

Martensitic transformation and magnetic ordering in as-cast Fe-Mn-Si-Ge and Fe-Mn-Si-Sn alloys

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Abstract:

Crystal structure, morphology, peculiarities of martensitic transformation and shape memory effect were investigated in Fe-Mn-(Si,Ge) and Fe-Mn-(Si,Sn) as-cast alloys. It was found that regularly substitution of atoms Si with the Ge or Sn in Fe-Mn-Si alloys dramatically change the martensitic transformation behavior that displayed in calorimetry, resistometry and dilatometry curves during the cooling and heating the alloys. Crystal structure changed as well. As a result of alloying by Ge and Sn the substructure of samples became more inhomogeneous, well developed dendritic structure appeared, finally $(\text{Mn}_{0.5}\text{Fe}_{0.5})_3\text{Sn}_2$ phase and hexagonal phase with the structure $P6_3/mmc$ have precipitated in Fe-Mn-(Si,Sn) and Fe-Mn-(Si,Ge) respectively. The effect of alloying with Si or Ge on $\gamma \rightarrow \epsilon$ temperatures of martensitic transformation, volume effect of transformation, Neel point caused by the influences of alloying components as well as the ferromagnetic phases appearing during as-cast process. KEYWORDS: MARTENSITIC TRANSFORMATION, SHAPE MEMORY EFFECT, AS-CAST ALLOYS, CRYSTAL STRUCTURE, VOLUME EFFECT, NEEL POINT, CALORIMETRY, RESISTOMETRY, DILATOMETRY

1. Introduction

Despite the perfect shape memory effect (SME) in Fe-Mn-Si-based alloys [1, 2, 3, 4], the effect of the magnetic ordering on the SME, as well as on the $\gamma \rightarrow \epsilon$ martensitic transformation (MT) remains a debatable issue [3, 5, 6, 4, 7]. Alloying Fe-Mn with Si enhances the localization of magnetic moments on Fe atoms [8] and increases the driving force $\gamma \rightarrow \epsilon$ transformation, because reduces the Neel temperature T_N [9, 10, 8]. We assumed that Ge and Sn are elements that can affect the localization of magnetic moments like Si. These elements have similar chemical and physical properties (Table 1). The electronic configuration of the outer electronic shell of the elements atoms is the same – s^2p^2 , so alloying in the sequence $\text{Si} \rightarrow \text{Ge} \rightarrow \text{Sn}$ should not significantly affect the position of T_N , but enhances the "metallization" of properties, which can increase the degree of occupancy of the d -band of Fe-Mn. Increasing the radius of the atom in this sequence can affect the position of the martensitic start point M_s as well as solubility of these elements in Fe-Mn. The goal of current study was to investigate the effect of the replacement Si in alloy with the Ge or Sn on MT, SME and magnetic ordering.

Table 1 Some properties of alloying elements of Fe-Mn alloys

	Si	Ge	Sn	Fe	Mn
Atomic radius, Å	1.46	1.52	1.72	1.72	1.79
Ionic radius (4^+), Å	0.42	0.53	0.71		
Electronegativity, eV	1.90	2.01	1.96	1.83	1.85
Crystal structure and electrical conductivity (m – metallic, s/c – semiconductor)	diam(s/c) ↓120kBar β -Sn(m) ↓160kBar BCC(m)	diam(s/c) ↓90kBar β -Sn(m) ↓130kBar BCC(m)	β -Sn(s/c) ↓-14°C β -Sn(m) ↓90kBar BCT(m)		

2. Experimental

The nominal composition of the studied alloys can be represented by the formulas $\text{Fe-22Mn-6}(\text{Si}_{1-x}\text{Ge}_x)$ at.% and $\text{Fe-22Mn-6}(\text{Si}_{1-x}\text{Sn}_x)$ at.% ($x = 0, 1.5, 3.0, 4.5, 6.0$). The composition and their label are shown in Table 2. The alloys were melted in an arc furnace in an argon gas atmosphere. As-cast samples cut, quenched into water from 950°C and investigated.

Crystal structure was investigated at room temperature using the X-ray Debye-Scherrer method on diffractometer Rigaku Ultima IV with $\text{Cu K}\alpha_{1,2}$ radiation. The temperature dependence of electrical resistance was measured by four-point method in a temperature interval between –196°C and 350°C. SME measurements were made by bending test using three-points bending described in details elsewhere [11].

Dilatometry measurements were made by Du Point TMA 934 dilatometer using liquid nitrogen to achieve temperatures below RT. Calorimetric measurements were made using modulated differential scanning calorimeter of TA instruments. Martensite morphology and microstructure was investigated by optical microscopy (OM) and scanning microscopy (SEM) with PSEM501 instrument equipped by Link System analyzer to determine the local chemical composition.

Table 2 The composition of Fe-Mn-Si-Ge and Fe-Mn-Si-Sn alloys

Alloys	Fe at. %	Mn at. %	Si at. %	Ge at. %	Sn at. %
R	71.31	22.36	6.33		
GDr	71.21	22.47	4.67	1.66	
GDk	71.05	22.36	3.15	3.43	
GL	71.13	22.61	1.63	4.63	
GP	70.61	22.61	0.14	6.64	
BDr	71.39	22.24	4.55		1.82
BDk	72.57	20.78	3.05		3.61
BL	72.77	20.29	1.50		5.44
BP	73.70	19.57	0.19		6.54

3. Results and discussion

3.1. Microstructure of Fe-Mn-Si-Ge and Fe-Mn-Si-Sn alloys

The reference alloy R had a well-developed dendritic structure (Fig. 1a). Weak chemical inhomogeneities (~ 1 at.% Si) in dendritic branches are sized $\sim 50 \mu\text{m}$. Martensite crystals in the form of flat plates, which formed a self-accommodating triangular structure of ϵ -martensite, cross the dendritic branches maintaining their orientation (Fig. 1b).

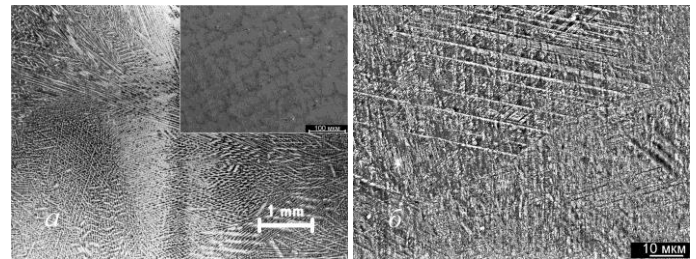


Fig. 1 Microstructure of alloy R: a) - dendrites (OM); composition stratification in dendrites (SEM) on insert; b) - plates of ϵ -martensite.

Replacement of Si with Ge caused stratification of alloys in composition, which increased with increasing Ge content (Table 3). The content of Ge + Si in the matrix was slightly < 5 at.%, in the inclusions

increased up to ~11at.% with increasing content of Ge in the alloys. Within one grain, one to three orientations of martensite crystals were observed. For all Fe-Mn-Si-Ge samples with a dendritic structure, the images of martensite crystals were not interrupted by dendrites or etching defects, but continued from one edge of the grain to another, as if the latter were "transparent" for martensite plates (Fig. 2). In most cases, the plates did not pass through the inclusions, but only wedged into them. A similar pattern of filling the whole grain with the martensitic phase and the cross section of dendrites was observed in Fe-Mn-Si alloys [12]. Such interaction of martensitic crystals with these inhomogeneities implies at least exact orientation relationship between the matrix and inclusions.

"The collision" of the plates of ε -martensite in some inclusions caused a weak striped contrast, while the direction of strips was $6\div8^\circ$ with the direction of ε -martensite plates (Fig. 2). According to XRD data strips in the inclusion could be crystals α -martensite. Because the plane of martensite crystals form self-assembling schemes with angles with each other close to 60° (Fig. 2a) the plane of the sample in Fig. 2a is close to $\{111\}_\gamma$. Because in most Fe-based alloys the gabitus plane of crystals α -martensite is $\{3,10,15\}_\gamma$ one can calculate the angles between the traces of ε - and α -martensite. Thus, a calculated angle between the traces of the plane $(\bar{1}11)_\gamma$ and $(3,10,15)_\gamma$, formed on the sample surface with normal $(111)_\gamma$ is 6.6° , confirming the hypothesis of the presence of crystals α -martensite in some inclusions.

Table 3 Chemical compositions of matrix and inclusions in Fe-Mn-Si-Ge and Fe-Mn-Si-Sn as-cast alloys

Alloy	Phase	Fe	Mn	Si	Ge	Sn
GL	Matrix	72.2 $\pm$ 1.4	23.1 $\pm$ 1.1	1.4 $\pm$ 0.1	3.4 $\pm$ 0.3	
	Inclusion	59.7 $\pm$ 1.7	30.7 $\pm$ 0.9	2.2 $\pm$ 0.1	7.4 $\pm$ 0.8	
GP	Matrix	73.5 $\pm$ 1.2	21.8 $\pm$ 0.9		4.7 $\pm$ 0.3	
	Inclusion	57.6 $\pm$ 1.6	31.4 $\pm$ 1.0		11.0 $\pm$ 0.7	
BDk	Matrix	75.3 $\pm$ 0.7	20.7 $\pm$ 0.5	3.0 $\pm$ 0.2		1.0 $\pm$ 0.2
	Inclusion	35.3 $\pm$ 2.7	34.9 $\pm$ 1.0			29.8 $\pm$ 1.7
BL	Matrix	74.1 $\pm$ 2.6	22.0 $\pm$ 1.2	1.9 $\pm$ 0.2		2.0 $\pm$ 1.4
	Inclusion	34.6 $\pm$ 1.0	34.5 $\pm$ 0.2			30.9 $\pm$ 0.8

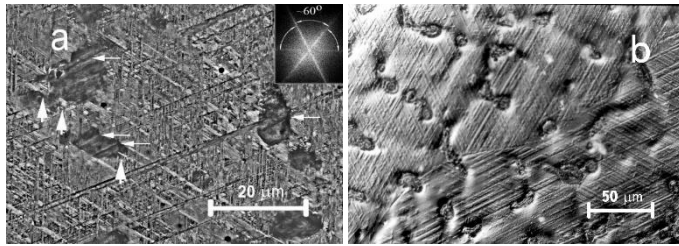


Fig. 2 As cast Fe-Mn-Si-Ge alloys: a) - SEM image of ε -martensite and inclusions in the GL alloy; vertical arrows indicate the plates of ε -martensite, which is wedged in the inclusion, horizontal - the plates of the α -phase inside them; Fourier image on the insert; b) - OM images of relief ε -phases that intersect the inclusion in the GDK alloy; deep grooves - etched dendrite structure formed by inclusions.

The replacement of Si with Sn caused the appearance of inclusions, recorded as deep etching on OM images in the BDr alloy (Fig. 3a) and irregular phases in BDk, BL, BP alloys (Fig. 3b,c,d). These inclusions formed a dendrite structure that became clearer with an increase Sn content. It was found that the inclusion in alloys is a ternary phase with a chemical composition close to $\text{Fe}_{0.35}\text{Mn}_{0.35}\text{Sn}_{0.3}$, which can be interpreted as $\text{Fe}_{0.33}\text{Mn}_{0.33}\text{Sn}_{0.33}$ as well as $(\text{Mn}_{0.5}\text{Fe}_{0.5})_3\text{Sn}_2$ (Table 3). Consequently, the stimulus to the concentration stratification in as-cast alloys increases in the Si $\rightarrow$ Ge $\rightarrow$ Sn sequence.

Only in BDr and BDk alloys plates of ε -martensite "flowed around" the inclusions (Fig. 3a,c). Penetration in the inclusions is not observed.

Instead, martensite crystals as if "stopped" nearby it, and "continued its movement" after obstacle at a certain distance (Fig. 3c). With an increase Sn content part of areas free from martensite became more (Fig. 3c,d). Certain areas in the alloy BL can be interpreted as free from martensite, in which wide plates of ε -martensite (marked with oblique arrow in Fig. 3d) penetrate. Morphology of martensite plates in alloys with high content of Sn is characterized by the presence of narrow and short plates, sometimes zigzag form (Fig. 3d). In the contact area with martensite plates, there was observed occasional fine plates. Their orientation was the same as in ε -martensite. These formations are not α -phase; twin plates or shear bands are not excluded.

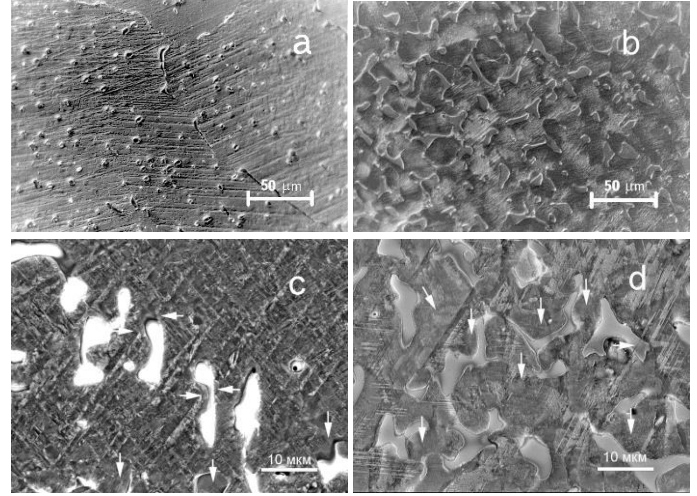


Fig. 3 a) - the relief on BDr alloy surface; b) - OM of BL alloy; c) - SEM of BDk alloy; d) - SEM of BL alloy; vertical arrows indicate areas free of crystals of martensite, horizontal - the places of "collisions" of ε -martensite with inclusions.

3.2. Crystal structure and phase composition

XRD studies have shown that the reference alloy R contained mainly ε and α phases with a small amount of residual γ phase (Fig. 4), which is a typical structure of martensite for thermally activated $\gamma\rightarrow\varepsilon$ MT in Fe-Mn alloys, where the α -phase is formed in the intersection of the plates of the ε -phase [13].

Replacement of Si with Sn causes a decrease in the intensity of reflexes from the ε -phase, the appearance and subsequent intensification of reflexes from the orthorhombic phase with the space group Pnma (Fig. 4, alloys BDr, BDk, BL). Most reflexes from the orthorhombic phase overlap with reflexes from the hexagonal phase with the space group $P6_3/mmc$. The presence of a hexagonal phase with the structure $P6_3/mmc$ isostructural either to $(\text{Mn}, \text{Fe})_{2-x}\text{Sn}$ ($x = 0\div0.35$) with $c/a > 1$ or to $(\text{Mn}_{1-x}\text{Fe}_x)_3\text{Sn}_{1-\delta}$ ($x \approx 0.5$, $\delta = 0\div0.35$) with $c/a < 1$ cannot be excluded (Fig. 4, BL alloy). Depending on the annealing temperatures and composition, both the hexagonal phase with the composition Mn_{2-x}Sn and the stoichiometric orthorhombic phase Mn_3Sn_2 can coexist in Mn-Sn alloys [14]. In addition, there are several orthorhombic phases in the vicinity of the Mn_{2-x}Sn composition [15]. All of them, including the hexagonal one, can be considered as intermediates between hexagonal structures of the NiAs and Ni_2In type. Therefore, some of the reflexes are well interpreted as belonging to both types of structures. Part of the reflexes can be interpreted as belonging to the hexagonal phase with $c/a < 1$ and lattice parameters close to that in phase $(\text{Mn}_{1-x}\text{Fe}_x)_3\text{Sn}_{1-\delta}$ [16] and Sn content 25 $\div$ 28at.%. Taking into account the composition of inclusion they are rather isostructural Mn_3Sn_2 with Pnma spatial group. The lattice parameters of the orthogonal phase are close to those found in [17, 15] in magnetocaloric alloys $\text{Mn}_{3-x}\text{Fe}_x\text{Sn}_2$. Reflexes from ε , α , and γ phases were observed in the spectra of Ge doped alloys with exception of GL and GP alloys (Fig. 4). After

immersion sample in liquid nitrogen, ϵ phase lines appeared in the GL alloy. The lines of both ϵ and γ phases in the GL alloy were widened, while in the GP alloy the peaks are narrow and clearly separated. In alloys with a lower Ge content, the volume of the unit cell of the ϵ phase is smaller than in the γ phase, while in the alloy GP the volume of the unit cell of a hexagonal phase is $\sim 4\%$ larger than in the γ phase. The lattice parameters of this phase are close to those in alloys $(\text{Mn}_{1-x}\text{Fe}_x)_3\text{Ge}_{1+\delta}$ ($0 < x < 0.34$, $-0.2 < \delta < 0.25$) [18]. It is natural to assume that the phase is enriched in Mn and Ge (Si) and is the one that has a $P6_3/mmc$ structure. The inclusions are isostructural to $(\text{Mn}_{1-x}\text{Fe}_x)_3\text{Ge}$ and have lattice parameters close to the ϵ -phase parameters ($a \approx 2 \cdot a_\epsilon$, $c \approx c_\epsilon$). This makes it "transparent" to martensite plates, in the sense that the stresses caused by the collision of the plates on one side of the inclusion are transmitted through them to the other side. The matrix phase, on the other hand, undergoes a $\gamma \rightarrow \epsilon$ transformation, and the α -phase can be formed at the intersections of the ϵ -phase plates [13] and at some points of collision of the ϵ -phase plates with inclusions (Fig. 3). It also contributes to the "transparency" of inclusions for martensite, and the role of the stress transducer is played by α -phase plates.

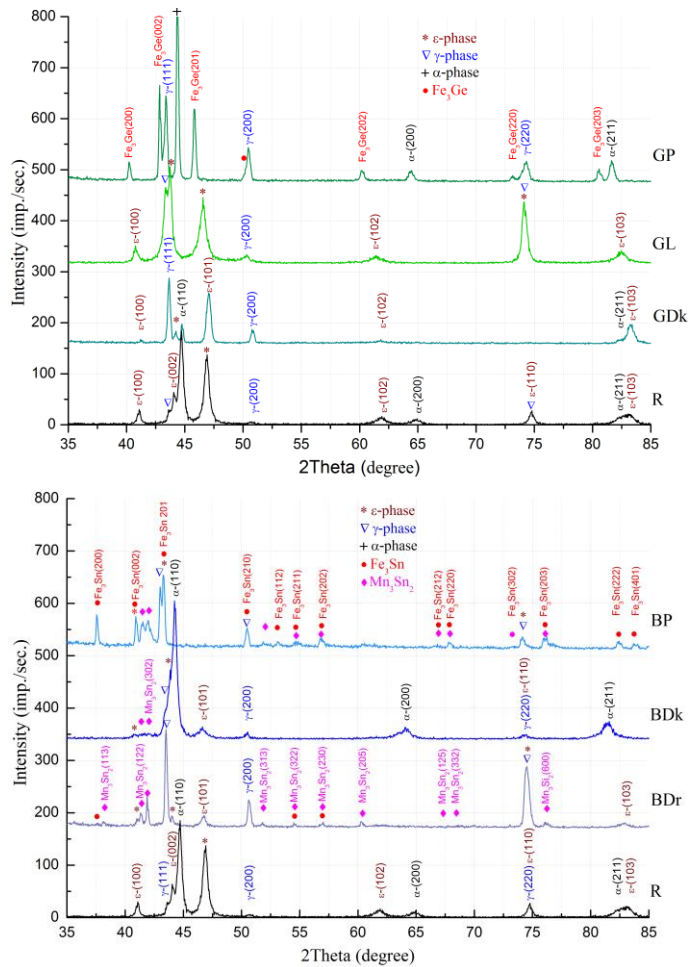


Fig. 4 XRD spectra of alloys Fe-22Mn-6(Si_{1-x}Gex) (top) and Fe-22Mn-6(Si_{1-x}Snx) (bottom)

3.3. Some physical properties and characteristic points of $\gamma \rightarrow \epsilon$ martensitic transformation and magnetic transformation

A comparative analysis of the temperature dependences of electrical resistance and sample elongation (dilatometry) (Fig. 5), the sample bending by four-point scheme (SME) and calorimetry (DSC) (Fig. 6) showed that there are two types of transformations in Fe-Mn-(Si, Ge, Sn) alloys. One of them is $\gamma \rightarrow \epsilon$ martensitic transformation with a

temperature hysteresis of 130-170 K, a significant heat effect, a negative volume effect, and which is responsible for the SME. The second transformation is revealed in alloys with a predominant content of Ge or Sn, characterized by a narrow hysteresis, negligibly small thermal effect and small positive volume effect. MDSC studies of the temperature dependence of heat capacity C_p clearly revealed another transformation localized in the range from 30 to 60°C (Fig. 7). The peculiarities of the temperature dependence of the BP alloy, where the $\gamma \rightarrow \epsilon$ transformation was suppressed (step, hysteresis is negligibly small), correspond rather to second order phase transition. At the same time, for alloy R and alloys with lower content of Si (BDk) and especially Ge (GP, GDk) the temperature dependence of heat capacity corresponds to the first order phase transition (peak heat flux, available hysteresis). Thus, the heat capacity jump is associated with the Neele temperature, which in alloys with a significant content of Ge and especially Sn is within the interval of direct $\gamma \rightarrow \epsilon$ MT. By the nature of the temperature dependence of C_p , the features on the resistometric, calorimetric and dilatometric curves, it rather corresponds to the transformation of paramagnetic (PM) $\rightarrow$ antiferromagnetic (AFM) in the γ phase.

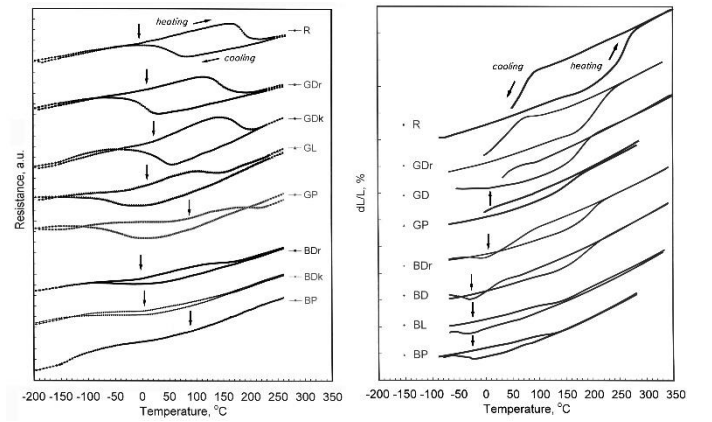


Fig. 5 Temperature dependence of electrical resistance (on a left); elongation of the sample (on a right). Arrows indicate non martensitic transformation.

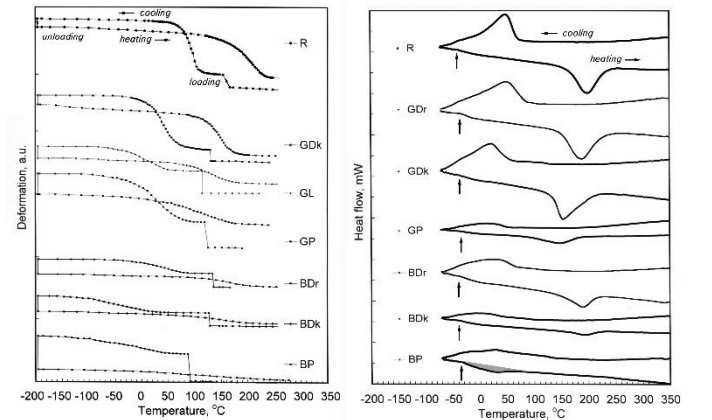


Fig. 6 Temperature dependence of the sample bending by four-point scheme (SME) (on a left); DSC analysis (on a right). Arrows indicate start of reverse martensitic transformation.

Another feature on the temperature curves was observed between -50 and -100°C. It can be associated with a paramagnetic $\rightarrow$ ferromagnetic (FM) transformation in the phase $(\text{Mn,Fe})_3 + \gamma\text{Sn}_{2-y}$ in alloys Fe-22Mn-6(Si_{1-x}Snx) (or in the phase enriched in germanium in alloys Fe-22Mn-6(Si_{1-x}Gex)), so with the magnetic transition from the antiferromagnetic to the paramagnetic state of the ϵ -phase. The nature of the change of volume effect sign is different in alloys with

Ge and Sn. It is due to the formation of the α -phase and with competing contributions to the dilatation effect of $\gamma \rightarrow \varepsilon$ and $\gamma \rightarrow \alpha$ transformation in the former. In the latter it is suddenly appears due to the deformation of the sample by the martensitic mechanism, stimulated by magnetostriction due to PM $\rightarrow$ FM transition [17] in $\text{Mn}_{3-x}\text{Fe}_x\text{Sn}_2$. The start temperatures of direct MT (M_s) and the finish of the inverse MT (A_f) decrease monotonically with increasing Ge and Sn until their values became equal to the Neele point T_N , determined from the resistance curves (R) and dilatometric curves (TMA), and then practically do not change (Fig. 8). This is due to the formation of $(\text{Mn}_{0.5}\text{Fe}_{0.5})_3\text{Sn}_2$ or inclusions with high content of Mn and Ge. The result is a stable matrix composition in alloys with a high content of Ge and Sn and at the same time a decrease in the volume available for the development of MT. Taking into account the composition of the matrix (Table 3) and comparing the predicted values of martensitic points with those in homogenized alloys with the same content of Mn and Si [19], we find that Ge and Sn reduce M_s on ~ 26 and $51^\circ\text{C/at.}\%$, respectively. First is close to the value of $21^\circ\text{C/at.}\%$ in a homogenized alloy of Fe-24Mn-6Ge [20, 21, 22]. There was also found complete suppression of MT, because the temperature $\gamma \rightarrow \varepsilon$ MT was significantly lower than T_N . Therefore, antiferromagnetic ordering suppresses $\gamma \rightarrow \varepsilon$ MT.

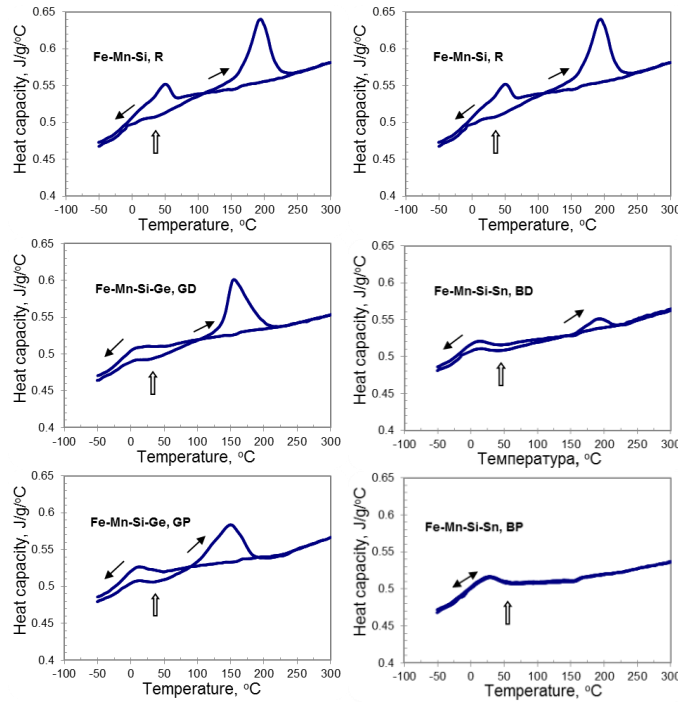


Fig. 7 Temperature dependences of C_p for Fe-Mn-Si-Ge and Fe-Mn-Si-Sn alloys. Contour arrows indicate the AFM ordering

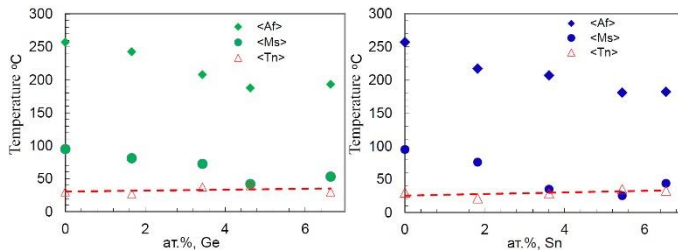


Fig. 8 Dependence of MT points and Neele point on Ge content in Fe-Mn-Si-Ge alloys (on a left) and Sn in Fe-Mn-Si-Sn alloys (on a right)

The decrease in MT temperatures is due to the increase in the atoms size of the alloying components in the Si $\rightarrow$ Ge $\rightarrow$ Sn sequence. For Fe-24Mn-(2-4)Ge at.% alloys [21] the lattice parameter of the γ -phase increases with increasing Ge content. This is equivalent to anisotropic

stretching of the lattice. Since during $\gamma \rightarrow \varepsilon$ MT specific volume decreases, the replacement of Si atoms by Ge and Sn atoms causes a decrease in M_s .

3.4. Effect of magnetic ordering and magnetic inclusions in Fe-Mn-Si-Ge and Fe-Mn-Si-Sn alloys on MT

Addition Ge to Fe-30Mn alloys reduces T_N on $\sim 15^\circ\text{C/at.}\%$ [23], while addition Si reduces T_N on $\sim 15^\circ\text{C/at.}\%$ for alloys with a Mn content of 28–32 at.% and up to $27^\circ\text{C/at.}\%$ for alloys with 22–25 at.% Mn [24]. Comparison of the values of T_N in the matrix, calculated by the empirical formula in [25], with the experimentally found ones confirms the assumption of a weak effect on T_N when replacing Si with Ge.

The depressing $\gamma \rightarrow \varepsilon$ MT due to the AFM ordering can be explained from the considerations illustrated in Fig. 9. Consider the orientation of the spins of 12 atoms from the vicinity of atom 4 in the FCC structure (Fig. 9b). The spin of each of those atoms $\vec{S}_i$ interacts with 12 others (four triplets), each of which has different direction: in the basal plane two triplets (in the corners of two triangles) and one triple in the upper and lower basal planes. The components of the spins of each of the triplets lying in the basal planes mutually compensate each other, and the sum of the components perpendicular to the basal planes is equal to $-\vec{S}_i$. Thus, the magnetic interaction of the spin of each atom with the spins of the 12 nearest neighbors in the FCC lattice is:

$$(1) \quad E_{antiferr}^{FCC} = -4J\vec{S}_i\vec{S}_i = -4JS^2$$

The orientation of the spins in the HCP structure, which is formed due to the shift of every second basal plane in one of the directions $\langle 112 \rangle$ (Fig. 2c), differs in that in one of the basal planes the sum of spins is equal to $-\vec{S}_i \neq \vec{S}_i$. That is, the magnetic interaction is:

$$(2) \quad E_{antiferr}^{HCP} = -3J\vec{S}_i\vec{S}_i - J\vec{S}_i\vec{S}_j$$

The difference between the energies of the magnetic interaction of the HCP and FCC structures

$$(3) \quad \Delta E = J\vec{S}_i\vec{S}_i - J\vec{S}_i\vec{S}_j = JS^2(1 - \cos \widehat{S_i S_j}) = JS^2(1 - \cos 109.47^\circ) = \frac{4}{3}JS^2$$

always greater than zero. Here, as in (1) and (2), J is the exchange integral, the value of which is positive for AFM interaction.

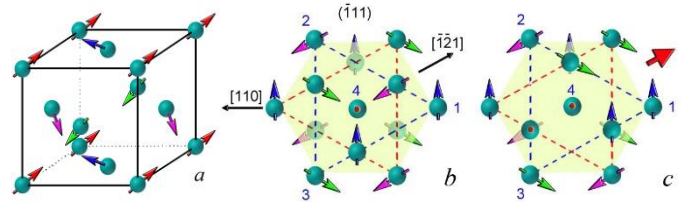


Fig. 9 a) AFM ordering of spins Fe-Mn alloys (antiferromagnetic structure, 3Q state) in the FCC lattice [26, 27]; b) the orientation of the spins of the 12 nearest neighbors of the central atom in three consecutive basal planes $\{111\}$ (the middle plane is highlighted in color); c) orientation of the spins after the shift in the direction $[112]$ of the upper plane with the formation of packing ABAB... (HCP lattice). Spins 1, 2, 3, the projections of which on the basal plane mutually compensate each other, have the sum of normal projections equal in modulus and opposite in sign to spin 4 (directed perpendicular to the plane (111)).

This is equivalent to an increase in the stacking fault energy, and hence a decrease in the driving force $\Delta G_{\gamma \rightarrow \varepsilon}$ $\gamma \rightarrow \varepsilon$ transformation. If the M_s is slightly above the T_N , the MT is further suppressed by AFM ordering in the residues of the γ -phase [5]. The decrease in $\Delta G_{\gamma \rightarrow \varepsilon}$ is not very sharp, because AFM ordering is a second order transition. The different path of the heating and cooling curves for alloys with a high content of Ge and Si also indicates $\gamma \rightarrow \varepsilon$ transformation at temperatures below T_N . Indeed, in [19] it was shown that martensite can be formed even after the γ -phase has undergone AFM ordering, i.e., in the case of $T_N > M_s$.

4. Conclusion

In Fe-20÷22Mn-(Si, Ge, Sn) alloys with a content of Si+Ge and Si+Sn ~6at.% $\gamma \rightarrow \varepsilon$ transformation with a temperature hysteresis of 130÷170K, a significant heat and negative volume effects is responsible for SME. Increasing the Ge or Sn content also manifests the PM→AFM transformation in the γ phase with a narrow hysteresis, negligibly small heat and positive volume effects. Increasing the Ge or Sn content reduces M_s to T_N on ~26 and 51°C/at.% respectively, due to increasing the size of the atoms in the Si→Ge→Sn sequence, which is equivalent to the negative hydrostatic pressure experienced by the alloy.

When Si is replaced by Sn, the phase $(Mn_{0.5}Fe_{0.5})_3Sn_2$ (Pnma) and the hexagonal phase isostructural to $(Mn,Fe)_{2-x}Sn$ are formed. When Si is replaced by Ge, the alloy stratifies into regions depleted with Si, Ge and with Mn content close to nominal and regions enriched in Mn and Ge (Si) isostructural to $(Mn_{1-x}Fe_x)_3Ge$ with lattice parameter values commensurate with such in ε -phases $a \approx 2 \cdot a_\varepsilon$, $c \approx c_\varepsilon$.

Due to the invariance of the Fe and Mn content in the matrix, the Néel point changes weakly, and the magnetic ordering in the γ -phase stabilizes $\gamma \rightarrow \varepsilon$ MT, because the magnetic interaction energy in HCP is higher than in FCC structure. In Fe-Mn-Si-Ge, the contributions to the dilatation effect of $\gamma \rightarrow \varepsilon$ MT in the matrix and $\gamma \rightarrow \alpha$ MT in inclusions enriched with Mn and Ge (Si) determine the course of dilatation and SME curves. In Fe-Mn-Si-Sn, as the Sn content increases, the deformation of the sample by the martensitic mechanism stimulated by the magnetostrictive effect of the magnetic transformation into $Mn_{3-x}Fe_xSn_2$ changes the sign of the volume effect.

In Fe-Mn-(Si,Sn) alloys ε -martensite plates do not stop with inclusions with a thickness of less than 1÷2 μ m, sometime shear bands are formed in places of "collision" in the inclusions. In Fe-Mn-(Si,Ge) the α -phase is formed at the points of collision of the ε -phase plates with inclusions. Areas comparable in the thickness with martensite crystals enriched in Mn and Ge(Si) are "transparent" for martensite due to either elastic stress transfer or stress transfer by α -phase plates.

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