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Obtaining of Nanocrystalline BCC-Phase in Ce-Ag Alloys

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Experimental investigations structure formation processes of $Ce_{100-x}Ag_x$ alloys ($x = 10 - 35$) in quenching from a liquid state conditions and the subsequent annealing of rapidly quenched amorphous foils has been realized. It is shown, that both at rapid cooling of melts, and at heating of preliminarily amorphized samples the metastable bcc-phase of an initial composition is formed in an explored concentration interval. It has micro- and nanocrystalline structure in fresh quenched and annealed foils, respectively. Features of the bcc-phase polymorphic crystallization revealed experimentally are explained by kinetic diagram „temperature - time - transformation”.

Key words: Ce-Ag alloys, quenching from the melt, amorphous foils annealing, metastable bcc-phase, micro- and nanostructures.

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Introduction

Quenching from a liquid state (QLS) is accompanied by a wide spectrum of metastable structural state formation, including amorphous phases without distant order in atom disposition [1 - 3]. Rapidly quenched amorphous alloys or metallic glasses (MG) possess valuable combinations of properties [4] which can be additionally refined at the expense of nanocrystalline structure forming at an early stage of MG crystallization [5 - 7]. Investigations of crystalline phase nature, appearing at heating of metal glasses and also phases which are fixed in a structure at subcritical rates of QLS and deviation of alloy composition from concentration ranges of a noncrystalline solidification, promotes deeper understanding of the overall picture of vitrescent alloy structure formation [8] and, besides that, they are important for development of new amorphous and nanocrystalline material production technologies.

In the given work the experimental investigations of metastable bcc-phase crystallization processes in alloys of Ce-Ag system which, according to data [9], shows higher competitiveness in comparison with equilibrium crystalline phases both at quenching out of a liquid state and at heating of rapidly quenched amorphous ribbons have been carried out.

I. Experimental Technique

Alloys of Ce-Ag system with concentration from 10 to 35 at. % Ag were melted of cerium with the total impurity content no more than 1 % and spectral-pure

silver in the vacuum electric furnace RVSE-12.5/25-43 at the residual pressure ~ 6 Pa. Quenching out of a liquid state was realized by a melt drop percussion with the rotating bronze cylinder interior surface. Cooling rate u_{-} of obtaining foils was estimated on their thickness l by empirical relation u_{-} (1) from work [10].

X-ray explorations were carried out by means of diffractometer DRGA-3 in monochromatized $CuK\alpha$ - emission. Amorphous alloy structural transformations at heating were studied by combination of X-ray-phase, resistor metric and differential thermal analyses. Specific electrical resistance (SER) was measured by a four-probe potentiometric method. The thermal graphic analysis was carried out with using of combined chromel-copel thermocouple. Samples by mass ~ 100 mg were composed from rapidly quenched foil fragments ($\sim 7 \times 7$ mm) with close thickness. Aluminum foil was applied as a comparison standard. Samples heating for SER measurement and thermal analysis were carried out in the universal vacuum post UVP-5M work chamber.

Bcc-phase forming at rapid cooling of melts.

According to data [11], phase composition of alloys Ce-Ag with Ag content up to 50 at. % in equilibrium conditions is described by a constitutional diagram fragment of eutectic type fragment. The eutectic reaction occurs at temperature 783 K and it is accompanied by mixture formation of cerium γ -modification with fcc-lattice ($a = 0.5161$ nm) and equiatomic compound CeAg of CsCl type lattice ($a = 0.375$ nm).

The analysis of X-ray diffraction spectrums of rapidly quenched foils of $Ce_{1-x}Ag_x$ ($x = 10 - 35$) alloys indicates, that at solidification out of liquid state in the explored sample structure the metastable bcc-phase is

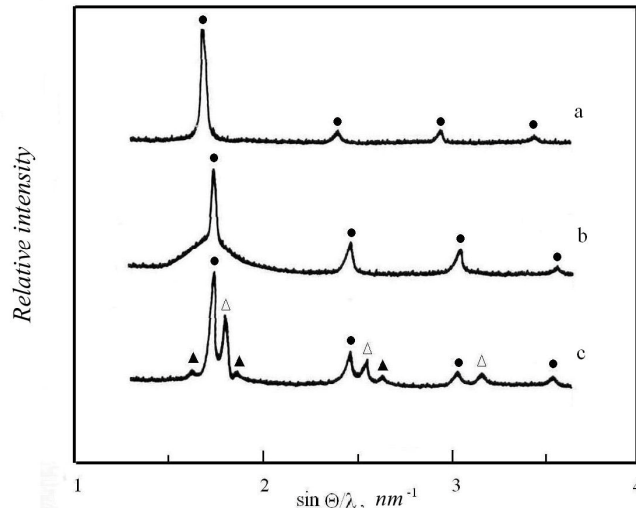


Fig. 1. Diffraction patterns of Ce-Ag alloys rapidly quenched foils with the thickness $l \approx 45 \mu\text{m}$ ($v \approx 5 \cdot 10^5 \text{ K} \cdot \text{s}^{-1}$): a – $\text{Ce}_{85}\text{Ag}_{15}$; b – $\text{Ce}_{70}\text{Ag}_{30}$; c – $\text{Ce}_{65}\text{Ag}_{35}$. ● – metastable bcc-phase; ▲ – $\gamma\text{-Ce}$; Δ – CeAg.

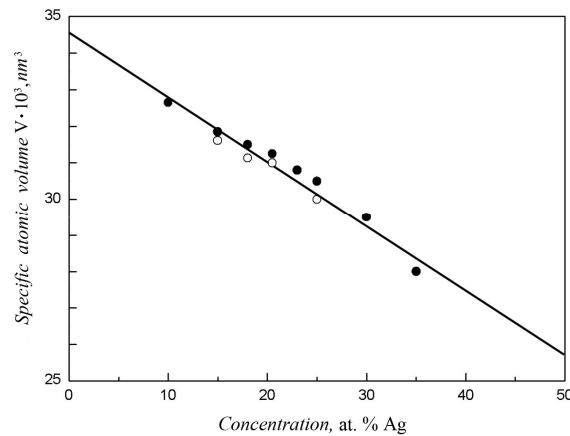


Fig. 2. Concentration dependences of specific atomic volumes of system Ce-Ag equilibrium phases (straight line) and the metastable bcc-phase (points) obtained by solidification from liquid state (●) and amorphous foils annealing (○).

fixed which subject to composition and cooling rate of melt can be obtained either in a pure state (fig. 1,a) or in a mixture with amorphous component (fig. 1,b) or with equilibrium eutectic phases (fig. 1,c). In silver-base alloys (16 - 22) at.% the bcc-phase is formed at minimum cooling rates $u_- \approx (2 - 5) \cdot 10^4 \text{ K} \cdot \text{s}^{-1}$ which are achieved in the foils by thickness $l = (80 - 100) \mu\text{m}$. By cooling rate increasing the detection range of the bcc-phase is extended and at QLS extreme conditions ($u_- > 3 \cdot 10^7 \text{ K} \cdot \text{s}^{-1}$, $l < 5 \mu\text{m}$) are stretched from 10 to 35 at. % Ag.

The specific atomic volume values, calculated on the bcc-phase lattice spacing, for all alloys explored with satisfactory accuracy are conformed with linear concentration dependence, built on crystallographic parameters of components and intermediate equilibrium Ce-Ag system phases (fig. 2). Hereof, the metastable bcc-phase has a wide range of homogeneity and at solidification out of a liquid state is crystallized with preservation of initial alloys concentration.

Metallographic estimations of effective grain sizes of bcc-phase give values from 50 to 100 μm which are typical for metal materials obtained by melt solidification with cooling rates $\sim 10^4 - 10^6 \text{ K} \cdot \text{s}^{-1}$ [12].

Within the detection range, bcc-phase is fixed only in the certain cooling rate span limited by lower (u_-)_k and upper (u_-)_k' critical values. At cooling rates, smaller (u_-)_k, rapidly quenched foils save the phase composition ($\gamma\text{-Ce} + \text{CeAg}$) corresponding to an equilibrium diagram (fig. 3,a). Therefore, the value (u_-)_k is meaningful as cooling rate at which the processes of diffusive separation component, necessary for mixture formation of eutectic phases are suppressed. At these conditions alloy crystallization is carried out on more kinetically profitable way, notably, it is accompanied by a metastable bcc-phase formation of initial composition (fig. 3,b). The further acceleration of QLS process firstly causes the partial bcc-phase crystallization suppression (fig. 3,c), and then (at

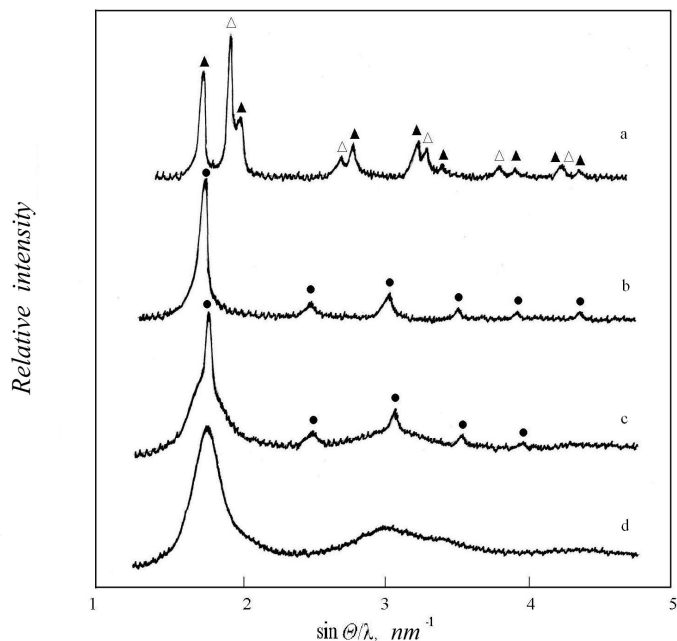


Fig. 3. Ce₈₂Ag₁₈ alloy diffraction pattern changes depending on the melt cooling rate U_- (K·s⁻¹): a - < 10³; b - ~10⁴; c - 10⁴ - 10⁵; d - >10⁵. ▲ - γ-Ce; Δ - CeAg; ● - metastable bcc-phase.

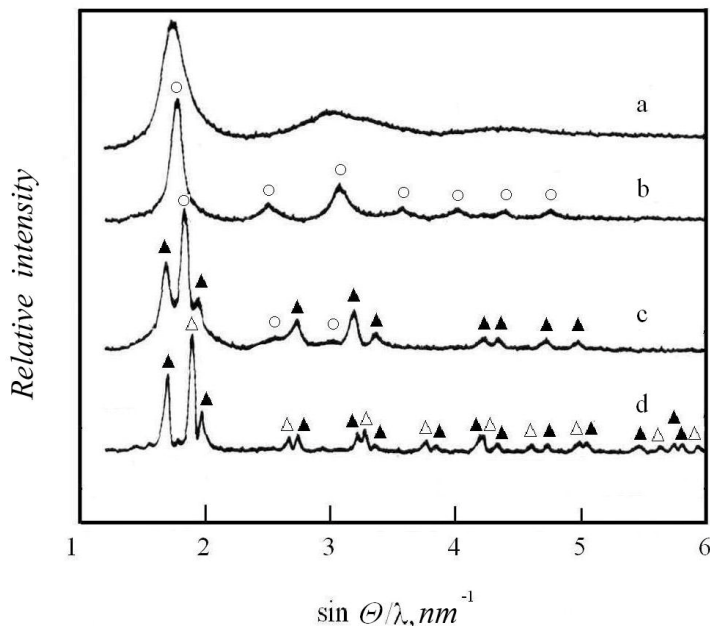


Fig. 4. Diffraction patterns of rapidly quenched ($U_- \approx 7 \cdot 10^5$ K·s⁻¹) foils of Ce₇₉Ag₂₁ alloy heated to temperatures (K): a - 353; b - 423; c - 533; d - 673. ○ - metastable bcc-phase.; ▲ - γ-Ce; Δ - CeAg.

$u_- \geq (u_-)'$ - the full one (fig. 3d). Therefore, the upper threshold value $(u_-)'_k$ corresponds to a critical cooling rate at which physical premises for realization of polymorphic crystallization*) process disappear and an amorphous state of alloys is fixed.

The values of critical quenching rates $(u_-)_k$ and $(u_-)'_k$ are resulted in table 1. It is shown that in the

alloys disposed according to composition in the neighborhood of eutectic point (18 at. % Ag), forming of equilibrium and metastable crystalline phases becomes impossible at cooling rates $\sim 5 \cdot 10^4$ K·s⁻¹ ($l \approx 100 \mu\text{m}$) and $4 \cdot 10^5$ K·s⁻¹ ($l \approx 50 \mu\text{m}$), respectively. However, on the boundaries of concentration range under study the metastable states (bcc and amorphous phase) are fixed only at cooling rates $\sim 10^7$ K·s⁻¹, close to maximum

*) According to the classification suggested by Koster [13], polymorphic crystallization means the process of crystal formation which save the maternal phase composition.

Table 1

Conditions of a metastable bcc-phase obtaining in rapidly quenched Ce-Ag alloys

Alloy composition, at.% Ag	Critical cooling rate, K·s ⁻¹	
	(u ₋) _к	(u ₋)' _к
10 – 12	10 ⁷	> 3·10 ⁷
15 – 21	5·10 ⁴	4·10 ⁵
25 – 28	2·10 ⁵	10 ⁷
30 – 35	8·10 ⁶	> 3·10 ⁷

Table 2

Results of resistometric, thermal and X-ray diffraction analyses of structural transformations at amorphous foils Ce₇₉Ag₂₁ alloy heating

$r_a \cdot 10^6$, Ω·m	$\frac{r_a}{r_e}$	$\frac{T_\kappa}{T_L}$	T_+ , K	T_i , K		Phase composition after heating	ΔT_a , K	$a \cdot 10^4$, K ⁻¹
				$i = 1$	$i = 2$			
1.91	0.9	0.45	358	398	493	Amorphous phase	298 – 358	-0.52
			398			bcc (a = 0.396 nm)	318 – 398	1.4
			653			γ-Ce + CeAg	513 – 643	8.9
			653			— — —	318 - 433	9.4

r_a , r_e - accordingly, SER of rapidly quenched foils in an amorphous state and after annealing on equilibrium phase composition. T_+ - heating temperature; ΔT_a - range of magnitude a .

for QLS method used in process.

Bcc-phase crystallization at the heating of amorphous foils.

As is shown above, in rapid solidification conditions with the cooling rates $\geq 10^7$ K·s⁻¹ alloys Ce_{100-x}Ag_x (x = 10 - 35) solidify with formation of amorphous structure. At postheating rapidly quenched amorphous samples experience decay which end result is equilibrium phase composition obtaining. Taking into account the analogy of structural transformations in the foils with various content of silver, we will consider the peculiarities of equilibrium transition by example of one of the explored alloys - Ce₇₉Ag₂₁.

The analysis of the experimental data obtained (fig. 4, tab. 2) argues that in the course of the starting-amorphous sample continuous heating with the rate $u_+ = 8 \cdot 10^{-2}$ K·s⁻¹ two stages of structural transformations which are accompanied by general SER decreasing in 1.9 times and exothermal effects with maximum heat release at temperatures T_i , equal 398 K (i = 1) and 493 K (i = 2), are successively developed.

At the first stage amorphous foils (fig. 4,a) are crystallized with formation of a metastable bcc-phase (fig. 4b) with lattice spacing $a = 0.396$ nm. The specific atomic volume of this phase practically coincides with corresponding linear concentration dependence for equilibrium phases of CE-Ag system (fig. 2), it indicates that crystallized bcc-phase conserves an alloy initial composition. The polymorphic crystallization begins at

the temperature T_K^*) which forms 0.45 from alloy equilibrium liquidus temperature T_L , and calls an absolute value increasing and sign change (from negative to positive) of electrical resistance temperature coefficient α (tab. 2). At the final stage of transformations the metastable bcc-phase undergoes the single-phase decay to a mixture γ -Ce and compound CeAg (fig. 4c).

As follows from fig. 4b, the diffraction pattern of the bcc-phase generated in the conditions of amorphous alloy Ce₇₉Ag₂₁ heating, differs from analogous patterns of fresh-quenched foils (fig. 1,a, 3,b) by higher degree of diffusivity. Particularly, the integral breadth β of maxima (110) only approximately in 3 times yields to the breadth of the first diffuse halo of amorphous alloy. Calculated on magnitude β effective crystallite sizes of the bcc-phase amounts 4.5 nm, indicating the nanocrystalline nature. Similar single-phase structures with nanoscale grain sizes are also formed at heating of amorphous foils with silver content from 15 to 25 at. % (light symbols on the fig. 2).

II. The experimental data discussion

The results of explorations performed argues that at solidification out of a liquid state with cooling rates $(u_-)_\kappa < u_- < (u_-)'_\kappa$ in Ce_{100-x}Ag_x (x = 10 - 35) alloys

*) The magnitude of T_K was taken equal to temperature of the first stage start of SER irreversible decrease.

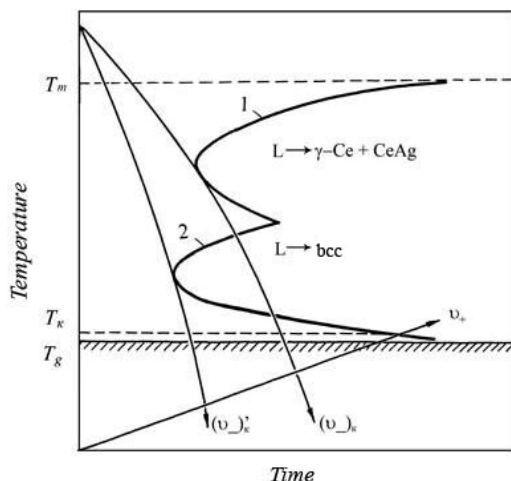


Fig. 5. The hypothetical TTT-diagram for Ce-Ag alloys which amorphized at quenching from a liquid state conditions. 1 - the "C-curve" corresponding to an equilibrium eutectic phases mixture forming; 2 - the "C-curve" corresponding to metastable bcc-phase polymorphic crystallization.

the metastable bcc-phase of initial composition is fixed. The same phase can be obtained at an early stage of structural transformations stimulated by rapidly quenched heating of amorphous foils and, in the latter case the bcc-phase gains the nanocrystalline structure. To explain the correlation and differences of the structures obtained at the QLS conditions and at warm of rapidly quenched amorphous alloys, the hypothetical diagram „temperature – time - transformation” (TTT) is represented on fig.5 which reflects the most possible relation of mixture rate forming of equilibrium eutectic phases (curve 1) and metastable bcc-phase (curve 2). Here are the schemes of cooling curves with rates $(u_-)_k$ and $(u_-)'_k$ at which the crystallization processes of equilibrium and metastable phases become impossible, respectively. As follows from figure, at relatively small cooling rates $u_- < (u_-)_k$ the melt crystallization (L) courses according to an equilibrium diagram of Ce-Ag system and it is accompanied by mixture of γ -Ce crystals and CeAg compound forming. The melt cooling rate increasing to values $(u_-)_k < u_- < (u_-)'_k$ results in the fact that the heterophase crystallization requiring essential redistribution of components, appears less competitive process in comparison with polymorphic crystallization of a metastable bcc-phase. If QLS rate exceeds the critical magnitude $(u_-)'_k$, in these conditions crystallization processes are completely suppressed, melt is supercooled lower than the temperature of glass transition T_g and solidifies in a noncrystalline structure.

Let's note, that bcc-phase forming in the conditions of QLS occurs at deep melt supercoolings comparatively melting temperature T_m (fig. 5) which provide high values of nucleation frequency. On the other hand,

transformation temperature $L \rightarrow bcc$ considerably exceeds point T_g that creates premises for the growth of nuclei forming and of microcrystalline structure formation typical for products of rapidly quenching.

Kinetic diagram presented on fig. 5 can be used for analysis of transformations occurring at heating of preliminarily amorphized alloys with some given rate U_+ . We can see, that in this case the first transformation which is developed right after devitrification of amorphous structure at temperature T_g , is the crystallization of metastable bcc-phase. As transformation occurs near to vitrification point in a high-viscosity environment, it is most probably that the processes of diffusive-controlled crystal growth will be significantly suppressed whereupon incipient bcc-phase crystals are "frozen" in the structure, conserving nanosizes.

Hence, according to the results of analysis realized the bcc-phase crystallizing in Ce-Ag alloys in conditions of amorphous foil heating, should differ from the same phase fixed by solidification out of liquid state by essentially smaller crystallites sizes that is proved by experimental data.

Conclusions

1. By means of structural investigations of $Ce_{100-x}Ag_x$ alloys ($x = 10 - 35$), obtained by solidification from a liquid state, the values of critical cooling speeds $(u_-)_k$ and $(u_-)'_k$ at which mixture forming processes of equilibrium eutectic phases (γ -Se + CeAg) and also a metastable microcrystalline bcc-phase of initial composition forming are suppressed, respectively, have been defined.

2. By combining of X-ray diffraction, thermal and resistor metric methods of analyses it was shown that rapidly quenched amorphous alloy transfer into structurally stable state is carried out by sequential development of polymorphic crystallization processes of bcc-phase with nanoscale crystallite sizes and its further single-phase decay on a γ -Ce mixture and CeAg compound.

3. Using the kinetic TTT-diagram the features of polymorphic crystallization of metastable bcc-phase at QLS conditions and warm of rapidly quenched amorphous foils which stipulate grain size differences of an explored phase observed experimentally, have been explained.

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- [1] В.В. Маслов, Д.Ю. Падерно. Получение аморфных металлических сплавов // *Аморфные металлические сплавы*. – Наукова думка, К., сс. 52-86 (1987).
- [2] H. Warlimont. Amorphous metals driving materials and process innovations // *Mater. Sci. Eng.*, **304**(306). pp. 61-67 (2001).
- [3] A. Inoue. Stabilization of metallic supercooled liquid and bulk amorphous alloys // *Acta Mater.*, **48**, pp. 279-306 (2000).
- [4] И.В. Золотухин. *Физические свойства аморфных металлических материалов*, Металлургия, М. 176 с. (1987).
- [5] M.E. McHenry, M.A. Willard, D.E. Laughlin. Amorphous and nanocrystalline materials for applications as soft magnets // *Progr. Mater. Sci.*, **44**, pp. 291-433 (1999).
- [6] А.П. Шпак, В.В. Маслов, В.К. Носенко. Ресурсозберігаючі технології виробництва нанокристалічних прецизійних матеріалів як складова інноваційного розвитку енергетичної та електронної галузей промисловості України // *Наука та інновації*, **1**(3), сс. 92-111 (2005).
- [7] H. Chen, Y. He, G.J. Shiffet, S.J. Poon. Mechanical properties of partially crystallized aluminium based metallic glasses // *Scr. Met. Mater.*, **25**(6), pp. 1421-1424 (1991).
- [8] Ю.А. Скаков, В.С. Крапошин. Затвердевание в условиях сверхбыстрого охлаждения и фазовые превращения при нагреве металлических стекол // *Итоги науки и техники. Металловедение и термическая обработка*. **13**, ВИНТИ, М. сс. 3-78 (1980).
- [9] А.А. Якунин, А.Б. Лысенко. Особенности образования и распада аморфных фаз в быстроохлажденных сплавах церий – серебро // *Известия АН СССР. Металлы*, (1), сс. 144-149 (1980).
- [10] А.Б. Лысенко, Г.В. Борисова, О.Л. Кравец. Расчет скорости охлаждения при закалке сплавов из жидкого состояния // *Физика и техника высоких давлений*, **14**(1), сс. 44-53 (2004).
- [11] S. Delfino, R. Ferro, R. Capelli, A. Borsese. Phase equilibria in the silver-cerium system // *J. Less-Common metals*, **41**, pp. 59-64 (1975).
- [12] E. Vogt, G. Frommeyer. Solidification parameters and microstructures of rapidly solidified Fe-Si and Fe-C melt spun ribbons. *Z. Metallkunde*, **78**(4), pp. 262-267 (1987).
- [13] У. Кёстер, У. Герольд. Кристаллизация металлических стекол // *Металлические стекла*. Мир, М. сс. 235-371 (1983).

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Отримання нанокристалічної ОЦК-фази у сплавах Се-Аг

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Виконано експериментальні дослідження процесів структуроутворення сплавів $\text{Ce}_{100-x}\text{Ag}_x$ ($x = 10 - 35$) в умовах загартування з рідкого стану та подальшого відпалу швидкозагартованих фольг. Показано, що як при швидкому охолодженні розплавів, так і при нагріванні попередньо аморфізованих зразків у концентраційному інтервалі, що досліджувався, формується метастабільна ОЦК-фаза вихідного складу, котра у свіжозагартованих та відпалених фольгах має мікро- та нанокристалічну будову, відповідно. Виявлені експериментально особливості поліморфної кристалізації ОЦК-фази пояснені за допомогою кінетичної діаграми "температура – час – перетворення"

Ключові слова: сплави Се-Аг, загартування з розплаву, відпал аморфних фольг, метастабільна ОЦК-фаза, мікро- та наноструктури.