium matrix produced using liquid metal, particularly stir casting. Metal matrix composites have a wide application due to their excellent mechanical properties with the combination of a hard reinforcement phase such as tungsten carbide (WC) and ductile matrix material aluminium. While current application for their class of materials are aerospace and automobile sectors with their continuous developments resulting with new products. Likely, as MMCs application continue to expand the spectrum of materials and process employed will remains relatively wide.

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