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High Temperature Structural Silicides

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Abstract:

Structural silicides have important high temperature applications in oxidizing and aggressive environments. Most prominent are MoSi_2 -based materials, which are borderline ceramic-intermetallic compounds. MoSi_2 single crystals exhibit macroscopic compressive ductility at temperatures below room temperature in some orientations. Polycrystalline MoSi_2 possesses elevated temperature creep behavior which is highly sensitive to grain size. MoSi_2 - Si_3N_4 composites show an important combination of oxidation resistance, creep resistance, and low temperature fracture toughness. Current potential applications of MoSi_2 -based materials include furnace heating elements, molten metal lances, industrial gas burners, aerospace turbine engine components, diesel engine glow plugs, and materials for glass processing.

Introduction:

Over the past few years, structural silicides have emerged as important elevated temperature structural materials for applications in oxidizing and aggressive environments (1-3). There are a relatively large number of silicides known, most of which have seen little characterization of their properties (4). For structural purposes, the silicides of most interest are the transition metal silicides, and more particularly molybdenum-based silicides.

In terms of structural materials that can be used in oxidizing environments, there is a temperature cutoff point at approximately 1000 °C. Below this temperature materials such as nickel and cobalt-based superalloys can be employed, as well as materials such as titanium and nickel aluminides and SiC fiber reinforced glass-ceramics. However, above 1000 °C, for oxidation-resistance and elevated temperature strength reasons, one must resort to materials such as the silicon-based structural ceramics Si_3N_4 and SiC, advanced high temperature intermetallics such as NiAl and NbCr₂, and the class of structural silicide materials, most notably MoSi₂.

Potentially interesting and important structural silicides are shown in Table I. MoSi₂ has been by far the most investigated due to its excellent oxidation resistance. WSi₂ forms a complete solid solution with MoSi₂. Mo₅Si₃ is adjacent to MoSi₂ in the Mo-Si phase diagram. NbSi₂ and TaSi₂ have exhibited single crystal ductility in some orientations at temperatures near room temperature. Ti₅Si₃ has a high melting point and low density.

Table I: Some Interesting Potential Structural Silicides

Silicide	Melting Point (°C)	Crystal Structure	Density (g/cm ³)
MoSi ₂	2030	Tetragonal	6.24
WSi ₂	2160	Tetragonal	9.86
NbSi ₂	1930	Hexagonal	5.66
TaSi ₂	2200	Hexagonal	9.10
TiSi ₂	1500	Orthorhombic	4.04
CrSi ₂	1490	Hexagonal	4.98
CoSi ₂	1326	Cubic	4.95
YSi ₂	1835	Rhombohedral	4.50
Mo ₅ Si ₃	2160	Tetragonal	8.24
Ti ₅ Si ₃	2130	Hexagonal	4.32

Characteristics of MoSi₂:

As has been indicated, MoSi₂ has received the most attention to date in the field of structural silicides. It is pertinent to ask the question: What is MoSi₂? In order to answer this question, it is first necessary to address the question: What is a ceramic? Although there have been many definitions of a ceramic put forward, a definition which is both comprehensive and succinct is the following (1): A ceramic is a solid, ionic-covalent, inorganic compound. Based on this definition of a ceramic, MoSi₂ is then a borderline ceramic-intermetallic

compound, since its atomic bonding is a combination of both covalent and metallic (5).

It is the collection of properties of MoSi_2 that make it interesting as a high temperature structural material (1). MoSi_2 has a high melting point of 2030 °C. It has superb high temperature oxidation resistance, essentially equivalent to that of SiC since it forms a thin coherent and adherent protective silica layer. In polycrystalline form, MoSi_2 exhibits a brittle-to-ductile transition in compression in the vicinity of 1000 °C or lower, although some orientations of single crystals actually show macroscopic ductility at much lower temperatures. The material is thermodynamically stable with a wide range of structural ceramics, including Si_3N_4 , SiC, Al_2O_3 , ZrO_2 , mullite, TiB_2 , and TiC. Thus, there is a significant potential for composite development. It can also be alloyed with other high melting point silicides such as WSi_2 , NbSi_2 , Mo_5Si_3 , and Ti_5Si_3 . Due to the metallic nature of its bonding, MoSi_2 can be electro-discharge machined, thus making it easier to machine than most structural ceramics. Finally, MoSi_2 is an abundant, relatively low cost material, which is also environmentally benign.

In terms of engineering properties, MoSi_2 has a thermal expansion coefficient close to that of Al_2O_3 . Its thermal conductivity is intermediate between that of Si_3N_4 and SiC. The elastic modulus of MoSi_2 is close to the elastic modulus of SiC. While the high temperature oxidation resistance of MoSi_2 is similar to that of SiC, maximum oxidation rates in MoSi_2 actually occur at the intermediate temperature of 500 °C.

Single Crystal MoSi_2 :

The crystal structure of MoSi_2 is tetragonal. The compressive deformation of single crystal MoSi_2 has been investigated as a function of temperature (6-8). Figure 1 shows the compressive yield stress of MoSi_2 single crystals as a function of temperature. There are two key points to be made about the data in Figure 1. First, elevated temperature strength in the [001] orientation is very high, essentially similar to that of c-axis sapphire. This suggests the potential for crystallographic texture development to increase high temperature mechanical strength, such as polycrystalline fiber or wire development with a [001] texture. The second key observation is that macroscopic compressive ductility occurs in some crystallographic orientations at temperatures as low as -100 °C. This presents the possibility of significantly lowering the ductile-to-brittle transition temperature of MoSi_2 by suitable alloying.

Figure 1: Compressive yield stress of MoSi_2 single crystals as a function of temperature (8).

The observed slip systems in MoSi_2 are $\{013\}\langle 331\rangle$, $\{110\}\langle 111\rangle$, $\{011\}\langle 100\rangle$, $\{010\}\langle 100\rangle$, and $\{023\}\langle 100\rangle$ (6-8). An anomalous behavior is observed for the $\{013\}\langle 331\rangle$ slip system, in that this slip system operates only at high temperatures for crystallographic orientations near $[001]$, yet is observed to be operative at low temperatures for other crystallographic orientations (8). This unusual behavior is likely due to dislocation core effects. If the $\{013\}\langle 331\rangle$ slip system can be made to operate in the $[001]$ orientation, then there is a significant possibility of markedly lowering the brittle-to-ductile transition of polycrystalline MoSi_2 (8). The alloying of MoSi_2 to promote this slip system is presently an active area of silicide research.

Figure 2 shows a room temperature Vickers indentation in single crystal MoSi_2 oriented in the $[001]$ direction (9). Both indentation cracks and dislocation slip lines are observed on the polished surface at room temperature. This indicates that MoSi_2 is a semi-brittle material somewhat analogous to MgO . The direction of the indentation cracks suggests that $\{100\}$ planes may be cleavage-type planes in MoSi_2 . If the slip trace planes are perpendicular to the plane of polish, then slip on $\{100\}$ and $\{110\}$ planes at room temperature is suggested.

Figure 2: Room temperature 1000 gm Vickers indentation in single crystal MoSi₂ (9).

Polycrystalline MoSi₂:

At the present time, polycrystalline MoSi₂ is brittle at room temperature, with a polycrystalline fracture toughness of approximately 3 MPa m^{1/2} (10). It has been shown that at room temperature, the fracture mode of MoSi₂ is 75% transgranular and 25% intergranular (10). The brittle-to-ductile transition of large grained, low oxygen content MoSi₂ has been investigated in both compression and bending (11). While a BDTT of approximately 1000 °C is seen in compression, the BDTT in bending occurs at approximately 1350 °C in bending. The BDTT of polycrystalline MoSi₂ is sensitive to both grain size and oxygen content, decreasing with decreasing grain size and increasing oxygen content. It has been shown that prestraining at 1300 °C can lower the BDTT of polycrystalline MoSi₂ to approximately 750 °C (12). This is due to the introduction of mobile dislocations by the high temperature prestraining treatment.

The elevated temperature creep resistance of polycrystalline MoSi₂ is highly sensitive to grain size (13). This effect is shown in Figure 3. The creep resistance of MoSi₂ has been shown to increase by three orders of magnitude with only an 11 μm increase in the grain size. A full explanation of this grain size sensitivity has not yet been obtained. However, the elevated temperature creep mechanisms in polycrystalline MoSi₂ are known to be a combination of grain boundary sliding and dislocation plasticity (13). This grain size effect on creep

resistance is important from the viewpoint of composite design for optimized creep properties.

Figure 3: Effect of grain size on the creep of polycrystalline MoSi₂ (13).

MoSi₂-based Composites:

For MoSi₂-based materials to be successfully employed in high temperature structural applications, both the high temperature creep resistance and the low temperature fracture toughness must be improved. The composite approach with ceramic reinforcements has been shown to yield such improvements, with no significant reduction in the oxidation resistance of these materials (1). Composites may be a MoSi₂ matrix reinforced with ceramic, or a ceramic matrix reinforced with MoSi₂.

Both SiC whisker and SiC particle reinforcements have been observed to significantly increase the elevated temperature creep resistance of MoSi₂-based materials, and moderately increase the room temperature fracture toughness (14-16). The addition of ZrO₂ particles to a MoSi₂ matrix can produce significant transformation toughening effects in MoSi₂ composites, with the maximum toughening observed for unstabilized ZrO₂ particles (17).

MoSi₂-Si₃N₄ Composites:

The MoSi₂-Si₃N₄ composite system is a very interesting and important one. MoSi₂ and Si₃N₄ are thermodynamically stable compounds (18). Additions of Si₃N₄ to a MoSi₂ matrix significantly improve the intermediate temperature oxidation resistance of MoSi₂ and its elevated temperature mechanical properties (19). Additions of MoSi₂ to a Si₃N₄ matrix allow for the electro-discharge machining of Si₃N₄, and also lead to improved fracture toughness and elevated temperature oxidation characteristics (20,21,22). Figure 4 shows the effects on room temperature fracture toughness and elevated temperature creep resistance of additions of MoSi₂ to a Si₃N₄ matrix (21).

Figure 4: Room temperature fracture toughness and elevated temperature creep resistance of MoSi₂ particle-Si₃N₄ matrix composites (21).

Boron-Mo₅Si₃:

The silicide compound Mo₅Si₃ is adjacent to MoSi₂ in the Mo-Si phase diagram, and has a high melting point of 2160 °C. A major drawback to its application has been the fact that its oxidation resistance is greatly inferior to that of MoSi₂ (2). Recently, it has been shown that small additions of boron to Mo₅Si₃ significantly improve the oxidation resistance of this material (23). These small additions of boron lead to the formation of a protective borosilicate glass oxidation layer. Additionally, the boron additions produce the formation of a multiphase composite material consisting of Mo₅Si₃B_x, Mo₅(SiB)₃, Mo₃Si, MoSi₂, and MoB, with the exact phase composition depending on the level of boron addition. The boron-Mo₅Si₃ materials have been reported to possess good elevated temperature creep resistance (24).

Applications of MoSi₂-based Materials:

MoSi₂-based materials are beginning to develop a broad base of important industrial applications. These applications are driven by the elevated temperature

mechanical properties of these materials, in combination with other properties such as electrical conductivity and oxidation/corrosion resistance.

Heating Elements:

MoSi₂ materials have been employed for a number of years as heating elements for air furnaces. The recent Kanthal Super 1900 heating elements can operate at an element temperature of 1900 °C in air and oxidizing environments. These Super 1900 elements are actually a solid solution alloy of MoSi₂ and WSi₂. The major problems with the MoSi₂-based heating elements are brittle fracture, which makes the elements difficult to handle, and high temperature creep, which causes the elements to deform. Both of these aspects limit element life, as well as affect furnace design. Current elements are U-shaped and typically hung vertically due to limitations in mechanical properties. As both the fracture toughness and creep resistance of MoSi₂-based materials continue to improve by composite and alloying approaches, there will be significant effects on enhanced furnace element lifetime as well as greater flexibility in furnace design.

Molten Metal Lances:

A number of foundry operations require that gases be injected into molten metals. Microlaminate MoSi₂-Al₂O₃ composite tubes were fabricated by plasma spray forming (25). These tubes were then tested as inert gas lances in molten aluminum alloy at 725 °C and molten copper at 1200 °C. The MoSi₂-Al₂O₃ composites performed very well in both molten metals (25). In the case of the molten copper, alternative tube materials of graphite and SiC were also tested for comparison. The graphite tube lasted for only fifteen minutes in the molten copper, while the SiC tube thermal shocked upon immersion in the molten copper. In contrast, the MoSi₂-Al₂O₃ microlaminate tube withstood four hours in the molten copper and could have lasted longer, however the test was terminated at the four hour mark. The composite tube was resistant to chemical attack by the molten copper due to the presence of the Al₂O₃ phase, while it exhibited thermal shock resistance and "graceful failure" type mechanical behavior due to plastic deformation of the MoSi₂ phase (25).

Industrial Gas Burners:

The industrial gas burner industry is in the process of developing gas burners which will burn oxygen-natural gas mixtures rather than air-natural gas mixtures, in order to reduce NO_x environmental emissions. Because such

oxygen-natural gas burners must operate at higher temperatures than air-natural gas burners, there is a need to develop new burner materials which are resistant to the oxygen-natural gas combustion environment. Studies have shown that MoSi_2 possesses significant resistance to oxygen-natural gas combustion at high temperatures (26). After an initial transient period, material stability is achieved through the formation of a stable Mo_5Si_3 layer. Stability occurs under both stoichiometric and fuel-rich combustion conditions. Prototype MoSi_2 gas burners have been fabricated by a plasma spray forming process (27).

Aerospace Gas Turbine Engines:

Pratt & Whitney has been developing advanced materials for a blade outer air seal (BOAS) hot section component of its gas turbine engines. In the engine, the BOAS is a stationary part which is located directly opposite of the rotating hot section turbine blades. The purpose of the BOAS is to maintain a small gap of stable dimensions between itself and the turbine blade. If this gap widens during operation of the turbine, it directly affects the turbine efficiency. Although stationary, the BOAS is exposed to high turbine gas temperatures and significant thermal stresses.

Gas burner testing by Pratt & Whitney has shown that MoSi_2 -SiC and MoSi_2 - Si_3N_4 composites possess significant thermal shock resistance in the simulated jet fuel combustion environment (28). These materials survived 250 cycles from room temperature to 1500 °C with no failures. Recent work at NASA-Lewis has concentrated on MoSi_2 - Si_3N_4 composites reinforced with SiC continuous fibers. Thermomechanical Charpy impact tests as a function of temperature (which are designed to evaluate the material resistance to foreign impact damage in the engine) have demonstrated that these composite materials absorb significant impact energy at both room temperature and elevated temperatures (29).

Diesel Engines:

MoSi_2 - Si_3N_4 composite diesel engine glow plugs have recently been developed by Toyota Central R&D in Japan (30). The MoSi_2 - Si_3N_4 glow plugs contain 30-40 vol.% MoSi_2 phase in a Si_3N_4 matrix. These glow plugs have two distinct practical advantages over metal glow plugs. First, they are highly resistant to the diesel fuel combustion environment and thus have a long lifetime of approximately thirteen years. Second, they can be heated at higher heating rates with the result that the diesel engine can be started faster. An inner composite cylinder with an interconnected MoSi_2 phase provides the necessary

electrical conductivity for the glow plug application. An outer, non-conducting sheath of the same $\text{MoSi}_2\text{-Si}_3\text{N}_4$ phase composition is employed as a cover for the inner conducting composite and has the same thermal expansion coefficient and thermal conductivity. This microstructural tailoring of the $\text{MoSi}_2\text{-Si}_3\text{N}_4$ composite allows for optimum performance of the diesel glow plug.

Glass Processing:

At the present time, metals and ceramic refractories are primarily employed in applications and components requiring contact with molten glasses. The refractory metal molybdenum is highly resistant to corrosion when immersed in molten glass. However, due to its poor oxidation resistance, it cannot be employed at or above the molten glass line. The precious metal platinum is also employed in contact with molten glasses, but this material is very expensive. The AZS multiphase refractory ceramic (Alumina-Zirconia-Silica) is also used for containing molten glasses, but suffers from relatively poor mechanical properties.

Recently, it has been shown that MoSi_2 is also a material which is quite resistant to corrosion by molten glasses (31-33). MoSi_2 shows excellent corrosion resistance below the glass line due to Mo_5Si_3 formation, and excellent oxidation resistance above the glass line due to SiO_2 formation. While corrosion rates of MoSi_2 are somewhat higher at the glass line than below the glass line, it has been reported that anodic protection of the MoSi_2 significantly lowers corrosion rates at the glass line (33).

This corrosion resistance of MoSi_2 to molten glasses in combination with its elevated temperature mechanical properties has recently lead to the Kanthal Corporation marketing a new MoSi_2 immersion tube for the injection of gases into molten glass (34). It has also initiated a Cooperative Research and Development Agreement (CRADA) between the Los Alamos National Laboratory and Schuller International Inc. (35). Schuller International is a major U.S. producer of fiberglass, and the objective of the CRADA is the development of MoSi_2 -based materials for fiberglass processing applications and components.

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