Indentation toughness of Mo5Si3-based alloys[①]

E. Ström[1], ZHANG Ji(张 继)[2], FENG Di(冯 荻)[2]

(1. Chalmers University of Technology, SE-412 96 Gothenburg, Sweden;
2. Central Iron and Steel Research Institute, Beijing 100081, China)

[Abstract] The indentation toughness of Mo5Si3-based phases was studied with regard to different alloying elements, amount of alloying addition as well as the presence of secondary phases. Cr, Ti, Nb, Ni and Co were added as alloying elements. The results show that the indentation fracture toughness of Mo5Si3 increases with the alloying additions, from 2. 4 MPa·m$^{1/2}$ for monolithic to just over 3 MPa·m$^{1/2}$ for highly alloyed Mo5Si3. Small volume fractions of brittle secondary phases may have a positive impact on the indentation toughness; while larger fractions seems to lower the toughness.

[Key words] indentation toughness; Mo5Si3; alloying

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1 INTRODUCTION

The demands for higher efficiency of energy converting systems necessitates for the maximum operating temperature to be increased. Consequently, there is an increasing need for structural materials that can withstand oxidizing environments at elevated temperatures. For structural use at temperatures higher than those used for today's Ni-based superalloys, any significant improvement will necessitate the development of new alloy systems.

Mo5Si3 has been considered a promising material for ultra-high temperature use regarding its high melting temperature of 2 180 ℃[1] and reasonable density of 8. 19 g/cm^3. Moreover, its creep strength has been shown to be several orders of magnitude higher than that for MoSi2[2]. However, there are some key issues for the future development of Mo5Si3. Firstly, it suffers from brittleness at ambient and elevated temperatures, probably as a result of the complex tetragonal crystal structure (space group I4/mcm, W5Si3-structure[3]) and strong bonding within the crystal. Secondly, cast materials of Mo5Si3 show severe cracking on both a macro- and microscopic level. This is proposed to be a result of the large mismatch in the coefficient of thermal expansion (α) between the a- and c- directions in the tetragonal unit cell (α_a = 5. 2 × 10^{-6} K^{-1} and α_c = 11. 5 × 10^{-6} K^{-1}[4]).

Generally, industrial applications require a fracture toughness of at least 10 MPa·m$^{1/2}$; while turbine applications require toughness values of 15 MPa·m$^{1/2}$ or higher[5]. However, the toughness values of most intermetallics are far from these levels, which has limited their use as structural materials. So far, three methods based on alloying process have been used in an attempt to overcome the brittle behaviour of intermetallics: control of ordered crystal symmetry, composition control to partially disturb the strong bonding within the ordered lattice, or by microstructure control, also referred to as in-situ composites[6~8].

To date, literature on alloyed Mo5Si3 has mainly been focused on solubility ranges[9~11]. Microhardness of Mo$_{5-x}$M$_x$Si3(x = 0. 5, 1, 2; M = Cr, Ti, Nb, Ni, Co) alloys were recently measured as a preliminary assessment of alloying process[12]. It was found that the hardness of annealed Mo$_{5-x}$M$_x$Si3 alloys decreased with increasing Cr content and that even Ni, although it had low solubility, decreased the hardness of the Mo5Si3 phase. The other alloying elements had a limited influence on the hardness. In the present study, indentation toughness of Mo5Si3-based phases is investigated with regard to different alloying elements, amount of alloying addition as well as the presence of secondary phases.

2 EXPERIMENTAL

The starting materials were a mixture of Mo and Si powders of eutectic composition (74% Mo, 26% Si, mass fraction) that were ground for 48 h and compacted by cold isostatic pressing followed by sintering at 1 500 ℃ in a hydrogen atmosphere. The intermediate alloy was then mixed with solid Mo and respective alloying element and arc melted in a non-consumable furnace under argon atmosphere to obtain the designed alloys. Each ingot was turned and remelted several times in an effort to obtain homogeneity. A sectioned ingot is shown in Fig. 1, in which

Fig. 1 Section of arc-melted ingot

the intergranular cracking that is produced during cooling as a result of the mismatch of thermal expansion coefficient is visible.

The alloys containing Cr, Ti, or Nb were annealed at 1 600 ℃ for 96 h. Ni and Co containing alloys were annealed at 1 150 and 1 350 ℃ for 96 h, respectively. This method was taken to avoid melting of low melting phases Ni_2Si and CoSi found in the as-cast Ni- and Co-containing alloys, respectively. Additionally, one of the Cr-containing alloys was annealed at 1 400 ℃ since evidence of melting was found in that alloy after the 1 600 ℃ heat treatment. The microstructural characterization, phase analysis and mi-

crohardness of the alloys is given elsewhere[12].

The indentation toughness was calculated using the formula[13]:

$$K_{IC}/(MPa \cdot m^{1/2}) = 0.203 \cdot (c/a)^{-3/2} \cdot HV \cdot a^{1/2} \quad (1)$$

where c is the average half-crack length, a is half of the average length of two indent diagonals, and HV is the corresponding Vickers hardness obtained with 5 N load. Hardness testing was performed using a Leitz microhardness tester equipped with a Vickers diamond. The radial cracks emanating from the indents were measured in a LEO 1550 Gemini scanning electron microscope (SEM). Hardness data was taken from previous work[12].

3 RESULTS AND DISCUSSION

The designed alloy compositions investigated in this study, and the resulting hardness values and corresponding indentation toughness values are given in Table 1 together with respective standard deviations. Data for alloys $Mo_3Ni_2Si_3$ and $Mo_3Co_2Si_3$ could not be obtained due to the low volume fraction of the Mo_5Si_3-based phase, as listed in the far right column. The Vickers indents were selectively put on single-phase areas for all the other samples, although the hardness values and, in particular, toughness values of the multi-phase alloys listed in Table 1 may be affected by the presence of second phases. Thus, toughness data for the multi-phase alloys may not

Table 1 Compositions of studied alloys and resulting hardness and indentation toughness of respective Mo_5Si_3-based phase

Alloy	HV/GPa	$K_{IC}/(MPa \cdot m^{1/2})$	Phase assemblage(volume fraction, %)
Mo_5Si_3	13.2 ±0.5	2.4 ±0.5	Mo_5Si_3
$Mo_3Cr_2Si_3$	11.0 ±0.9	3.2 ±0.6	$(Mo, Cr)_5Si_3$
$Mo_4Cr_1Si_3$	12.3 ±0.8	2.6 ±0.9	$(Mo, Cr)_5Si_3$
$Mo_{4.5}Cr_{0.5}Si_3$	12.9 ±0.4	2.1 ±0.8	$(Mo, Cr)_5Si_3$
$Mo_3Ti_2Si_3$	13.0 ±0.7	3.1 ±0.8[2]	91.5($Mo, Ti)_5Si_3$-8.5($Ti, Mo)_5Si_3$
$Mo_4Ti_1Si_3$	12.8 ±0.8	2.0 ±0.7	$(Mo, Ti)_5Si_3$
$Mo_3Nb_2Si_3$	13.1 ±0.4	3.1 ±1.3	$(Mo, Nb)_5Si_3$
$Mo_4Nb_1Si_3$	13.1 ±0.3	3.1 ±0.7	$(Mo, Nb)_5Si_3$
$Mo_{4.5}Nb_{0.5}Si_3$	12.8 ±0.4	3.1 ±0.5	$(Mo, Nb)_5Si_3$
$Mo_3Ni_2Si_3$	–	–	28.5 Mo_5Si_3-63.0 MoNiSi-8.5 $MoSi_2$
$Mo_4Ni_1Si_3$	12.1 ±1.2	1.8 ±0.5[2]	66.6 Mo_5Si_3-33.4 MoNiSi
$Mo_{4.5}Ni_{0.5}Si_3$	12.2 ±1.1	2.9 ±0.4[2]	93.4 Mo_5Si_3-6.6 MoNiSi
$Mo_3Co_2Si_3$	–	–	28.9 Mo_5Si_3-71.1 MoCoSi
$Mo_4Co_1Si_3$	12.9 ±0.5[1]	2.3 ±0.8[2]	69.4 Mo_5Si_3-30.6 MoCoSi

(1) —Obtained on two-phase areas
(2) —Value is or may be affected by presence of secondary phases

reflect the toughness of pure (Mo, M)$_5$Si$_3$ phases, but rather for an Mo$_5$Si$_3$-based in-situ composite.

For comparison with reported data, the toughness of monolithic Mo$_5$Si$_3$ was calculated using the formula by Anstis et al[14]:

$$K_{IC}/(MPa \cdot m^{1/2}) = 0.016(E/HV)^{1/2} \cdot p/c^{3/2} \tag{2}$$

where $E = 323$ GPa[5]. The value obtained in this study using Eqn. (2), 2.0 MPa·m$^{1/2}$, is in accordance with the values reported for single crystals of Mo$_5$Si$_3$(2.0~2.5 MPa·m$^{1/2}$, depending on orientation of the crystal and indenter) by Chu[4]. However, it can be noted that K_{IC} is slightly higher using Eqn. (1) than Eqn. (2) on the same sample of Mo$_5$Si$_3$. Since there is no available data of elastic modulus of alloyed Mo$_5$Si$_3$, however, Eqn. (1) was used in this work.

3.1 Single-phase alloys

For the alloying elements that are dissolved by large amounts in Mo$_5$Si$_3$(Cr, Ti, Nb), it can be noticed from Table 1 that, generally, the indentation toughness increases with the alloying addition. For Nb-containing alloys, however, the toughness seems to be higher than for monolithic Mo$_5$Si$_3$ independent of the Nb content.

In Fig. 2(a), cracks can be observed in the transverse direction of the Cr-rich, dark areas of alloy Mo$_3$Cr$_2$Si$_3$ annealed for 96 h at 1400 ℃. The cracks in Fig. 2(a) suggest that the dark dendrites are oriented in the c-direction of the tetragonal cell, since the thermal expansion coefficiency is larger in this direction than in the a-direction ($\alpha_c/\alpha_a \approx 2.2$[4]). Also, the predominant cracking of the Cr-rich areas indicates that the Cr-content affects the thermal expansion coefficiency. Figs. 2(b) ~ (d) indicate that Mo$_5$Si$_3$-based materials fracture in an anisotropic manner: the main cracks do not emanate from the corners of the indent but rather along preferred crystal orientations. It is interesting to note that the cracks that emanate from the corners of the indent in Fig. 2(c) are quite small, while the crack going across the dendrite direction is much larger.

3.2 Multi-phase alloys

For alloy Mo$_4$Ni$_1$Si$_3$ having a Mo$_5$Si$_3$-MoNiSi two-phase microstructure as shown in Fig. 3(a) and (b), the following observations are made: if the second phase is small, the crack propagates across the
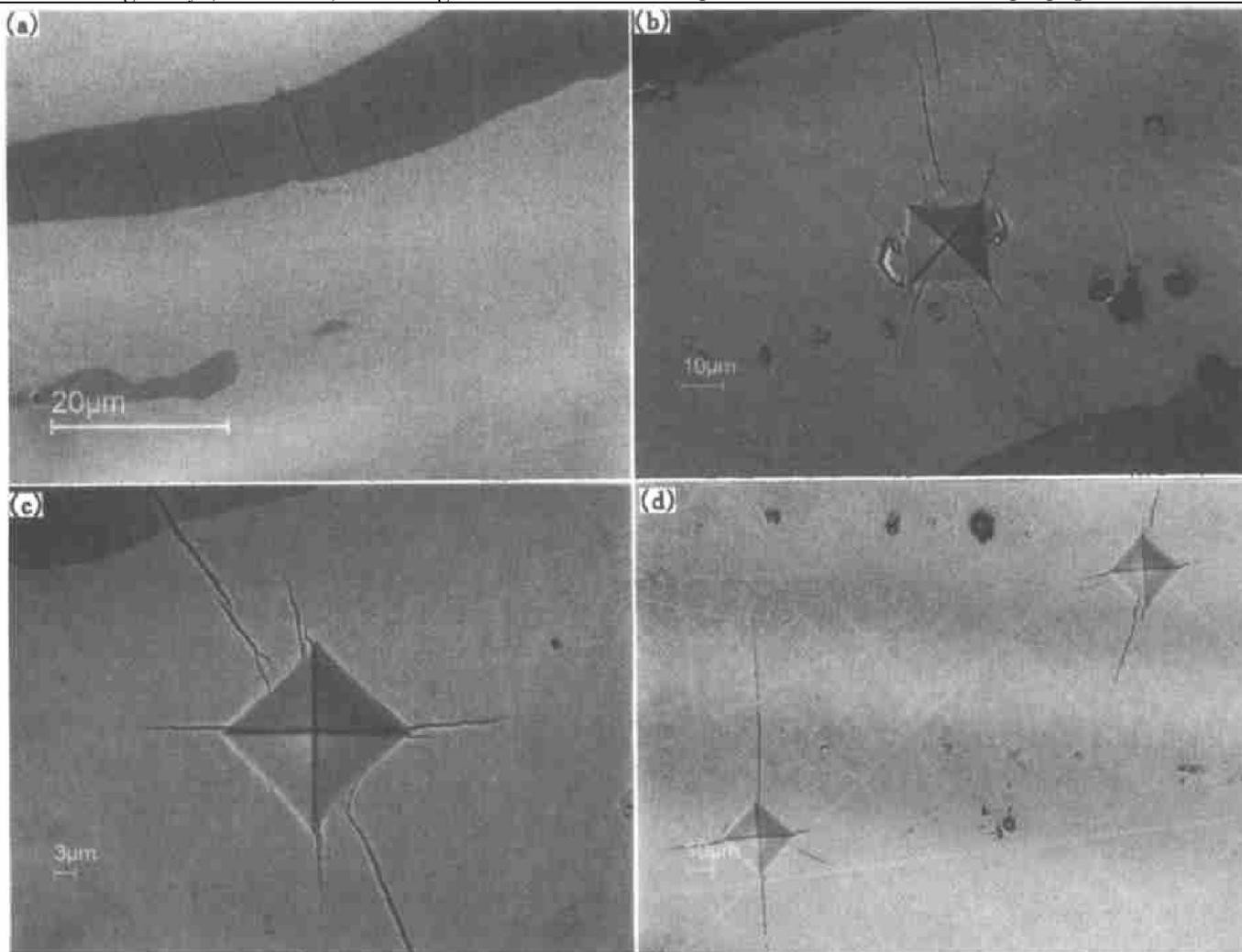
Fig. 2 Backscattered electron micrographs of alloy Mo$_3$Cr$_2$Si$_3$ annealed for 96 h at 1 400 ℃ (a),
Vickers indents in alloy Mo$_3$Cr$_2$Si$_3$ annealed at 1 600 ℃((b) and (c)) and Mo$_4$Cr$_1$Si$_3$ alloy (d)
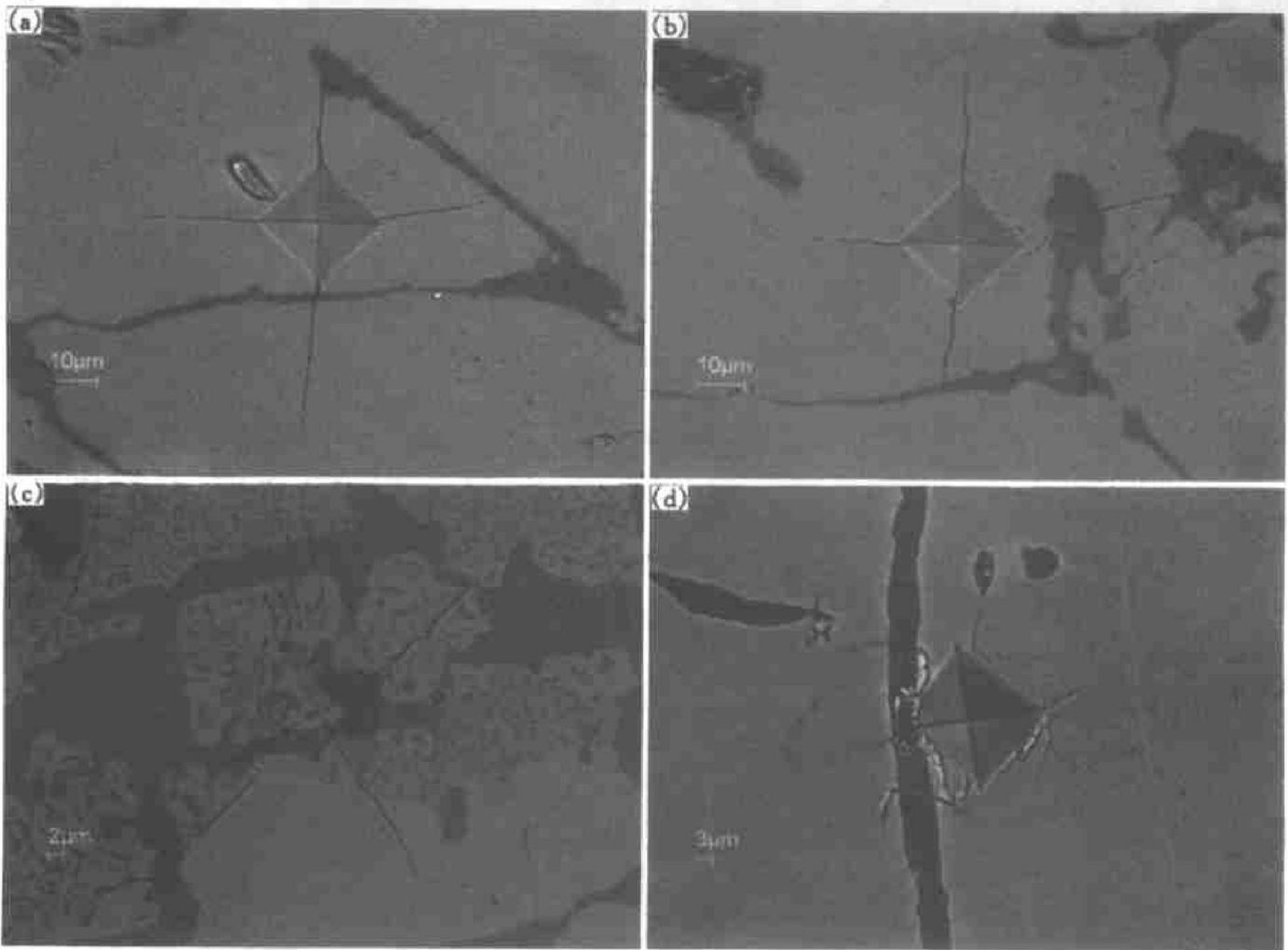
Fig. 3   Backscattered electron micrographs of $Mo_4Ni_1Si_3$ and $Mo_3Ni_2Si_3$ alloys
(a) —$Mo_4Ni_1Si_3$; (b) —Shear ligaments in MoNiSi phase; (c) —Pronounced crack deflection in
Mo_5Si_3-MoCoSi microstructure; (d) —Crack arrest in(Ti, Mo) $_5Si_3$ phase

second phase without losing much energy (shown in Fig. 3(a)). When the second phase becomes larger, shear ligaments can be formed. This behaviour seems to absorb some of the crack propagation energy. Finally, if the second phase is large, bending or deflection of the crack can occur, as seen in Fig. 3 (b). In the fine two-phase microstructure of alloy $Mo_4Co_1Si_3$, [shown in Fig. 3(c)], the cracks are deflected along the phase boundaries, while in areas of the same alloy having coarser microstructure, cracks are not deflected significantly. The second phase can somehow deflect the crack as in $Mo_4(Ni/Co)_1Si_3$, but the crack length in single phase Mo_5Si_3 is still shorter even though it follows a straighter path. In addition, when comparing the toughness values of the Ni-containing alloys in Table 1, it can be noticed that the toughness is higher for $Mo_{4.5}Ni_{0.5}Si_3$ than for $Mo_4Ni_1Si_3$. The latter alloy contains more MoNiSi Laves phase than the former, and this indicates that the brittle Laves phase damages the overall toughness of the alloy when its content becomes too large. Generally, the values obtained in this study suggest that the two-phase

Mo_5Si_3-Mo(Ni/ Co) Si microstructure is more brittle than monolithic Mo_5Si_3. An exception is that the toughness of $Mo_{4.5}Ni_{0.5}Si_3$, which has a low volume fraction of second phase, is higher than for monolithic Mo_5Si_3. Moreover, the two-phase alloy $Mo_3Ti_2Si_3$[as shown in Fig. 3 (d)] displays among the highest toughness values obtained in this study. These results indicate that a low fraction of secondary phase, although brittle, may increase the fracture toughness of Mo_5Si_3.

4   CONCLUSIONS

1) The indentation fracture toughness of Mo_5Si_3 increases with the alloying additions, from 2. 4 for monolithic to just over 3 $MPa•m^{1/2}$ for highly alloyed Mo_5Si_3.

2) The indent cracks in Mo_5Si_3 seem to follow certain crystallographic directions, suggesting that Mo_5Si_3 has a very anisotropic fracture behaviour.

3) Small volume fractions of brittle secondary phases may have a positive impact on the indentation

toughness; while larger fractions seem to lower the toughness.

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