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BUDAPEST

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АННОТАЦИЯ

Представлены результаты серии низкотемпературной термообработки, проведенной при различных температурах для изучения процесса старения. Процесс изучался при помощи измерений статической коэрцитивной силы /H_c/ и микротвердости /HV/. H_c и HV не изменяются монотонно под действием старения и указывают на механические напряжения, вызванные перегруппировкой атомов. После длительного старения дыры наблюдались даже в том случае, если образец по результатам рентгеновского исследования образца оставался аморфным.

KIVONAT

Az öregedés hatását vizsgáltuk különböző alacsony hőmérsékletü hőkezelések segitségével. Statikus koercitiv erő (H_c) és mikrokeménység (HV) mérésekkel vizsgáltuk a hatást. Öregités hatására ezek nem változtak monoton módon és azt mutatják, hogy mechanikai feszültségeket okoz az atomok átrendeződése. Hosszuidejü öregités után lyukakat figyeltünk meg akkor is, ha a minta röntgen vizsgálat alapján amorf maradt.

ABSTRACT

The results are presented of a series of aging heat treatments, carried out at different temperatures. Static coercive force /H_c/ and microhardness /HV/ measurements were made. H_c and HV do not change monotonically during the aging thereby showing that stresses arise from the atomic regrouping. After long-term aging the formation of holes was observed even though the specimens remained X-ray amorphous.

INTRODUCTION

Relatively few data have been published in the literature on the results of long-term aging processes despite the fact that this type of information seems to be valuable in the experimental estimating of thermal stability [1]. In this paper the results are described of series of long-term heat treatments performed on different iron-based metallic glasses at different temperatures including natural aging. The static coercive force and the microhardness were measured and the results correlated with structural changes observed by optical and electron-microscopy.

EXPERIMENTAL

Sample preparation is described elsewhere [2]. Natural aging was carried out at room temperature in a dry box to avoid corrosion. The heat treatments were performed at 433 K, 473 K and 573 K in air and Ar atmosphere respectively. Among the heat treatments the natural aging and the heat treatment at 433 K were long term, 10000 h and 5000 h respectively.

Amorphicity was checked after each heat treatment by X-ray diffraction. Microhardness were measured by a Wickers instrument /HV 200/, and the coercive force by a Foner-type magnetometer.

RESULTS

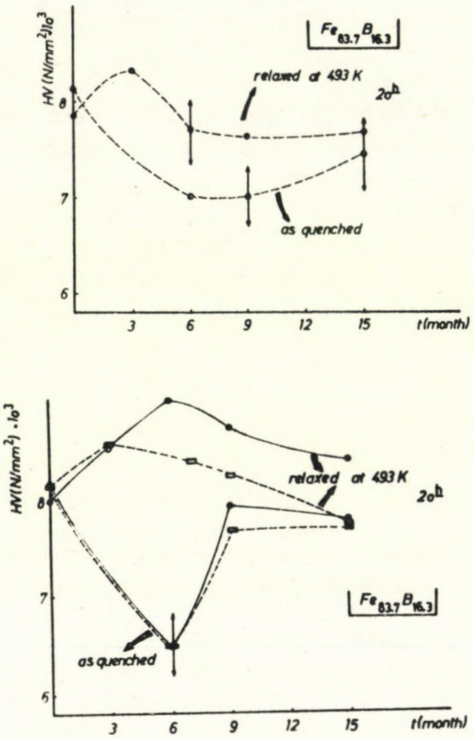

Fig. 1a,b
Microhardness /HV 200/ of eutectic FeB ribbons versus the time of natural aging. /0 and ▭ pre-annealed and then naturally aged,• and ■ only naturally aged after the preparation/

Fig. 1a,b shows the change in microhardness measured on eutectic FeB ribbons during the natural aging for 15 months. The ribbons were quenched with slightly different cooling rates consequently HV in the as-quenched state was nearly the same. HV of the as-quenched specimens decreases with time and show minima at about 6 months. As opposed to this, microhardness for the pre-annealed specimens /20 h, 470 K/ increases and shows maxima at this time. HV measured on the previously relaxed ribbons was always higher than the as-quenched ones in the period investigated, though the values approach each other. At temperatures higher than room temperature, a maximum in HV appears during the aging /*Fig. 2.*/. If the temperature is increased the maximum is reached earlier indicating that thermal activated processes are involved. The appearance of the maximum can be described by single activation energy supposing a simple Avrami-type kinetics. The corresponding activation energy is 12.6 Kcal/mol, which is significantly lower than values found for the stress relaxation in different iron-based metallic glasses [3]. In *Fig.3.* the changes in H_c are

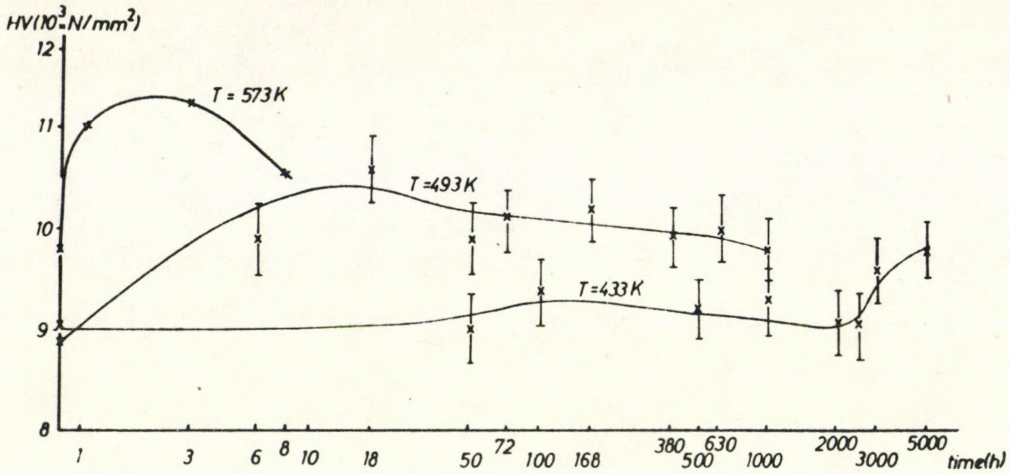

Fig. 2. HV /200/ of $Fe_{83.7}B_{16.3}$ versus time of aging at different temperatures.

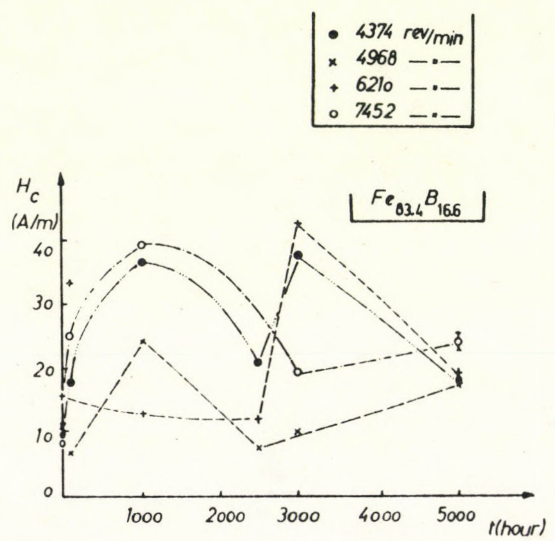

Fig. 3.
Static coercive force during the aging at 433 K. The ribbons were quenched with different cooling rate.

plotted for the eutectic FeB ribbons /temperature of heat treatment: 433 K/. A characteristic of these H_c/time curves is that they highly depend on the cooling conditions applied by the preparation of the ribbons, however, there is an increase in H_c in the first period of the annealing in most cases. Of course this not monotonic change in H_c is also a consequence of thermally activated processes, consequently the instantaneous value of H_c is practically a function of the processing history until the relaxation is completed. As *Fig. 4.* shows, at sufficiently high aging temperature the maxima in H_c disappear and H_c decreases monotonically with

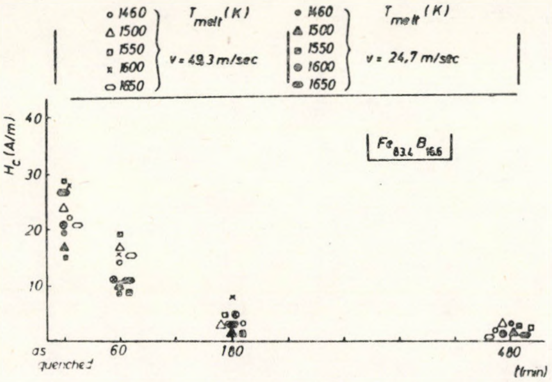

Fig. 4.
Change of static coercive force of eutectic FeB ribbons /quenched with different cooling rate/ during the aging at 470 K.

time up to the onset of crystallization. The differences in H_c caused by the processing conditions also disappear gradually /T = 573 K/. These non-monotonic altering of H_c during the low temperature aging seems to be a general feature of the rapidly quenched iron and cobalt based metallic glasses. This is presented in *Fig. 5.* /the only exception is $Fe_{80}B_{15}Si_5$, for which a monotonic increase in H_c was observed/.

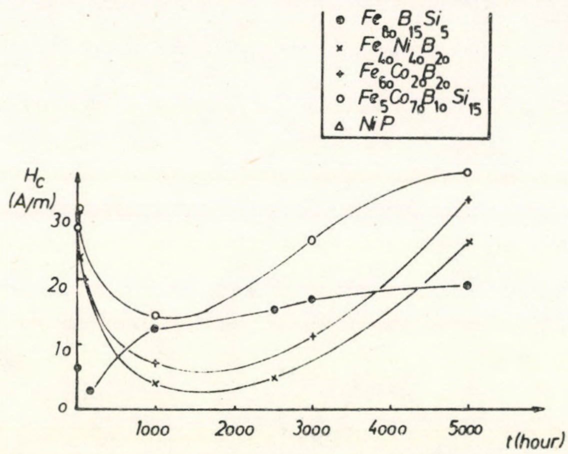

Fig. 5.
H_c for different iron-cobalt based amorphous alloys versus time of aging at 433 K.

The structural changes during the aging process were followed in the cause of the heat treatment at 433 K. Some specimens were found to be X-ray amorphous even after the 5000 h aging, but in those held under stress traces of crystalline phases were already found at this time. Both in the as-quenched state and after the annealing a typical "globular structure" could be observed on the specimens after ion-etching similarly to those observed in evaporated amorphous films [4]. The only difference is that globular structure "ripend" after the long term aging. Furthermore after the long heat treatments the formation of holes and micro-cracking were observed on several specimens. The cracking was often arranged in the form like the grain boundaries in crystalline metals /*Fig. 6.*/

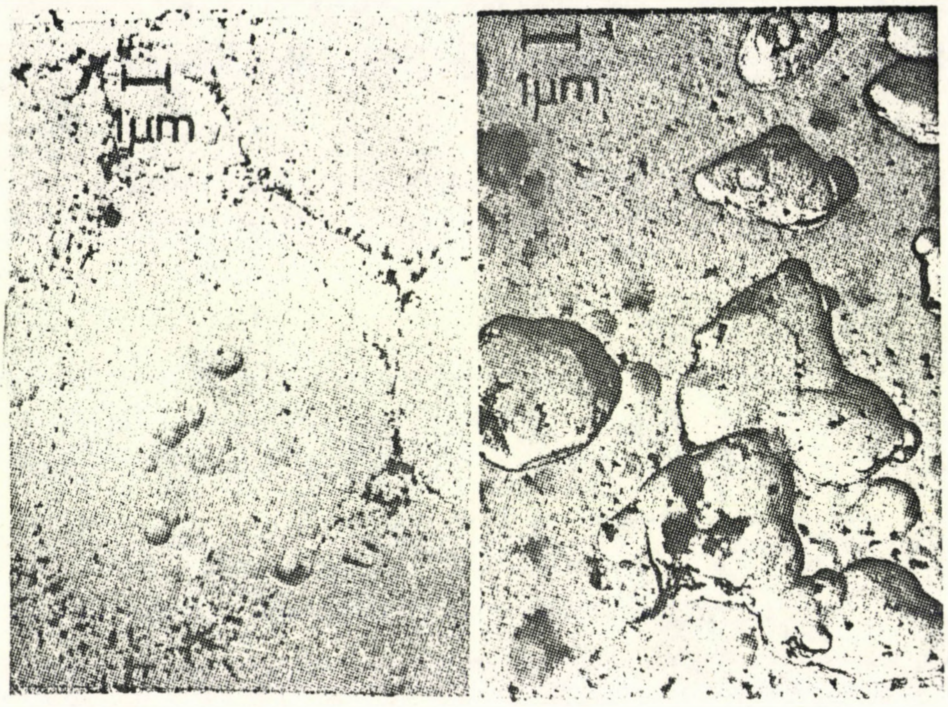

Fig. 6. Photomicrographs of holes and microcracks in FeB eutectic ribbons after aging at 433 K.
a./ as quenched b./ after 5000 h aging at 433 K.

DISCUSSION

In order to make any comparison between the metallic glasses on the bases of their microhardness, related to other physical properties, all factors determining the HV must be considered.

These are: 1. Methodological [5-6]. The role of applied load as well as the ribbon thickness.

2. Physical

a./ The role of composition and the nature of chemical bonding. Although only a qualitative tendency, it is generally found that increasing the covalent bonding- character in metallic glasses by raising the concentration of the metalloid elements results in greater hardness [7].

b./ Similarly to crystalline alloys, HV is also very sensitively influenced by the presence of the extended defects and by the stresses caused by precipitation or inhomogenities.

The latter are determined by the "processing or thermal history" [8] which causes deviations from the ideally amorphous material being chemically and physically homogeneous up to the dimensions of short range order. The high role of stresses is also supported by the marked change in hardness below the crystallization temperature. On the basis of our results we can state that the non-monotonic change of HV and H_c are not connected with any crystallization phenomena, because the applied temperature was too low to cause any crystallization, but it is the consequence of the induced and disappearing stresses. Maybe there is a close connection between the ripening of the observed "globular structure" and the induced stresses, but this is not proven at present. It was found by several authors that the kinetics of stress relief as well as the relaxation of magnetic anisotropy are characterized by a quick change in the first 5-10 minutes of annealing, which was followed by a relative slow change in the same properties [9-10]. In the present experiment this sudden change in HV and H_c was not found.

SUMMARY

1. During low temperature aging processes the change of HV and H_c is not monotonic showing maxima and minima.
2. These changes are not connected with crystallization but are the consequence of the induced stresses caused by the regrouping of atoms. The appearance of the first maximum in HV can be described by a single activation energy.

3. After the heat treatment at 433 K for 5000 h the investigated alloys remained X-ray amorphous, but microcracks were formed in the specimens showing that the effect of the atomic rearrangements are more extended in the specimens than the first coordination of the atomic neighbourhood.

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