The Interactions between Ta-Nb Ferroalloys and Sulfate-carbonate Melts

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Z. Naturforsch. 56 a, 725–729 (2001); received August 20, 2001

Presented at the NATO Advanced Study Institute, Kas, Turkey, May 4 - 14, 2001.

The reactions of pure metals Ta, Nb, V, Fe, Si, etc. and Ta-Nb-containing ferroalloys with sodium (calcium) sulfate (carbonate) melts are characterized by large exothermic effects and formation of solid, liquid and gaseous products. The liquid phases formed reduce diffusion restrictions and result in catastrophically large rates of metal oxidation.

Keywords: Oxidation; Component; Sulfate; Melt.

The oxidation of Ta-Nb containing ferroalloys takes place during pyrochemical processing of tantalum-niobium ores and secondary raw materials [1, 2]. Molten salts, in particular sulfates, carbonates and their mixtures can be used as oxidizers. In the present work we studied the interaction between sodium and calcium sulfates (carbonates) and multicomponent Ta-Nb-containing ferroalloys as well as their individual components.

Thermodynamic modelling, thermogravimetric (TG), differential-thermal (DT), and high-temperature X-ray diffraction (XRD) methods were employed in the present study. The X-ray diffraction patterns were measured on heating with linear heating rate of 10 degrees/min. The extent of interaction (α) was calculated from the ratio of the measured mass change of the molten mixture to the initial SO₃ content of the system.

The metals and alloys were used as powders (particle size < 0.1 mm). The purity of the individual metals was > 99.9%. The experiments were performed under an inert atmosphere or under vacuum. Chemically pure sodium and calcium sulfates and sodium carbonate were calcined for 2 h at 973 K prior to use.

Thermodynamic analysis of the systems M - Na₂SO₄ (M = Ta, Nb or V) has indicated many possible reactions. Some of the basic ones are:

\[ 2M + 5Na₂SO₄ = 5Na₂O + M₂O₅ + 5SO₂, \]  
\[ 8M + 5Na₂SO₄ = 5Na₂S + 4M₂O₅, \]  
\[ 8M + 8Na₂SO₄ = 8NaMO₃ + 4Na₂O + 2SO₂ + 3S₂, \]  
\[ 2M + 3Na₂SO₄ = 2NaMO₃ + 2Na₂O + 2SO₂ + 0.5S₂, \]  
\[ 4M + 4Na₂SO₄ = 4NaMO₃ + Na₂S + S₂. \]  

In order to determine the exact way of the rare metals oxidation a detailed experimental investigation has been carried out.

The DT analysis showed only one exothermic effect on the differential-thermal heating curves (Fig 1b) occurring at 999 K for Ta and at 1023 K for Nb, irrespectively of the amount sodium sulfate added to the initial M-Na₂SO₄ mixtures. The results show that the amplitude of the peak on the thermograms increases as the metal to oxygen ratio in the mixture approaches the stoichiometric value required for pentoxide formation. The large reaction enthalpies resulted in an increase of the temperature of the reacting mixture by 150 - 300 degrees.

The behaviour of the reacting mixture was investigated under an optical microscope. It was found that the process was accompanied by formation of liquid phases. The melting points of Na₂SO₄ (1158 K), V₂O₅ (947 K), Nb₂O₅ (1783 K) and Ta₂O₅ (2143 K), and the formed compounds Na₃O and M₂O₅ (M = V, Nb), indicate the formation of complex multicomponent melts.
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Fig. 1. a: Thermogravimetric (TG) and b: differential-thermal (DT) analysis of the interaction between sodium sulfate and rare metals. Ta / Na<sub>2</sub>SO<sub>4</sub>: 1: (8 / 5), 3: (2 / 5), V / Na<sub>2</sub>SO<sub>4</sub>: 2: (8 / 5), 4: (2 / 5). \( \alpha \) is the extent of interaction, calculated as the ratio of the measured mass decrease of the melt to the initial SO<sub>3</sub> mass in the mixture.

Fig. 2. The effect of temperature on the relative intensity of the maxima of the X-ray diffraction patterns of pressed 8M + 5Na<sub>2</sub>SO<sub>4</sub> mixtures. 1: M = V, 1: M = Nb, 1: M = Ta. \( I / I_0 \) is the relative intensity.

Fig. 3. The effect of sample preparation and the Ta / Na<sub>2</sub>SO<sub>4</sub> ratio on the starting temperature of reaction. \( I / I_0 \) is the relative intensity of a maximum of X-ray diffraction. 1: pressed 2Ta + 5Na<sub>2</sub>SO<sub>4</sub> mixture, Ta / Na<sub>2</sub>SO<sub>4</sub>: 1: (1 / 2.5), 3: (1 / 0.125), 4: (1 / 0.625).

Fig. 4. Changes of the relative intensity of X-ray diffraction maxima upon heating of a pressed 8Ta + 5Na<sub>2</sub>SO<sub>4</sub> mixtures. 1: Ta, 2: Na<sub>2</sub>SO<sub>4</sub>, 3: NaTaO<sub>3</sub>, Nb, Ta) indicate that only vanadium-containing products are liquid. For interactions including niobium and tantalum, initial melting of sodium sulfate is more probable. Formation of liquid phases enhances diffusion and results in very high rates of metal-oxidation. A similar conclusion can be drawn from the TG data (Fig. 1a). The periodic blocking of the metal surface by crystalline products makes the process similar to unstable combustion of exothermic mixtures.

The results of the high-temperature XRD measurements (Figs. 2, 3) showed that the integrated intensities of metal peaks remain constant so long as there is no product formation on the surface of the metal sample absorbing part of the \( \gamma \)-radiation. The temper-
The effect of temperature on the extent (a) and rate (b) of interaction in Ta+CaSO$_4$ mixtures. Ta / CaSO$_4$ 1: (1/5), 2: (2/5), 3: (4/5).

Fig. 5. The effect of temperature on the extent (a) and rate (b) of interaction in Ta+CaSO$_4$ mixtures. Ta / CaSO$_4$ 1: (1/5), 2: (2/5), 3: (4/5).

ature at which the interaction and the fast decrease of the intensity of the metal peaks in the XRD patterns begins depends on the ratio of the components in the mixture and the intimacy of their contact (Fig. 3).

When the M/O ratio in the mixture is close to that stoichiometrically required for M$_2$O$_5$ formation, the intensity of the diffraction lines of the reacting metals also decreases faster, in agreement with the DT data. The interaction of the studied metals with sodium sulfate under vacuum begins at 743 - 773 K.

As the temperature is further increased (up to 823 K) the intensity of the XRD lines of tantalum and niobium decreases (Fig. 4) with the simultaneous increase of the intensity of the NaTaO$_3$ and NaNbO$_3$ diffraction maxima. At temperatures between 823 and 903 K the intensities of the diffraction lines remain constant. On heating above 903 K, the rate of the reactions accelerates so much that at 1023 K the process is complete. In the case of vanadium oxidation the dependence $J/J_0$ on $T$ does not exhibit horizontal regions. The reaction slowly develops at 773 - 843 K and then vigorously finishes between 853 - 863 K. This more intensive vanadium oxidation (in comparison with tantalum and niobium) can be explained by the formation of low-melting vanadium pentoxide and sodium vanadates.

The reactions of sodium sulfate with Fe, Mn, Si, W, and Sn followed similar patterns as described above for the group 5 metals. In this case, the large enthalpy changes of the reactions also promoted the local temperature increase and melting not only of the low-melting products and eutectics but also of Na$_2$SO$_4$-particles. The highest reaction rates were observed for M/O ratios close to that stoichiometrically required for the formation of oxides (sulfides) containing M in the highest oxidation state.

When calcium sulfate was used as oxidant, large exothermic effects and very high reaction rates were observed again. However, in this case the process began at temperatures by 200 - 300 degrees higher than in Na$_2$SO$_4$-containing systems. The determining role in the process was played by the formation of liquid products capable of dissolving calcium sulfate, by the reactions on the gas-solid interface and also by the durability of the oxide films present on the metal surface. The tantalum oxidation was, for example, accompanied by the formation of $\beta$-Ta$_2$O$_5$, CaTa$_2$O$_{11}$, CaTa$_2$O$_6$, TaS$_2$, CaO, CaS and SO$_2$ (Fig. 5). The rather fast tantalum oxidation was promoted by gaseous products such as oxygen, sulfur and sulfureic anhydride taking part in the reactions, and also by continuous exposure of the tantalum surface due to cracking of the layer of $\beta$-Ta$_2$O$_5$ and the tantalates formed. It has been reported that $\beta$-Ta$_2$O$_5$ plays a significant role in high-temperature oxidation of tantalum by oxygen [3].
Table 1. Oxidation of the multicomponent alloys.

<table>
<thead>
<tr>
<th>Test No</th>
<th>Oxidizer to initial alloy (wt.%)</th>
<th>Composition (wt.%)</th>
<th>Extraction (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{Na}_2\text{SO}_4 )</td>
<td>( \text{Na}_2\text{CO}_3 )</td>
<td>( \text{Secondary alloy} )</td>
</tr>
<tr>
<td>1</td>
<td>–</td>
<td>50</td>
<td>50</td>
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<tr>
<td>2</td>
<td>40</td>
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</tr>
<tr>
<td>7</td>
<td>15</td>
<td>–</td>
<td>60</td>
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</tbody>
</table>

Fig. 6. Thermodynamic modelling of the effect of the wt-ratio of sodium sulfate to alloy on the composition of the alloy after oxidation of this alloy at 1573 K.

The results obtained so far on the oxidation of pure metals allow to assume that high rates of reactions and small diffusion restrictions can be expected during liquid interaction between sodium (calcium) sulfate and multicomponent Ta-Nb-containing alloys. In this case, a selective oxidation of the components of such alloys is possible using a limited amount of the oxidizing agent. The theoretical predictions were checked by studying the interaction of the ferroalloy containing (wt. %) 42.0 Nb, 2.41 Si, 3.13 Al, 3.34 Mn, 5.62 Sn, 0.64 Ti, and 0.32 Zr with a sulfate-carbonate melt. It is known that sodium carbonate is a weak oxidizer and all the same was used as diluent, capable of forming low-melting compounds with refractory products. The thermodynamic computer modelling of the process (based on the principle of minimizing the free energy of the system) has shown that selective oxidation of the above ferroalloy by sodium (calcium) sulfate is possible with a sulfate salt load of 50 - 60% with respect to the weight of the alloy. In this case of the new (secondary) alloy containing (wt. %) 75 - 80 Fe, 15 - 20 Sn and less than 1 of the remaining elements can be obtained (Fig. 6). If sodium carbonate is used in place of sulfate as the oxidant, the amount of oxidizer (\( \text{Na}_2\text{CO}_3 \)) required for the above selective oxidation to yield the secondary alloy is 15 times greater than in the sulfate-containing system (Fig. 7).

To confirm the thermodynamic predictions the experiments were performed on a laboratory scale using \( \text{Na}_2\text{SO}_4 + \text{Na}_2\text{CO}_3 \) and \( \text{CaSO}_4 + \text{Na}_2\text{CO}_3 \) mixtures (Table 1). The experiments were carried out as follows. An alumina crucible was charged with 20 - 50 g of a chosen reaction mixture and lowered into an open vertical tube furnace preheated to 1573 - 1623 K. The temperature was risen to 1673 - 1723 K, the melt formed was kept in this temperature range for 10 - 15 min, and then it was cooled. The interaction proceeded rather vigorously and was completed within some minutes.
The data presented in Table 1 and Fig. 6 show that the results of experimental tests are close to those predicted by the thermodynamic calculations, and the deviations observed probably arose from the atmospheric oxygen participating in the oxidation. Good separations of tin and other metals (e.g., niobium) were observed using salt mixtures containing 50 - 60% Na$_2$CO$_3$ and 40 - 50% Na$_2$SO$_4$ (CaSO$_4$). When sodium sulfate was used, the oxidation was more exothermic and produced a less viscous slag.

We have thus established that high-temperature reactions between metals and sodium (calcium) sulfate are characterized by a variety of processes and large exothermic effects. The high reaction rates result in a fast completion of the interactions, therefore allowing effective use of such salts for the oxidation of multicomponent alloys, in particular the Ta-Nb-containing ones studied here.