PHASE EQUILIBRIUM IN THE Sb$_2$Te$_3$-HoTe$_3$ SYSTEM


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Summary: The phase equilibrium of the Sb$_2$Te$_3$-HoTe$_3$ system was studied by means of physical and chemical analysis methods DTA, RFA, MQA, as well as density and microhardness measurements, and its phase diagram was constructed. It has been determined that the Sb$_2$Te$_3$-HoTe$_3$ system is a partial quasi-binary cross section of the ternary Bi$_2$Ho-Te system. The system undergoes a process of eutectic equilibrium and peritectic transformation. In the Sb$_2$Te$_3$-HoTe$_3$ system at room temperature, of the based Sb$_2$Te$_3$ solid solutions extend to 4.5 mol % and of the based HoTe$_3$ solid solutions have practically not been established.

Keywords: phase, solid solution, eutectic, syngony, microhardness.

The ternary system of antimony and holmium chalcogenides has not been studied in detail in the literature. It should be noted that the physicochemical and physical properties of holmium chalcogenides have not been studied in detail. It is noted that HoTe, Ho$_2$Te$_3$, Ho$_3$Te$_5$ and HoTe$_3$ compounds are obtained in the Ho-Te system. Only the crystallographic properties of these compounds have been studied. It is known that chalcogenides of rare earth elements and double and triple compounds have been studied. It is known that chalcogenides of rare earth elements and triple compounds and solid solution alloys based on them are magnetic, photoelectric, thermoelectric and luminescent materials and are widely used in semiconductor technology [1-10].

Unlike holmium chalcogenides, a large number of systems involving antimony chalcogenides have been studied. Sulfide and selenide compounds of antimony and ternary compounds based on them and solid solution alloys show high photoelectric properties [11-15]. Antimony telluride compounds are materials with medium resistance thermoelectric properties [16-19]. From this point of view, the study of the chemical interaction of Sb$_2$Te$_3$ and HoTe$_3$ chalcogenides is of scientific and practical importance. The Sb$_2$Te$_3$-HoTe$_3$ system is being studied for the first time.

The aim of this work is to construct the phase diagram of the Sb$_2$Te$_3$-HoTe$_3$ system by studying its phase equilibrium. The following information is available on the initial components of the system: The Sb$_2$Te$_3$ compound melts congruently at 622°C and crystallizes in the rhombohedral-hexagonal system of the Bi$_2$Te$_3$ type, lattice parameters: \( a_0 = 4.264 \, \text{Å}, c_0 = 30.42 \, \text{Å}, \beta = 235^\circ34', \text{sp. gr. K3-m-D}^5_{2d}[20] \). The HoTe$_3$ compound melts incongruently at 780°C and crystallizes in the tetragonal system, lattice parameters: \( a = 4.292 \, \text{Å}, c = 25.40 \, \text{Å}, \text{sp. qr. Bmnb} [10] \).

Experimental part

Alloys of the Sb$_2$Te$_3$-HoTe$_3$ system were synthesized by fusing the components Sb$_2$Te$_3$ and HoTe$_3$ in a quartz ampoule evacuated to 0.133 Pa. The synthesis was carried out in the temperature range 800-1000°C. Taking into account the peritectic nature of the formation of the HoTe$_3$ compound, annealing was carried out below 20°C at the peritectic temperature to obtain its full composition. The samples were heat treated at 400°C for 350 hours to achieve equilibrium. Homogenized samples were investigated by methods of physicochemical analysis (DTA, XRD, MSA, as well as by measuring density and microhardness).

Differential thermal analysis (DTA) of the alloys was carried out on an HTR-73 low-frequency pyrometer. Al$_2$O$_3$ was used as a standard, the heating rate was 10°C.

X-ray diffraction patterns of the alloys were taken on a D2 Phaser X-ray device using CuKα radiation. The microstructural analysis of the alloys was carried out on an MIM-8 metallographic microscope. To reveal the microstructure of the alloys, we used an etchant with the composition HNO$_3$ conc.: H$_2$O$_2$ = 2: 1, etching time was 10 s.

The microhardness of each phase was measured on a PMT-3 device at a load of 0.15 N. The density for the samples was determined by the pycnometric method.

Results and its discussion

The synthesized alloys of the Sb$_2$Te$_3$-HoTe$_3$ system are in a compact mass. Rich samples with Sb$_2$Te$_3$ are silver, the rest are gray. The system alloys are resistant to air, water and organic solvents. They are readily soluble in acids HNO$_3$, H$_2$SO$_4$ and strong alkalis (NaOH, KOH). After the homogenization of the samples was completed, a physicochemical analysis was carried out. According to the results of differential thermal analysis of the samples, it was found that the thermograms of alloys of the Sb$_2$Te$_3$-HoTe$_3$ system contain two and three endothermic effects. High thermal effects in the system are due to the decomposition of HoTe$_3$ as well as complex interactions.
The results of microstructure analysis (MSA) of the alloys show that the samples in the concentration range of 0-4.5 mol % HoTe₃ are single-phase, and the rest of the samples are two-phase. HoTe₃-based solid solutions are practically undefined. In Fig. 1 shows the microstructures of alloys of the Sb₂Te₃-HoTe₃ system. The 4 mol % HoTe₃ sample is a solid solution based on the Sb₂Te₃ compound. Samples with 30 and 70 mol % HoTe₃ are two-phase.

Fig. 1. Microstructures of alloys of the Sb₂Te₃-HoTe₃ system.
1-4, 2-30, 70 mol % HoTe₃.

To determine the accuracy of the DTA results and analyze the microstructure, an X-ray phase analysis of the alloys of the system was carried out. For this, Fig. 2 shows the results of X-ray phase analysis of HoTe₃ samples with 4 and 80 mol %. As seen from Fig. 2, diffraction patterns of samples with 30 and 70 mol % HoTe₃ consist of diffraction lines of the initial components. The diffraction lines in the diffraction pattern of the alloy containing 4 mol % HoTe₃ are identical to the diffraction lines of the Sb₂Te₃ compound and differ insignificantly in interplanar distances. This sample is a solid solution based on Sb₂Te₃ (Fig. 2).

Fig. 2. Diffraction patterns of alloys of the Sb₂Te₃-HoTe₃ system.
1-Sb₂Te₃, 2-4, 3-80, 4-100 mol% HoTe₃.

The phase diagram of the Sb₂Te₃-HoTe₃ system was constructed based on the results of physicochemical methods of analysis (Fig. 3). The Sb₂Te₃-HoTe₃ system was found to be, as expected, a partial quasi-binary section of the Sb-Ho-Te ternary system. The liquidus of the system is surrounded by monovariant curves of the equilibrium of an α-solid solution based on Sb₂Te₃ and a Ho₂Te₅ compound in liquid equilibrium. Eutectic equilibrium and peritectic transformation take place in the system.
Since the HoTe$_3$ compound is peritectic, splitting in this region leads to the formation of three-phase regions above the solidus line. There are three-phase fields in the concentration range 12-40 mol % HoTe$_3$ (M + α + Ho$_2$Te$_5$) and in the range 40-100 mol % HoTe$_3$ (M + Ho$_2$Te$_3$ + HoTe$_3$). The intersection of the α and Ho$_2$Te$_5$ liquidity curves in the system is 20 mol % HoTe$_3$ and 550°C. At this moment, a three-phase equilibrium M↔α + Ho$_2$Te$_5$ is formed. Primary crystals of the Ho$_2$Te$_5$ compound are separated from the liquid in the concentration range of 20–100 mol % HoTe$_3$. In the system, the four-phase peritectic transformation M + Ho$_2$Te$_3$↔α + HoTe$_3$ occurs on an isothermal line with a temperature of 400°C. At room temperature, solid solutions up to 4.5 mol % are formed in a system based on Sb$_2$Te$_3$, while solid solutions based on HoTe$_3$ are practically not established. Two-phase alloys α + HoTe$_3$ crystallize in the range of 4.5 - 100 mol % HoTe$_3$ below the solidus line. Some physicochemical properties of alloys of the Sb$_2$Te$_3$-HoTe$_3$ system are given in Table 1.

**Table 1. Results of DTA, measurements of microhardness and determination of the density of alloys of the Sb$_2$Te$_3$-HoTe$_3$ system**

<table>
<thead>
<tr>
<th>Composition, mol%</th>
<th>Thermal effects, °C</th>
<th>Density, 10$^3$kg/m$^3$</th>
<th>Microhardness, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb$_2$Te$_3$</td>
<td>HoTe$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0.0</td>
<td>622</td>
<td>6.51</td>
</tr>
<tr>
<td>95</td>
<td>5.0</td>
<td>540.615</td>
<td>6.53</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>450.600</td>
<td>6.56</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>400.560</td>
<td>6.60</td>
</tr>
<tr>
<td>70</td>
<td>30</td>
<td>400.520,575</td>
<td>6.62</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>400.640</td>
<td>6.65</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>400.500,680</td>
<td>6.67</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>400.575,710</td>
<td>6.69</td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>400.650,750</td>
<td>6.72</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>400.700,770</td>
<td>6.76</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>400.725,790</td>
<td>6.80</td>
</tr>
<tr>
<td>0.0</td>
<td>100</td>
<td>780,800</td>
<td>6.82</td>
</tr>
</tbody>
</table>

As can be seen from the table, two different values of microhardness were determined when measuring the microhardness of alloys in the system. The value of microhardness (1200-1260) MPa corresponds to the...
microhardness of the α-solid solution formed on the basis of Sb₃Te₃, the value of (1160-1190) MPa corresponds to the microhardness of the new HoTe₃ compound. The density of the alloys increased monotonically in the two-phase field between the solid solution area.

**Conclusion**

By studying the chemical interactions in the Sb₂Te₃-HoTe₃ system, its phase diagram is constructed. It was found that the Sb₂Te₃-HoTe₃ system is a partial quasi-binary region of the Sb-Ho-Te ternary system. The system is undergoing a process of eutectic equilibrium and peritectic transformation. It was found that, at room temperature, solid solutions based on Sb₂Te₃ reach 4.5 mol %, while solid solutions based on HoTe₃ are practically not found. Since the HoTe₃ compound is peritectic, it decomposes at a higher peritectic temperature, which leads to the formation of three-phase regions (M+α+Ho₂Te₃) and (M+Ho₂Te₃+HoTe₃) above the solidus line. In the concentration range 4.5–100 mol.% HoTe₃ below the solidus line, two-phase alloys consisting of α + HoTe₃ crystallize.

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