## SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

# Particle Size Effects on Calorimetric and Magnetic Properties of the Ferromagnetic Phase in the Eutectic Composite Alloy of ZnSnAs<sub>2</sub>-MnAs System

S. F. Marenkin<sup>*a*, *b*, \*, P. A. Chernavskii<sup>*c*</sup>, A. I. Ril<sup>*a*</sup>, G. V. Pankina<sup>*c*</sup>, I. V. Fedorchenko<sup>*a*</sup>, and V. V. Kozlov<sup>*d*</sup></sup>

<sup>a</sup>Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia
<sup>b</sup>Moscow Institute of Steel and Alloys (National University of Science and Technology), Moscow, 119991 Russia
<sup>c</sup>Department of Chemistry, Moscow State University, Moscow, 119991 Russia
<sup>d</sup>Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 119991 Russia

*\*e-mail: marenkin@rambler.ru* Received May 27, 2019; revised June 10, 2019; accepted July 17, 2019

Abstract—Magnetic and calorimetric properties of a eutectic alloy of  $ZnSnAs_2$ —MnAs system are studied depending on particle size in the range of magnetostructural transition temperatures of the ferromagnetic phase MnAs. The particle sizes are varied by using different cooling rates as measured by a temperature-control device. The cooling rate is ~0.05°C/s under ordinary conditions and ~90°C/s under quenching with salt systems having high heat conductivity. Simultaneous phase solidification, typical of eutectics, under high cooling rates yields nanosized ( $\leq$ 50 nm) MnAs grains. DSC curves for quenched samples, unlike for samples prepared under ordinary conditions, have no thermal feature associated with  $\alpha$ – $\beta$ -MnAs magnetostructural transformation. The magnetization and Curie temperature have considerably different values in quenched samples and in samples prepared in an ordinary manner. The Curie temperature rises to 337 K and the coercive force increases as the particle size increases.

**Keywords:** hardening, microstructure, Curie temperature **DOI:** 10.1134/S0036023619120088

## INTRODUCTION

In the 1980s, Academician Tananaev added particle size to the three factors in the basic formula of physicochemical analysis: composition-structureproperty [1-3]. The effect of particle size was shown both on bulk and on film samples of various materials [4, 5]. A number of monographs and articles by various authors showed that the properties of materials begin to change dramatically when the crystallite sizes reach ~100 nm [5–16]. Temperature-dependent studies of properties in nanosized items are appreciably complicated due to their high reactivity. Sintering or recrystallization changes the particle-size composition, so composites, where phase boundaries reduce mass transfer and reduce the possibility of the above processes, are better subjects for an unbiased study of particle size effects [4]. The study described here is concerned with particle size effects on the calorimetric and magnetic properties of an eutectic alloy of ZnSnAs<sub>2</sub>-MnAs system in the range of magnetostructural transformation temperatures of ferromagnet MnAs. ZnSnAs<sub>2</sub>-MnAs system is of interest due to the fact that manganese-doped compounds  $A^{\rm II}B^{\rm IV}C_2^{\rm V},$ 

EXPERIMENTAL The eutectic alloy of ZnSnAs

uent phases.

The eutectic alloy of  $ZnSnAs_2$ –MnAs system (55 mol %  $ZnSnAs_2$ , 45 mol % MnAs) [23, 24] was directly alloyed from high-purity constituent elements (arsenic, zinc, tin, and manganese), where the total impurities were  $\leq 10^{-3}$  wt %, in graphitized silica glass ampoules. The ampoules were degassed to a residual

one being ZnSnAs<sub>2</sub>, were regarded as dilute magnetic semiconductors with high Curie temperatures and as

The preparation of nanosized samples is an

important problem in particle-size studies. Usually,

high solidification rates of overheated melts can serve

for this purpose, as shown in the preparation of nano-

sized metal structures [22]. In our case, it was expedi-

ent to choose the eutectic composition. Firstly, this

composition is easier to overheat, in view of the fact

that the phases of ZnSnAs<sub>2</sub>-MnAs system involve vol-

atile components. Secondly, eutectic solidification

involves the simultaneous solidification of the constit-

promising spintronic materials [17–21].



Fig. 1. Eutectic ingot of ZnSnAs<sub>2</sub>-MnAs system.

pressure of  $10^{-2}$  Pa and then sealed off. The ampoules with samples, which were weighed accurate to  $10^{-4}$  g. were placed in a vertical resistance furnace with a minimum temperature gradient (the temperature gradient in the area of the synthetic ampoules did not exceed  $1^{\circ}$ ). This excluded the transfer of volatile components from the reaction zone. The total weight of a sample was 50 g. Given the high vapor pressure of arsenic, the following temperature-and-time synthesis mode was chosen: heating to 620°C at 40°C/h, followed by heating to  $760^{\circ}$ C at  $20^{\circ}$ C/h, then the heating rate was reduced to 10°C/h and the temperature was brought to 790°C, followed by four-day exposure to this temperature. Cooling was in the switched-off furnace mode. The cooling rate was about 0.05°C/s. The as-synthesized samples were dense, low-porosity ingots (Fig. 1). Their identification was by means of X-ray powder diffraction DTA, and microstructure observation. Figure 2 shows the microstructure of an as-synthesized sample, whose pattern is typical of textured eutectic microstructures. These samples were used in experiments to prepare composites with nanosized ferromagnetic inclusions. For this purpose, special thinwalled ampoules were made to carry out ultrafast solidification of overheated eutectic melts. The quenching media were air, water, molten tin, and an aqueous salt mixture of high heat conductivity. Quenching was modeled to estimate cooling rates.

Table 1. Determination of cooling rates in various media in the range  $850-550^{\circ}C$ 

Quenching medium*	Cooling rates, °C/s			
	850–750°C	750–650°C	650–550°C	
1	17	10	7	
2	29	25	24	
3	40	30	18	
4	90	70	44	

\*1—Air,  $T = 24^{\circ}$ C; 2—water,  $T = 20^{\circ}$ C; 3—molten tin,  $T = 300^{\circ}$ C; 4—aqueous salt mixture,  $T = -30^{\circ}$ C.



Fig. 2. Eutectic microstructure of ZnSnAs<sub>2</sub>-MnAs system.

A Termodat temperature controller with integrated software was used in experiments with quenching ampoules. The results of these experiments appear in Table 1. Molten tin and aqueous salt mixture as quenching media had the higher cooling rates in the suggested range of  $ZnSnAs_2$ –MnAs eutectic solidification temperatures (800–650°C). They were further used as quenching media.

The preparation of quenched samples involved the following stages: heating to  $850^{\circ}$ C at  $30^{\circ}$ C/h, followed by 2-h exposure at this temperature and then quenching. Quenching medium no. 4 (Table 1) was the aqueous salt mixture cooled to  $-38^{\circ}$ C by liquid nitrogen; quenching medium no. 3 (Table 1) was molten tin at  $300^{\circ}$ C.

### **METHODS**

X-ray powder diffraction (XRD) was used to identify samples. XRD experiments were carried out in the Shared Facilities Center of the Kurnakov Institute on a Bruker D8 Advance diffractometer (Cu $K_{\alpha}$  radiation,  $\lambda = 0.1540$  nm, U = 40 kV, I = 40 mA). Diffraction patterns were recorded in 0.005° steps in the range  $2\theta = 10^{\circ}-90^{\circ}$ ; the exposure time per point was 2 s. The basis for processing was the powder diffraction database ICDD PDF-2 and Diffrac, Suite EVA, and Topas software.

MnAs nanocluster sizes were estimated as the peak areas in diffraction patterns using the Debye–Scherrer relation for all MnAs peaks featured on X-ray diffraction patterns. The reliability factors were: expected  $R_{exp} = 3.71$ , weighted-profile  $R_{wp} = 4.42$ , and profile  $R_p = 3.48$ ; GOOF = 1.19. Figure 3 shows diffraction patterns for three types of samples with the fragments used to determine MnAs grain sizes in the inset: for sample 1, ~5 µm; for sample 2, ~60 nm; and for sample 3, ~50 nm.



**Fig. 3.** Diffraction patterns for eutectic samples of  $ZnSnAs_2$ –MnAs system: (1) cooling in a switched-off furnace, (2) quenching to molten tin, and (3) quenching to aqueous salt mixture. In the inset: a fragment of the diffraction pattern with the MnAs [102] peak in the range  $2\theta = 42^{\circ}-43^{\circ}$ .

The heat and temperature range of the structural transition in manganese arsenide were determined on a Q20 TA Instruments differential scanning calorimeter in the heating—cooling mode from 270 to 350 K at rate of 0.1 K/s. The temperature and heat measurement errors were  $\pm 1.0^{\circ}$  and  $\pm 2\%$ , respectively.

The magnetic properties of samples were determined on a setup designed on the basis of a vibrating-sample magnetometer [25, 26] in the range 280–400 K; the sample weight was 7-8 mg. The magnetic field intensities were up to 0.63 T.

## **RESULTS AND DISCUSSION**

The calorimetric and magnetic properties of measured samples are considerably differentiated and depend on the manganese arsenide grain size. For sample 1, where the melt was solidified at ~0.05 K/s, DSC curves feature an endotherm of the hexagonalto-orthorhombic structural transformation in MnAs (Fig. 4a). For samples 2 and 3, which were solidified in the quenching mode, the DSC curves are featureless (Fig. 4b).

The results of magnetic measurements (Table 2) complement the DSC data. The decreasing grain size brings about a decrease in specific saturation magnetization and an increase in coercive force (Fig. 5). This

effect verifies the transition from micro- to nanosized inclusions of the ferromagnetic phase in the composite alloy under study; the highest coercive force is, as a rule, observed when the ferromagnet inclusion size reaches some critical value. In this case, all ferromagnetic particles are single-domain centers, and magnetization reversal (or demagnetization) requires the highest external field energy due to the rotation of the magnetic moment of each particle, as opposed to

**Table 2.** Magnetic properties of the eutectic in ZnSnAs<sub>2</sub>– MnAs system depending on the solidification rate, where  $H_c$  is coercive force,  $\sigma_s$  is saturation magnetization, and  $\sigma_r$  is residual magnetization

Sample no.	<i>T</i> <sub>c</sub> , K	H <sub>c</sub> , Oe	$\sigma_{s}$	$\sigma_{\rm r}$
			Erg/(G g)	
1	311	31	30.56	0.77
2	322	40	30.1	0.86
3	337	58	25.7	0.97



Fig. 4. DSC data for samples: (1) cooling in a switched-off furnace and (2) quenching to molten tin.



**Fig. 5.** Specific magnetization versus magnetic field at 300 K for: (1) cooling in a switched-off furnace, (2) quenching to molten tin, and (3) quenching to aqueous salt mixture.

magnetization reversal in multidomain particles via the displacement of domain boundaries. In association, the Curie temperature rises to 337 K (Fig. 6). The change in calorimetric and magnetic properties in response to increasing particle size in eutectic composite alloys of ZnSnAs<sub>2</sub>-MnAs system is associated with the increasing effect of the phase interfaces to change the domain structure of a magnetically ordered system, induced by the decreasing MnAs grain sizes.



**Fig. 6.** Specific magnetization versus temperature for: (1) cooling in a switched-off furnace, (2) quenching to molten tin, and (3) quenching to aqueous salt mixture.

#### CONCLUSIONS

We have elaborated a method to prepare nanosized manganese arsenide crystallites in a eutectic composite alloy of  $ZnSnAs_2$ –MnAs system to show the effect of particle size on calorimetric and magnetic properties. We have studied the effects of various quenching media on the melt cooling rate in various temperature

ranges, in particular, at the solidification temperature of the eutectic alloy in  $ZnSnAs_2$ –MnAs system. We have shown that the cooling rate increases when an aqueous salt mixture is used, and reaches 90°C/s. This value is far higher than the quenching rates in ice water, commonly used in quenching experiments. Overall, our study confirms the fundamental idea of Academician Tananaev about the effect of particle size on various aspects of matter.

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#### REFERENCES

- 1. I. V. Tananaev, *Physical Chemistry of Ultradisperse Systems* (Nauka, Moscow, 1987) [in Russian].
- N. T. Kuznetsov, N. N. Chudinova, and I. A. Rozanov, Vestn. Ross. Akad. Nauk 74, 460 (2004).
- Yu. A. Buslaev, L. M. Zhukova, and S. V. Semenova *Ivan Vladimirovich Tananaev* (Nauka, Moscow, 1979) [in Russian].
- 4. A. I. Gusev, *Nanomaterials, Nanostructures, Nanotech*nologies (Fizmatlit, Moscow, 2005) [in Russian].
- A. D. Pogrebnjak and V. M. Beresnev, *Hard Nanocomposite Coatings, Their Structure and Properties* (2012). https://doi.org/10.5772/50567.
- C. P. Poole and F. J. Owens, *Introduction to Nanotechnology* (Wiley, New York, 1996; Tekhnosfera, Moscow, 2004).
- 7. A. B. Yaroslavtsev, *The Chemistry of Solids* (Nauchnyi Mir, Moscow, 2009) [in Russian].
- 8. J. Whitesides, D. Eigler, R. Anders, *Vision for Nanotechnology R&D in the Next Decade* (IWGN Workshop Report, Moscow, 2002).
- 9. Yu. F. Komnik, *Physics of Metal Films. Size and Structure Effects* (Atomizdat, Moscow, 1979).
- 10. D. Brandon and W. D. Kaplan, *Microstructural Characterization of Materials* (Wiley, Weinheim, 1999; Tekhnosfera, Moscow, 2004).
- E. P. Simonenko, N. P. Simonenko, I. A. Nagornov, et al., Russ. J. Inorg. Chem. 63, 1519 (2018). https://doi.org/10.1134/S0036023618110189

- A. A. Eliseev and A. B. Lukashin, *Functional Nanomaterials*, Ed. by Yu. D. Tret'yakov (Fizmatlit, Moscow, 2010) [in Russian].
- 13. A. G. Padalko, *The Practice of Hot Isostatic Pressing to Manufacture Inorganic Materials* (Akademkniga, Moscow, 2007) [in Russian].
- 14. L. V. Kozhitov, V. G. Kosushkin, T. T. Magkoev, et al., *Technology of Microengineering Materials* (Severo-Osetinsk. Gos. Univ., Vladikavkaz, 2018) [in Russian].
- L. V. Kozhitov, I. V. Zaporotskova, D. G. Muratov, et al., *Physical Synthetic Methods for Preparing Metal Alloy and Composite Nanoparticles Based on Transition Metals* (VolGU Press, Volgograd, 2018) [in Russian].
- E. S. Kulikova, D. V. Drobot, V. G. Yarzhemsky, and E. G. Ilyin, Russ. J. Inorg. Chem. 63, 1446 (2018). https://doi.org/10.1134/S0036023618110116
- G. A. Medvedkin, K. Hirose, T. Ishibashi, et al., J. Cryst. Growth 236, 609 (2002). https://doi.org/10.1016/S0022-0248(01)02396-X
- K. Hirose, G. A. Medvedkin, T. Ishibashi, et al., J. Cryst. Growth 237–239, 1370 (2002). https://doi.org/10.1016/S0022-0248(01)02185-6
- V. M. Novotortsev, S. F. Marenkin, I. V. Fedorchenko, and A. V. Kochura, Russ. J. Inorg. Chem. 55, 1762 (2010). https://doi.org/10.1134/S0036023610110136
- I. V. Fedorchenko, A. V. Kochura, S. F. Marenkin, et al., IEEE Trans. Magn. 48, 1581 (2012). https://doi.org/10.1109/TMAG.2011.2175482
- S. V. Murashov, V. G. Yarzhemsky, V. I. Nefedov, and E. N. Murav'ev, Russ. J. Inorg. Chem. 52, 1243 (2007). https://doi.org/10.1134/S0036023607080141
- 22. A. M. Glezer and I. E. Permyakova, *Nanocrystals Quenched from Melt* (FIZMATLIT, Moscow, 2012) [in Russian].
- I. V. Fedorchenko, A. N. Aronov, S. F. Marenkin, et al., J. Alloys Compd. 626, 9 (2015). https://doi.org/10.1016/J.JALLCOM.2014.11.147
- I. V. Fedorchenko, L. Kilanski, I. Zakharchuk, et al., J. Alloys Compd. 650, 277 (2016). https://doi.org/10.1016/J.JALLCOM.2015.08.006
- P. A. Chernavskii, B. S. Lunin, G. V. Pankina, et al., Instrum. Exp. Technol. 57 (1), 78 (2014). https://doi.org/10.1134/S0020441214010035
- P. A. Chernavskii, G. V. Pankina, and V. V. Lunin, Russ. Chem. Rev. 80, 579 (2011). https://doi.org/10.1070/RC2011V080N06ABEH004187

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