Phase Composition of Mo-Si-V Hypoeutectic Alloys

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Abstract
Thermodynamic modeling (TDM) of phase formation was performed with vanadium doping of the hypoeutectic Mo-Si alloy. It was found that the thermochemical properties of vanadium silicides (presented in the HSC Chemistry 6.12 database), when modeling Mo-Si-(14.5-12.2)-V(5.0-20.0) alloys, lead to inadequate results regarding Mo-Si-V diagram state indicators. The simulation results agree satisfactorily with the Mo-Si-V diagram with the following values of $\Delta H_{298}^{0}$: for $V_3Si = -180.4$ kJ / mol, for $V_5Si_3 = -433.6$ kJ / mol, for $VSi_2 = -124.5$ kJ / mol. According to the results of TDM and X-ray phase analysis (XRD) of the obtained alloys, it was found that vanadium in Mo-Si-V ternary alloys can be found both in the form of silicides, $(Mo,V)_3Si$, and in the composition of the solid solution $(Mo,V)_x$. Their ratios depend on the vanadium additives in the alloys. With an increase in the content of vanadium in model alloys, the ratio of the metal phase to the silicide phase increases from 0.78 to 1.60 (according to TDM) and from 0.78 to 1.27 (according to XRD data).

Keywords: in situ composites, molybdenum, silicon, silicide, doping, vanadium, thermodynamic analysis, X-ray phase analysis

1. Introduction

According to Russian and foreign researchers, a worthy alternative to nickel-based heat-resistant alloys is alloys of Nb-Si and Mo-Si systems, capable of forming structures for natural (in situ) composites with high strength and heat resistance [1–3]. However, molybdenum and its alloys, like niobium-silicon composites, are not resistant to oxidation and are prone to embrittlement. The literature widely presents the results of studies for the composite materials based on MoSi$_2$, which is most resistant to oxygen compared to molybdenum silicide with a lower Si content but has low fracture toughness [4]. Hybrid composites with matrix hardening by silicon carbides and nitrides [5] have been proposed to increase the crack resistance and yield strength at high temperature but this hardening of brittle phases has proved to be unreliable. There are attempts to reduce the oxidizability of Mo-Si alloys by doping with zirconium [6] and aluminum [7].
Information on high-temperature composites based on Mo-Si of the hypoeutectic composition is extremely limited and relates to a greater degree to the determination of phase equilibrium in the region of the Mo – Si diagram rich in molybdenum, as well as the properties of Mo₃Si [8]. Earlier [9–13], we studied the effect of rare-earth metals (Sc, Y, Nd) on the formation of the structural-phase state for Mo – Si intermetallic alloys of hypoeutectic composition. It is established that with the introduction of up to 3.0 at. % of Sc, Y, or Nd in hypoeutectic alloy Mo - 15.3 at. % Si forms a structure that is characteristic for natural (in situ) composites, consisting of a solid solution based on α-Mo and a hardening silicide phase consisting of Mo₃Si and particles of complex composition enriched by REE. The introduction of alloying additives significantly increases the dispersion of the microstructure and changes the morphology of the metal and silicide phases, increases the volume ratio of Mo₃Si/Mo₃Si.

To increase the strength ratio of the Mo₃Si-Mo₃Si hypoeutectic composite to its specific mass, while maintaining the two-phase structure, it is proposed to study the possibility of the replacing for the part of molybdenum with vanadium. It is known that the introduction of vanadium in steel reduces their brittleness, increases the ductility during hot-forming method and increases the resistance to corrosion cracking by 4-6 times [14]. The properties of vanadium and REE as structural modifiers are implemented in the production of steel [15].

The V-Mo-Si system was studied by the scientists of IMET named after the A.A. Baikov under the supervision of Academician E.M. Savitsky [16, 17]. The studies revealed the existence of a continuous series of (V,Mo)₃Si solid solutions in the cast state and after annealing at 800°C. The isomorphism of vanadium substitution by molybdenum in the silicide lattice is shown. It has been established that the unlimited solubility of molybdenum in vanadium becomes extremely limited with the introduction of silicon. At about 2 at. % of silicon in V-Mo alloys beneficiated in vanadium, a second phase appears - a solid solution based on the (V,Mo)₃Si compound. In this case, the melting point of (V,Mo)₃Si is lower than the melting points of the corresponding pure binary compounds. Also were clarified data on the parameters of the elementary cell of the annealed solid solution (V,Mo)₃Si and on its microhardness, the maximum value of which was 1560 kg / mm² at 25–35 at. % Mo. The data on the elemental composition of double silicide (V,Mo)₃Si are not given.

Recently, the attention of researchers focused on the study of the interactions for vanadium with silicide of MoSi₂ and Mo₃Si₃ [18–22]. Meanwhile, the area of hypoeutectic alloys (Mo,V)₃-(Mo,V)₃Si may be interesting not only to study and for the clarification of
the phase equilibria in the Mo-V-Si system but also as the most promising to search for new composites compositions.

2. Materials and Methods of Experiment

To assess the phase equilibrium compositions for the hypoeutectic Mo-Si alloy (15.3 at.%) doped with vanadium, the method of complete thermodynamic analysis was used. The calculations were performed using the HSC Chemistry 6.12 (Outokumpu) software package [23], the database of which contains information on the values of three main thermodynamic properties — heat of formation $\Delta H_{f}$, entropy $\Delta S$, and coefficients of temperature dependence for heat capacity $C_p$ [24]. When performing model calculations, the possibility of the formation for intermetallic compounds in accordance with the state diagrams of Mo-Si and V-Si binary systems was taken into account [25]. The thermochemical characteristics of molybdenum silicide (Mo$_3$Si, Mo$_5$Si$_3$, MoSi$_2$) in the database of the HSC program were replaced by the values borrowed from the work of O. Kubashevskiy [24]. The importance for such a replacement is explained in [9].

The models of probable phase formation upon vanadium doping with the Mo – Si alloy (15.3 at.% Si) were calculated for the Mo$_3$Si–Mo–V system in the temperature range 25–2500°C in inert atmosphere (argon). Additives of metallic vanadium varied on the basis of its content in the “base” alloy — BA (Mo$_3$Si – 56.0 wt. %, Mo – 44.0 wt. %) — from 3.0 to 13.0 wt. % or from 5.0 to 20.0 at. %, respectively (Table 1). The choice of BA composition is justified in [9, 11].

An ingot of a binary BA weighing 980 g is melted in a C-3443 furnace from a compressed mixture of metal powders. Doped samples weighing ~ 10.0-11.5 g were obtained from BA with the addition of metallic vanadium shavings on a laboratory arc melting furnace 5SA Centorr / Vacuum Industries on a copper hearth in a helium atmosphere using a non-consumable tungsten electrode. The ingots were subjected to 4-fold remelting, sufficient to achieve a chemically homogeneous composition of model alloys. For the synthesis, high-purity metal powders (99.9% wt) and semiconductor silicon (99.999% wt) were used. Samples were not subjected to stabilization (annealing) or any special treatment. The calculated compositions for model alloys are given in Table 1.

Determination of the phase composition for the samples was performed by X-ray phase analysis (XRPA). The survey was carried out in monochrome Cu-Kα radiation on an XRD 7000C diffractometer (Shimadzu, Japan). Phases were identified according to the ICDD PDF-2 database.
TABLE 1: Calculated composition of Mo-Si-V alloys.

<table>
<thead>
<tr>
<th>№</th>
<th>Alloy</th>
<th>Charge, wt. %</th>
<th>Content in the alloy</th>
<th>wt. %</th>
<th>at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mo</td>
<td>Si</td>
<td>V</td>
</tr>
<tr>
<td>1</td>
<td>BA</td>
<td>95Mo + 5.00Si</td>
<td>95.00</td>
<td>5.00</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>BA(5V)</td>
<td>100BA + 3.13V</td>
<td>92.12</td>
<td>4.84</td>
<td>3.04</td>
</tr>
<tr>
<td>3</td>
<td>BA(10V)</td>
<td>100BA + 6.61V</td>
<td>89.11</td>
<td>4.69</td>
<td>6.20</td>
</tr>
<tr>
<td>4</td>
<td>BA(15V)</td>
<td>100BA + 10.5V</td>
<td>85.97</td>
<td>4.53</td>
<td>9.50</td>
</tr>
<tr>
<td>5</td>
<td>BA(20V)</td>
<td>100BA + 14.88V</td>
<td>82.70</td>
<td>4.35</td>
<td>12.95</td>
</tr>
</tbody>
</table>

3. Results and Discussion

Thermodynamic simulation (TDS) of phase formation during a BA (5V) alloy melting showed that V₅Si₃ is present in the silicide phase in the entire studied temperature range (Fig.1a), which contradicts the data [16, 17, 26] on the formation in this region for the Mo-Si-V system of continuous series for solid solutions (V,Mo)₃Si. According to [23], the thermochemical characteristics of vanadium silicide in the HSC Chemistry 6.12 software package database are borrowed from [27–30]. The values of the enthalpies of formation for vanadium silicide, according to various literature data, differ considerably (Table 2). A comparative analysis of the modelling results obtained using ΔH°₂⁹₈ data from various sources showed that the temperature dependence of the equilibrium phases composition in the Mo(80.5)-Si(14.5)-V(5) alloy (at.%) is in a good agreement with the findings of E.M. Savitsky (Fig. 1b), if the calculations are based on the data of V.N. Yeremenko [31–33]. As can be seen from the figure, in the high-temperature region, the formation of the V₅Si₃ phase, which is richer in silicon, is possible; however, during the crystallization of the alloy, when interacting with metal vanadium, it completely turns into V₃Si. The main phases resulting from the interaction of BA with metallic vanadium (5.0 at.%) are elemental molybdenum and Mo₃Si. In the temperature range above 500°C, the existence of the Mo₃Si₃ silicide is also possible. The presence of elemental vanadium in the melt indicates the formation of a solid solution (Mo, V)₃Si, the thermochemical data of which, like the thermochemical data of solid solutions of the type (Mo, V)₃Si, are not in the database of the HSC Chemistry 6.12 software and were not found by us in literary sources.

Figure 2 shows the results of equilibrium thermodynamic simulation in systems (Mo-Mo₃Si)-V(5-20 at.%), at the temperature of 500°C. According to calculations, the ratio of the mass fractions for the metal and silicide phases increases with an increase in the...
Figure 1: Temperature dependence of the equilibrium composition for the metallic phase of the BA (5V) alloy: a, b calculated according to [23] and [31–33], respectively. (E) - Eremenko V.N.

share of vanadium in the alloy - \((\text{Mo,V})_2/(\text{Mo,V})_3\) = 0.9; 1.1; 1.3 and 1.6 for BA (5V) - BA (20V) alloys, respectively. In the base alloy, this ratio has a value of 0.78.

The results of chemical and X-ray phase analyses of model Mo-Si-V alloys melted in a vacuum arc furnace are given in Table 3. The deviation of the chemical analysis data from the calculated ones for V lies in the range from -4.6 to +1.6 wt. %, for Si - from +1.6 to +7.6 wt. %. The consequence of this may be, the error in the method of determining elements in chemical analysis, and the loss of part of the material during vacuum arc remelting. Weight loss after melting was about 1.0 %.

By the X-ray phase analysis method for powders of Mo-Si-V model alloys, it was established that all the studied alloys are two-phase and are represented by solid solutions \((\text{Mo,V})_2\) and \((\text{Mo,V})_3\). The semi-quantitative assessment of the phase composition for the samples according to X-ray spectra showed that the mass fraction ratio \((\text{Mo,V})_2/(\text{Mo,V})_3\) with increasing of the vanadium in BA increases and for the BA alloy

<table>
<thead>
<tr>
<th>Literature</th>
<th>(\Delta H_{298}^\circ), kJ/mole</th>
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<tbody>
<tr>
<td>HSC database [23]</td>
<td>V(_2)Si</td>
</tr>
<tr>
<td>Eremenko [31–33]</td>
<td>V(_5)Si(_3)</td>
</tr>
<tr>
<td>Meschel [34]</td>
<td>V(_5)Si(_2)</td>
</tr>
<tr>
<td>Gorelkin [35]</td>
<td></td>
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<td>Zhang [36]</td>
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</table>
(20V) it reaches 1.27, which is 25.0% less than the value calculated by the results of TDS (Fig. 3). Nevertheless, the obtained dependences do not contradict each other, and the differences can be caused by the following factors: 1) thermodynamic models do not take into account the rate of alloys crystallization, the heat loss and the part of the material during the smelting process; 2) in the HSC Chemistry 6.12 database there is no information about the thermochemical properties of solid solutions formed in the Mo-Si-V system; 3) the error in calculation of the ratio for the mass fractions of phases according to the results of XRP A analysis.

Thus, according to the results of thermodynamic and X-ray phase analyses, the additive of up to 20.0 at. % of vanadium in the Mo\textsubscript{0.85}Mo\textsubscript{0.15}Si alloy practically doubles the proportion of the metal phase in relation to the silicide phase in it, while maintaining the two-phase nature of the system. This will undoubtedly have a significant impact on

![Figure 2: Equilibrium compositions for model Mo-Si-V alloys. (E) - Eremenko V.N.](image)

**Table 3: Chemical and phase compositions of Mo-Si-V alloys.**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>Phase composition (wt. fraction, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt. %</td>
<td>at. %</td>
</tr>
<tr>
<td></td>
<td>Mo</td>
<td>Si</td>
</tr>
<tr>
<td>BA(5V)</td>
<td>92.18</td>
<td>4.92</td>
</tr>
<tr>
<td>BA(10V)</td>
<td>88.65</td>
<td>5.05</td>
</tr>
<tr>
<td>BA(15V)</td>
<td>86.20</td>
<td>4.62</td>
</tr>
<tr>
<td>BA(20V)</td>
<td>83.06</td>
<td>4.50</td>
</tr>
</tbody>
</table>
the structure and physical-mechanical properties of vanadium-doped Mo-Si alloys of hypoeutectic composition in comparison with binary ones.

4. Conclusions

1. The values of the heat formation for vanadium silicide incorporated in the HSC Chemistry 6.12 database, when simulating Mo-Si(14.5-12.2)-V(5.0-20.0) alloys (at. %), lead to results that contradict the Mo-Si-V state diagram for alloys of this composition. The modelling results are in satisfactory agreement with the Mo-Si-V phase diagram if the calculations are based on the $\Delta H_{298}^0$ values given in the works of V.N. Yeremenko [31–33].

2. The results of TDS adequately describe the phase formation processes during the smelting of Mo-15.3Si alloys doped with vanadium (up to 20.0 at.%), which is confirmed by the results of X-ray phase analysis of the synthesized Mo-Si-V alloys.

3. It has been established that the investigated Mo-Si-V alloys are two-phase and consist of solid solutions $(Mo,V)_{ss}$ and $(Mo,V)_3Si$. According to TDS and XRPA data, with an increase in the content of vanadium in model alloys, the ratio of the metal phase to the silicide phase increases from 0.78 to 1.60 and from 0.78 to 1.27, respectively.
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References


