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Cermets, structure and development

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مأخص

يقدم هذا البحث مضمون النظريات السائدة حول الترابط و البنية في المواد المركبة السيراميكية-المعدنية (السيرميت) التي توضّح سبب امتلاكها الخصائص الميكانيكية الفريّدة لكل من المعادن و المواد السراميكية من قساوة ومرونة عالية و مقاومة تآكل مميّزة -ممّا يعطيها عمر التّشغيل الطويل- عند درجات الحرارة المرتفعّة بالإضافة للناقلية الكهربائية و الحرارية العاليّة، مع مناقشة نتائج الدراسات التجريبية حول طرق التصنيّع المختلفة للقطّع السيرمتية مع تبيّان الفروق بينها و تطورها مع الزمن للاستفادة منها في عمليات و قطّاعات مختلفة كأدوات لنحّت الأجزاء الفولاذية المختلفة الأشكال التي تطلب دفّة عالية في العمل و كطبقات مانّعة للتآكل في المحركات و كوقود نووي عاليّ الفعاليّة و قوالب للتخلص من وقود اليورانيوم المستنفذ.

1. Introduction

Materials are probably more deep-seated in our culture than most of us realize. Transportation, housing, clothing, communication, recreation, and food production virtually every segment of our everyday lives is influenced to one degree or another by materials. Historically, the development and advancement of societies have been intimately tied to the members' ability to produce and manipulate materials to fill their needs. In fact, early civilizations have been designated by the level of their materials development (Stone Age, Bronze Age, Iron Age).

The development of many technologies that make our existence so comfortable has been intimately associated with the accessibility of suitable materials. An advancement in the understanding of a material type is often the forerunner to the stepwise progression of a technology.

In recent few decades, production environments (machining, oil industry) have been representing aggressive conditions, which gave the motivation to develop new materials that can stand this harder and harder work conditions.

Specification and the use of materials which combine erosion and corrosion resistances with high mechanical strength is a fundamental requirement in industrial applications leading to be the focus of interest in numerous researches.

Subsequently, the development and production of appropriate materials was of a great economically and engineering importance.

Up to date, although numerous practical machining operations and several progresses have been made in various materials, cermets have been considered as the most promising candidates due to their high high-temperature hardness, low reactivity and many desirable properties that make cermets an applicable material in different domains to provide high-performance machines and work pieces.

So, is cermet an adequate material that possess the sufficient strength and hardness to be used in the aggressive work environment along with the low-cost manufacturing process, If so, what causes this remarkable properties?

2. Chapter one: ceramic to metal bonding

2.1 The Need for Cermet

Having high wear and corrosion resistance is crucial for a part to survive long periods of time in the high wear environments like aerospace manufacturing industry of aircraft and the oil industry. If the part is able to continually successfully survive during use at these conditions it not only reduces costs in repairing and replacement but it also increases the safety factor of the structure as a whole. Although having a highly corrosive resistant material is very important, having a mechanically sound material is equally as essential. Two key characteristics that one must consider when selecting a suitable material is therefore the hardness and toughness behavior because without having respectable performances in these areas the integrity of the structure would quickly be compromised, especially at the extreme working conditions they are immersed in. Finally, environmentally friendly processes and materials are important, so as to not cause unneeded contamination to the working environment and to meet the strict rules and regulations set by the industry.

There are many different types of materials that meet some combination of the required properties, but there are very few that meet all of the requirements together. One family of materials that meets essentially all of these needs is ceramic-metal composites, which are often referred to as 'cermets'. These composites were first developed by the allies during the Second World War in the search for a material that had the high temperature resistance of ceramics along with the toughness and ductility of cemented carbides (i.e. WC-Co). The term 'cermet' comes from the combination of a relatively brittle but hard ceramic matrix with a tough metallic 'binder'. Typical applications of cermets include use as a protective coating layer on the inside of pipelines that carry oil and gas, machining and tooling purposes (including cutting tools and compaction/forming dies), high performance braking systems for cars, and also as a form of ballistic protection for equipment and personnel in the military.

2.2 Manufacturing

The mechanical properties of cermets are closely related to their complex structure. Many factors determine the final morphology of the material, such

as the choice of the raw material, the presintering production steps and finally the careful control thermodynamic of the parameters such as temperature, pressure and time during the sintering process. A lot of research during the last 20 years has been dedicated to the improvement of the processing in order to reach a better control and predictability of the microstructure and morphology and consequently of the material properties[1].

One of the general production processes called liquid phase sintering (LPS) - is briefly described as follows:

The raw material is constituted of pure or pre-alloyed powders of hard metal carbides, the binder metal (cobalt here) and carbon black. sometimes А polymeric binder is added to obtain a more stable body after pressing. All ingredients are mixed in ball mills with alcohol (or another solvent) to facilitate the homogenization of the powders. The grain size of the carbides is reduced during milling to 1-3 µm that of Figure 1:general production process the cobalt even down to nanometer size.



The alcohol is removed during spray drying, when the powder forms granules. The obtained powder mixture is pressed to the desired shape, the so-called green body. The porous green bodies are placed on graphite plates sintered in special furnaces with a well-defined temperature-time and program in order to achieve full densification. The sintering atmosphere and pressure is changed during the sintering process, a flow of gases like N₂ or CO, for example, can prevent from de-nitrification or de-carburization.

A typical sintering process is shown in Figure 1. The first part of the sintering is a slow heating with several dwells, where the polymeric binder is removed and the outgassing of adsorbed gases and gaseous reduction products takes place, while the material still presents open porosity. Solid state sintering occurs below the eutectic temperature.



Figure 2: General sintering cycle showing the important sintering stages and the corresponding changes in the microstructure.

Some amount of the hard phase is dissolved in the still solid binder, new phases may be formed and material transport through surface and bulk diffusion leads to decreasing porosity. The next sintering stage, the liquid phase sintering, starts when the temperature rises above the ceramic-metal eutectic melting point. An extensive dissolution-precipitation process takes place, where bigger grains grow on expense of small ones. The grain growth continues even during the final solid state sintering until the temperature becomes too low and the structure is frozen in. The sintering time at high temperature must be long enough to reach full densification of the structure, but it should be as short as possible to limit grain growth, which is detrimental for the mechanical properties[2].

2.2.1 Liquid Phase Sintering

Liquid phase sintering (LPS) is a process for forming high performance, multiple-phase components from powders. It involves sintering under conditions where solid grains coexist with a wetting liquid. Many variants of are applied to a wide range of engineering materials. Example LPS applications for this technology are found in automobile engine connecting high-speed metal cutting inserts. Scientific rods and advances in understanding LPS began in the 1950s. The resulting quantitative process models are now embedded in computer simulations to enable predictions of the sintered component dimensions, microstructure, and properties.



Figure 3 : evolution of microstructure in a simulated 3D system during LPS with an initial solid fraction of 0.7, liquid phase is not shown

Packed particles heated their melting near temperature bond together by sintering. As diffusion accelerates higher at sintering is temperatures, manifested by bonding between contacting particles. Sintering occurs over a range of temperatures, but is accelerated the as particles approach their melting range. It takes place faster as the particle decreases, size since diffusion distances are shorter and curvature stresses are larger. For solid-state sintering, it is appropriate to think of sintering with respect to

the melting temperature. Snow sinters to form ice at temperatures near -15 °C, while alumina requires temperatures in excess of 1000 °C.[3]

A widely applied variant relies on forming a liquid during the sintering cycle. Liquid phase sintering (LPS) is applied to alloys and composites that melt over a range of temperatures. In the typical situation, the solid grains are soluble in the liquid. This solubility causes the liquid to wet¹ the solid, providing a capillary force that pulls the grains together. At the same time, the high temperature softens the solid, further assisting densification. Highdiffusion rates are associated with liquids, giving fast sintering or lower sintering temperatures. Since the final product is a composite with customized properties, LPS is the dominant commercial sintering process.

LPS processing spread to a diverse range of applications oil well drilling tips, porcelain jacketed dental crowns, automotive valve seats, wire drawing dies, high-temperature bearings, electrical contacts, electronic capacitors, radiation shields, diesel engine turbochargers, electronic insulator substrates, golf clubs balance weights, ultrasonic transducers, electronic solders, and grinding abrasives.

¹ The wettability is the capability of solids to build interfaces with liquids

2.2.2 Structure and Microstructure

Hardmetals used for the production of cutting tools consist of a majority of ceramic hard phase and a small amount of metallic binder. A typical structure of a cemented carbide and a cermet, each with 10 vol.% cobalt binder, is shown in Figure 3. Depending on the volume fraction (usually 80 vol.% or higher), the hard phase forms a continuous structure throughout the sample, called the ceramic skeleton. For lower volume fractions, the hard phase is present in form of single grains or clusters of grains entirely surrounded by the metal phase, which leads to mechanical properties dominated by the metal phase. In general, also the binder phase forms a continuous network structure. A schematic representation of the two interconnected phases is shown in Figure 4. The degree of connectivity is quantitatively described by the contiguity, which is the ratio of the ceramic/ceramic interfacial area to the total interface surface area. It has a range of values from 0 (totally dispersed) to 1 (fully agglomerated). As the contiguity increases, hardness increases and the fracture toughness simultaneously decreases. The equation used to calculate the contiguity is:

$$C = \frac{2N_{cc}}{2N_{cc} + N_{cb}}$$

Where N_{cc} is the average number of intercepts per unit length of a test line which intersects carbide/carbide boundaries and N_{cb} is the number of intercepts of binder/carbide interfaces.



Figure 4: SEM micrographs using back-scattered electrons of a) cemented carbide and b) cermet, each with 10 vol.% cobalt binder. The cobalt appears dark in WC-Co and light in TiCN-Co.



Figure 5: Cermets and cemented carbides are formed of a main ceramic phase bond by a metal binder. Both metal and ceramic phase form continuous interpenetrated skeletons.

2.3 Bonding and Structure in Ceramic/Metal Joints

The use of ceramics and ceramics based composites in industrial applications mainly for high temperature has received extensive attention recently. However, the utilization of the full capabilities of ceramics demands an ability to join ceramics to themselves or metals. Significant differences in the mechanical properties of ceramics and metals make it extremely difficult to obtain ceramic/metal joints with adequate mechanical integrity. Silicon nitride (Si_3N_4) and tungsten carbide (WC) are two of the most attractive advanced ceramics materials for specific applications since the resulting microstructure of these ceramics after sintering is similar to that of particulate-reinforced composites, respectively. Joining ceramics to metals is a key of technology in the use of advanced ceramics in complex structures. Moreover, the use of advanced ceramics depends on the reliability of ceramic/metal joining processes and the properties of the resulting interfaces. Several methods for joining ceramics to metals have been developed, some need an intermediate liquid phase, brazing, thermal spraying, and others are produced by solid state bonding and co-sintering.

In all cases some problems have to be overcome: (i) morphological adaptation of the surfaces in contact; (ii) formation of bonds: van der Waals bonds, chemical bonds by simple recovery of the molecular orbital or by chemical reaction, where new phases are grown at the interface; (iii) strict control over the residual stresses developed in both materials; (iv) changes in mechanical properties of the alloy and ceramic close to the interface.

Ceramic/metal joining can only be accomplished with temperature, pressure, and time sufficient to promote mobility and interdiffusion of reacting species, producing adequate interfacial contact between the ceramic and the metal. Initially, the two components contact only at their asperities. In the first stage of the bonding process, more intimate contact is achieved by plastic deformation, which results in two partly joined surfaces with residual voids in between. When ceramic/metal bonds are being formed, and deformation of the metal is permissible, plastic flow generally occurs within the metal, and in the second stage of the bonding process, creep and diffusion eliminate the voids. The key step in the formation of a ceramic/metal interface is to achieve adequate contact between the two materials at the interface. The driving force for the formation of a ceramic/metal interface is the reduction in free energy when intimate contact is established between the ceramic and metal surfaces. In order for this to occur, both surfaces have to be brought into intimate contact, which is usually accomplished by controlling the temperature and atmosphere during interface formation. The application of pressure results in displacement of impurities and adjustment of irregularities due to localized deformation.

2.3.1 Solid-State Diffusion Bonding

Diffusion bonding is а solid-state process for the fabrication of metalmetal. ceramic-ceramic and ceramicmetal is conceptually joints that simple. The process requires no localized melting of components or introduction of foreign bonding materials. but merelv that mating surfaces are brought into intimate, atomic scale contact that so an interface can be formed by interdiffusion to create structural а Such continuum. interfaces. whether between metals, ceramics or between a metal and a ceramic, can have good mechanical integrity even high at The simplest temperatures. form of diffusion bonding involves the application of a low pressure at a high temperature to achieve bonding of the components. It is important they have smooth and well-matched mating surfaces. Understanding the relationship between processing, structure and properties of metal/ceramic interfaces is becoming



Figure 6: Sequence of events during metal-ceramic diffusion bonding.

increasingly important as performance requirements demand a combination of these different materials in applications ranging from electronic packaging to high temperature aircraft structures[4].

There are two possible mechanisms of the solid phase bonding of ceramics to metals without the intermediary of a liquid filler metal: when the solid-phase ceramic and metal are brought into contact, the metal may undergo plastic deformation, enter the surface irregularities of the ceramic, adhere and bond to the ceramic. In another possible mechanism, the metal may diffuse through the interface, react with the ceramic and form a continuous layer.

There are several advantages of solid-state joining. When ceramic have to be bonded to metals, it is a common practice to introduce a metal interlayer between the components. The interlayer should be ductile so that it can deform readily to achieve intimate contact with both mating surfaces at various pressures and temperatures, that it should act as a stress relieving buffer layer if the thermal expansivities of the metal and ceramic components differ significantly, and of course that it should adhere strongly to both the metal and ceramic components. The technique has been applied, so far, mainly for the joining of Al_2O_3 and SiO_2 , but its utility has also been demonstrated for joining of Si₃N₄ and other new engineering ceramics like WC. The technological advantages of diffusion bonding are low deformation which enables parts to be joined with little distortion, the ability to join large applicability diffusion bonded joints high areas. the of at service the for joining and possibilities temperatures, materials in а none conventional way, However, the major disadvantages of diffusion bonding are high capital costs, and the restricted joint geometries that can be produced. In addition, specific problems exist when applying diffusion bonding to Si₃N₄. The misfit in the coefficient of thermal expansion (CTE) of the joining materials can result in areas of high residual stresses at the interface during the cooling process.

In case, the metal-ceramic interaction was not sufficient to bond the two phases, commonly an intermediate layer is presented to the metal-ceramic interface to provide metal-ceramic bonding like glassy intermediary layers and polycrystalline intermediary layers[5] or, it could be alloys contain active elements such as titanium and cerium, that can be reacted directly with the ceramic which provide an appropriate layer can adhesive to the metal phase and vice versa.



Figure 7: Stainless Steel - Alumina Joint Indicating metal to ceramic bonding using intermidiate layer

2.3.2 Effect of Bonding Temperature

The solid-state diffusion bonding is controlled by many parameters. The main variables affect the process are pressure, temperature, time and surface roughness. Temperature is the most important parameter in the bonding process due to the fact that: (i) in thermally activated processes, a small change in temperature will result in the greatest change in process kinetics, diffusion, creep, compared with other parameters; and (ii) virtually all mechanisms in diffusion bonding are sensitive to temperature, plastic deformation, diffusion, creep. Temperature increases interaction across a metal/ceramic interface by increasing the mobility of atoms and also the mobility of dislocations in the metal during bonding. Since the mobility of dislocations increases with temperature and the flow stress correspondingly decreases, the pressure

required for bonding decreases with increasing temperature. In general, the temperature required to obtain sufficient joint strength is typically within the



Figure 8:Cross-section of the Si3N4/Nb interface for a sample hot-pressed at a) 1400°C for 120 minutes and b) 1600°C for 60 minutes in vacuum

range 0.6 and $0.95 T_m$, where T_m is the absolute melting point of the base material. The effect of temperature is shown for Si_3N_4/Nb joints in Figure 8. It is seen that the interface in samples hot-pressed at 1400°C consists of a layer with one phase and thickness average of 2 µm, however the interface in samples hot-pressed at 1600°C consist of one layer with two intermixed phases and thickness average of 18 µm.

On joining of metals to silicon nitride (Si_3N_4) , an additional difficulty is introduced by the presence of nitrogen gas at the interface. Nitrogen gas is formed upon the dissociation of Si_3N_4 , and it may or may not diffuse into the metal, depending on its solubility at the bonding temperature. In general the chemical reactions occurring when silicon nitride is in contact with a metal (Me) follows one of the following three routes:

 $Me + Si_3N_4 \rightarrow Me \ silicide + Me \ nitride$ (1)

$$Me + Si_3N_4 \rightarrow Me \ silicide + N_{2(g)}$$
 (2)

$$Me + Si_3N_4 \rightarrow Me \ silicide + Si$$
 (3)

Comparing the thermodynamic stability of Si3N4 with those of metal silicides and nitrides, it is possible to predict the likely products of diffusion bonding. When the bonding temperature is above the minimum temperature required for reaction (2), it proceeds and forms intermetallic compounds at the interface. The free nitrogen produced by this reaction diffuses into the metal when it has a high solubility for nitrogen. However, strong nitride formers, such titanium (Ti) and niobium (Nb), promote reaction (1) above the minimum temperature of reaction (2) and below the minimum temperature in the case of reaction (3).

3. Chapter Two: Cermet in Action

3.1 Ti(C, N) Cermets

Because of the combination of the desirable properties of both metal and ceramic, the cermets exhibit excellent properties, such as high strength, high hardness and wear resistance. Since the TiC-based cermets were developed in the early 1970s, a kind they have become of important materials in the

applications of high speed cutting tools but the coarsening tendency



Figure 9: Ti(C,N) cermet in action

and instability of the microstructure at higher temperature limited their wide applications. Compared with the *TiC*-based cermets, the *Ti(C,N)*-based cermets possess a fine and stable microstructure with higher hot hardness, higher transverse rupture strength and enhanced oxidation resistance. Therefore, more and more *TiC*-based cermets have been replaced by the Ti(C,N) based cermets in the commercial cutting applications[6].

3.1.1 Microstructure and Mechanical Properties of Ti(C, N) Cermets

So far, it was commonly accepted that, the compound TiCN (titanium carbonitride) is a kind of non-oxide material. TiC and TiN are isomorphous both having an FCC (face centered cubic) NaCl type structure, therefore a continuous solid solution can be prepared: $Ti(C_{1-x}N_x)$ with $0 \le x \le 1[7]$.

In some ways, The correct description on its structure can be based on *TiN* structure with occupation of N sites by C, resulting in a FCC or tetragonal structure, which depends on how the substitution takes places.

As mentioned above, $Ti(C_{1-x}N_x)$ is a continuous solution of TiC and TiN. Thus the properties of TiCN vary with x, which means that they are dependent on the properties of both TiC and TiN. Commonly, with decreasing x, the unit cell parameter of TiCN decreased linearly, and the micro-hardness would drop down; yet the toughness would be enhanced on the contrary. Table 1 lists the specific properties of TiC and TiN.

In conclusion, TiCN possesses both the properties of TiC and TiN: high hardness, high melt point, good corrosion resistance, excellent wear resistance, good chemical stability, high thermal and electric conductivity, and so on. However, pure TiCN is much brittle due to its very low toughness and strength. So TiCN is often used as a hard phase in cermets or as composites for the wide demanding applications

Properties	TiC	TiN
Molecular weight	59.9	61.9
Crystal structure type	NaCl	NaCl
Unit cell parameter (nm)	0.4318-0.4328	0.4240-0.4249
Melt point (K)	3340-3530	3223
Density (g/cm ³)	4.90-4.93	5.39-5.44
Thermal conductivity $(W \cdot m^{-1} \cdot K^{-1})$	17-24	29
Coefficient of thermal expansion (10 ⁻⁶ /K)	7.40-7.95	9.35
Micro-hardness (HV, GPa)	30-32	20-20.5
Modulus of elasticity (GPa)	315-450	251

Table 1: The properties of TiC and TiN.

3.1.2 Core-rim Structure of TiCN-Based Cermets

Commonly, cermets are composed mainly of three phases: hard phase, metal binder phase and surrounding phases. in TiCN-based cermets, there is commonly a core-rim structure. And sometimes, the rim consists of two parts, which was called the outer rim and the inner rim, respectively. Normally, the composition of the core in TiCN-based cermets, namely the hard phase, is believed to be TiCN or TiC, which was deemed to be the residues of un-dissolved raw materials. And the rim, i.e. the surrounding phase, is a sort of complicated (Ti,W,..)(C,N) solution, which has a similar crystalline structure with the core but with much more heavy metal atoms than those in the core. For this, it has been observed in SEM-BSE images that, the rim is grey while, sometimes, the core is black. As it was known, the white brightness in SEM-BSE means a much higher content of heavy elements. A typical microstructural schematic of a commercial cermet, imaged via SEM, is shown in Figure 10 [8, 9]; And as mentioned about the two rims, it was generally considered that, the inner rim was a solution originated from the diffusion of W,Mo and other atoms during the solid sintering, and the core was all surrounded by the inner rim. However, the out rim was a similar solution as the inner rim but just with less W,Mo and other heavy elements originated from the dissolution-precipitation through the liquid sintering. In a word, the components of both the inner and outer rims of TiCN based cermets are the same, only a matter of that, their contents are different.



Figure 10: (A): a typical core/rim structure. (B): Schematic representation of the SEM image of a typical commercial TiCN-based cermet.

According to thermodynamic principles, the solubility of the smaller hard phase grains in the liquid was much higher than that of the bigger ones. Consequently, when the smaller atoms have reached the saturation point, the bigger ones still have a long way to go yet. It has been suggested that, smaller TiCN grains dissolved in the liquid continually and the dissolved ones kept precipitating on the undissolved bigger ones. At the same time, other additives like metal carbides also precipitated in the form of complicated solution of (Ti,W,M)(C,N) (M represents for the metal element added in the cermets) surrounding the undissolved particles. Besides, with the temperature elevating, the N atoms derived from the decomposition of (W,Mo,M)(C,N), thus forming the outer rim.

the present of surrounding phase could improve the wettability of the hard phases with the binders and bond the two phases well, thus enhancing the toughness of the cermets. Moreover, the surrounding phase would inhibit the approaching of TiCN particles with each other, hindering the growth and conglomeration of TiCN grains. For this reason, the hard phase grains would be fine and disperse evenly. As referred to in Ref[10]: a much complete surrounding phase would strengthen the bonding between the hard phase and binder phase, thus suppressing the crack propagation in the cermets. As a result, the bending strength of the cermets would be improved. However, the rim phase was actually a kind of quite brittle phases, and when the thickness of the rim was larger than $0.5 \,\mu$ m, the strength would turn to decrease sharply.

3.1.3 Influence of C or N on TiCN-Based Cermets

After the addition of small amount of C (no more than 0.5 wt.%) into the raw materials for preparing TiCN-based cermets, the η phase (Ni₃Ti) and TiO phase, remained by incomplete deoxidization, would be formed, thus

deteriorating the bending strength and toughness of the cermets. Moreover, in this case, the binder phase could not thoroughly wet the hard phase, which would induce the grain growth of TiCN, thus reducing the cermet toughness. After the addition of medium amount of C (in a range of 1–1.5 wt.%), the solid solubility of heavy metal elements in the binder phase increased and the wettability of the hard phases in the cermets was improved along with the thickness of the rim decreased. As a result, the bending strength increased while the hardness presented a decrease. When the addition of C in the cermets is beyond its saturation (about 2.5 wt.%), the dissociative carbon phase appeared along with more pores and looser microstructure in the cermet matrix, which would result in decreasing bending strength and hardness. The appropriate amount of C addition may be 1 wt. %

In a similar note, N also plays an important role in both ambient-temperature and high-temperature mechanical properties of TiCN-based cermets. Since that, bringing N into the cermets would be always crucial. However, the added N should be in the form of TiCN, TiN or some other solutions. the addition of TiN, the core size became finer and the thickness of the rim turned out to be thinner. Accordingly, both the strength and hardness of the cermets increased. However, when the addition amount of TiN exceeded a certain amount, maybe 12 wt.% or 15 wt.%, the wettability of the hard phase in the cermets was deteriorated, the rim structure became imperfect and the core size grew up, which would lead to deteriorated mechanical properties. Furthermore, it has been observed that the TiCN-based cermets modified by TiN would possess a higher thermal shock resistance than the ones without TiN.

3.1.4 Influence of Binder Metals on TiCN-Based Cermets

In most TiCN-based cermets, the binder phase is mainly composed of Ni or Co, and the solid solution hardening of binder phase plays a vital role in the application of cermets. In TiCN-Ni-Mo cermets, an increased addition of Ni would result increased bending strength and decreased hardness. in Nevertheless, the addition of Co into TiCN-based cermets would result in a higher toughness and resistance to oxidation, owing to the higher toughness of Co than that of Ni and the improved wettability to hard phase in the cermets.

However, the resistance to corrosion of TiCN-based cermets with Co is inferior to that of cermets with Ni. The atom radius of Mo is much larger than that of Ni; hence, after the addition of Mo as binder into TiCN-based cermets, the solid solubility of Ti in Ni will be reduced, resulting in a much stable carbonitride and a rim of (Ti,Mo)C or (Ti,Mo)(C,N) -rich Mo, which can hold up the growth of TiCN grains and suppress the re-crystallization. In consequence, the relative density, the resistance to plastic deformation as well as the strength of the cermets would increase. However, the optimal Mo content is still an open question, because too much addition of Mo will lead to a sharp decrease in the fracture toughness and bending strength of cermets.

3.1.5 Influence of Secondary Carbides on TiCN-Based cermets Commonly, a better wetting between the binder phase and hard phase is quite necessary to a better binding of chemical bonds. Typically in TiCN-based cermets, in order to improve the wetting, several carbides have to be added into TiCN-based cermets. The most commonly used secondary carbides included WC, VC, NbC, Cr_3C_2 , TaC, Mo_2C and the similar. It is worth mentioning that, good wetting between the hard phase and binder phase is dependent on low stability of the secondary carbides, which can be judged from the formation enthalpy of the carbides.

As seen from Table 2, the addition of Mo_2C and WC could greatly improve the wetting between the binder phase and hard phase. Additionally, NbC and TaC have the same cubic structure as TiCN, so they will readily form a uniform solid solution with TiCN. VC and Cr_3C_2 have much higher solubility in the binder phase, thus they could inhibit the growth of the hard phase (core).

Carbides	TaC	NbC	VC	Cr ₃ C ₂	WC	Mo ₂ C
Formation enthalpy (KJ/mol)	- 183.7	- 142.3	- 126.4	89.7	- 35.1	- 17.6

Table 2: The formation enthalpy of typical carbides at 298 K.

With addition of medium amount of WC (10–20 wt. %), the wettability between the hard phase and binder phase can be improved, the carbonitride grains would become finer and the core-rim structure would be readily formed as well. In consequence, the fracture toughness, bending strength and hardness of the cermets increased.

3.1.6 Reactive Sintering

Most industrial TiC powders are fabricated through the reduction of TiO_2 with carbon at the temperature of 1900 - 2300 °C for 10 - 20 hours in an inert atmosphere. These then require crushing using jaw crushers and fine-milling thereafter. However, such methods have serious disadvantages due to high cost of equipment and high power consumption because of very high reaction temperature.

Recently, a novel process for producing TiC based cermets – named as reactive sintering – was developed to produce cermet parts. When conventional powder metallurgical manufacturing uses ceramic powders of titanium carbide (TiC) and mixes it with elemental nickel (Ni) for binder and

molybdenum (Mo) for alloying before final sintering then reactive sintering uses elemental titanium (Ti) and carbon black (C) instead of TiC. This means that the formation of the carbides occurs in situ in the sintering of the sample in one cycle. Therefore an expensive titanium carburizing step is no longer required.

The microstructure of reactive sintered cermets consists of two phases – (Ti,Mo)C grains without "core-rim" phase within a Ni matrix[11, 12].



Figure 11: reactive sintered (Ti, Mo)C-Ni cermet.

3.2 Uranium Ceramics-Metal Cermets

the requirements of high-performance and low cost nuclear fuel and a spent nuclear fuel casks gave the motive to develop techniques to fabricate refractory metal and ceramic cermets to withstand the aggressive condition in nuclear application like Nuclear Thermal Propulsion (NTP) and spent-nuclear-fuel (SNF)[13, 14].

Methods are being investigated to manufacture cermet casks to be used for storage, transport, or disposal of spent-nuclear-fuel (SNF) casks.

The functional requirements for An SNF cask include a handling Package for the SNF, radiation shielding, cooling of the SNF to limit its peak temperatures, physical protection, and – for waste packages (WPs)- delaying the degradation of SNF over long periods of time.[15]

In the same context, Significant advances have been made in the area of high-temperature cermet fuel processing since Rover/NERVA. Cermet materials offer several advantages such as retention of fission products and fuels, thermal shock resistance, hydrogen compatibility, high conductivity, and high strength. Recent NASA funded research (among this research is Nuclear Cryogenic Propulsion Stage (NCPS) project was initiated in

October, 2011, with the goal of assessing the affordability and viability of Nuclear Thermal Propulsion (NTP). Many believe that NTP is the best near term propulsion option for crew and cargo missions to the Moon, near earth objects, Mars and other deep space destinations) has demonstrated the net shape fabrication of W-Re-HfC and other refractory metal and ceramic components that are similar to UN/W-Re cermet fuels. Several processing methods including Vacuum Plasma Spray (VPS) and conventional PM processes are being evaluated to fabricate material property samples and components

Cermet fuels consist of ceramic fuel particles such as uranium dioxide (UO_2) or uranium nitride (UN) embedded in a metal matrix, which is typically tungsten (W) due to a high melting point and excellent compatibility with hot hydrogen. CERMET samples subjected to long term hot flowing hydrogen, irradiation, and transient reactor testing during the GE-710 and ANL programs showed good robustness and retention of fuel particles[16].

Testing during the GE 710 and ANL programs demonstrated the capability of W/UO_2 based cermet fuels to operate at temperatures up to 3000 K in hot hydrogen for several hours. Early in the GE 710 program, W/UO_2 cermet fuels clad with W-25Re were tested for 50 hours in hydrogen at 2860 K and remained leak tight. W/UO_2 -ThO₂ cermets clad with W-25Re were also tested at 3270 K for 1 hour, 3170 K for 3 hours, and 3070 K for 10 hours without damage. All tests showed no reaction or sensitivity to flowing hydrogen.

Most of the initial cermet development work was done with UO_2 because of the experience base. However, oxygen migration issues and fuel density limitations led to the consideration of UN as an alternate fuel; Also, there was some indication of de-bonding between UO_2 fuel particles and the tungsten matrix during testing at 3000 K, which is likely the result of a thermal expansion mismatch.

More recent cermet fuel development efforts have focused on UN as an alternative to UO_2 . UN fuels have several advantages over UO_2 such as a uranium content, higher specific higher thermal conductivity, lower coefficient of thermal expansion (CTE), and higher operating temperature capability. High uranium content is an important consideration because of difficulties in the processing of high volume percent fuel particle cermets (>50 volume %). A tungsten 72 volume % UN cermet is equivalent to pure $U0_2$ in terms of uranium loading. The main disadvantage of UN is dissociation into free uranium and nitrogen at high temperatures and the absence of a nitrogen overpressure. However, studies have shown that UN is stable in tungsten at >3000 K as long as the tungsten forms a diffusion barrier to prevent the escape of nitrogen and thus prevent UN decomposition. Ultimately, UN performance could exceed that of UO_2 because of the better CTE match, which reduces cracking and matrix/fuel particle de-bonding from thermal cycling. If cladding failures occur in space, the fuel will gradually vaporize whether it is UN or UO_2 . This behavior is well understood for UO_2 but more work is necessary to establish similar data for UN.

CERMETS are typically formed by consolidation or densification of powders using Powder Metallurgy (PM)processes. Complex tungsten based CERMETS with hafnium nitride (HfN) and zirconium oxide $(Zr0_{2})$ surrogate ceramic particles have been fabricated to near 100% density at MSFC using Hot Isostatic Press (HIP) techniques. During HIP, the CERMET powders are consolidated in sacrificial containers at 2000°C and pressures up to 30 ksi. The HIP container design, powder size and shape, powder loading, sealing, and HIP processing parameters significantly affect the quality and repeatability of the part. Figure shows typical final 12 a cermet microstructure and image of a net shape HIP consolidated part.



Figure 12:(a) Micrograph of a W/60 vol% ZrO2 CERMET with integral W claddings (b) Consolidated W/40 vol% HfN CERMET sample.

It was noticed during the tests on uranium cermets that fuel loss from tungsten cermets involves one or more of the following mechanisms:

- Loss by vaporization of exposed and interconnected fuel particles
- Thermal decomposition of fuel/matrix and subsequent migration of products
- Diffusion through micro-pores and/or micro-cracks
- High vapor pressures exerted by impurities present in consolidated parts
- Differences in thermal expansion of tungsten and fuel particles

The materials and process approaches being studied to minimize or inhibit fuel loss are:

- Size of the fuel particles and resultant shape in the consolidated part
- Tungsten coating of spherical UO_2 particles prior to consolidation
- Complete surface cladding with tungsten
- Addition of small amounts of fuel particle and matrix stabilization materials

3.2.1 Spherical Uranium Dioxide (UO₂)

A critical part of CERMET fuels fabrication is developing high quality, spherical UO_2 feedstock. While no specific requirement exists for the desired particle sizes, information from historical W-UO₂ cermet programs suggest that the particles should range in size from $10 - 200 \,\mu\text{m}$.

The technics for production of small sized spherical depleted and natural UO_2 particles are available but, its cost is very high; the Y-12 laboratory currently has affordable methods of fabricating UO_2 particles at approximately 100 µm and larger. However, the UO_2 particles are not spherical.

A Plasma Spheroidization System (PSS) was designed to spheroidize the UO_2 particles. The PSS will spheroidize the particles by passing them through a plasma torch that is fully contained in a vacuum chamber. During processing, the particles are partially melted by the plasma, re-solidified to a spherical shape, and collected at the bottom of the chamber.

3.2.2 Chemical Vapor Deposition (CVD) Tungsten Coated UO₂ Particles

A fluidized bed chemical vapor deposition (CVD) process is being developed to pre-coat the UO2 with the tungsten matrix material. Coated particles are preferred for CERMETS with high volume percent fuel to improve the particle distribution. The tungsten coating prevents UO_2 particle to particle contact, agglomeration, and coalescence during consolidation. CVD coatings also develop a columnar grain structure with a low grain boundary misorientation angle that prevents the deleterious build-up of hydrogen in the grain boundaries. The CVD process uses hydrogen reduction of tungsten hexachloride (WCl₆), which deposits on the UO₂ particles in a fluidized bed.



Figure 13: Tungsten coated ZrO2 particles.

3.2.3 Hot Isostatic Press (HIP) Fabrication of Prototypical CERMET Elements

Early development of prototypical fabrication techniques is required to demonstrate affordability, develop material specifications, and rapidly converge on design requirements. Figure 14 shows images of a 331 channel hexagonal fuel element sample during HIP fabrication. The fabrication process includes inert glovebox welding of niobium HIP can components, assembly of sacrificial mandrels in the can, powder filling, and vacuum closeout. After HIP consolidation, the sacrificial mandrels are preferentially removed using chemical etching.



Figure 14: hexagonal fuel element sample produced using HIP process.

Ultimately, the use of cermet technology in fuel elements or waste packages of depleted uranium provide a high quality pieces and rise the safety factory due to the remarkable mechanical features of cermets like hardness and toughness and the high thermal conductivity. The research for developing of this technic is proceeding rapidly which gives the optimal efficiency of these materials while providing a safe and environment-friendly method to get rid of nuclear wastes.

4. Chapter three: Modern Applications

The applications of cermet spread widely to various domains as the result of its remarkable properties, which made the research on its applicability to be used in the development in different technologies such as solar cells, space crafts and Revitalization of mechanical parts

4.1 CerMet Technology in Revitalization Friction Pairs Surfaces

4.1.1 A new discovery

In the late 1950's. In the outreach of Siberia, A group of geological engineers had discovered a new phenomenon while deep drilling into the Earth's crust and mantle layers. During these expeditions, at certain depths, they noticed their drill bits were not wearing out as usual. In fact, they looked brand new. After close scientific study, it was determined that a certain combination of minerals, coupled with the grinding of these minerals to nanoparticle size, and utilizing the energy from the friction of drilling as a catalyzer caused a phenomenal chemical reaction to take place.

This chemical reaction, briefly explained, actually modified the atomic structure of the metal's top surface layer to become "ceramic-like" in property. It also created atomic attractors that would re-attach the minute metal particles floating around in the surrounding lubrication forming a much harder and smoother "ceramic-metal" layer, thus dramatically reducing friction, extending part life, and actually rebuild and renew the worn out areas of the metal surface.

The military kept this secret from the general public and worked with this discovery for decades, perfecting its abilities and its use. For years this technology was used throughout the Pacific Fleet to repair and revitalize engines, gears, bearings without disassembly. In the 1990's, after the collapse of the Soviet Union this technology was introduced to the general scientific community. Since then CERMET LAP CO. was the world leader in the nano-particle metal revitalization technologies, production and science.

4.1.2 The science related to CerMet

CERMET mainly reverses friction-based wear out process, dramatically reduces friction and builds metal-ceramic layer, thus drastically reducing internal losses of any mechanism or assembly where friction is present. CERMET truly does what could hardly have been imagined before. It actually transforms the metal surface into a "ceramic-metal" mix that not only restores the geometry of the part, but also hardens and smoothes the surface thus drastically reducing friction. The removal of friction

dramatically improves efficiency, saves energy and resources, revitalizes and extends the life of the engine, gears, bearings and metal parts.

The term "Revitalization" (from Latin "vita"=life) literally means "returning to life". CERMET's revitalization process is based on unique nano-particle technology unlike anything in the world today. CERMET physicochemical processes take place in any metal-to-metal friction zone and actually transform the metal surfaces at the atomic level. CERMET hardens the metal's crystal lattice at the surface up to 30 microns. This new hardened surface emulates the properties of pure ceramic and will reduce friction up 100-300%.



Figure 15: the stages of revitalization of an engine part using CERMET technology.



Figure 16: Electron Microscope comparison between the surface before and after the treatment with CERMET.

One of the phenomena surrounding CERMET's is the fact that "atomic attractors" are also created at the metal's surface. Utilizing the friction energy, these atomic attractors will re-attract the minute metal particles floating around inside the lubrication and attach themselves back onto the worn part inside the friction zone where it is needed most. This in-turn is an ongoing rebuilding process that will renew the metal parts and never over-build. To explain – once both surfaces of a friction pair have been transformed to this

new cermet layer there will not be enough friction energy to activate the chemical process to continue the rebuilding process.

5. Conclusion

our lives is governed in one way or another by the degree of material science developing and the ability to obtain the optimal performance of it, Besides, the requirements of different industries and the higher criteria for the work pieces; the cermet composed materials emerged as the solution.

The increasing research about cermets revealed its remarkable properties of high high-temperature hardness, low reactivity, high toughness and ductility, relatively simple manufacturing routs and -Of course- its long operating time before wearing compared to normal work pieces which gives it its economic importance.

The routes of production obtained the main focus in former studies due to its relation to the final mechanical properties and the cost of production and i.e. the quality of the product; numerous methods were discussed to provide cermets Powder metallurgy, liquid phase sintering and reactive sintering to mention a few. However, the production rout must be chosen considering the type of cermet (binder and ceramic), its shape, and its role in the machine.

The cermet technology spread widely to find it applicable in many domains including nuclear fuel, spent nuclear fuel casks and recently in medical cutting tools, it showed an astonishing performance in all of them.

In the end, the cermet technology provides many advantages that were considered impossible in one time; it gathered the attention of researchers around the world which provided a rich literature about it. The development of cermet materials is undergoing, but for now, cermet is an ultimate performance material which we have a clear knowledge of its structure, properties and manufacturing methods.

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