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Directional crystallization of $MoSi_2$ and some compositions based on it

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Abstract

It has been shown that by directional crystallization of pseudobinary compositions of molybdenum disilicide ($MoSi_2$) with some other refractory compounds, particularly with diborides of transition metals (composite materials having a disilicide matrix and extended in crystallization direction diboride inclusions) can be obtained that may improve the mechanical properties of the matrix material. © 1997 Elsevier Science S.A.

Keywords: Directional crystallization; Silicides

1. Introduction

Molybdenum disilicide ($MoSi_2$) has attracted the attention of both scientists and technologists over the last few decades due to its excellent oxidation resistance at high temperatures. Having a moderate density and a high melting point, it could occupy a respectable position among compounds for new construction materials [1–5].

Unfortunately, in its individual state it has two substantial disadvantages — a high brittleness at room and moderate temperatures and a low creep resistance at high temperatures, particularly in the region where its unusual high oxidation resistance may be utilized.

Then the main efforts of scientists were geared towards the creation of different $MoSi_2$ based composite materials for plastification at moderate temperatures and strengthening at high temperatures. They studied different strengthening materials, particularly refractory metals, oxides, non-oxygen refractory compounds. Several technological methods were used including powder metallurgy, self-propagating high-temperature synthesis, plasma-spray processing, solidstate displacement reactions and crystallization from melted solutions, etc. [6,7].

Among the strengthening materials investigated that do not lower the oxidation resistance of matrix material the most promising appear to be some diborides of transition metals and silicon carbide.

It could be assumed that further improvements in the composition, structure and properties of $MoSi_2$ based composite materials may be made using combinations of several technological methods. Using this technique it is possible to obtain a desirable quantity, configuration of introduced phases and their distribution in the matrix phase.

One promising method in the formation of real structures of composite materials that favors their essential strengthening is directional crystallization of eutectic compositions.

This method may be considered as a combination of zone melting and melted solution methods and allows us to obtain the strengthening phase in the form of uni-axial crystals, distributed in the matrix of the main phase.

The closer to the eutectic point the composition of

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the composite, the more regular should be the structure obtained and may result in improved mechanical properties.

It has previously been shown that during directional crystallization of LaB_6–MeB_2 eutectic systems the single crystal matrix of lanthanum hexaboride is formed with single crystal fibers or whiskers of some diboride phase regularly distributed in it, that can be determined by peculiarities in the diboride phase crystal structure [8,9].

The pseudobinary constitutional diagrams including $MoSi_2$ with other refractory compounds have not been studied in detail, but it is known that some of them, particularly with titanium and zirconium diborides, have a eutectic character [10]. Thus it may be supposed that a similar structure may also be realized in such composites.

2. Materials and methods

The directional crystallization process both for individual $MoSi_2$ and its mixtures with some transition metal diborides, i.e. TiB_2, ZrB_2 and ScB_2 was studied.

Also, mixtures of $MoSi_2$ with erbium ($ErSi_2$), tantalum ($TaSi_2$) and tungsten disilicides (WSi_2) were investigated for stabilization of definite (hexagonal or tetragonal) $MoSi_2$ modification; some experiments were made with the addition of silicon or tungsten carbides.

The directional crystallization process was performed using sintered rods of individual or composite materials. This was carried out by induction crucibleless zone melting, the zone movement rate was in the range 1–5 mm/min. To prevent silicon evaporation, inert (argon) gas under pressure up to 0.5 MPa was used.

The quenching of melted drops of composite materials into a cold copper crucible was used for obtaining a preliminary estimation of the possibility in the formation of elongated inclusions of strengthening phase into the matrix phase of molybdenum silicide. This method may be used as a fast qualitative evaluation of possible real structure configuration that may be realized by direction crystallization.

The composition of obtained samples was studied by chemical, X-ray and optical spectra analysis. Real structure and fracture surface were researched using

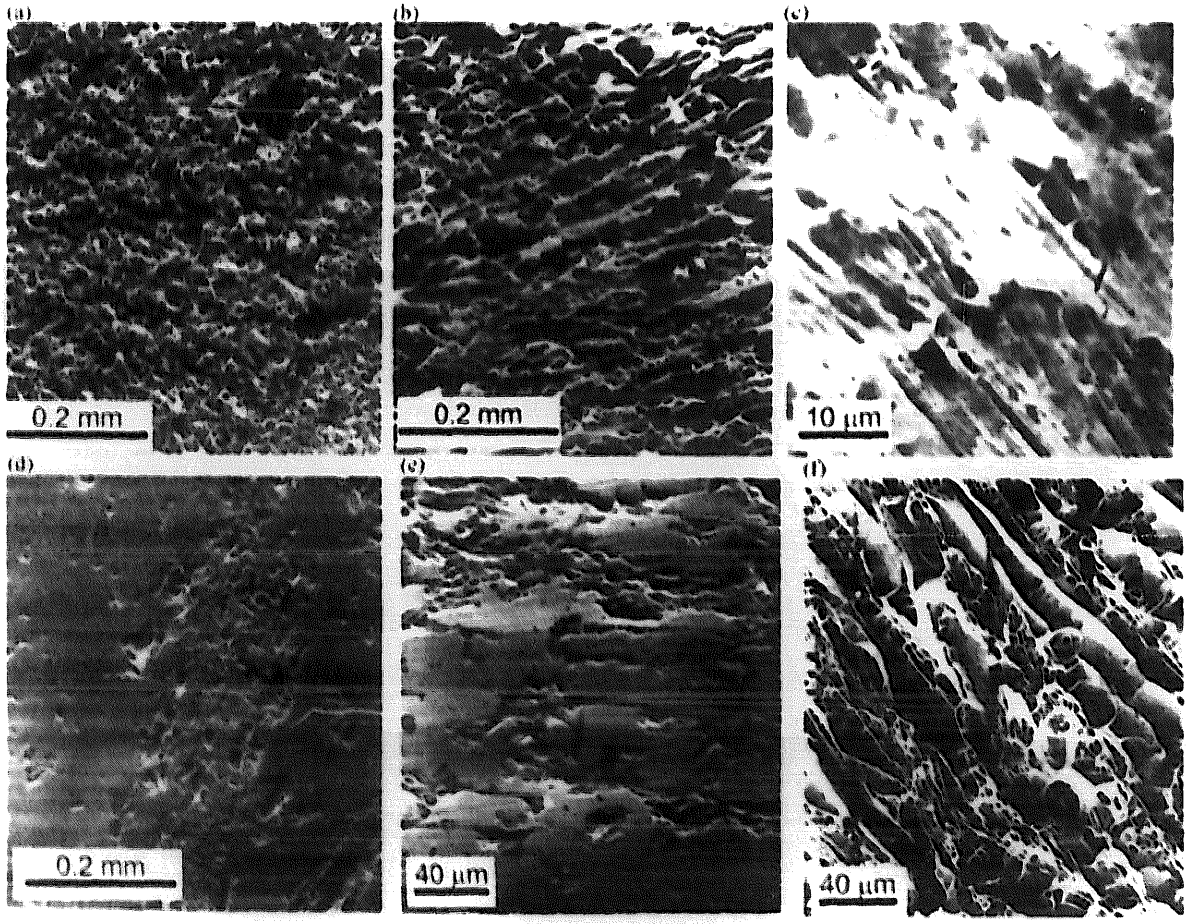

Fig. 1. Microstructures of quenched drops of $MoSi_2$-based composite materials (a) +20 vol.% ScB_2; (b) +27 vol.% LaB_6; (c) +80 vol.% WC; (d) +5.5 vol.% SiC; (e) +20 vol.% Si_3N_4; (f) +5 vol.% $TaSi_2$.

scanning electron microscopy with X-ray microanalyses.

3. Results and discussion

There are some contradictions in published data [11] about the existence or absence of polymorphous transitions of individual molybdenum disilicide close to its melting point. If this occurs, then the resulting oriented structure that may be formed under directional crystallization at the solidification point after such a solid state phase transformation may be distorted.

Firstly, the crystallization of individual molybdenum disilicide was studied.

X-ray structure investigations of specimens that were obtained at different cooling rates (quenched drops, zone melted and directional crystallized samples) have shown that in all cases only the tetragonal structure was fixed, which agrees with recently published data [11]. These results confirm the possibility of using the directional crystallization technique for molybdenum disilicide composite materials.

Next the structures of quenched drops of molybdenum disilicide compositions were studied.

The structure of a quenched drop of molybdenum disilicide with the addition of scandium diboride (20%, v/v) has shown the absence of any specific orientation of phases, only a practically isotropic fine grain structure was formed (Fig. 1a).

In the molybdenum disilicide–lanthanum hexaboride mixture a very small mutual orientation of component phases was seen (Fig. 1b).

The structure of a quenched drop of a mixture of molybdenum disilicide with tungsten carbide (80%, v/v) has shown some orientation (Fig. 1c).

The structure of a quenched drop of $MoSi_2$ with the addition of silicon carbide (5.5%, v/v) shows the absence of mutual structure orientation. A matrix phase based on $MoSi_2$ with some inclusions of silicon carbide is seen (Fig. 1d). A similar structure was formed in a composite of molybdenum disilicide with silicon nitride (20%, v/v) (Fig. 1e).

The microstructure of a rapidly quenched drop of composite that contains $TaSi_2$ (10%, v/v), demonstrates a heterogeneous structure, that consists of substantially large crystals of the matrix phase ($MoSi_2$) and eutectic colonies occupying approximately half of the figure area. The general structure orientation is connected with the direction of maximal heat flow.

12.5, 20 and $MoSi_2$ based composites having ZrB_2 (25%, v/v) were studied.

The structure of a quenched drop of a mixture of

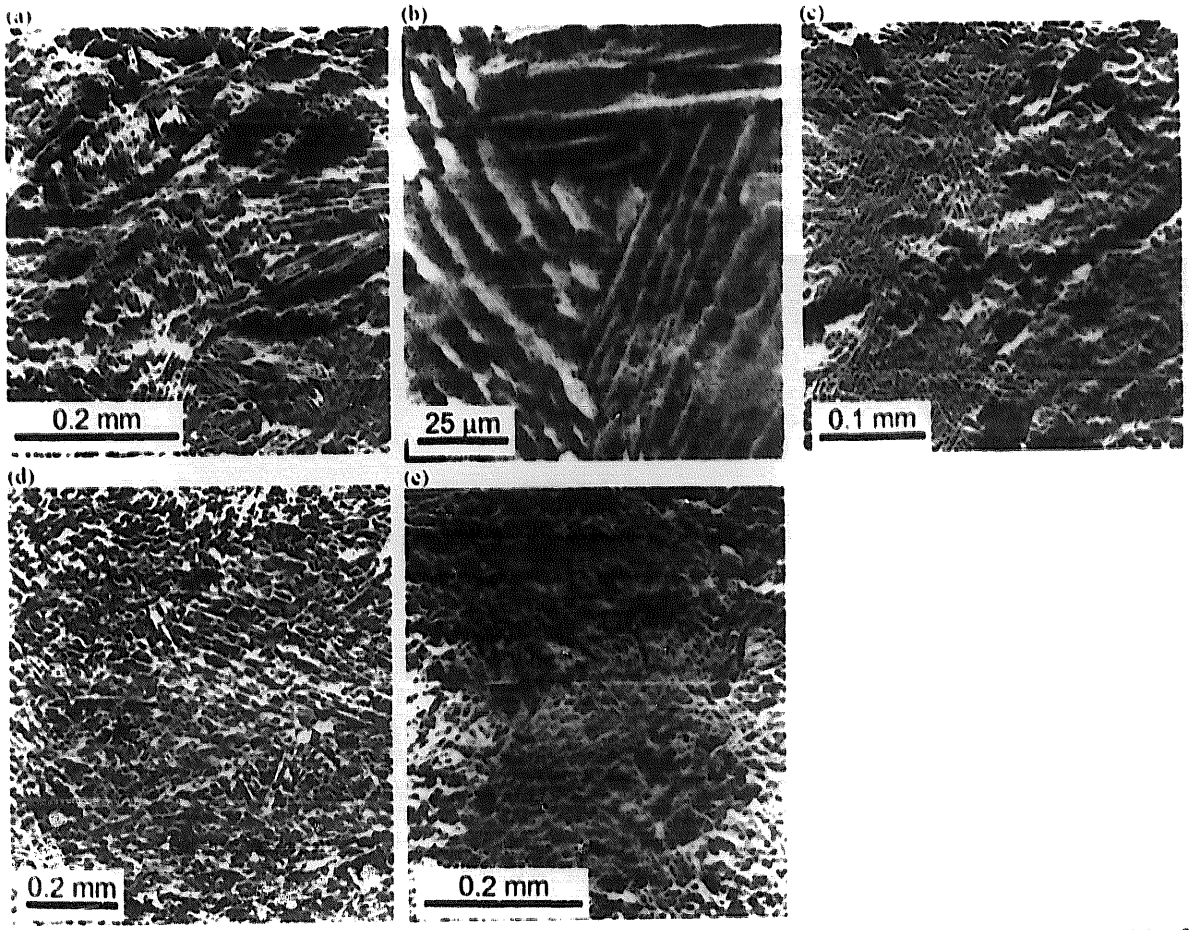

Fig. 2. Microstructures of quenched drops of $MoSi_2$–MeB_2 composite materials: (a) + 12.5 vol.% ZrB_2; (b) + 12.5 vol.% ZrB_2; (c) + 20 vol.% ZrB_2; (d) + 25 vol.% ZrB_2; (e) + 20 vol.% TiB_2.

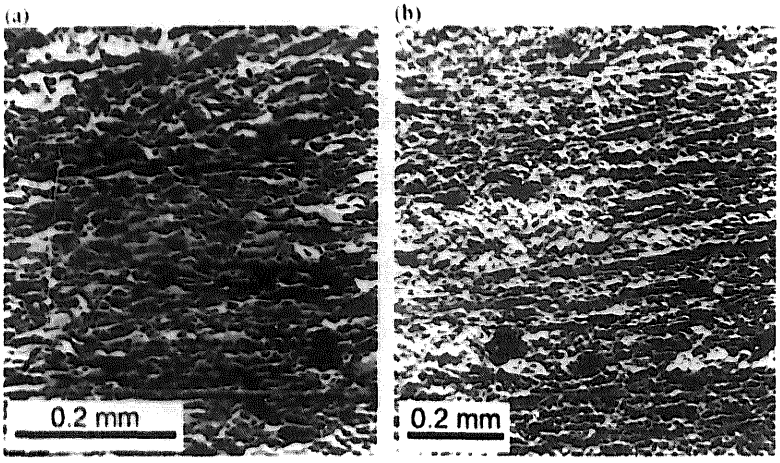

Fig. 3. Microstructures of directional crystallized composites $MoSi_2$–ZrB_2 by different crystallization rate (a) 3.5 mm/min; (b) 8.5 mm/min.

$MoSi_2$ and ZrB_2 showed the presence of many mutually penetrating crystals, where more coarse grains of molybdenum disilicide are pierced by plates or needles of zirconium diboride (ZrB_2), in some cases the aggregates of plates or needles are surrounded by extra matrix disilicide phase (Fig. 2a), in most cases in limits of each grain or agglomerate the definite orientation exists (Fig. 2b).

The increase in ZrB_2 content up to 20% (v/v) does not change the structure of the material (Fig. 2c). With the addition of 25% (v/v) the visible orientation of phases is only in some parts of samples, in general the structure appears more fine-grained (Fig. 2d).

A similar picture was received in the case of additions of titanium diboride (TiB_2) (Fig. 2e).

A change of directional crystallization process parameters, particularly an increase in the crystallization rate leads to obtaining materials with a more clearly defined orientation structure. It is clearly seen during the formation of composite materials on the base of $MoSi_2$ with the addition of ZrB_2 (Fig. 3).

It may therefore be supposed that the most promising composites based on the $MoSi_2$ matrix from the point of view of oriented structure formation are possible with additions of some transition metal diborides, particularly zirconium or titanium diborides.

These results in combination with known data about increasing of mechanical properties of $MoSi_2$–TiB_2 composites, prepared by other methods, confirm the efficiency of the directional crystallization process for such compositions [12].

Some experiments in the co-crystallization of $MoSi_2$ mixtures with some other silicides having other crystal structures were performed. Particularly, as a strengthening phase, erbium disilicide was chosen as it has the same structure as transition metal diborides, i.e. AlB_2 type. By directional crystallization of the $MoSi_2$–$ErSi_2$ (20%, v/v) composition, an oriented structure was obtained which did not have an uniaxial but a plate form of the second phase (Fig. 4a). It can be seen that the studied composition is far from eutectics.

During directional crystallization of an alloy that contains a $TaSi_2$ (5%, v/v) phase, the structure formed, which is characterized by extended grains (in

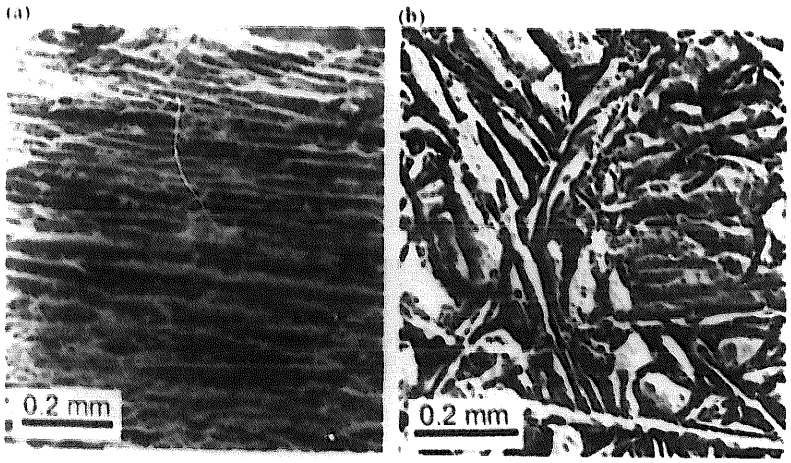

Fig. 4. Microstructures of directional crystallized composites in $MoSi_2$–$MeSi_2$ systems: (a) + 20 vol.% $ErSi_2$; (b) + 10 vol.% $TaSi_2$.

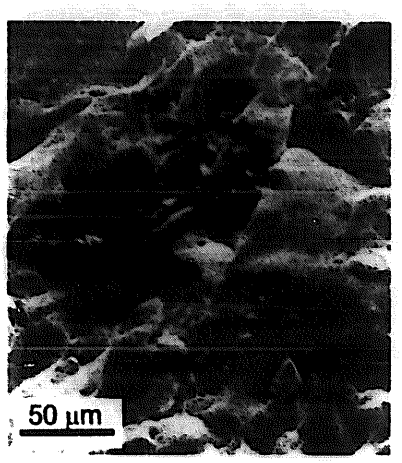

Fig. 5. Fracture surface of composite 80 vol.% $MoSi_2$ and 20 vol.% TiB_2.

some cases they are needle-like), located randomly. In some cases the colonies of eutectic structures are located along the grain boundaries (Fig. 4b).

It can be seen that the complete orientation of the strengthening phase was not achieved. The degree of structure orientation is determined by the cooling rate; under used rates of directional crystallization the regularity of the structure is less than for quenched drops of the same material. Then it may be supposed that the regularity of structure may be improved by raising the cooling rate.

The evaluation of some mechanical and oxidation characteristics of directional crystallized composites, $MoSi_2$–TiB_2 and $MoSi_2$–ZrB_2 were performed.

The fracture of these materials has a mixed character, transcrystalline fracture of coarse $MoSi_2$ grains and intercrystalline fracture of diboride phases are seen (Fig. 5). Fracture toughness measured with standard 2.5 × 2.5 × 25-mm sample having a 1.7 mm cutting was near 4 $MPa \cdot m^{1/2}$, that is close to hot pressed materials.

The oxidation behavior of directional crystallized $MoSi_2$–TiB_2 and $MoSi_2$–ZrB_2 rods was evaluated in conditions which approach real heating element exploitation. The rods were maintained outdoors at 1500°C for 82 h by means of current pass through the samples. The mass gain was approximately 0.01 mg/cm^2 per hour, that is less than for individual $MoSi_2$ and much less than it was obtained for similar hot-pressed composites according to Cook et al. [7]. It is possible that the reason is in a more perfect structure of our directionally crystallized samples. Apart from them, according to Serebriakova et al. [13], forming during oxidation borosilicate glass coating is a better protective barrier against oxygen diffusion than individual silicate.

Studied compositions of $MoSi_2$ based composites were chosen arbitrarily. By approaching the eutectic composition, that are realized in some pseudobinary systems with $MoSi_2$, the increase in structure regularity and the raising of physical properties should be forthcoming.

It may be concluded that there are grounds in suggesting that the method of directional crystallization, as applied to eutectic $MoSi_2$– MeB_2 compositions, that in turn still require determination, may be used for obtaining new composite materials.

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