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Nanocrystalline alloys with high magnetic properties and high temperature stability

N.I.Noskova, V.V.Shulika, A.P.Potapov

Institute for Metal Physics, RAS Ural Branch, 18 S.Kovalevskaya St., 620041 Ekaterinburg, Russia

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The structure, magnetic properties and the temperature-time stability of nanocrystalline soft magnetic alloys have been studied. The influence of the preliminary low-temperature annealing during nanocrystallization on the structure and the magnetic properties of the nanocrystalline alloys under study has been revealed. It has been shown that the chemical composition of the precipitating phases influences not only the alloy magnetic properties but also the temperature stability. The nanocrystalline alloy $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ shows the highest temperature-time stability.

Исследованы структура, магнитные свойства и температурно-временная стабильность нанокристаллических магнитомягких сплавов. Обнаружено влияние предварительного низкотемпературного отжига при нанокристаллизации на структуру и магнитные свойства исследуемых нанокристаллических сплавов. Показано, что химический состав выделяющихся нанофаз влияет не только на магнитные свойства, но и на температурную стабильность сплавов. Наиболее высокой температурно-временной стабильностью обладает нанокристаллический сплав $Fe_{73,5}Cu_1Nb_{1,5}Mo_{1,5}Si_{13,5}B_9$.

1. Introduction

Much success has been achieved recently in development and preparation of nanocrystalline soft magnetic alloys having high magnetic properties [1–4]. Today, the use of nanocrystalline soft magnetic materials with preset functional characteristics is among the ways to improve the electrical and radio equipment, expending the application field of nanocrystalline alloys in high-frequency devices, thus providing an enhanced electrical resistance. More interest is revealed simultaneously in a better understanding of the structure and parameter stability of nanocrystalline alloys [5, 6].

The nanocrystalline alloy $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ shows high static magnetic properties. Its dynamic characteristics were improved in [2] by a partial substitution of Co for Fe atoms. Small Mo additives were used to enhance its temperature stability. However, the data concerning the influence of Co and Mo additions on the microstructure and the magnetic properties of the Fe–Cu–Nb–Si–B alloy are scarce, while the correlation between the structure and the magnetic properties has been not studied in essence.

The nanostructure parameters are determined mainly by the size of nanophases, their chemical composition, the presence of the free volume, and the level of internal elastic stresses.

The magnetic characteristics of nanocrystalline materials depend to a large extent on the nanostructure parameters and are defined by structural homogenization and stabilization of the domain structure, which is caused by the induced magnetic anisotropy [3]. Therefore, it would be of interest to study the variation of the nanostructure and the magnetic properties and examine the temperature-time stability of modified nanocrystalline alloys after thermal and thermomagnetic

(TM) treatments aimed at optimization of functional characteristics thereof.

2. Experimental

Amorphous ribbons of the $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$, $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$. and $Fe_{69}Cu_1Nb_{1.5}Mo_{1.5}Co_{4.5}Si_{13.5}B_9$ alloys were made by the melt spinning on a copper disk. The ribbons were 20–25 μm thick and 5 mm wide. The samples were shaped as toroids with outer and inner diameters of 22 mm and 16 mm, respectively. To remove the quenching stresses, the amorphous samples were annealed in vacuum at 400°C for 30 min. To form a nanocrystalline structure, the samples were annealed in vacuum at 520–540°C, with the annealing time being varied from 5 min to 6 h.

The TM treatments were performed in longitudinal constant or alternating (f = 50 Hz and f = 80 kHz) magnetic fields. The TM treatment included the following operations: an amorphous sample was heated to 520°C or 540°C, depending on the alloy chemical composition, exposed to a field for 30 min at the same temperature, and cooled in the magnetic field to room temperature at a rate of 200°C/h. The magnetic field intensity during the TM treatment was 10–20 H_c, where H_c is the sample coercive force. The TM treatment was combined with the alloy transition from the amorphous state to the nanocrystalline one. The TM treatment of the alloy $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$, is more efficient when the magnetic field is applied to the sample during its transition from the amorphous state to the nanocrystalline one [4].

The initial magnetic permeability μ_0 and the static and dynamic hysteresis loops were measured on toroidal samples. The dynamic hysteresis loops were recorded using the stroboscopic method [8]. The initial magnetic permeability was determined at a frequency of 80 Hz in a field of 0.05 A/m. The Curie temperature T_c and the crystallization one T_x of the nanocrystalline alloys were measured using standard techniques: T_c, from the temperature dependence of the saturation magnetization; and T_x, from the temperature trend of the electrical resistance, the samples heating rate being 5°C/min. The ribbon structure was studied by the transmission electron microscopy under a JEM-200KX microscope in the high-resolution mode. The foils with the thinnest portions being 150–200 nm thick were prepared by electrolytic polishing for examination in the electron microscope. The Curie temperatures T_c and the crystallization temperatures T_x of the nanocrystalline soft magnetic alloys $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$, $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ and $Fe_{69}Cu_1Nb_{1.5}Mo_{1.5}Co_{4.5}Si_{13.5}B_9$ are presented in Table 1.

Table 1. Curie temperature (T_c) and the nanocrystallization temperature (T_x) for iron-based nanocrystalline alloys

Alloy	T_c, °C	T_x, °C
$Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$	570	540
$Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$	570	540
$Fe_{69}Cu_1Nb_{1.5}Mo_{1.5}Co_{4.5}Si_{13.5}B_9$	470	520

3. Results and Discussion

It is known that structural features of amorphous alloys are very important when a nanocrystalline structure is formed through crystallization of the amorphous state [9]. Therefore, the effect of preliminary low-temperature annealing of $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$, $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ and $Fe_{69}Cu_1Nb_{1.5}Mo_{1.5}Co_{4.5}Si_{13.5}B_9$ amorphous ribbons on the magnetic properties of nanocrystalline samples prepared of these ribbons was studied.

Fig. 1 presents the static hysteresis loops for samples of the $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ alloy. It is seen that the preliminary low-temperature annealing and subsequent thermal treatment at 540°C even for as short time as 5 min result in a considerable decrease in the coercive force as compared with H_c after annealing at 400°C (H_c becomes 5.5 times lower). Without the preliminary annealing at 400°C, the coercive force decreases insignificantly after the thermal treatment at 540°C for 5 min.

In Table 2, presented is the dependence of H_c for a nanocrystalline $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ alloy sample (measured in static and dynamic magnetization reversal modes) on the holding time during nanocrystallizing annealing preceded by low-temperature annealing at 400°C. It is seen that the annealing at 540°C during the period from 5 min to 1.5 h in the static magnetization reversal mode provides minimum H_c values. However, the dynamic properties of the alloy after nanocrystallization at 540°C for 5 min are not optimal as compared to those after annealing at 540°C for 0.5–1.5 h. Nanocrystallization of the $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ alloy at 540°C

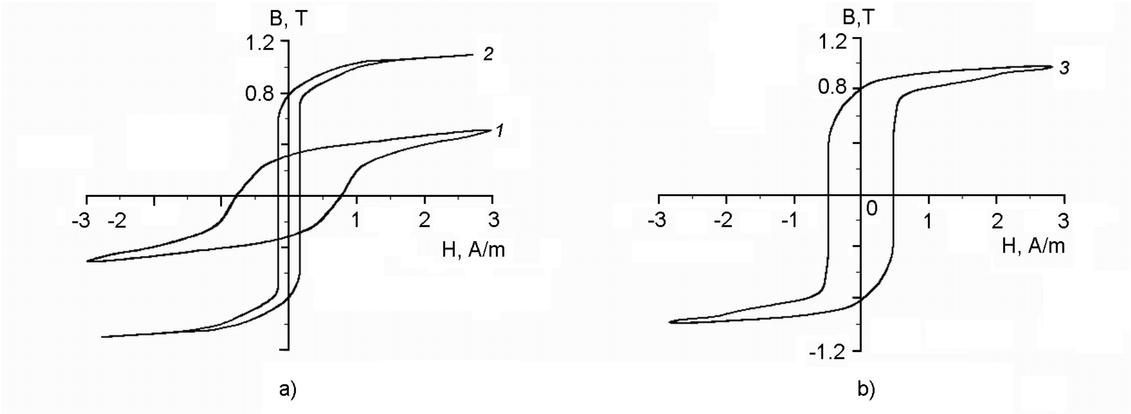

Fig. 1. Hysteresis loops for samples of $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ alloy annealed: (a) at 400°C for 30 min (*1*), at 400°C for 30 min and then at 540°C for 5 min (*2*); (b) at 540°C for 5 min (*3*).

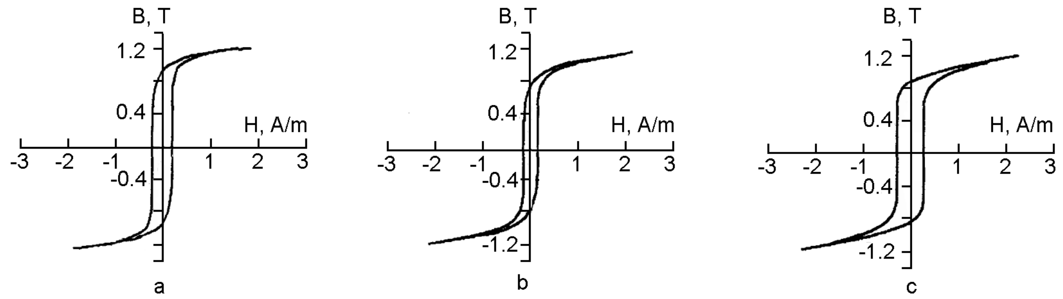

Fig. 2. Static hysteresis loops for $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ alloy samples after different thermomagnetic treatments: (a) in alternating field (f = 50 Hz);(b) in high-frequency field (f = 80 kHz);(c) in DC magnetic field.

Table 2. Dependence of H_c (A/m) on the annealing time (t) at 540°C (with preliminary low-temperature annealing) in static and dynamic conditions of magnetization. Alloy $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$

F, kHz	t				
	5 min	30 min	1.5 h	4.5 h	6.0 h
0	0.25	0.25	0.25	0.73	1.4
40	2.4	1.6	1.6	1.75	2.25
80	5.6	3.6	3.6	4.25	4.6

* The force H_c was measured at B_m = 1.0 T in the static regime and B_m = 0.5 T in the dynamic regime of the magnetization reversal.

for 0.5–1.5 h provides the best static and dynamic magnetic properties. If the holding time exceeds 4.5 h, both the static and dynamic magnetic properties of the nanocrystalline alloy $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ are impaired. The analysis of the alloy microstructure has shown that the observed impairment of the properties is due to the growing size of the α–Fe–Si, Fe_3Si and Fe_3B nanophases and the precipitation of the Fe_2B nanophase.

Fig. 2 presents the static hysteresis loops of the $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ nanocrystalline alloy after a complex treatment (annealing at 400°C for 30 min followed by annealing at 540°C for 30 min in a magnetic field, i.e. the nanocrystallizing annealing and the TM treatment being performed concurrently). The comparison of the hysteresis loops after the TM treatment in an alternating magnetic field (a), a high-frequency magnetic field (b), and a constant magnetic field (c) shows what follows. The TM treatment in a magnetic field alternating at a frequency of 80 kHz is seen to result in appearance of rounded hysteresis loops with the lowest H_c. The TM treatment in a constant magnetic field increases H_c as compared to its value after the TM treatment in the alternating (f = 50 Hz and f = 80 kHz) magnetic fields. The observed change of the magnetic properties of the samples can be explained as follows. The annealing in a high-frequency magnetic field does not cause any magnetically induced anisotropy because at magnetization reversal frequencies over 50 kHz the magnetization reversal occurs through an inhomogeneous rotation of the magnetization, and the domain structure is not stabilized [4]. Therefore, this treatment results in formation of a rounded hysteresis loop with a low coercive force. The TM treatment of the $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ nanocrystalline alloy in a constant magnetic field of 10–20H_c intensity causes a uniaxial magnetic anisotropy and increased pinning of domain boundaries. The domain structure stabilization decreasing the mobility of the domain boundaries during the magnetization reversal influences negatively the hysteresis properties. It follows from Fig. 2 that the hysteresis loop for the sample subjected to the TM treatment in an alternating (50 Hz) field deviates more from the rectangular shape and H_c is less as compared to characteristics of the sample TM treated in a constant field. This can be explained rather likely by different uniaxial magnetic anisotropies arising in these TM treatment conditions. Similar results were obtained for the nanocrystalline alloys $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ and $Fe_{69}Cu_1Nb_{1.5}Mo_{1.5}Co_{4.5}Si_{13.5}B_9$.

The temperature and time stability of the magnetic properties for the nanocrystalline alloys $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$, $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ and $Fe_{69}Cu_1Nb_{1.5}Mo_{1.5}Co_{4.5}Si_{13.5}B_9$ was studied. It was found that the $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ alloy shows the highest temperature-time stability. The magnetic properties, namely, the initial magnetic permeability and the

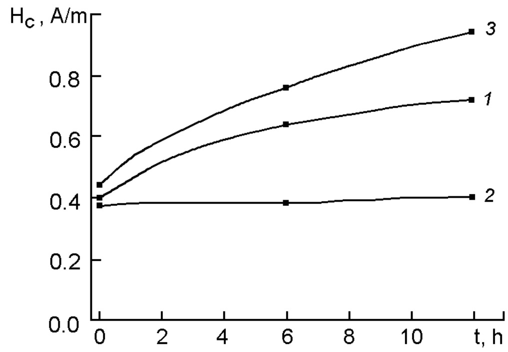

Fig. 3. Dependences of coercitivity on the exposure time in vacuum at 300°C for nanocrystalline alloys preliminarily annealed at 400°C, 30 min and then at 540°C, 30 min: *1*, $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$; *2*, $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$; *3*, $Fe_{69}Cu_1Nb_{1.5}Mo_{1.5}Co_{4.5}Si_{13.5}B_9$ (annealing at 400°C, 30 min and then at 520°C, 30 min).

coercive force of the $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ nanocrystalline alloy change only insignificantly after testing the temperature-time stability at 180°C for 60 h in different media (in vacuum and in air). Fig. 3 shows the H_c of the $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ alloy (curve *1*) as a function of the holding time in vacuum at 300°C. The H_c is seen to remain essentially constant even at a rather high temperature. For comparison, Fig. 3 presents the coercive force dependences on the holding time t for the nanocrystalline alloys $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ (curve *2*) and $Fe_{69}Cu_1Nb_{1.5}Mo_{1.5}Co_{4.5}Si_{13.5}B_9$ (curve *3*) at

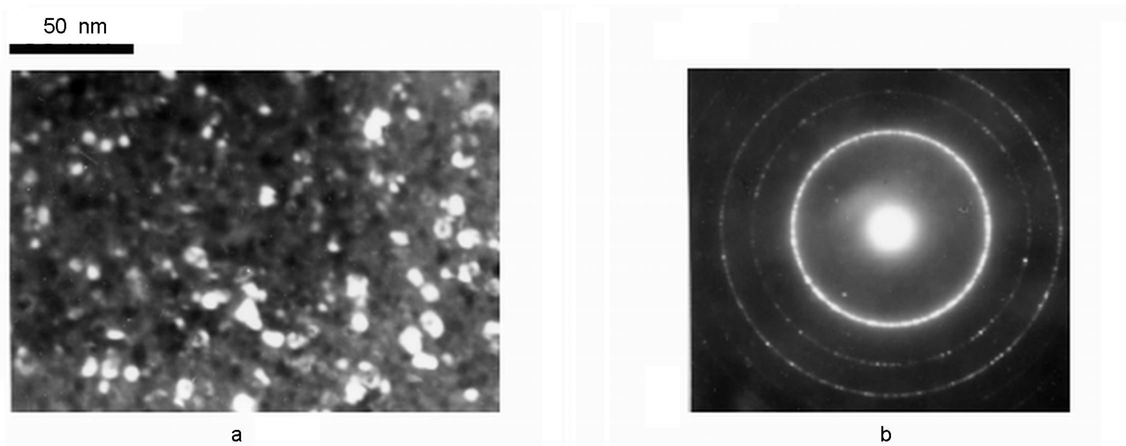

Fig. 4. Electron micrograph of structure (a) and electron diffraction pattern (b) for $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ nanocrystalline alloy after annealing at T = 400°C, 30 min and then at T = 540°C, 30 min. In the structure micrograph, it is seen an electron contrast in the form of rings and on diffraction pattern, the reflexes within the position of the first diffuse halo due to Fe(Nb,Mo)B phase.

the same test temperature (300°C). It follows from Fig. 3 that the nanocrystalline alloy $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ is more thermally stable than the $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ and $Fe_{69}Cu_1Nb_{1.5}Mo_{1.5}$-$Co_{4.5}Si_{13.5}B_9$ ones.

The nanostructure study of the $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ alloy shows that the high temperature-time stability of the magnetic properties is due to the precipitation of the Fe(Nb,Mo)B nanophase (Fig. 4) at the "α–Fe–Si phase-matrix" interface in the alloy. This nanophase has a high thermal stability and impedes the further growth of the α–Fe–Si nanophase.

Note that two nanocrystallization temperatures 520°C and 610°C are used for the $Fe_{69}Cu_1Nb_{1.5}Mo_{1.5}Co_{4.5}Si_{13.5}B_9$ alloy [7]. The nanocrystallization at the lower temperature (520°C) (Fig. 3) does not provide high thermal stability of the properties because the precipitation of a Fe-depleted Fe(Co,Nb,Mo)B nanophase (Fig. 5), which is less thermally stable qas compared to the Fe(Nb,Mo)B phase. Nanocrystallization at 610°C improves the thermal stability, but the coercive force increases considerably [7]. The cause is that the thermally stable Fe(Nb,Mo)B and Co_2B nanophases precipitate at the high nanocrystallization temperature. Note that the Co_2B nanophase causes the increase of H_c.

4. Conclusion

Studied has been the influence of specific nanostructure features on the magnetic properties of modified Fe-based nanocrystalline soft magnetic alloys after nanocrystallization in different conditions. It has been found that preliminary low-temperature (400°C) annealing improves the magnetic properties of the $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$, $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$, and $Fe_{69}Cu_1$-$Nb_{1.5}Mo_{1.5}Co_{4.5}Si_{13.5}B_9$ alloys during subsequent nanocrystallization. The effect of preliminary low-temperature annealing during subsequent nanocrystallization is due to the relaxation of internal elastic stresses as well as to accelerated nucleation of crystallization centers. The effect of thermomagnetic treatment conditions on the magnetic characteristics of the nanocrystalline alloys under study has been considered. It has been shown that materials with different functional properties can be obtained by varying the the magnetic field frequency during the TM treatment. The temperature-time stability of the nanocrystalline alloys

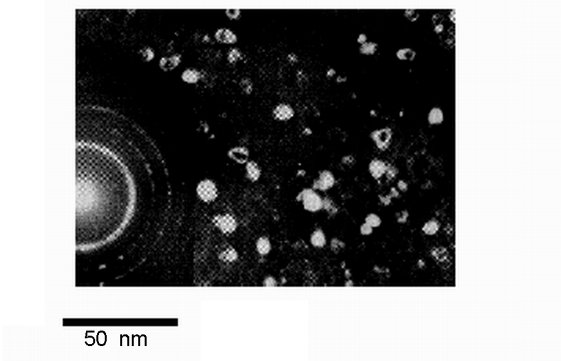

Fig. 5. Electron micrograph of structure and electron diffraction pattern for $Fe_{69}Co_{4.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ nanocrystalline alloy after annealing at T = 400°C, 30 min and then at T = 520°C, 30 min. In the structure micrograph, it is seen an electron contrast at the boundary of precipitating phases in the form of diffuse rings and in diffraction pattern, reflexes practically close the first diffuse halo, due to Fe(Co,Nb,Mo)B phase.

$Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$, and $Fe_{69}Cu_1Nb_{1.5}$-$Mo_{1.5}Co_{4.5}Si_{13.5}B_9$ has been studied. The highest temperature-time stability was observed in the $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ alloy after the thermal treatment consisting in annealing at 400°C for 30 min and nanocrystallization annealing at 540°C for 30 min. The high temperature-time stability of the $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$ alloy is due to the precipitation of the Fe(Nb,Mo)B nanophase in the alloy, with this nanophase having a high thermal stability and impeding the growth of the main α–Fe–Si nanophase. The magnetic characteristics of this alloy have been shown to be stable over the temperature interval of 20°C to 300°C.

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Нанокристалічні сплави з високими магнітними властивостями та високою термостабільністю

Н.І.Носкова, В.В.Шуліка, А.П.Потапов

Досліджено структуру, магнітні властивості та температурно-часову стабільність нанокристалічних магнітно-м'яких сплавів. Виявлено вплив попереднього низькотемпературного відпалу при нанокристалізації на структуру та магнітні властивості нанокристалічних сплавів, що досліджувалися. Показано, що хімічний склад нанофаз, що виділяються, впливає не тільки на магнітні властивості, але й на температурну стабільність сплавів. Найвищу температурно-часову стабільність має нанокристалічний сплав $Fe_{73.5}Cu_1Nb_{1.5}Mo_{1.5}Si_{13.5}B_9$.