Max Phase Materials- Review of an Exciting Class of Ternary Carbides and Nitrides

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Abstract— MAX phase materials are layered ternary carbide or/and nitride compounds with general formula Mₙ₊₁AXₙ where M is an early transition metal, A is a Group IIA or IIIA element and X is C or N. These materials combine certain properties of metals, such as good electrical and thermal conductivity, low hardness, machinability, damage tolerance and thermal shock resistance with those of ceramics, such as high temperature strength, high elastic moduli, oxidation and corrosion resistance. These properties are a result of an inherently nano-laminated crystal structure, with Mₙ₊₁Xₙ slabs intercalated with pure A-element layers. This paper is an attempt to review the crystal structure, synthesis, physical properties, mechanical properties and current & potential applications of MAX phase materials. The future scope for these materials include synthesizing and characterizing existing ones and higher order MAX phases, also facilitating their industrial applications.

Keywords— MAX phases, Ternary compounds, Crystal structure, Mechanical Properties.

I. INTRODUCTION

The term “MAX Phases” have become known in the late 1990’s to apply to a emerging class of ternary carbides and nitrides that bridge the gap between properties typical of metals and ceramics. They are also known as metallic ceramics and possess the general formula Mₙ₊₁AXₙ, where ‘M’ represents an early transition metal, ‘A’ represents an ‘A’ group element, ‘X’ represents ‘C’ and/or ‘N’, and n=1 to 3. Depending on the value of n, the M₂AX, M₃AX₂ and M₄AX₃ phases are usually referred to 211, 312 and 413 phases respectively. Experimental or calculated evidence has also been advanced for the existence of higher order MAX phases such as 514, 615 and 716 [6]. The figure 1 shows most commonly known MAX phase compounds.

Although Nowotny and co-workers in the 1960s discovered most of the MAX phases known to date in powder form, only after Barsoum & El-Raghy reported on the synthesis of phase pure bulk Ti₃SiC₂ samples and its unusual properties renewed interest in these solids [7]. Since then, research on the MAX phases has increased exponentially.

1.1 Why MAX Phase Materials?

The main reason for the growing interest in the MAX phases lies in their unusual, and sometimes unique, set of properties [5, 7] that can be traced back to their atomic bonding and structural characteristics. Like their corresponding binary carbides and nitrides, the MAX phases are elastically stiff, are good thermal and electrical conductors, are resistant to chemical attack, and have relatively low thermal expansion coefficients [5].
Mechanically, however, they cannot be more different; they are relatively soft (2–8 GPa) [5] and most readily machinable, thermal shock resistant, and damage tolerant [2]. Moreover, some are fatigue, creep, and oxidation resistant. At room temperature, they can be compressed to stresses as high as 1 GPa and fully recover upon removal of the load while dissipating 25% of the mechanical energy. However, at higher temperatures, they undergo a brittle-to-plastic transition (BPT), and their mechanical behaviour is a strong function of deformation rate [7].

II. CRYSTAL STRUCTURE

The MAX phases are layered hexagonal crystal structures (----- space group P63/mmc-----) and have two formula units per unit cell, as illustrated in figure 2; for ‘n’ equal to 1 to 3. The unit cells of the MAX phases are characterized by near close – packed M layers interleaved with layers of a pure A – group element, with the X atoms filling the octahedral sites between the former. The M₆X octahedra are identical to those found in the rock salt structure of the corresponding binary MX carbides. The A group elements are located at the centers of trigonal prisms, which are slightly larger, and thus better able to accommodate the larger A atoms, than the octahedral sites. The figure 2 shows the unit cells of MAX phase compounds for n=1,2 and 3.

When n = 1, the layers are separated by two M-layers. When n = 2, they are separated by three layers ; M₂AX₂ in fig.2(b). Further, when n=3, they are separated by four layers; M₃AX₃ in fig.2(c). There are roughly 50 M₂AX or 211 phases and five M₃AX₂ or 312 phases, namely Ti₃SiC₂, Ti₃GeC₂, Ti₃AlC₂, Ti₃SnC₂ and Ta₃AlC₂.

The number of M₃AX₃ or 413 phases has been reported by Barsoum et al [7] to have grown since that structure was established in Ti₃AlN₄. The A-group elements are mostly III A and IV A (i.e, groups 13 to 16); the most versatile of these elements is Al because it forms nine compounds including two nitrides, one 312 phase, and four 413 phases. Ga also forms nine 211 phases, six of which are carbides and three are nitrides.

DFT calculations of the electronic structure and chemical bonding in the MAX phases show that:

- Similar to MX phases, MAX phase bonding is a combination of metallic, covalent and ionic bonds.
- In most MAX phases, the M-A bonds are relatively weaker than the M-X bonds. [5,7]

III. SYNTHESIS

While hot-pressing has remained an important method for bulk synthesis for research purposes, pressureless sintering may be more commercially viable. Other methods for processing of bulk MAX phases are variations of self-propagating high-temperature synthesis spark plasma sintering or pulse discharge sintering and solid liquid reaction synthesis. Per Eklund et al have reported that recent innovative approaches to bulk synthesis include three-dimensional printing, the use of Al or Sn, respectively, as catalysts for growth of Ti₃SiC₂ and Ti₃AlC₂, and design of crystalline precursors for solid phase reaction synthesis [4].

The production of MAX phase powders provides an alternate route for the development of bulk single MAX phases, as well as more applications such as to MAX phase based composites [6]. The synthesis of MAX phase films are carried out using deposition techniques like CVD or PVD techniques. While bulk MAX phase compounds can be developed using MAX phase powders as mentioned above, they can synthesized using combustion reaction, Hot Isostatic Pressing (HIP), Pulsed Laser sintering etc. A few synthesis methods of MAX phase materials are discussed below.

3.1 Synthesis Methods – Reports of Study

Barsoum et al [4] carried out the synthesis of Ti₃SiC₂ powders by combustion reaction process. A solid–liquid reaction process with NaF addition [4] and a fluctuation synthesis method were applied to synthesise Ti₃SiC₂ powders [6]. In both cases, the Ti₃SiC₂ content in the as synthesised powders was 85 wt-%. The solid–liquid reaction process was also used to synthesise nearly single phase Ti₃SnC powders with small amounts of metallic Sn.
Highly phase pure Ti3SiC2 (99.3 wt-%) powders were obtained by isothermal heating of Ti–Si–TiC powder mixtures [6].

The early CVD work on the deposition of Ti3SiC2 films resulted in single phase samples with anomalous properties [6]. But these processes had drawbacks in terms of phase purity and process control. Much more rapid and fruitful results were obtained when the attention was turned from CVD to physical vapour deposition (PVD). Ti3SiC2 films were successfully synthesised by magnetron sputtering [4].

Magnetron Sputtering is a deposition process in which plasma is created and positively charged ions from the plasma are accelerated by an electrical field superimposed on the negatively charged electrode or target. Similar results were obtained in the Ti–Ge–C, Ti–Al–C, and Ti–Al–N systems. The figure 3 illustrates the principle involved in Magnetron Sputtering process.

While combustion synthesis is merited by its rapid reactions, in as short as a few seconds, but with sacrificed product quality, Barsoum et al [4] employed hot pressing (HP) or HIP for the synthesis of nearly single phase bulk Ti3SiC2 polycrystalline samples. The HIP process subjects a component to both elevated temperature and isostatic gas pressure in a high pressure containment vessel. The pressurizing gas most widely used is argon. An inert gas is used, so that the material does not chemically react. The chamber is heated, causing the pressure inside the vessel to increase. Many systems use associated gas pumping to achieve the necessary pressure level. Pressure is applied to the material from all directions (hence the term "isostatic"). Such processes were soon extended to the synthesis of many other MAX phases, such as Ti3GeC2, Ti2AlC, Ti2AlN, Ti3GeC, V2AlC, Ta2AlC and Nb2AlC. The following figure shows one of the commonly used sintering processes for the synthesis of bulk MAX phase compounds of high purity and relative density. The figure 4 shows a common type of Hot Isostatic Pressing process.

The synthesis of bulk MAX was also carried out using pulse discharge sintering (PDS), also known as spark plasma sintering. The PDS process employed for the synthesis of the MAX phases is similar to reactive Hot Pressing, however, with some advantages over the latter. The PDS process was used to fabricate bulk Ti3SiC2, starting with various molar ratios of reactants, such as Ti/Si/C, Ti/ SiC/C, Ti/Si/TiC, Ti/SiC/TiC, and Ti/TiSi/TiC [6].

However, these reactive sintering processes cannot easily be applied to the mass production of MAX phase parts. Pressureless sintering from powder green compact without mechanical pressure, i.e. pressureless sintering, is much more economical and scalable. Early attempts of pressureless sintering were first made via mechanical alloying (MA) and sintering process, which all ended up with a high content of unwanted secondary phases.
Sun et al [6] reported on the successful synthesis of high phase purity and density Ti₃SiC₂, by reactive pressureless sintering (patented). Such pressureless sintering processes from the respective phase pure compound powders are a promising practice for application.

IV. PHYSICAL PROPERTIES

This section deals briefly with the electrical and optical properties, thermal property and chemical stability of MAX phase materials. The electrical conductivities of MAX compounds are due to impurity phases and compositional variation while their optical properties are due to the delocalised electrons. These materials exhibit good thermal conductivities, low thermal expansion co-efficient and do not melt congruently at high temperature.

4.1 Electrical Properties

Most of the MAX phases are excellent electrical conductors, with electrical resistivities that mostly fall in the narrow range of 0.2–0.7 μΩ·m at room temperature [5]. The low resistivities measured, for example, in Ti₃SnC have been difficult to reproduce, which has been attributed to compositional variation and the presence of impurity phases in the microstructure [6].

Many MAX phases are compensated conductors, i.e., both electrons and holes contribute in approximately equal number to electrical conductivity. This is evidenced by measurements of the Hall and Seebeck coefficients, where the measured results tend to fluctuate around zero and give either slightly positive or slightly negative values [4]. Such fluctuations can only occur for compensated conductors. There are exceptions; for example, Ti₃AlC and Ti₃AlN are primarily hole conductors [11], and Ti₂SC [10] is mainly an electron conductor.

4.2 Optical Properties

The optical properties of the MAX phases are dominated by delocalized electrons [5]. Magnetically, most of them are Pauli paramagnets, wherein the susceptibility is, again, determined by the delocalized electrons and, thus, is neither very high, nor temperature dependent [10].

4.3 Thermal Properties

Thermally, the MAX phases share much in common with their MX counterparts, that is, they are good thermal conductors because they are good electrical conductors. At room temperatures their thermal conductivities fall in the 12–60 W/(m·K) range [7].

The coefficients of thermal expansion (CTE) of the MAX phases fall in the 5–10 μK⁻¹ range and are relatively low as expected for refractory solids. The exceptions are some chromium-containing phases with CTEs in the 12–14 μK⁻¹ range [5].

At high temperatures, the MAX phases do not melt congruently but decompose peritectically to a rich liquid and Mₙ[Xₐ] carbides or nitrides. Thermal decomposition occurs by the loss of the A element and the formation of higher n-containing MAX phases and/or MX. Some MAX phases, such as Ti₃SiC₂, are quite refractory with decomposition temperatures above 2300°C [6].

The coefficients of thermal expansion of the MAX phases range from 7.2-13.3 x10⁻⁶ K⁻¹ [6]. Currently, the highest coefficients of thermal expansion were reported in Cr₂AlC and Cr₂GeC [6], which is one reason the former, is a good candidate for large area coatings on steels. Measurements of the thermal expansion of the MAX phases in different orientations were performed using high temperature X-ray diffraction [6] or synchrotron X-ray diffraction. The graphs in the below figure 5 shows the effect of temperature on the resistivities and thermal conductivities of select MAX phases.

![Figure 5: Temperature dependence of (a) electrical conductivity and (b) thermal conductivity of select MAX phases. [5]](image)

V. CHEMICAL STABILITY AND OXIDATION RESISTANCE

Like traditional ceramics, many Al-containing MAX phases are stable in inert atmospheres up to at least 1500 °C [12]; However when exposed at high temperature to oxidizing environments, the MAX phases form oxide scales that depend on their chemistry.
The excellent oxidation resistance stems from the formation of a thin tenacious, adherent, alumina layer. The oxidation resistances of MAX phase materials determine their usefulness in air. In most cases, MAX phases oxidize according to Eqn (1) [5].

\[ M_{n+1}AX_n + \alpha O_2 = (n+1) MO_{n+1} + AOy + X_{n}O_{2b-x} \]  

Consequently, their oxidation resistance depends on nature of the oxides that form. The most oxidation-resistant MAX phase is Ti$_2$AlC, because it forms a stable and protective Al$_2$O$_3$ layer that can withstand thermal cycling up to 1,350°C for 10,000 cycles without spallation or cracking [5]. The oxidation resistance of Cr$_2$AlC also is superb because it also forms a protective Al$_2$O$_3$ layer; however, the oxide spalls off during thermal cycling [11]. The figure 6 shows the micrograph of Al$_2$O$_3$ oxide layer after 10,000 thermal cycles up to 1,350°C showing no spallation or cracking of the oxide layer.

![Figure 6: Micrograph of the Al$_2$O$_3$ oxide layer [5]](image)

VI. MECHANICAL PROPERTIES

The M$_{n+1}$AX$_n$ compounds exhibit unusual and unique combination of properties. Much like their corresponding binary carbides and nitrides counterparts, they are elastically stiff, have good thermal and electrical conductivities, relatively low thermal expansion coefficients and are resistant to chemical attack. But they are relatively soft (1–5 GPa) and most readily machinable, damage tolerant and thermal shock resistant. Some MAX phase compounds are fatigue and creep, and oxidation resistant and they go through a ductile-to-brittle transition at high temperatures. At room temperature, they exhibit compressive strength as high as 1 GPa and fully recover upon removal of the load, while dissipating 25% of mechanical energy [9].

The MX and MAX phases despite being similar in terms of physical properties exhibit striking differences in their mechanical properties.

While MX phases are some of the hardest known solids, they are brittle, not easily machinable, damage intolerant, and susceptible to thermal shock. The MAX phases on the other hand are exceedingly damage tolerant and thermal shock resistant, and most are readily machinable [5]. This major difference in behaviour is due to the mobile dislocations in their crystal structures.

The property of excellent machinability of MAX phases can be attributed to their low hardness and their layered nature. The reported data of the hardness of the MAX phases range from 1.4 to 8 GPa [6]. The MAX phases have higher compressive than tensile or flexural strengths like conventional ceramics exhibiting compressive strengths upto 1.9GPa [6].

The MAX phases are reported to be elastically quite stiff [7]. Their specific stiffness values are high and have low densities ranging from 4-5 g/cc [7]. Despite having higher stiffness values MAX phases exhibit excellent machinability [13]. Their excellent electrical conductivities also allow them to be readily machined by electron discharge [14].

The polycrystalline MAX phases are softer than most structural ceramics, but harder than most metals. They exhibit Vickers hardness values in the range of 2–8 GPa [5].

The fatigue behavior data of MAX phases is quite limited and have been reported only in Ti$_2$SiC$_2$ which exhibits cyclic fatigue crack propagation behavior. It is characterized by higher threshold stress intensity factors and lower crack growth rates that are superior to conventional structural ceramics. The high fatigue resistance is reportedly due to the heterogeneous and laminated structure [6]. The graphs shown below in figure 7 illustrate the variations of compressive stresses and flexural stresses at different temperatures and strain or displacement for Ti$_2$SiC$_2$ compound.

![Figure 7: Mechanical properties of Ti$_2$SiC$_2$ prepared by reactive PDS process [6].](image)
VII. APPLICATIONS

Barsoum et al. [3] opine that probably the greatest potential impact these materials will have will be on the transportation sector, keeping in mind the need to increase the efficiency of our cars and airplanes and the fact that MAX phases like Ti$_3$SiC$_2$ possess roughly half the density of the alloys used in today’s jet engines and maintains its strength to temperatures that would render the best nickel-based superalloys on the market unusable.

Some of the potential markets where Ti$_3$SiC$_2$ and possibly some of the other ternaries could find applications are structural materials for high temperature applications, substitute for machinable ceramics, kiln furniture, wear and corrosion protection, heat exchangers, applications where rotating parts are used [16]. Other potential applications include electrodes, exhaust gas filters for automobiles, free-cutting elements, microelectronics, biomaterials, damping materials (high stiffness and up to high temperatures), corrosion resistant materials, surface coatings, defence applications; such as armor, nuclear applications, low dimensional materials and substrates for CVD Diamond [6]. The figure 8 illustrates some of the many applications of MAX phase compounds in recent times.

VIII. FUTURE POTENTIAL OF MAX PHASES

With the futuristics demanding more research to meet the needs of land and air transportation engineering in the form of lighter and high temperature resistant materials and in addition towards meeting the needs of high temperature tooling industry, defense applications, kiln furniture, heat exchangers and the like, the research work done so far have highlighted that the MAX phase materials could be a promising class of materials for such demands. More market penetration by these metallic ceramics will lead to increased attention on these classes of materials and also broadening their horizon of applications.

REFERENCES


Fig.: 8 (a) Ti$_3$AlC and Ti$_3$SiC$_2$ powders and parts fabricated by Sandvik Heating Technology, Sweden, and commercially available under the trade name MAXthal 211 and MAXthal 312 [5]; (b) Maxthal 211 heater glowing at 1723K (Courtesy 3-ONE-2 LLC) [6]; (c) gas burner nozzles made of Maxthal 211 and 353MA steels after one year in furnace at 1773 K (courtesy 3-ONE-2, LLC and Kanthal)[6].


