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Oxidation Behavior of Mo-Si-W Ternary Alloys in the Temperature Range of 400°C-900°C

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Abstract:

The intermetallic compound, $MoSi_2$ and ternary Mo-Si-W alloys - $MoSi_2$-25 wt% WSi_2 and $MoSi_2$-50 wt% WSi_2 were processed by reaction hot pressing at 1500°C. The microstructure of $MoSi_2$ with 25 and 50 wt% WSi_2 alloys showed $(Mo,W)Si_2$ phases, which were either rich in Mo or in W, as well as Mo_5Si_3 and W_5Si_3. Oxidation experiments were carried out in the temperature range of 400° C – 900° C for 24 hours in dry air, kinetic study was carried out by observing the change in mass at different intervals of time. The oxide scales in $MoSi_2$were comprised of MoO_3, Mo_9O_{26} and SiO_2. In addition to these scales WO_3 was observed in case of the $MoSi_2$-25 wt% WSi_2 and $MoSi_2$-50 wt% WSi_2 alloys. In $MoSi_2$-25 and 50 wt% WSi_2 alloys, the oxidation behavior was characterized chiefly by mass gain at temperatures less than 700°C and partial mass loss at higher temperatures. The gain in mass is more in the $MoSi_2$-50 wt% WSi_2 alloy, compared to the former, because of higher activity of W contributing to a larger volume fraction of WO_3 in scale. At higher temperatures, net mass loss was observed in the initial stages, because of the volatilization of MoO_3.

Keywords*: Oxidation, $MoSi_2$, volatilization, rate constant*

1. Introduction:-

$MoSi_2$ undergoes pesting, a phenomenon of accelerated oxidation induced disintegration, between 400^0C and 600^0C [1-3]. Pesting occurs because of the internal stress caused by volume expansion during selective oxidation at the grain boundaries, cracks and porosities. Intermetallics such as silicides, aluminides and berylides suffer from the pesting phenomenon. The pest oxidation to stress-enhanced oxidation because of the high residual stress introduced via cooling anisotropic materials from the melt [4, 5]. The catastrophic nature of the pest oxidation was the result of preferential inter-granular diffusion of a gaseous element (most probably oxygen or nitrogen) coupled with grain boundary embrittlement [6]. The oxidation of Mo and Si at the initial cracks with a large volume expansion induced the pesting of $MoSi_2$. However single-crystals

and crack-free polycrystalline $Mosi_2$ prepared by hot isostatic pressing (HIP) did not disintegration [7, 8]. The former [7] suggested that the susceptibility of near-stoichiometric $MoSi_2$ to pest disintegration increased with decreasing density; while the latter proposed that pest did not occur in dense(>95%) $MoSi_2$ for exposure times up to 688 h at 400-600^{0}C [9]. Form thermodynamic considerations [10], it follows that Si in $MoSi_2$ should be selectively oxidized to SiO_2 because its affinity for oxygen in much greater than that of Mo. The mass gain followed by large mass loss during the initial heating to the test temperature can be attributed to oxidation of silicon and molybdenum, followed by sublimation of MoO_3. It also suggested that plate-like MoO_3 grows by vapor deposition. The amorphous Mo-Si-O and Mo-Si-W-O oxides, which were formed during initial stages of this study, have composition of metal elements close to that in the initial intermetallics.

$$2MoSi_2 + 7O_2 = 2MoO_3 + 4SiO_2 \text{……..(1)}$$

The calculated volume change involved in reaction (1) is about 212 vol% [1].

2. Experimental Procedure:-

For $MoSi_2$, Mo and Si, and for $MoSi_2$-25 and 50wt% WSI_2 alloys, Mo, W and Si powders were mixed in stoichiometric ratios in pots in a planetary ball mill. The powder mixtures were subsequently reaction hot pressed at 1500^{0}C in argon atmosphere with pressure of 26 MPa for 1 hour at the DMRL, Hyderabad. These hot pressed plates were electro-discharge machined (EDM) to bar type specimens of rectangular cross-section with dimensions, 12 mm x 6 mm x 4.5 mm. The specimen bars were first polished and cleaned and then subsequently the samples were suspended inside the quartz tube chamber of the oxidation furnace, using a nichrome wire, which again is hung from the pan of the weight balance kept on a platform above the furnace. The oxidations of the samples were carried out at the temperature 400 – 900^{0}C.

2.1. Characterization:-

The samples were studied using bright field and polarized light optical microscopy to study the distribution of porosities and measure grain size, XRD was performed to identify the phases present. Subsequently, the microstructures were observed using secondary electron (SE) and backscattered electron imaging modes on SEM and EPMA.

3. Results and Discussions:-

3.1.$MoSi_2$.

The XRD patterns, using Cu Kα radiation, is shown in fig.3.1.1 depicted the XRD pattern of $MoSi_2$ alloy exposed at 700^{0}C for 24 hrs shows the peaks of MoO_3, Mo_9O_{26} and SiO_2 and (Mo, W)Si_2 originating from the alloy substrate. The SEM images of $MoSi_2$ alloy exposed at 700^{0}C were shown in fig.3.1.2.

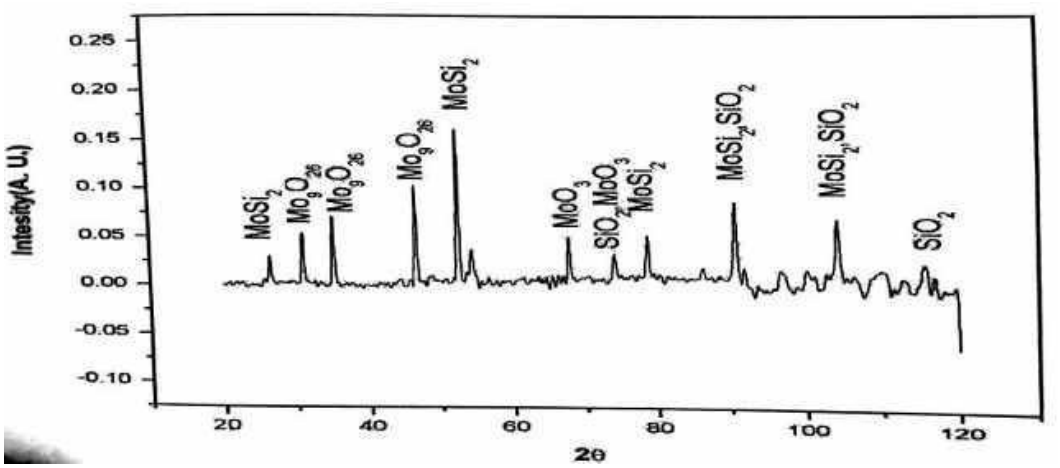

Fig. 3.1.1 *XRD pattern of $MoSi_2$ alloy exposed at temperature of 700^0C.*

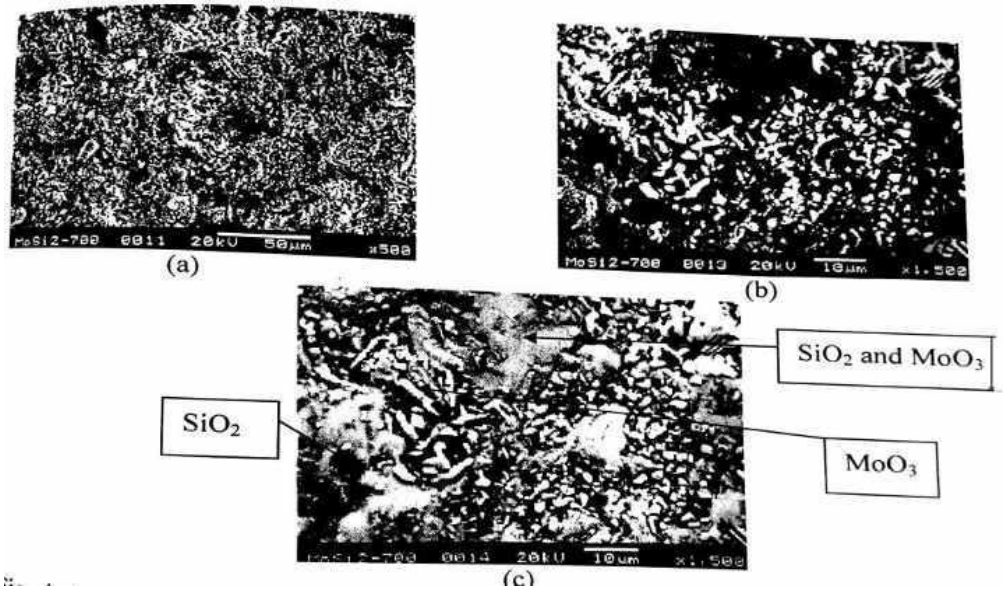

Fig. 3.1.2 *SEM micrographs of $MoSi_2$ alloy exposed at 700^0C for 24 hrs (a) SE mode, (b) SE mode at higher modification and (c) BSE mode.*

3.2. $MoSi_2$-25wt%WSi_2 alloy.

The XRD pattern of the alloy $MoSi_2$-25wt%WSi_2 as shown in fig.3.2.1(a) shows prior to oxidation of alloy and fig.3.2.1 (b) shows after exposed at 700^0C for 24 hrs. From fig.3.2.1 displays that the peaks of MoO_3, Mo_9O_{26}, WO_3, SiO_2 and (Mo, W)Si_2. The shift in peak position of (Mo, W)Si_2 with respect to that of $MoSi_2$ is found to be negligible. Fig.3.2.2 represents a polarized light optical micrograph before oxidation showing the grain size to be around 12 μm where as the fig.3.2.3 shows SE and BSE images of alloy $MoSi_2$-25wt%WSi_2 at different magnifications. The EPMA (WDS)

analysis have revealed the brightest phase to be riched in W (atomic number=74) with concentration in the range of 16-26 at%. The matrix, which appears to be dark compared to the W-rich phase, is enriched in Mo (atomic number=42) having concentration of W being about 5-8 at%. The phase appearing dark and globular is indentified to be SiO_2.

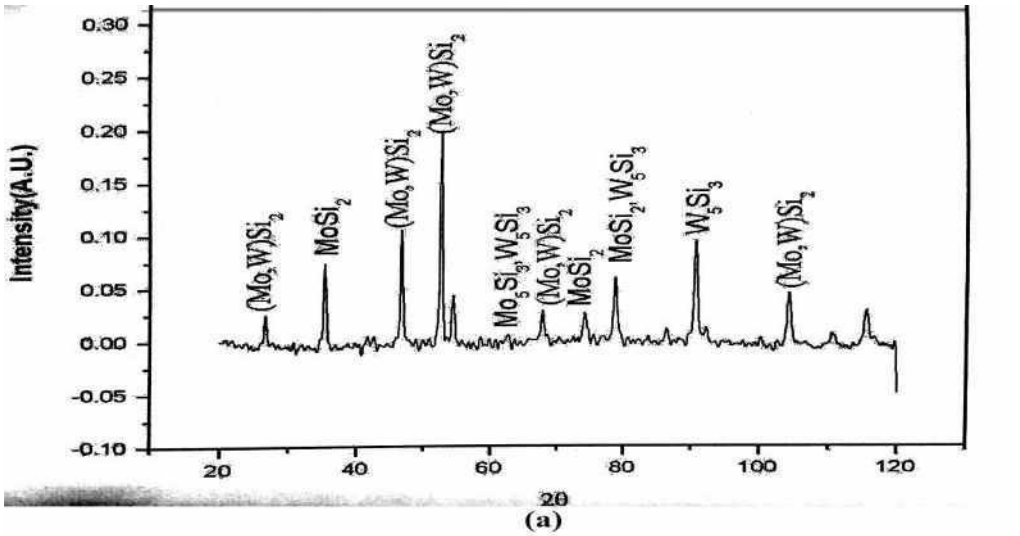

Fig. 3.2.1(a) *XRD pattern of $MoSi_2$-25 wt% WSi_2 alloy before oxidation.*

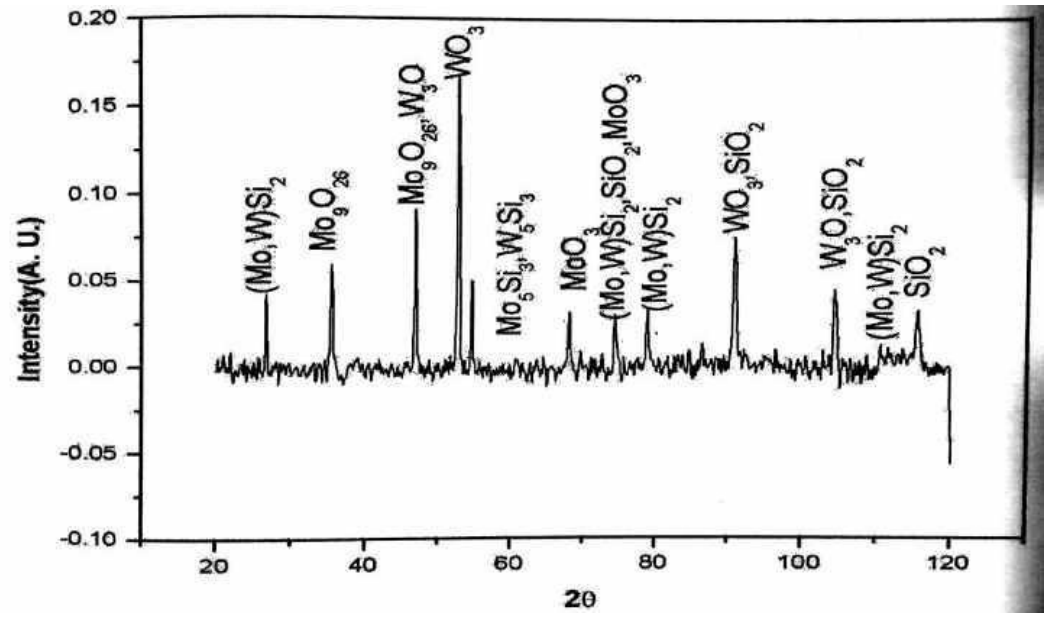

Fig. 3.2.1(b) *XRD pattern of $MoSi_2$-25 wt% WSi_2 alloy after oxidation.*

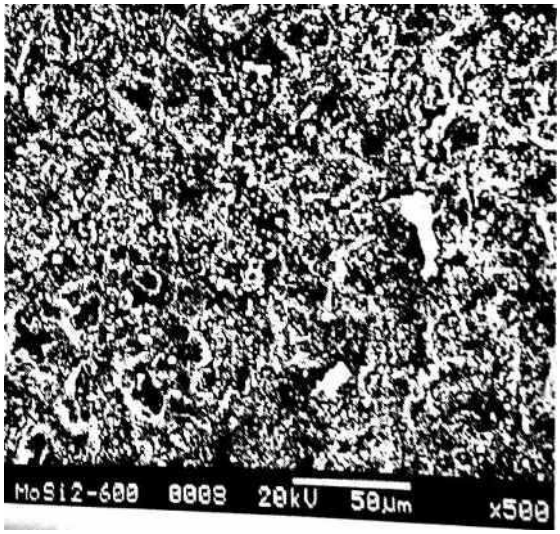

Fig. 3.2.2 *Polarized light optical micrograph of $MoSi_2$-25 wt% WSi_2.*

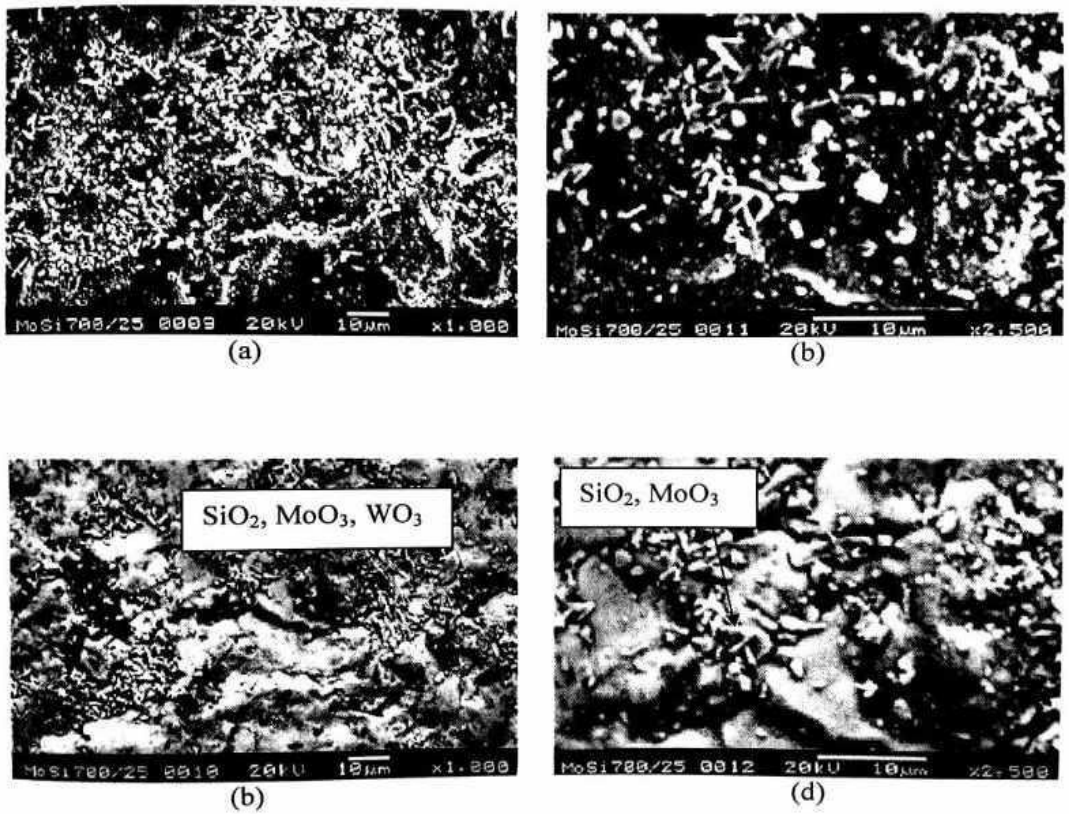

Fig. 3.2.3 *SEM micrographs of $MoSi_2$-25 wt% WSi_2 alloy exposed at 700^0C for 24 hrs (a) SE mode, (b) SE mode at higher modification and (c) and (d) are BSE images at lower and higher magnification.*

3.3. $MoSi_2$-50wt%WSi_2 alloy.

Chemical composition obtained from EDAX analysis of $MoSi_2$-50wt% WSi_2 alloy is shown in table-1. Fig.3.3.1shows the XRD pattern of $MoSi_2$-50wt%WSi_2 alloy exposed at 700^0C respectively. These XRD pattern indicates the peaks of $MoSi_2$, W_5Si_3, MoO_3 and WO_3 in addition to (Mo, W)Si. In fig. 3.3.2 shown the WDS analysis have revealed the W-rich region contain 28 at% W, while W-lean regions about 10 at%.

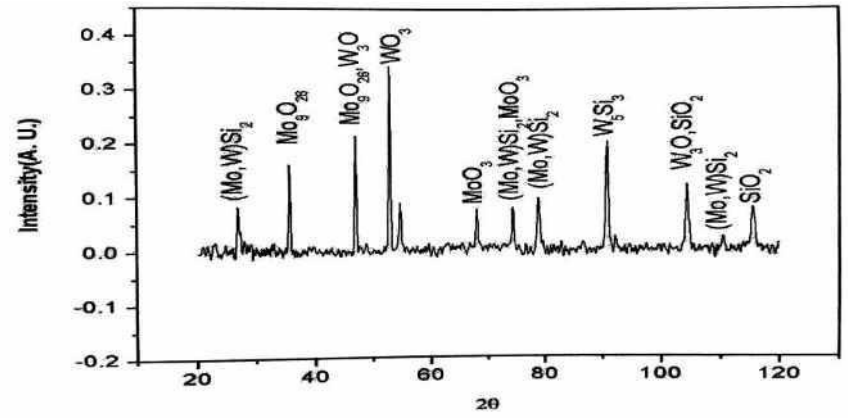

Fig. 3.3.1 *XRD pattern of $MoSi_2$-50 wt% WSi_2 alloy after oxidation.*

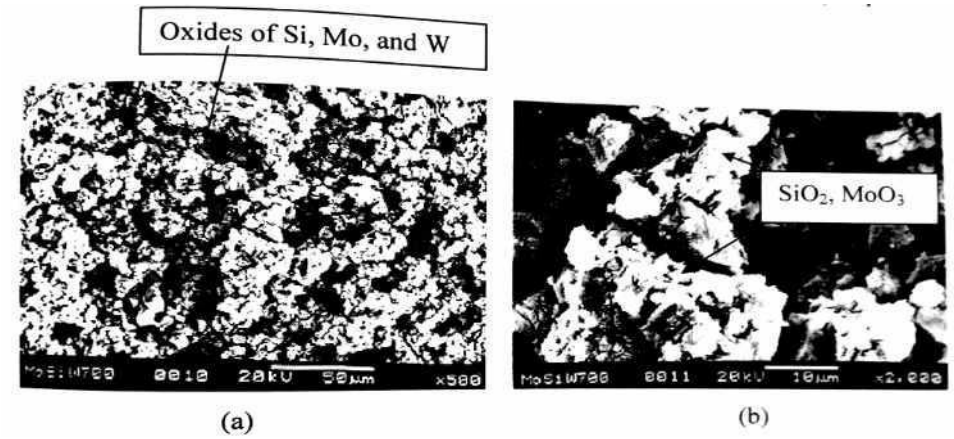

Fig. 3.3.2 *and (b) SEM micrograph of $MoSi_2$-50 wt% WSi_2 exposed to 700^0C at different magnifications.*

4. Oxidation Kinetics of three alloys.

Fig.4 shows the plots describing the kinetics of oxidation of $MoSi_2$, $MoSi_2$-25 wt.% WSi_2 and $MoSi_2$-50 wt.% WSi_2 alloys exposed at 700^0C in dry air for 24 h. Oxidation at all temperatures are characterized by a rapid rate of gain in mass during the first two hours, followed by a reduced rate for all alloys. The rate of mass gain is least in $MoSi_2$-25 wt.% WSi_2 alloy followed by $MoSi_2$-50 wt.% WSi_2 alloy and $MoSi_2$.

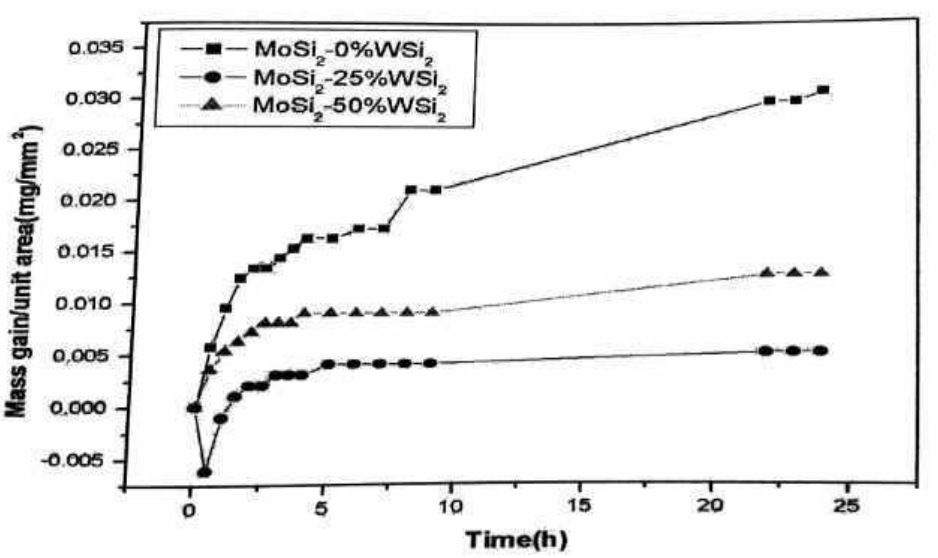

Fig.4. *Plots of oxidation kinetics of $MoSi_2$, $MoSi_2$-25 wt.% WSi_2 and $MoSi_2$-50 wt.% WSi_2 alloys exposed at 700^0C for 24 h.*

XRD analysis has confirmed the oxidation products to chiefly consist of MoO_3, WO_3 and SiO_2 phases. Below the oxidation temperature of 700^0C the mass gain is due to the formation of four oxides i.e. MoO_3, WO_3, SiO_2 and MoO_3 where as at above 700^0C, MoO_3 is volatile and oxidation kinetics involves partial loss in mass.

5. Conclusions:-

- The microstructures of $MoSi_2$-25 wt.% WSi_2 and $MoSi_2$-50 wt.% WSi_2 alloys showed primarily (Mo, W)Si_2 phase, as well as Mo_5Si_3 and W_5Si_3. Dispersed particles of SiO_2 would observe both in the $MoSi_2$ and Mo-Si-W alloys.
- Oxidation behaviour of MoSi2, $MoSi_2$-25 wt.% WSi_2 and $MoSi_2$-50 wt.% WSi_2 alloys in the temperature range of 400^0C – 900^0C in dry air demonstrated two principal time regimes. The initial exposure period exhibited a rapid rate of reaction while the second stage usually showed reduced rate of oxidation suggesting the formation of protective scales.
- The oxide scale chiefly consisted of SiO_2, MoO_3 and Mo_9O_{26} in $MoSi_2$ alloy and SiO_2, MoO_3, WO_3 and Mo_9O_{26} oxides are existed in $MoSi_2$-25 wt.% WSi_2 and $MoSi_2$-50 wt.% WSi_2 alloys. MoO_3 could not detect at 800^0C and 900^0C due to its volatilization.

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