Isothermal Section of the Ho–Cu–Sn Ternary System at 670 K

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The interaction of the components in the Ho–Cu–Sn ternary system was investigated at 670 K over the whole concentration range using X-ray diffraction and EPM analyses. Four ternary compounds were formed in the Ho–Cu–Sn system at 670 K: HoCuSn (LiGaGe type, space group P63mc), Ho,CuSn (Gd,Cu(Fe,Cu)-type, space group Immm), HoCuSn (CeCu(AlCu)-type, space group Pnma), and Ho,SbCuSn (Dy3,CuSbSn3-type, space group P63/mmc). The formation of the interstitial solid solution based on HoSn2 (ZrSi2-type) binary compound up to 5 at. % Cu was found.

Keywords: Intermetallics; Phase diagrams; X-ray diffraction; Crystal structure.

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I. Experimental details

The samples were prepared by a direct twofold arc melting of the constituent metals (holmium, purity of 99.9 wt.%; copper, purity of 99.99 wt.%; and tin, purity of 99.999 wt.%) under high purity Ti-gettered argon atmosphere on a water-cooled copper crucible. The weight losses of the initial total mass were lower than 1 wt.%. The pieces of the as-cast buttons were annealed for one month at 670 K in evacuated silica tubes and then water quenched. The temperature of annealing was taken into account the low melting temperature of Sn (232 °C) and of the R-Sn binaries at high Sn content. Phase analysis was performed using X-ray powder patterns of the synthesized and annealed samples (DRON-2.0, Fe Kα radiation). The observed diffraction
Fig. 1. Isothermal section of the Ho–Cu–Sn system at 670 K.

Fig. 2. SEM pictures of the alloys from Ho–Cu–Sn system (the alloys are numbered according to Table 1): a) 4. Ho$_{30}$Cu$_{55}$Sn$_{15}$ (HoCuSn—grey light phase, HoCu$_5$Sn$_{1}$—grey phase, HoCu$_2$—dark phase); b) 5. Ho$_{40}$Cu$_{40}$Sn$_{20}$ (HoCuSn—light phase, Ho$_5$Sn$_3$—grey phase, HoCu$_2$—dark phase); c) 7. Ho$_{30}$Cu$_{44}$Sn$_{26}$ (HoCuSn—light phase, HoCu$_5$Sn$_3$—dark phase); d) 13. Ho$_{20}$Cu$_{33}$Sn$_{47}$ (Ho$_3$Cu$_4$Sn$_4$—light phase, Cu$_3$Sn—dark phase, Sn—dark phase); e) 14. Ho$_{30}$Cu$_{55}$Sn$_{15}$ (Ho$_3$Cu$_4$Sn$_4$—grey phase, HoCuSn—grey light phase, Cu$_3$Sn—dark phase).
### Table 1

Phase composition of the selected Ho-Cu-Sn alloys

| N | Nominal alloy composition (at.%) | Phases | Phases | Phases |
|---|---------------------------------|--------|--------|--------|
|   | Ho | Cu | Sn | 1<sup>st</sup> phase | 2<sup>nd</sup> phase | 3<sup>rd</sup> phase |
| 1 | 17 | 78 | 5  | HoCu<sub>5</sub>Sn<sub>1</sub>  |
|   |     |     |   | Ho=0.7048(2) nm | HoCu | HoSn<sub>3</sub> |
|   |     |     |   | a=0.4277(4) nm  | |
|   |     |     |   | b=0.6758(3) nm  | |
|   |     |     |   | c=0.7269(5) nm  | |
| 2 | 40 | 53 | 7  | HoCu<sub>2</sub>Sn<sub>1</sub>  |
|   |     |     |   | Ho=0.5055(4) nm  | HoCuSn | HoCu<sub>2</sub> |
|   |     |     |   | a=0.4470(3) nm  | |
|   |     |     |   | b=0.7153(4) nm  | |
| 3 | 17 | 68 | 15 | HoCuSn |
|   |     |     |   | Ho=0.7152(3) nm  | HoCu<sub>5</sub>Sn<sub>1</sub> |
|   |     |     |   | a=0.8189(4) nm  | |
|   |     |     |   | b=0.4960(4) nm  | |
|   |     |     |   | c=1.0568(6) nm  | |
| 4 | 30 | 55 | 15 | HoCuSn |
|   |     |     |   | Ho=0.8844(4) nm  | HoCu<sub>2</sub> |
|   |     |     |   | a=0.7038(3) nm  | |
|   |     |     |   | b=0.6759(5) nm  | |
|   |     |     |   | c=0.7270(5) nm  | |
| 5 | 40 | 40 | 20 | HoCuSn |
|   |     |     |   | Ho=0.7152(3) nm  | HoCu<sub>1.9</sub>Cu<sub>9.2</sub>Sn<sub>2.8</sub> |
|   |     |     |   | a=0.4470(3) nm  | |
|   |     |     |   | b=0.7153(4) nm  | |
| 6 | 15 | 65 | 25 | HoCu<sub>1.9</sub>Cu<sub>9.2</sub>Sn<sub>2.8</sub> |
|   |     |     |   | Ho=0.5054(4) nm  | HoCu<sub>1.9</sub>Cu<sub>9.2</sub>Sn<sub>2.8</sub> |
|   |     |     |   | a=0.4470(3) nm  | |
|   |     |     |   | b=0.7153(4) nm  | |
| 7 | 30 | 44 | 26 | HoCu<sub>5</sub>Sn<sub>1</sub> |
|   |     |     |   | Ho=0.7153(3) nm  | CuSn |
|   |     |     |   | a=0.4470(3) nm  | |
|   |     |     |   | b=0.7152(3) nm  | |
| 8 | 25 | 55 | 20 | HoCuSn |
|   |     |     |   | Ho=0.7154(4) nm  | HoCu<sub>5</sub>Sn<sub>1</sub> |
|   |     |     |   | a=0.4473(3) nm  | |
|   |     |     |   | b=0.7155(3) nm  | |
| 9 | 15 | 55 | 30 | HoCu<sub>5</sub>Sn<sub>1</sub> |
|   |     |     |   | Ho=0.4317(3) nm  | CuSn |
|   |     |     |   | a=0.4421(3) nm  | |
|   |     |     |   | b=0.6940(6) nm  | |
|   |     |     |   | c=1.4549(8) nm  | |
| 10| 50 | 13 | 37 | HoCuSn |
|   |     |     |   | Ho=0.8845(4) nm  | HoCu<sub>5</sub>Sn<sub>1</sub> |
|   |     |     |   | a=0.4470(3) nm  | |
|   |     |     |   | b=0.7154(4) nm  | |
| 11| 12 | 50 | 38 | HoCuSn |
|   |     |     |   | Ho=1.0151(6) nm  | CuSn |
|   |     |     |   | a=0.4420(4) nm  | |
|   |     |     |   | b=0.6936(5) nm  | |
|   |     |     |   | c=1.4548(8) nm  | |
| 12| 45 | 10 | 45 | HoCuSn |
|   |     |     |   | Ho=1.1519(5) nm  | HoCuSn |
|   |     |     |   | a=0.4471(3) nm  | |
|   |     |     |   | b=0.7153(5) nm  | |
| 13| 20 | 33 | 47 | HoCuSn |
|   |     |     |   | Ho=1.5024(6) nm  | CuSn |
|   |     |     |   | a=0.4419(3) nm  | |
|   |     |     |   | b=0.6938(6) nm  | |
|   |     |     |   | c=1.4545(8) nm  | |
| 14| 40 | 10 | 50 | HoCuSn |
|   |     |     |   | Ho=1.6193(5) nm  | HoCuSn |
|   |     |     |   | a=0.4471(3) nm  | |
|   |     |     |   | b=0.7156(3) nm  | |
| 15| 30 | 15 | 55 | HoCu<sub>5</sub>Sn<sub>1</sub> |
|   |     |     |   | Ho=0.4397(4) nm  | HoCuSn |
|   |     |     |   | a=0.4419(3) nm  | |
|   |     |     |   | b=0.6938(6) nm  | |
|   |     |     |   | c=1.4547(8) nm  | |
Crystallographic characteristics of the Ho-Sn binary phases (670 K)

| Compound       | Space group | Structure type | Lattice parameters, nm |
|----------------|-------------|----------------|-----------------------|
|                |             |                | $a$       | $b$       | $c$       |
| HoSn$_3$       | Amm2        | GdSn$_2$-type  | 0.4338(3) | 0.4389(3) | 2.1756(7) |
| Ho$_2$Sn$_3$   | $Pmmm$      | Er$_3$Ge$_2$   | 0.4305(1) | 0.4385(5) | 1.8903(1) |
| HoSn$_2$       | $Cmcm$      | ZrSi$_2$       | 0.4382(2) | 1.6193(3) | 0.4290(2) |
| Ho$_2$Sn$_{10}$| $I4/mmm$    | Ho$_1$Ge$_{10}$| 1.1526(5) | 1.6768(6) |           |
| Ho$_2$Sn$_4$   | $Pnma$      | Sm$_5$Ge$_4$   | 0.7963(3) | 1.5302(5) | 0.8053(2) |
| Ho$_3$Sn$_3$   | $P6_3/mcm$  | Mn$_2$Si$_3$   | 0.8846(2) | 0.6453(3) |           |

Crystallographic characteristics of the ternary compounds in the Ho-Cu-Sn system

| Compound       | Space group | Structure type | Lattice parameters, nm |
|----------------|-------------|----------------|-----------------------|
|                |             |                | $a$       | $b$       | $c$       |
| HoCu$_3$Sn     | $Pnma$      | CeCu$_3$Au     | 0.81883(7) | 0.49599(4) | 0.50652(8) |
| Ho$_3$Cu$_9$Sn$_{10}$ | $P6_3/mmc$ | Dy$_1$Cu$_2$Sm$_3$ | 0.5056(3) | -         | 2.0581(6)  |
| HoCu$_3$Sn     | $P6_3/mmc$  | LiGaGe         | 0.4474(2) | -         | 0.7155(3)  |
| Ho$_2$Cu$_4$Sn$_4$ | $Imm2$    | Gd$_2$Cu$_4$Ge$_4$ | 0.44197(1) | 0.69065(1) | 1.45799(3) |

Table 3

Atomic positional and isotropic displacement parameters of the HoCu$_3$Sn compound ($R_p = 0.0358$, $R_{wp} = 0.0565$, $R_I = 0.0448$)

| Atom | Wyckoff position | $x/a$ | $y/b$ | $z/c$ | $B_{iso}$ $\cdot 10^2$ (nm$^2$) |
|------|------------------|-------|-------|-------|----------------------------------|
| Ho   | 4c               | 0.2530(2) | 0.25  | 0.5630(1) | 1.49(3) |
| Cu   | 8d               | 0.0688(2) | 0.4997(3) | 0.3110(2) | 1.07(4) |
| Cu   | 4c               | 0.0597(3) | 0.25  | 0.0977(3) | 1.25(5) |
| Cu   | 4c               | 0.3190(3) | 0.25  | 0.2410(2) | 1.16(6) |
| Cu   | 4c               | 0.4162(3) | 0.25  | 0.0143(2) | 1.15(6) |
| Sn   | 4c               | 0.1386(2) | 0.25  | 0.8605(1) | 0.88(2) |

II. Results

2.1. Isothermal section of the Ho-Cu-Sn system.
Phase equilibria in the Ho-Cu-Sn system have been studied using X-ray analysis and scanning electron microscopy of 15 binary and 29 ternary alloys annealed at 670 K (Fig. 1). The phase compositions of the selected samples are listed in Table 1, the SEM-pictures of some alloys are shown in Fig. 2.

The presence of all binary compounds in the Ho-Cu and Cu-Sn systems corresponding to the reference data was confirmed at 670 K. Taking into account the reported data on Ho–Sn system including experimental study and thermodynamic optimization, and previously known binaries [23-27], the samples with compositions corresponding to the reference data were synthesized and analyzed by X-ray powder diffraction. The performed analysis confirmed the formation of Ho$_2$Sn$_3$ (Mn$_3$Si$_3$-type), Ho$_2$Sn$_4$ (Sm$_3$Ge$_2$-type), Ho$_2$Sn$_{10}$ (Ho$_2$Ge$_{10}$-type), HoSn$_3$ (ZrSi$_3$-type), Ho$_2$Sn$_4$ (Er$_2$Ge$_2$-type), and Ho$_3$Sn$_3$ (Gd$_3$Si$_2$-type) binaries. However, two binaries Ho$_2$Sn$_3$ and Ho$_2$Sn$_7$ were not identified at temperature of annealing, corresponding samples contained only...
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Obtained results are in agreement with last version of Ho-Sn phase diagram [27]. Crystallographic characteristic of the Ho-Sn binary compounds are given in Table 2. The formation of the substitutional solid solution based on the HoCu$_5$ binary compound (AuBe$_5$-type) up to 5 at.% Sn was found (a = 0.7028(2) nm for HoCu$_5$, a = 0.7048(2) nm for Ho$_{17}$Cu$_{78}$Sn$_5$). The limiting composition was confirmed by EPMA data (Ho$_{17.62}$Cu$_{77.55}$Sn$_{4.83}$, Fig. 2a). The interstitial solid solution HoCu$_x$Sn$_2$ (up to 6 at.% Cu) based on the HoSn$_2$ (ZrSi$_2$-type) binary compound was observed similarly to Ref. [32] (a = 0.4393(3), b = 1.6197(5), c = 0.4298(4) nm for Ho$_{31/5}$Cu$_{5}$Sn$_{63/5}$). No significant solubility of the third component in the other binary compounds was observed under used in our work conditions.

According to performed X-ray and microprobe analyses the phase relations in the Ho-Cu-Sn system at 670 K are characterized by the formation of four ternary compounds listed in Table 3. All ternary compounds are characterized by narrow homogeneity regions at investigated temperature. Among formed ternary compounds Ho$_3$Cu$_4$Sn$_4$ contains the higher Sn content (36 at. %), and we checked this phase with the differential scanning calorimetric analysis (DSC). No thermal peak corresponding to decomposition of Ho$_3$Cu$_4$Sn$_4$ compound was observed on DSC curve up to 1023 K.

2.2. Crystal structure.

The existence of the HoCu$_x$Sn compound with CeCu$_6$ structure type and its lattice parameters were reported earlier [21]. In our work the crystal structure of HoCu$_5$Sn stannide was refined by X-ray powder diffraction method (STOE STADI P diffractometer, WinCSD program package). After Rietveld refinement it was deduced that this compound belongs to the CeCu$_5$Au type structure (ordered variant of CeCu$_6$-type, space group Pnma, a=0.81889(7), b=0.49599(4), c=0.50652(8)
nm) with ordered distribution of the all atoms. Refined atomic coordinates and displacement parameters are listed in Table 4. The observed, calculated and difference X-ray patterns of HoCu$_5$Sn compound are shown in Fig. 3. The interatomic distances in the HoCu$_5$Sn structure are close to the sum of the atomic radii of the components.

Table 5

| Atom  | Wyckoff position | $x/a$  | $y/b$  | $z/c$  | $B_{iso} \times 10^2$ (nm$^2$) |
|-------|------------------|--------|--------|--------|-------------------------------|
| Ho1   | 4j               | 1/2    | 0      | 0.3692(1) | 1.25(6)                       |
| Ho2   | 2a               | 0      | 0      | 0      | 1.20(8)                       |
| Cu    | 8l               | 0      | 0.3075(4) | 0.3283(2) | 1.04(8)                       |
| Sn1   | 4i               | 0      | 0      | 0.2152(1) | 0.59(7)                       |
| Sn2   | 4h               | 0      | 0.2020(3) | 1/2 | 0.68(4)                       |

Fig. 5. Package of polyhedra for rare earth atoms in CeCu$_5$Au (a) and CeNi$_5$Sn (b) structures.

Fig. 6. The observed, calculated and difference X-ray patterns of HoCu$_5$Sn compound.
Crystal structure model of the HoCu₅Sn compound is shown in Fig. 4. CeCu₅Sn structure type similarly to CeNi₅Sn in which RNi₅Sn stannides with light rare earths crystallize [17], is related to CaCu₅ structure. Both structures contain the fragments of CaCu₅ type [33, 34]. Package of polyhedra for rare earth atoms in CeCu₅Au (a) and CeNi₅Sn (b) structures is shown in Fig. 5.

During present work, the crystal structure of Ho₃Cu₄Sn₅ stannide was refined by X-ray powder diffraction method (STOE STADI P diffractometer, WinPLOTR program package). Performed calculation confirmed that Ho₃Cu₄Sn₅ belongs to the Gd₃Cu₄Ge₄ structure type (space group Immm, a = 0.44197(1) nm, b = 0.69065(1) nm, c = 1.45799(3) nm). Refined atomic coordinates and displacement parameters are listed in Table 5. The observed, calculated and difference X-ray patterns of Ho₃Cu₄Sn₅ compound are shown in Fig. 6.

**Final remarks**

Comparing investigated Ho-Cu-Sn and previously studied R-Cu-Sn systems with heavy rare earths, it should be note a close analogy in stoichiometry and crystal structure of the most formed compounds. Similarity in the interaction of the elements in all investigated systems is demonstrated by the formation of the compounds RCu₅Sn, R₂Cu₅Sn₄, R₁₉₃Cu₄Sn₂₈ and R₃Cu₅Sn (except Lu). Crystal structure of the studied HoCu₅Sn compound is characterized by ordered distribution of the all atoms corresponding to CeCu₅Au-type in comparing to reported previously isotypic compound with Er (CeCu₅-type), the stoichiometry of which weakly deviates from ErCu₅Sn to ErCu₅Sn₁₅ [21]. The equiatomic RCu₅Sn compounds exist with all rare earths, but depending on the valence state and size of rare earth element they crystallize in different structure types - LiGaGe-type (or CaIn₃-type) (Y, La-Sm, Gd-Er, Lu) [35-38], CeCu₅-type (Eu) [39], TiNiSi-type (Yb) [40] and ZrBeSi-type (La, Ce) [35, 41]. The structure type Sm₃Cu₅Sn₅ realizes in the systems with Gd, Tb and Dy. The stannides with MgCu₅Sn-type are typical for Y-Cu-Sn and Yb-Cu-Sn systems.
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Ізотермічний переріз потрійної системи Ho–Cu–Sn при 670 K

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Взаємодія компонентів у потрійній системі Ho–Cu–Sn досліджена за температури 670 K в повному концентраційному інтервалі методами рентгенівської дифракції та рентгеноспектрального аналізу. При 670 K в системі відбуваються чотири тернарні сполуки: HoCuSn (структурний тип LiGaGe, простора група P63/mmc), Ho3Cu4Sn4 (структурний тип Gd3Cu4Ge4, простора група Immm), HoCu5Sn (структурний тип CeCu5Au, простора група Pnma) і Ho3–Cu9–Sn2–8 (структурний тип Dy3–Cu9–Sn2–8, простора група P63/mmc). Установлено утворення твердого розчину включена на основі бінарної сполуки HoSn2 (структурний тип ZrSi2) до вмісту 5 ат. % Cu.

Ключові слова: інтерметаліди; фазові діаграми; рентгенівська дифракція; кристалічна структура.