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АННОТАЦИЯ

Исследовались металлические стекла при помощи электронной Оже-спектроскопии /AES/ путем измерения распределения компонентов в плоскости и по глубине на обеих сторонах ленты. Результаты показывают обогащение атомов Ni и обеднение атомов B на поверхности. Глубина неоднородных областей составляет около 100 нм, а изменение концентрации внутри ленты для всех компонентов меньше, чем 1 ат %. В некоторых случаях в приповерхностных областях наблюдалась квазипериодичная флуктуация состава в релаксационных образцах.

KIVONAT

Fémüvegeket vizsgáltunk Auger elektron spektroszkóppal (AES) mérve a komponensek sikbeli és mélységi eloszlását a fémüveg szalag mindkét oldalán. Az eredmények azt mutatják, hogy Ni feldusulás és B elszegényedés lép fel a felületeken. Az inhomogén tartományok mélysége kb. 100 nm és a szalag belsejében a koncentráció változás valamennyi komponensre kisebb mint 1 at.%. Néhány esetben a felület közelében különleges kvazi-periodikus összetétel fluktuációt figyeltünk meg a relaxáltatott mintákban.

ABSTRACT

Metallic glasses were investigated by Auger electron spectroscopy (AES) measuring the in-plane and in-depth distribution of the different components on both sides of the ribbons. The results show a Ni-enrichment and a reduction of the B content at the surfaces. The depth of the inhomogeneous regions is about 100 nm and the variation of the concentration within the ribbons was found less than 1 at.% for all components. In some cases near the surface a peculiar quasiperiodic concentration fluctuation was detected in the relaxed samples.

INTRODUCTION

Metallic glasses prepared by melt spinning or other quenching method may have inhomogeneous distribution of the different components. Such kind of inhomogeneity may affect strongly both the magnetic and mechanical properties of the ribbons. The investigation of the nature and origin of these inhomogeneities may help in producing high quality metallic glasses.

One of the most powerful methods for investigating the inhomogeneous distribution of components on the surfaces and within the ribbons is AES. In spite of it very few AES measurements can be found in the literature made on metallic glasses [1,2]. We have used this method to investigate two metallic glasses produced by melt spinning the composition of which were $Fe_{17}Ni_{63.8}B_{19.2}$ (material I) and $Fe_{31.5}Ni_{49.2}B_{12.3}Si_7$ (material II).

The spectrometer used was the scanning Auger microscope, SAM-PHI-545. It was operated at a primer electron energy of 5 KeV, a beam current of $9 \cdot 10^{-7}$ A and a beam diameter of 5 μm. The in-depth and in-plane distribution of the different components were measured on both sides of the ribbons. The measurements were

carried out in the as-quenched and in the relaxed state. The relaxation annealings were performed in vacuum (~ $1.3 \cdot 10^{-2}$ Pa) at 525 K for 15 ks and 563 K for 15.9 ks in the case of material I and II respectively.

In some cases the whole energy spectra were also taken to get informations about the presence of other elements or impurities besides the basic components. During the measurements of these spectra Ar-ion sputtering was applied to clean the surface so the appearance of Ar peak in the spectra is expected.

RESULTS AND DISCUSSION

1.) Impurities

From the spectra obtained on the different samples the following conclusions may be drawn on the existence of impurities:

I. Fe-Ni-B alloy

Impurities were found at several spots on the surface at the roller side of the as-quenched ribbon. The spots contained oxygen, carbon and sulphur. On the free side of the same sample and on both sides in relaxed state the impurities did not exceed several tenth of percent. On the basis of this observation it may be stated that the low temperature heat treatment gets the surface free from impurities.

II. Fe-Ni-B-Si alloy

On the roller side of the as-quenched sample, carbon contamintaion is significant at the surface. The structure of the AES peak of carbon shows that it is in chemical bond with the basic components or at least with some of them. The situation is similar on the free side except that the chemically bonded carbon can be observed only in the deeper layers and not at the surface.

2.) Basic components

The in-depth concentration distribution was measured on both sides of the samples up to about 500 nm depth. These measurements

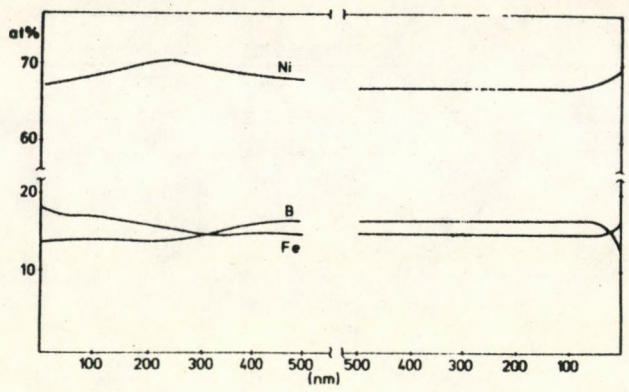


Fig. 1. In-depth profile curves at the roller side /left/ and the free side /right/ of as-quenched $Fe_{17}Ni_{63.8}B_{19.2}$ metallic glass

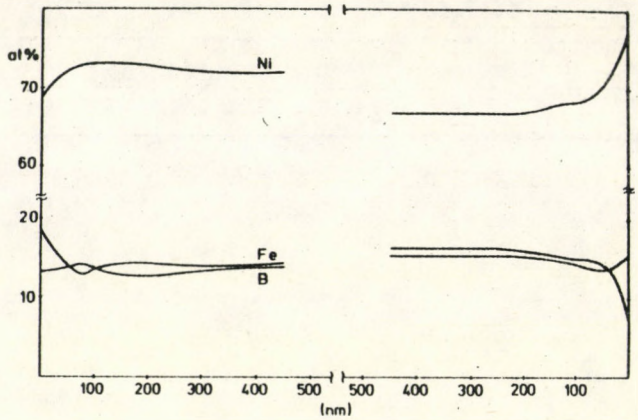


Fig. 2. In-depth profile curves of $Fe_{17}Ni_{63.8}B_{19.2}$ sample relaxed at 525 K for 15 ks

were performed at two spots in every cases except the relaxed Fe-Ni-B sample, where it was made only at a single spot. Some of the in-depth profiles obtained for as-quenched and relaxed Fe-Ni-B samples are shown in Fig. 1 and Fig. 2, respectively and the same curves for Fe-Ni-B-Si alloy are drawn in Figs 3 and 4.

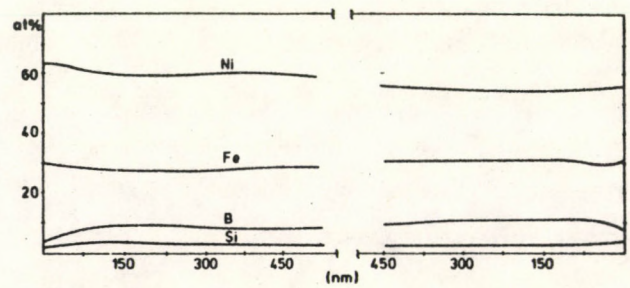


Fig. 3. In-depth profile curves of as-quenched $Fe_{31.5}Ni_{49.2}B_{12.3}Si_7$ sample

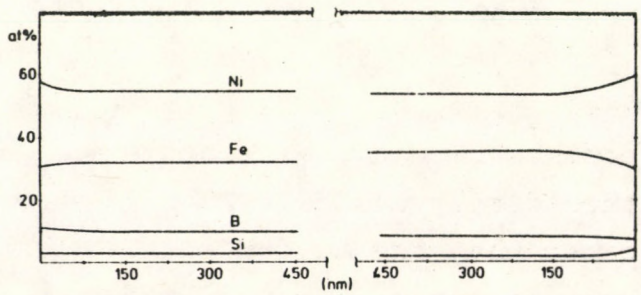


Fig. 4. In-depth profile curves of $Fe_{31.5}Ni_{49.2}B_{12.3}Si_7$ sample relaxed at 573 K for 15.9 ks

In Table I the deviations of the surface concentrations from the bulk one are collected in a qualitative manner. The signs (+) or (-) denote the cases when the content of the component in question is higher or lower at the surface than in the bulk, respectively. The double signs show stronger deviations (3-7 at.%) while the triple signs correspond to the extremly high deviations (>7 at.%).

Table I.

Element	As quenched		Annealed	
	Roller side	Free side	Roller side	Free side
	I. Fe-Ni-B		First spot	
Ni	O	+	- -	+ + +
Fe	-	+	+ +	O
B	+	- -	O	- - -
	I. Fe-Ni-B		Second spot	
Ni	O	+		
Fe	+	O		
B	-	-		
	II. Fe-Ni-B-Si		First spot	
Ni	+ +	+	+	+ +
Fe	+	O	-	- -
B	- -	- -	+	-
Si	-	+	O	+
	II. Fe-Ni-B-Si		Second spot	
Ni	+ +	+	-	+ +
Fe	+	-	O	- -
B	- -	O	O	-
Si	-	+	+	+

When the content of a component obtained at the surface was approximately the same as in depth of 400-500 nm the note o was used. As it can bee sen in the Table I and from the in-depth profile curves the Ni content is generally higher at the surface then deeply inside. (From 14 measurements there were only two cases when the Ni content was lower at the surface and two cases when it did not change at all.)

We have not found such an unambigous tendency in the Fe concentration. Only the Fe-Ni-B-Si metallic glass exhibits a little depletion of the Fe content at the free side, which tendency becomes more significant in the annealed sample.

In the case of B the tendency of depletion was found as significant as the enrichment of Ni. Comparing the results for the as-quenched and relaxed samples it may be established that due to the annealing the tendency becomes more apparent.

The Si has the most peculiar behaviour. In the case of as--quenched sample, the Si content decreases at the roller side and increases at the free side of the ribbon. In the relaxed sample,

the Si enriched at both surface.

Summarizing the conclusions we have to admit that the number of measurements is too low to check these tendencies statistically. That is, why we must say that from the results of this investigation only the increase of Ni concentration and depletion of boron at the surfaces seems to be a general rule.

In the case of the other components deviations from the bulk concentration were also observed but the magnitude and sign of them scatter in such a way which overspreads any tendency if it exists at all. Because of that scatter (which exists in the case of Ni and B as well), it is necessary to suppose the existence of in-plane concentration fluctuations at the surfaces which may have the same order of magnitude as the in-depth variations observed for Ni and B.

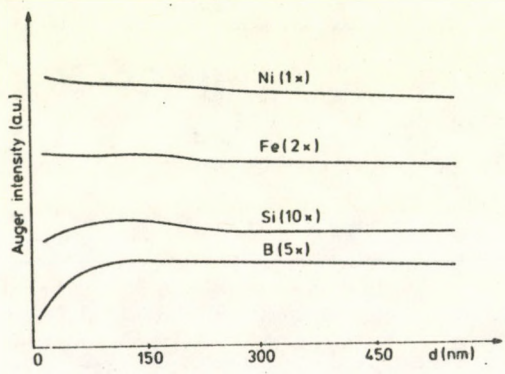


Fig. 5. In-depth change of Auger peak intensity of various elements at the roller side of as-quenched $Fe_{31.5}Ni_{49.2}B_{12.3}Si_7$ sample. The numbers in brackets show the relativ amplification of the spectrometer.

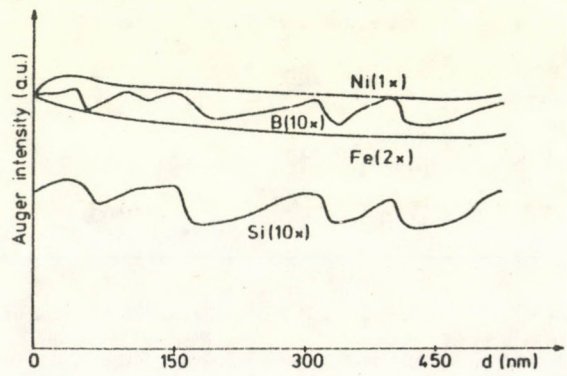


Fig. 6. In-depth change of Auger peak intensity of various elements at the roller side of relaxed $Fe_{31.5}Ni_{49.2}B_{12.3}Si_7$ sample.

In Figures 5 and 6 a very interesting phenomenon, observed in Fe-Ni-B-Si samples is shown. In these in-depth profiles the values of the Auger peak intensity are shown. Comparing the curves of as quenched and relaxed samples, it can be recognized that in-depth concentration fluctuations exist which are more pronounced in the relaxed sample then in the as-quenched one. The amplitude of this fluctuation converted it into concentration is less than $\pm$1 at.% which is nearly the same as the accuracy of the determination of concentration by AES. The fluctuations seem to be more

evident regarding the metalloid curves, but this is only an apparent effect caused by the higher amplification used in the spectroscope.

CONCLUSIONS

a) At both surfaces of the melt spun ribbons one can observe concentrations which are different from the bulk ones. The concentration differences arise mainly from the Ni enrichment and B depletion at the surfaces.

b) The depth of such inhomogeneous distribution of different elements is generally several hundreds of nanometer. In the layers further off from the surface the material can be regarded as homogeneous.

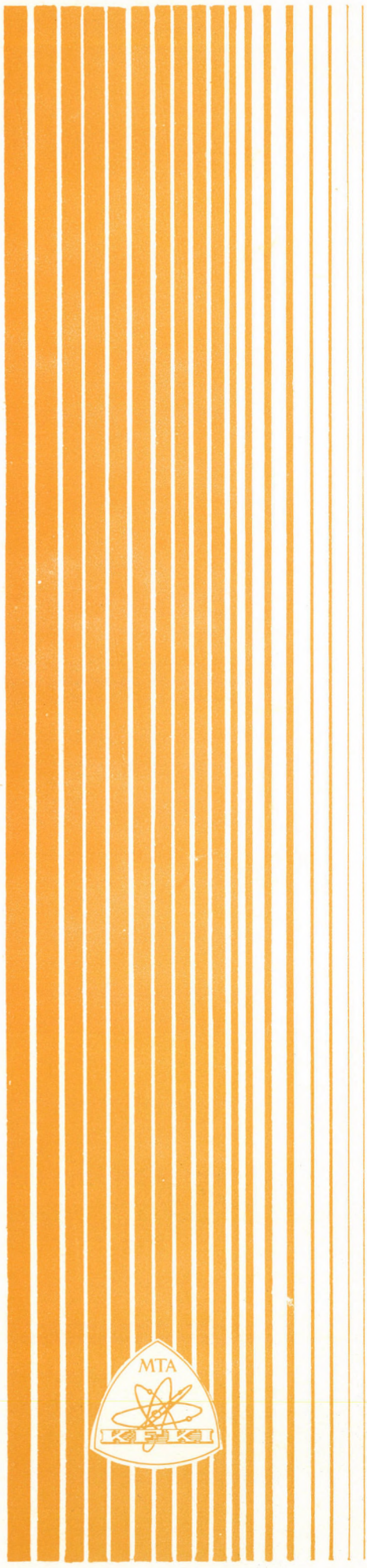
c) The in-plane distribution at the surface is also inhomogeneous. The amplitude of the concentration fluctuations is the same order of magnitude as that of in-depth inhomogeneities near the surface.

d) In some cases one can observe in-depth concentration fluctuations. Its amplitude is at least an order of magnitude less than that of in-plane fluctuations. As this phenomenon was observed mainly in relaxed samples it may be supposed that the relaxation processes might lead to such quasiperiodic concentration fluctuations which may be regarded as a special phase separation in the amorphous state.

REFERENCES

[1] Horowo G. Suzuki and Koichi Yamamoto, Material Science and Engineering 33 (1978) 57

[2] Lance A. Davis, Conference on Metallic Glasses, Budapest, 1980



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