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Phase Relations and Equilibrium Copolymerization in the Se–S System

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The phase relations in the Se–S system were investigated by the appearance of phase method, differential thermal analysis, and differential scanning calorimetry. High purity selenium melts at 216 ± 2°C. A peritectic exists at 85 at.% Se and 168 ± 2°C; the peritectic isotherm extends from 92 to 73.5 at.% Se. A temperature minimum of 102 ± 1°C exists at a composition of 35 ± 1 at.% Se. High purity sulfur melts at 114 ± 1°C and polymerizes at 160 ± 2°C. Addition of 10 at.% Se lowers the polymerization temperature to 118 ± 3°C. The Se–S system shows complete liquid miscibility and in this respect it differs from the majority of selenide type systems that generally show one or more fields of liquid immiscibility. The complete liquid miscibility in the Se–S system can best be explained by the equilibrium copolymerization theory. Investigation of the subsolidus relations in the Se–S system shows a miscibility gap in the Se-rich part of the system. The eutectoid proposed by W. E. Ringer (*Z. Anorg. Chem.* **32,** 183 (1902)) in the S-rich part of the system was not detected.

Introduction

The phase relations in the S–Se system were investigated at the beginning of this century by Ringer (*17*) by thermal and dilatometric methods. Though more adequate experimental techniques for study of sulfide and selenide type systems and characterization of the phases in these systems have been developed, no attempt was made to reinvestigate the phase equilibria in the system. Six decades after Ringer's investigation of the S–Se system Hawes (*11*) correctly stated that "the phase relationships in the sulfur–selenium system are obscure and difficult to interpret." Adequate determination of the phase relations in the S–Se system is a prerequisite for investigating phase equilibria in ternary systems that contain the sulfoselenides of important elements such as Fe, Cu, Zn, and Hg that form economic mineral deposits and have important industrial applications.

The structures of S–Se solid solutions crystallized from melts and from CS_2 solutions were studied by DeHann and Visser (*6*) and Fergusson *et al.* (*10*). The liquid–vapor equilibrium in the S–Se system was studied by Devyatykh *et al.* (*7, 8*), who suggested that the system does not behave as an ideal solution.

The polymerization of S–Se liquids was studied experimentally by Ward (*22*) and by Ward and Meyers (*23*) using Raman spectroscopy and differential scanning calorimetry. A theoretical discussion of poly-

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merization of S–Se solutions was given by Tobolsky and Owen (*20*) and recently by Kennedy and Wheeler (*12*).

The purpose of the present investigation is to redetermine the phase relations in the S–Se system and study the equilibrium polymerization in S–Se liquid solutions.

The Elements

The elements S and Se have been a subject of interest to physical chemists for many years. In this section a survey of pertinent data on their behavior in the solid, liquid, and vapor states is presented.

Sulfur

At room temperature orthorhombic or α-sulfur is thermodynamically stable. According to Tuller (*21*), it inverts to monoclinic or β-sulfur at 95.4°C. The melting temperatures of the orthorhombic and monoclinic forms are 110.0 and 115.2°C, respectively. Kullerud (*14*) reported a temperature of 102 ± 1°C for the $\alpha \rightarrow \beta$ inversion and a melting temperature of 114 ± 1°C for the monoclinic form on the basis of DTA experiments on high purity sulfur. The inversion of α- to β-sulfur is sluggish and usually leads to some variability in the melting temperature (113–115°C) depending upon the proportions of the two forms present in the solid on melting.

Both α- and β-sulfur contain eight atom rings, which upon melting form eight atom chains. According to Wierorowski and Touro (*24*), the proportion of rings to chains decreases with temperature rise. When the polymerization temperature of 159°C is reached there no longer are enough rings to associate with the eight atom chains, which start to join each other forming long chains. The chains become progressively longer with increase in temperature. The polymerization of S is an equilibrium reversible process (*19*). At any temperature, however, the equilibrium condition among the ring and chain molecules and among the chain molecules of different lengths is established very slowly. Any sudden change in temperature results in a nonequilibrium distribution of rings and chains that leads to the formation of metastable forms of sulfur.

Sulfur vaporizes appreciably at 100°C, and its vapor pressure reaches one atmosphere at 444.6°C. According to Berkowitz and Marquart (*3*) the saturated vapor of sulfur contains the molecular species S_2, S_3, S_4, S_5, S_6, S_7, and S_8 together with small but detectable amounts of S_9 and S_{10}. These authors studied the distribution of the various species from room temperature to the boiling point of liquid S. They found that S_8 is the most important constituent over the entire temperature range, although S_6 and S_7 are present in considerable amounts, especially at high temperatures.

Selenium

Four modifications of Se are known, but only the trigonal gray or metallic Se is thermodynamically stable at room temperature. Trigonal Se has a structure consisting of infinite polymeric chains that are arranged parallel to the *c* axis. Two monoclinic modifications of Se are known: α and β monoclinic Se. They are produced, respectively, by slow and fast evaporation of a CS_2 solution of vitreous Se at room temperature. The two monoclinic modifications are made of Se_8 rings, and they transform to trigonal Se in the temperature range between 115 and 130°C. The fourth modification of Se is the red amorphous form which is obtained by condensation of Se vapor on a cold surface. The chain structure of trigonal Se is also present in this modification (*1*).

The melting temperatures of trigonal Se and monoclinic Se are 221.0 and 140°C, respectively (*18, 25*). The melting temperatures, however, are known to be dependent on the degree of purity of Se, the type of impurities it contains in solid solution, and their concentrations.

Liquid Se is composed of an equilibrium mixture of Se_8 rings and long polymeric chain, flexible, linear macromolecules which is retained upon quenching to glassy or vitreous Se. On reheating vitreous Se, the Se_8 rings start to associate forming polymer chains. The threshold polymerization temperature below which only Se_8 rings should be stable in the amorphous state as calculated by Eisenberg and Tobolsky (*9*) on the basis of the equilibrium polymerization model is 83°C which is 53°C above the glass transition temperature and 138°C below the melting temperature of trigonal Se. Shu and Wunderlich (*18*), however, did not observe during their heat capacity measurements on liquid Se an endothermic effect at 83°C corresponding to the threshold polymerization temperature estimated by Eisenberg and Tobolsky (*9*) and their calculation shows that the Se_8 ring concentration at this temperature is 59% rather than 100%. Shu and Wunderlich (*18*) suggested that the thermal effects in their DSC experiments can be easily explained if a threshold temperature well below the glass transition temperature is accepted. On the basis of a disordered chain model composed of *cis–trans* conformations (i.e., the first and fifth Se atoms are on the same or on opposite sides of the plane formed by the second, third, and fourth Se atoms). Misawa and Suzuki (*15*) estimated that the Se_8 ring concentration reaches 100% at a calculated threshold temperature of 125°K. Despite the disagreement on the threshold temperature of polymerization of Se, it is clear that Se polymerizes in the solid state. In this respect it differs from S which polymerizes above its melting temperature.

The saturated vapor over liquid Se is an equilibrium mixture of $Se_{(n)}$ where $n = 1$ to 8. In the temperature range 250–425°C $n =$ 5, 6, 7, and 2 are the main species in the vapor in a decreasing order of abundance (*18*). Berkowitz and Chupka (*2*), however, reported that in the temperature range 177–827°C the contents of Se_2 and Se_3 increase with temperature while the contents of Se_n with $n = 6$ to 8 show a continual decrease. The content of Se_5 in the vapor increases with temperature up to 477°C and then decreases slightly above this temperature, whereas that of Se_4 is negligible. Se_2 is the most predominant species during fast evaporation (*16*). Measurable dissociation of Se_2 to atomic Se was observed at temperatures higher than 1004°C (*5*).

Experimental Approach

The techniques used in investigating the phase relations in the Se–S system are similar to those used by Boctor and Kullerud (*4*) in studying the Hg–Se system. American Smelting and Refining Company "Special high purity" sulfur (99.999 ± wt%), Na, and Cl are present in amounts not exceeding 1 ppm and selenium pellets grade A-58 (99.999 + at%, As = 1 ppm, Ta, Cu, and Si < 1 ppm, Cl and S total < 0.0005%) were used as reactants.

S–Se solutions of different compositions were synthesized from high purity elements in evacuated silica tubes and held at 400°C for 2 days to ensure homogenization. The homogeneous liquids were quenched and were left to crystallize at room temperature. When it was difficult to crystallize the glasses at room temperature, they were annealed below their solidus temperatures. The crystalline products were studied by differential thermal analysis (DTA) and occasionally by differential scanning calorimetry (DSC). When it was desirable to examine crystallization effects, Se–S glasses were used instead of their crystalline products in DTA experiments. During cooling cycles in DTA experiments, no thermal effects were observed. The liquidus temperatures were therefore determined by the appearance of phase method which involves heating each composition in evacuated silica tubes at different temperatures above its anticipated liquidus temperature. Each run was quenched to room temperature in ice water in a matter of seconds. The quenched products were examined immediately under a binocular microscope to determine whether only a quenched liquid or a liquid + crystals were present. A portion of the quenched product was mounted in cold setting epoxy, polished, and examined by reflected light microscopy, about 10 min after quenching to verify the binocular microscope identification. In the sulfur-rich part of the system the quenched products were also examined immediately after quenching in transmitted light as grain mounts in immersion oil. The liquidus temperature was taken to be the one at which incipient appearance of crystals nucleating from the liquid is observed. X-ray diffraction patterns were prepared for quenched products that contained crystals.

TABLE I

EXPERIMENTAL RESULTS IN S–Se SYSTEM

At.% Se	Solidus[a] (°C)	Peritectic[a] (°C)	Liquidus[b] (°C)
10	112	—	114
16.5	110	—	112
20	110	—	112
30	104	—	108
35	102	—	102
40	107	—	112
50	116	—	131
55	122	—	140
60	124	—	148
65	131	—	155
70	136	—	162
73.5	141	167	169
80	149	167	190
83	153	168	196
85	—	168	200
87	—	167	205
90	—	168	209
92	—	168	213
95	188	—	216

[a] Determined by DTA, temperature ±1 to 2°C.

[b] Determined by appearance of phase method, temperature ±2 to 3°C.

Phase Relations

DTA experiments (Table I) performed on high purity Se showed an exothermic effect at 75 ± 2°C which corresponds to the crystallization of amorphous Se to the trigonal form, and an endothermic effect at 216 ± 2°C which is the melting temperature of Se. The difference in the melting temperature of Se in this investigation and that reported by Shu and Wunderlich (*18*) may be attributed to their use of single crystals of trigonal Se in their melting experiments and to the heating of the samples in their DTA experiments in air under atmospheric conditions, rather than in evacuated silica tubes as in our experiments.

A peritectic exists at 85 at.% Se and a temperature of 168 ± 2°C. The peritectic isotherm extends from 92 to 73.5 at.% Se. The peritectic in the phase diagram determined by Ringer (*17*) was at 160°C and 83 at.% Se, and his peritectic isotherm extended from 87 to 73.5 at.% Se.

A temperature minimum of 102 ± 1°C exists at a composition of 35 ± 1 at.% Se. Ringer (*17*) reported a eutectic at 40 at.% Se and 105°C and suggested the possibility of the existence of a eutectoid at 75°C and 16.5 at.% Se. Compositions in the range 16.5 to 50 at.% Se showed no endothermic effects that correspond to the eutectoid reported by Ringer (*17*) whether prior to their study by DTA, they were quenched from the liquid state or cooled slowly over a period of 8 hr to room temperature, where they were left to crystallize for periods up to one year. No thermal effects at 75°C were observed when the same compositions were annealed at 60°C within the solid state miscibility gap reported by Ringer (*17*) for periods up to 6 months prior to their study by DTA. The only thermal effects observed for solid solutions in the compositional range 16.5 to 50 at.% Se were those resulting from melting. The melting behavior of these compositions is suggestive of a temperature minimum at 35 ± 1 at.% Se rather than a eutectic at 40 at.% Se.

The DTA experiments on high purity sulfur showed three endothermic effects at 102, 114, and 160°C. These are similar to the thermal effects reported by Kullerud (*14*) for the orthorhombic to monoclinic inversion, the melting, and the polymerization of S. The DSC experiments on high purity S, however, showed four thermal effects at 95, 108, 113.7, and 160°C. The temperature of 95°C represents the α–β inversion in S; the small endothermic effect at 108°C represents the melting of a small amount of uninverted orthorhombic S; the large endothermic effect at 113.7°C corresponds to the melting of monoclinic S; and the thermal effect at 160°C is the polymerization temperature of S.

Addition of Se was found to lower the temperature of the α–β inversion. Thus the temperature of inversion was lowered to 84 ± 2°C for S containing 12 at.% Se in solid solution.

Cooling cycles in DTA experiments showed no thermal effects. An exothermic effect was observed, however, at 71°C in S containing 10 at.% Se on cooling in DSC experiments about 40°C below the solidus temperature for this composition. The appearance of this effect was found to be independent of the cooling rates used in these experiments. The liquidus temperatures determined by the appearance of phase method are given in Table I. No liquid immiscibility was detected over the entire compositional range from pure S to pure Se from above the melting temperatures to 400°C. The phase relations in the S–Se system are presented in Fig. 1.

Polymerization of S–Se Solutions

Addition of Se tends to lower the polymerization temperature of S. DSC experiments showed that 10 at.% Se in solution in S lowers the temperature of polymerization to 118 ± 3°C. This result is in agreement with a value of 115.5°C given by Ward and Meyers (*23*) for this composition. No polymerization effects were observed when the Se concentrations were increased above 10 at.% in the present experiments. Ward and

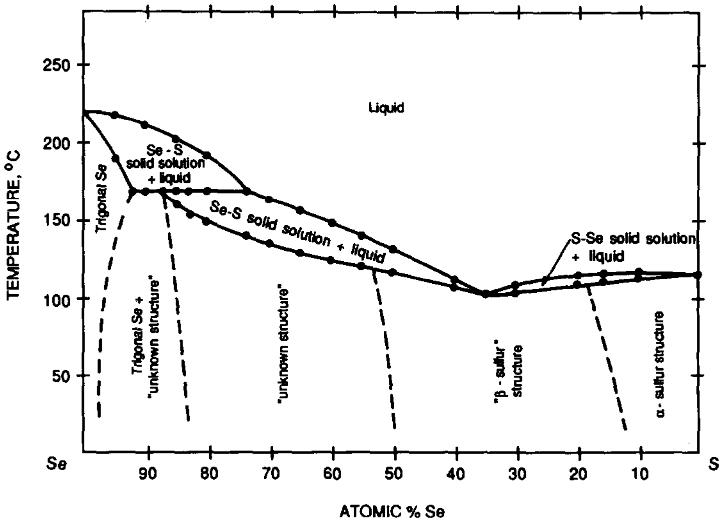

FIG. 1. Phase relations in the condensed Se–S system.

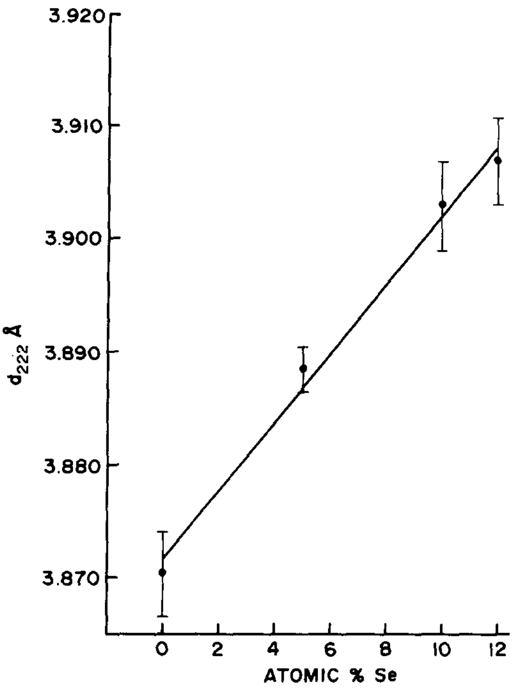

FIG. 2. Variation in the d_{222} spacing as a function of at.% of Se in Se–S solid solutions containing up to 12 at.% Se.

Meyers (*23*), however, were able to observe polymerization in their DSC experiments in the compositional range from pure S to sulfur with 12 at.% Se in solid solution. The polymerization temperature for the most Se-rich composition ($S_{88}Se_{12}$) was 110°C.

S–Se Solid Solutions

An X-ray study of S-rich solid solutions was conducted to detect whether there is, as suggested by Ringer (*17*), a solid state miscibility gap in the compositional range between 12 and 50 at.% Se.

Sulfur containing up to 12 at.% Se in solid solution showed X-ray patterns similar to that of orthorhombic sulfur. A shift in the line positions toward low 2θ values with increase in Se content is observed in all X-ray patterns of S–Se solid solutions in that compositional range. The shift in d_{222} reflection as a function of Se content is shown in Fig. 2. Each value reported for d_{222} is the average of eight measurements obtained by the oscillation method with Lake Toxaway quartz as an internal standard. The standard deviation of the measurements on each point are represented by vertical bars in Fig. 2. The best line fit for the data points was obtained by linear regression. The standard error of estimate for the regression line was 0.0018.

In the compositional range of 13–16.5 at.% Se, the solid solutions showed X-ray reflections of α-sulfur as well as β-sulfur. It is not clear whether there is a true miscibility gap in this compositional range or whether the coexistence of the two structures is due to failure to attain equilibrium. Evidence of metastability was detected during the study of S containing 10 to 12 at.% Se. When those compositions were quenched from the liquid state and studied by X-ray diffraction one day after quenching, they showed X-ray reflections corresponding to both α- and β-sulfur. X-ray patterns obtained from the same smear mounts after 2 months showed only lines characteristic of α-sulfur. Reflections of both α- and β-sulfur, however, were observed in the X-ray patterns for solid solutions containing 16.5 at.% Se after leaving it at room temperature for a period of 6 months. It is likely that due to kinetic effects the $\beta \rightarrow \alpha$ transition is retarded with increase of Se content, and the β-sulfur structure is persisting metastably.

S–Se solid solutions containing between 20 and 50 at.% Se showed the same X-ray pattern with systematic shift in the positions of the X-ray reflections toward low 2θ values with increase of Se content. The *d* values of the strongest reflection in these patterns are plotted in Fig. 3 as a function of Se content. The standard error of the regression line for the data points shown in Fig. 3 was 0.0014.

Fergusson *et al.* (*10*) found that S–Se

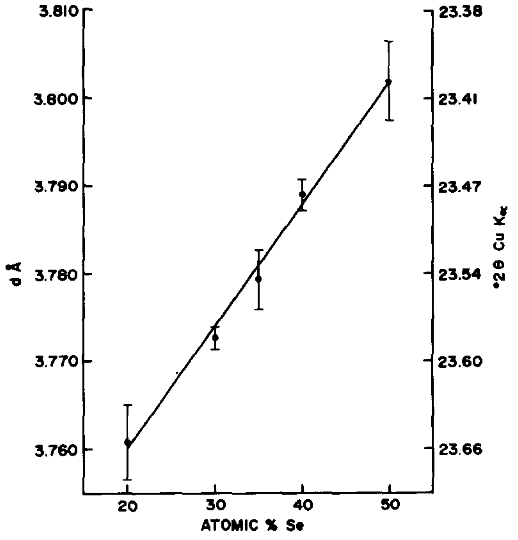

FIG. 3. Variation in the values of *d* and 2*θ* of the strongest reflection in Se–S solid solutions containing between 20 and 50 at.% Se.

solid solutions in the compositional range 0–14 at.% Se showed the α-sulfur structure, whereas those containing 17–55 at.% Se showed the β-sulfur structure, which was identified on the basis of cell dimension determinations in single crystal photographs. No indices for the X-ray reflections were given by these authors. The X-ray patterns obtained for compositions containing 20 to 50 at.% Se did not exactly match the pattern of β-sulfur, but no lines corresponding to the α-sulfur structure or the "unknown structure" of Fergusson *et al.* (*10*) were detected. Microscopic investigations of compositions with 20–50 at.% Se also showed a single homogeneous phase. In this investigation the use of solvent extraction by carbon disulfide solutions to improve the crystallinity was avoided, because it could change the composition and the crystal structures of the phases under investigation. The crystal structure of Se–S solid solution in the 20 to 50 at.% Se compositional range needs verification.

Melts containing more than 50 at.% Se quenched to glasses which devitrified very slowly when left at room temperature. The rate of devitrification decreased with increasing Se contents. Thus melts containing between 80 and 90 at.% Se showed only incipient devitrification after being left at room temperature for a period of 2 years. Annealing these glasses at temperatures below their solidus temperatures accelerates crystallization. The patterns obtained after annealing, however, showed poor crystallinity. In the compositional range from 55 to 83 at.% Se, the main X-ray reflections of the unknown structure reported by Fergusson *et al.* (*10*) were observed. Compositions in the range from 0 to 5 at.% Se gave X-ray patterns similar to those of trigonal Se. Compositions within the miscibility gap in the Se-rich portion of the system showed X-ray reflections of both the unknown structure and trigonal Se. Phase III (α-selenium structure) or phase IV (modified hexagonal selenium structure) reported by Fergusson *et al.* (*10*) were not detected in this investigation and they are likely to be metastable phases.

Discussion

The newly determined phase relations in the Se–S system are quite different from those determined by Ringer (*17*). The data presented here do not confirm the presence of the eutectic and the eutectoid which Ringer reported in the S-rich portion of the system. The peritectic isotherm in our phase diagram is of larger extent than that reported by Ringer (*17*).

The investigation of Se–S liquids was extended to a temperature of 400°C and showed no evidence of liquid immiscibility. In this respect the Se–S system is similar to the Se–Te system, and both differ from the sulfide–selenide-type systems that show either one or more fields of liquid immiscibility (*13*). The lack of liquid immiscibility in the Se–S system can be attributed to the fact that both elements are monomers forming long chain polymers, and can best be explained in the light of the equilibrium copolymerization theory (*12, 20*). In equilibrium copolymerization chain propagation is reversible and involves more than one type of monomer. Copolymer chains and monomer units coexist in thermodynamic equilibrium. The extent of polymerization and the length, composition, and sequence distribution of copolymer chains are temperature dependent. Tobolsky and Owen (*20*) suggested that the copolymer chains in the S–Se system form by joining S_8 and Se_8 monomer units. The threshold temperatures of polymerization calculated on the basis of the Tobolsky and Owen model are not in agreement with the experimentally determined temperatures. Kennedy and Wheeler (*12*) developed a lattice model for Se–S copolymerization in which the volume of the system is divided into cells on a regular lattice. Each cell is occupied by either an eight-membered ring or an eight-membered linear chain that may, or may not, be part of a longer copolymer chain. Each of the eight subunits in a cell may be either an S or an Se molecule. Ward and Meyer (*23*), however, found that their experimental results can best be explained if it is assumed that Se is not present as Se_8 rings, but enter sulfur substitutionally to give species of the type S_xSe_{8-x} where $8 > x > 4$. The polymerization threshold temperatures calculated by Ward and Meyer (*23*) assuming S_8 and S_6Se_2 monomer species were in good agreement with the experimentally determined values.

The study of the subsolidus phase relations in the Se–S system and the determination of the crystal structures of Se–S solid solutions of certain compositional ranges were hampered by the very sluggish reaction rates at low temperatures and our inability to obtain single crystals of Se–S solid solutions by crystallization from melts. Hydrothermal synthesis of single crystals of Se–S solid solutions that show the unknown structure and the β-sulfur structure should be attempted for crystal structure determination. Our investigation of the subsolidus relations in the S–Se system reduces the number of stable structures of Se–S solid solutions to form: the α-sulfur structure, the "β-sulfur" structure, the "unknown structure," and the trigonal selenium structure. The phases with the α-selenium structure and the modified hexagonal selenium structure that were reported by Fergusson *et al.* (*10*) to crystallize from melts with 60 and 66.66 at.% Se, respectively, appear to be unstable in the condensed Se–S system. These phases on heating are reported to decompose to phases that show the α-selenium structure and the unknown structure at 160°C. On solvent extraction by CS_2, however, at 46 and 160°C they decompose to compounds with the α-selenium structure, the α- and β-sulfur structure, and a residue with the modified hexagonal selenium structure (*10*). These results suggest that they are metastable phases. Intermediate compounds such as Se_2S_6 and Se_4S_4 that were prepared by Hawes (*11*) by solvent extraction in benzene of fusion products of S and Se mixtures of appropriate compositions were not encountered in this investigation of the subsolidus relations in the condensed Se–S system. This study clearly demonstrates that extraction by organic solvents is not a viable technique in the investigations of the condensed Se–S system. Because these organic solvents form ligands with both S and Se, the compositions of the initial solid solutions change during the extraction process and crystallization takes place of phases that do not crystallize from melts of similar initial composition in the condensed system.

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