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Investigation of the Property Change in FINEMET Alloy After Conventional, Pulse and Mechanical Stress Annealing

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Abstract

In the present work the comparison of the effect of traditional, pulse and stress annealing is made by monitoring the important mechanical and magnetic properties of FINEMET type amorphous precursor alloy. The magnetic properties were determined from the shape of magnetization curve (coercive force, anisotropy) during various heat treatments and the mechanical properties were measured using brittleness test. The traditional heat treatments were performed in resistance furnace and the magnetic measurements were performed in astatic magnetometer. The pulse and stress annealing (as well as their combinations) were carried out inside in the magnetometer. The temperature of pulse heat treatments is regulated with the length of current pulse flowing through the sample. After each pulses the magnetization curves were measured in-situ, in the magnetometer.

Keywords*: pulse heat treatment, FNEMET, amporphous, nano-crystalline, brittleness.*

1. Introduction

In recent decades, Fe-based nanocrystalline alloys have become fundamental in the production of soft magnetic materials. The excellent properties are developed via thermal decomposition of the FINEMET ($Fe_{73,5}Si_{13,5}B_9Nb_3Cu_1$), amorphous precursor [1]. It is believed, that the nanometer-size α-Fe (Si)) grain structure plays a basic role in the development of the extra-ordinary properties [2]. The onset-temperature of amorphous-phase decomposition can be altered even in the same crystallization reaction, resulting in different size distribution [3]. The minimum grain-size is expected to be formed when the temperature of crystallization is around the 0.5 times the melting point of the alloy in question [4]. The magnetic softness is reflected in the magnitude of coercivity which exhibits an inverse-like relation in several soft magnetic alloys of average grain size. However, this relation breaks down in the range of 100-1 nm grain diameters in FeSiB-alloys. This exceptional behaviour is attributed to the coincidence between the magnetic correlation length and the grain diameters. The rapid drop is believed to be the consequence of an averaging of crystal anisotropy within the domain wall thickness in these alloys [2]. This grain-size lowering is extremely sharp in the case of Fe(SiB) based glasses.

The phenomenon is attributed to the coincidence between the magnetic correlation length and the average grain diameters causing the crystal anisotropy averaging over the dimension of the domain wall thickness (~100 nm in these alloys).

However the nanometer-sized grain dimension is not the only reason for the development of excellent magnetic softness. Only those of nano-crystalline alloys exhibit magnetic ultrasoft-

ness, in which the nanograin system is developed from the glassy precursor via “primary reaction” [5]. This reaction is the first step during the amorphous phase decomposition of hypo-eutectic Fe-B glasses. Hence, this two-step mechanism can be regarded as the proto-type for the nano-crystallization in FINEMET ($Fe_{73,5}Si_{13,5}B_9Nb_3Cu_1$) precursors [6]. This transformation has been analysed in several references [7–9]. There is general agreement concerning the importance of separation of the first and second steps of crystallization, because magnetically hard, inter-metallic particles precipitate during the second crystallization step, destroying the soft magnetic character of the alloy. This separation is enhanced by the addition of appropriate alloying elements into the precursor glass. The addition of the nucleating element (Cu) (enhancement the nucleation of α-Fe particles) has an outstanding significance from the point of view of ensuring homogeneous distribution of nuclei formation [10], but also contributes to separation of crystallization steps belonging to the α-Fe(Si) and Fe_3B formation. The Nb addition contributes to the retardation of Fe_3B precipitation (crystalline inter-metallic compound) avoiding the magnetic hardening[11]. The Si addition ensures the overall stabilization of the glassy state.

The temperature of α-Fe nucleation in hypo-eutectic Fe-B glassy alloys is lowered by the Cu addition [12]. The essence is the “cathalytic” mechanism of eutectoid type decomposition of the fcc environments being entrapped during liquid quenching [13]. The preferential solubility of Cu in fcc (γ) Fe environments, γ-Fe type symmetries are quenched into the amorphous matrix, which are inactive during the magnetization process, i.e. the domain wall displacement is hindered. As the temperature increases during heat treatment, the γ-centres decompose at first, via an eutectoidic mechanism, as the activation energy of Cu diffusion is low [14, 15]. The outlined mechanism is also supported by the experiments [6]. Hence, itself this nucleation phenomenon also contributes to the suppression of coercivity prior to the development of nanocrystalline structure [13].

The traditional nanocrystallizations are performed by isothermal heat treatments at around 540 °C, 1h, when the DO3 ordered phase is formed, which is α-Fe (Si) solid solution. The Nb and B are enriched in the remaining amorphous phase. Recently, “pulse heat treatments” and stress annealing (annealing combined with longitudinal stress) [16] were also studied for tailoring the soft magnetic properties.

Though several outlined methods are applied even in the industrial praxis already, some details of the physical background of property tailoring is still open. Mainly the knowledge of atomic level mechanism of coercivity and brittleness evolution is insufficient during the various heat treatment types. This topic is the focus of the present paper.

2. Experimental

2.1. Materials, heat treatments and measuring methods

The well-known FINEMET alloys are applied in the experiments. The samples purchased were 10 mm width, 30 μm thickness and length was set to 100 mm with scissors. Impulse heating was performed by alternating the current pulses with the peak current of approximately 10A, the frequency was set to 50Hz. Pulse duration was 0.08-0.12 sec. Samples were heat treated with this method without applying forced air cooling. The estimated cooling rate was about 100 K/s and the thermal heating rate was about 1000 K/s. The magnetic measurements were performed in-situ during the heat treating process in an astatic magnetometer. The coercive force (H_c) was determined from the magnetization curves, which are plotted after each individual pulse.

In **Figure 1** examples are shown for the time dependence of temperature caused by individual pulses of different length, representing different energies. The details of measurement and the evaluation of results are described in [16].

The relative strain at fracture (ε_f) is determined from simple bending test by bending the ribbons of thickness d between two parallel plates to a semicircle of radius r = D/2, where D denotes the distance between the two plates. At fracture, ε_f is evaluated from the expression $\varepsilon_f = d / (D - d)$ described in [17, 18].

Stress annealing was also applied using case external uniaxial stress (σ = 0, 2 and 4 MPa) combining the traditional or pulse treatments with longitudinal stress during the time-period of sample heating. The longitudinal stress was applied to the weights placed on the samples inside in the magnetometer.

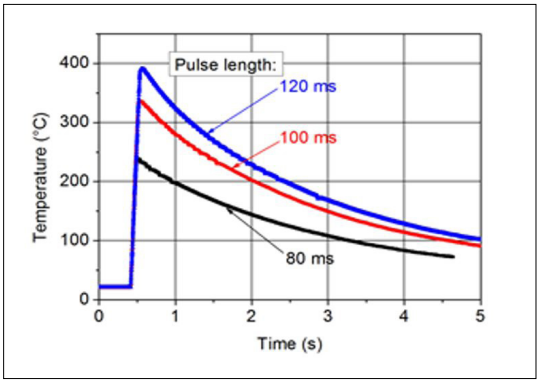

Figure 1. *The time dependencies of temperature using pulses of different length measured on sample FINEMET* **[16].**

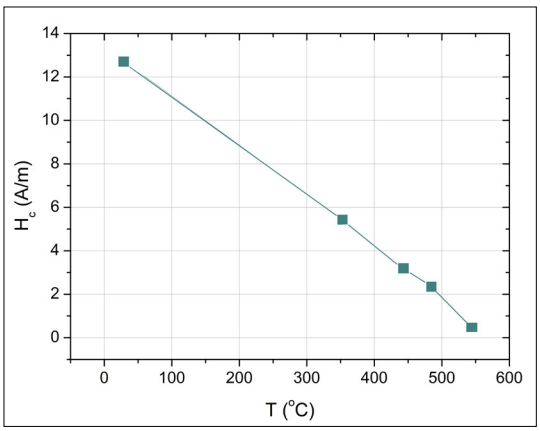

Figure 2. *AThe change of H_c in FINEMET precursor versus the temperature of isothermal 1h heat treatments* **[19].**

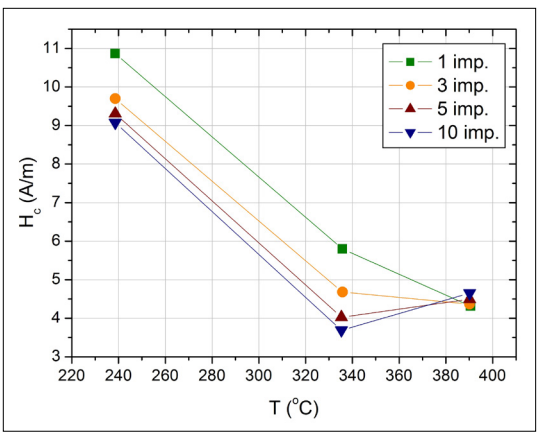

Figure 3. *Correlation between coercivity and the maximum temperature attained by different pulse number and pulse length.*

3. Results and discussion

3.1. Temperature dependence of coercivity during isothermal heat treatments

The change of magnetic properties during amorphous nanocrystalline transformation are reported in several papers **[6, 18]**. A typical trend is illustrated in **Figure 2**, where the H_c of FINEMET samples are plotted versus the temperature of isothermal (1h) annealing. This result is regarded as reference tendency for the appreciation of the impact of pulse treatments.

The net Hc decrease originates from two, slightly overlapping physical processes: In the low temperature range the Hc lowering arises solely from the structural relaxation (T_{anneal} < 350 °C), which consists of short range arrangement, containing also bond reorientation between the frozen contacting atoms, without long range diffusion. More, than the 50 % of the total H_c decrease originates from this process. No trace of crystal nucleation is detected in this temperature range. Beyond 400 °C the additional H_c decrease arises from crystal nucleation and growth of nano-crystals. In this process diffusion over medium range order is also involved.

The further decrease of H_c by nearly a magnitude treatment is typical in these alloys. Within this temperature interval nanometer-sized DO3 type grain assembly is developed, which is Fe (Si) solid solution. This process is completed at around 540 °C. The H_c lowering in the early stage of crystallization is unexpected in the Fe-B alloys. Just the opposite tendency is experienced in the binary glasses **[20]**. The significant lowering is interpreted by the enhanced elimination of γ-trapping centers by the entrapped Cu-atoms via the eutectoidal reaction, so the mechanism of catalytic effect of Cu-atoms on the γ-center elimination is an eutectoidal reaction, starting from the fcc environments.

In **Figure 3** the H_c evolution is depicted versus the increasing peak temperature for several independent series of pulses (see **Figure 1.**). It was detected that peak temperature depends predominantly on the pulse length (**Figure 1.**), Consequently, the highest H_c depression is expected at the highest peak temperature applied in the experiments. At the 0.1 s pulse length, the peak temperature is nearly 350 °C. The impact of a single pulse on H_c suppression is nearly the same as that for the 1h isothermal heat treatment at the same temperature, indicating that magnetic stress re-

laxation is an extremely rapid process, presumably of the non-diffusive nature of this relaxation mechanism.

This observation is also supported by the series of measurements, collected in **Figure 4.** Here, the H_c lowering is plotted for different (increasing) pulse lengths (0.08 s, 0.10 s and 0,12 s). Again, these independent measurements were performed in-situ in the magnetometer, subsequently the individual pulses. It is remarkable, that H_c decrease is negligible during the pulse series, except the first heat pulse. On the other hand, it is also clear, that peak temperature (or the magnitude of activation energy) has a dominant role in the kinetics of H_c decrease. In the period of structural relaxation, the H_c decrease is coupled solely with short range atomic rearrangements within these – sterically independent – quenched-in stress centres. As the peak temperature of pulses is high enough, the population density of these centres rapidly decreases.

3.2. Pulse heat treatments in external (axial) field

A longitudinal external field was also applied in order to study the interaction between the thermal activation and the outer magnetic field in the evolution of coercivity during the series of individual pulses. The easy direction of magnetization in soft magnetic rapidly quenched ribbons is along the ribbon length. The direction of magnetic field produced by the magnetometer is parallel with this easy direction of magnetization of the ribbon.

If the longitudinal magnetic field is applied during the heat pulse, the slope of H_c curves increases versus the pulse number, which means that longitudinal field (similarly to the traditional heat treatments) promotes the H_c decrease (see **Figure 6.**). In these experiments 0.08 s pulse length is applied. In such circumstances (≈240 °C peak temperature) grain nucleation and growth is excluded, only stress relaxation is the uncial mechanism in the Hc lowering. The role of the longitudinal field is similar at higher, 0.1 pulse length (see **Figure 7.**), but after successive 0.12 s pulses, the value of H_c is identical with that obtained after 1h isothermal heat treatment at the appropriate temperature ≈ 400 °C (reaches the Hc measured in nano-crystalline state) (see **Figure 6.**).

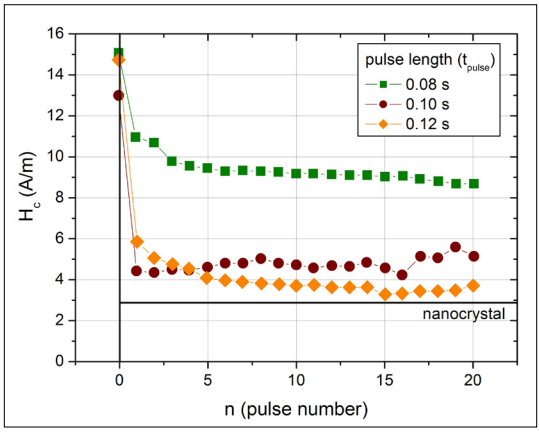

Figure 4. *Coercivity change versus the applied pulse number in the case of different pulse length (peak temperature).*

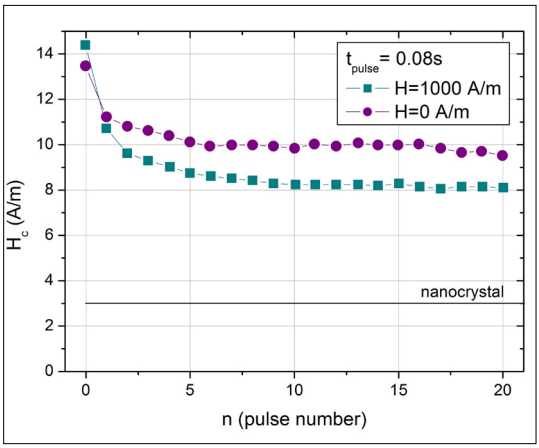

Figure 5. *The role of 1000 A/m field on H_c evolution during the series of 0.08 s length pulses.*

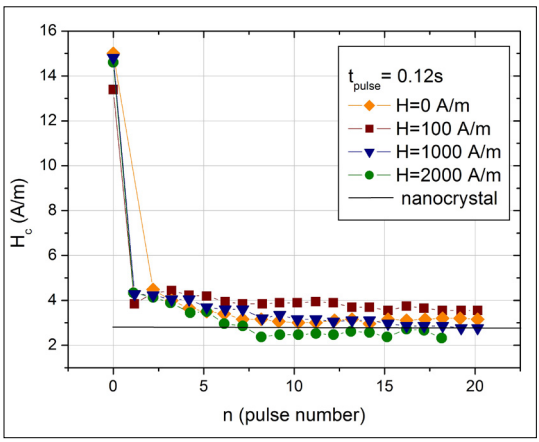

Figure 6. *The influence of field strength on H_c during the series of 0.12 s length pulses.*

3.3. Pulse heat treatments in axial field and load

From a thermodynamic point of view the metallic glasses are a single phase homogeneous continuum. In spite of this, many physical properties do exhibit significant macroscopic anisotropy (difference in mechanical properties in longitudinal and rectangular direction, or the difference in the mechanical response to the hydrogen absorption at the opposite side of ribbon surfaces).

Such effects hint at the difference between the local cooling rate on the opposite side of ribbons. One can suppose a coupling between the local cooling rate, the population density and distribution of the quenched-in stress centres, which can be coupled with the stress sensitive properties like Hc or even the quenched-in anisotropy. Such tendencies can be recognized in the **Figure 7**, where the coercive force is monitored during the series of pulse annealing of FINEMET alloys.

The measurement was carried out also in a longitudinal magnetic field and under longitudinal mechanical stress. As **Figure 7** shows, the H_c of quenched ribbons (0 pulse) slightly decreases, when longitudinal field or stress was applied during the measurements due to the small positive magnetostriction of this alloy. The role of longitudinal field and load is obvious: It is remarkable, that H_c breaks down due to the applied load already after the first impulse (peak temperature ≈330 °C, 0.1 s pulse length) approaches the value of completely nano-crystallized structure in spite of the obvious absence of nano-crystalline structure at this temperature.

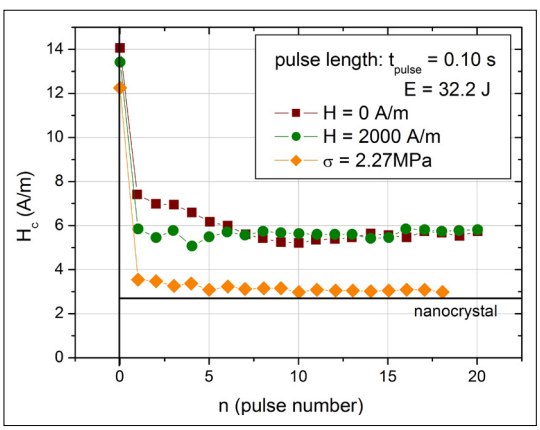

Figure 7. *The evaluation of H_c versus the series of isotherm pulses during the independent measurements-longitudinal field and stress were also applied.*

3.4. The origin and evolution of brittleness of glassy alloys

Several atomic level mechanisms do contribute to the evolution of brittleness in metallic glasses. The significant brittleness difference between metallic glasses originates partially from the different composition or from the various thermal history **[21]**. The brittleness of Fe-based as quenched glasses arise dominantly from the metalloid contents which ensures simultaneously the sufficient glass forming ability (mainly the B, P and Si content). Hence, the ductility or the degree of brittleness **[18]** is mainly composition specific in transition metal-metalloid based glasses, i.e. no direct relation exists between the crystal nuclei formation and the brittleness evolution. A typical example is the Fe100-xBx binary system. When the hypo- and hyper-eutectic glasses (low and high B-content) are compared, the hyper-eutectic glasses are less flexible (more brittle) in spite of the perfectly X-ray amorphous nature of ribbons. The reason is the increasing covalent bonding character with the increasing B-content in the hyper-eutectic region of Fe100-xBx glasses. In general, the tendency of brittleness is in direct correlation with the hardness (HV) of the as quenched Fe-B samples **[21]**. Increasing brittleness is also experienced at the crystallization onset, being also supported by the high resolution diffraction techniques.

The theoretical treatment of brittleness evolution is based on the free volume theory of glass formation **[22, 23]**. The macroscopic shear viscosity is supposed to describe the connection between the shear viscosity $\eta(T)$ and the average free volume v per atom. ΔG_m is the activation energy of displacement, v^* the critical free volume fluctuation, γ a geometrical factor between 0.5 and 1, and C is a constant:

$$\eta(T) = CRTexp\left(-\frac{\Delta G_m}{RT}\right)exp\left(\frac{\gamma v^*}{v}\right) \qquad (1)$$

This macroscopic tendency of viscosity change is considered as the phenomenological background for the evolution of brittleness in the rapidly quenched sample. According to **[22, 23]**, there is a coupling between the kinetics of annealing out of the quenched-in free volume and the brittleness. The free volume is cooling rate dependent, resulting stress gradient across the sample thickness.

According to the outlined consideration, the evolution of brittle behaviour is the consequence of different rates of free volume annihilation

between opposite surfaces, which also manifested in the spontaneous deformation of the samples during heat treatments.

In the case of the investigated FINEMET alloys the development of (magnetically and mechanically) hard particles precipitates at high temperature (T_{anneal} ≈ 600 °C) so this sudden increase of brittleness (see in **Figure 8.**) seems to arise from relaxation (T_{anneal} ≈ 330 °C). The outlined considerations are experimentally supported by the **Figure 8.** The change of brittleness versus the pulse number for various pulse length is illustrated in **Figure 9.** The series of 0.08 sec pulse length (max. peak temperature is around 240 °C) the flexibility of ribbons is sustained over the entire period of pulse series (20 pulses) i.e. no brittleness can be detected. In spite of this, significant H_c decrease occurs during the same circumstances (see **Figure 5.**). In contrast, when the pulse length is slightly increased (pulse length 0.09 s, with peak temperature of 292 °C) sudden breakdown of flexibility is experienced even after the first pulse. As the pulse length approaches 0.1 s, the brittleness also approaches the values obtained after isothermal heat treatments. According to the **Figures 8** and **9** the temperature of heat treatment has a dominant role in the degree of brittleness, the duration of heat treatment has only secondary significance.

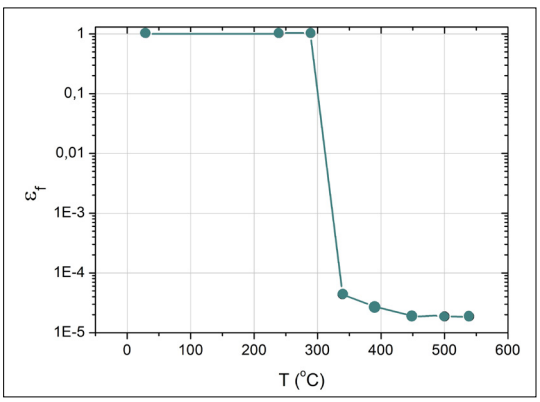

Figure 8. *The change of brittleness of FINEMET sample during isothermal heat treatments.*

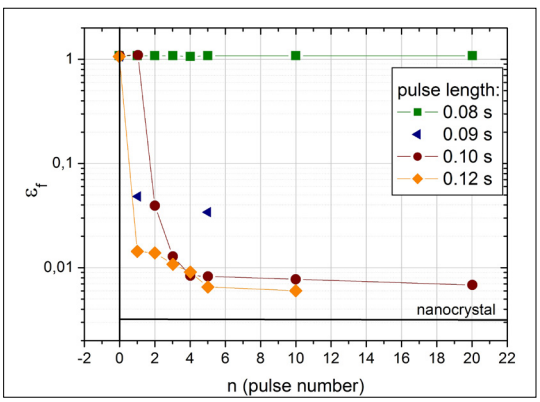

Figure 9. *The change of brittleness of FINEMET sample versus the pulse number for various pulse length.*

The degree of brittleness is generally lower in the case of pulse heat treatments (compare **Figure 8** and **9.**).

4. Conclusions

The impact of traditional (isotherm) impulse and stress annealing was compared in the property evaluation of FINEMET alloys. Pulse and stress annealing (as well as their combinations) were carried out inside in a magnetometer, where the magnetic measurements were carried out after each pulses, in-situ. The temperature of pulse heat treatments was regulated with the length of current pulse. In the experiments a coercive force lowering and HV increase can be detected already during the structural relaxation phase, however a more significant HV increase and H_c decrease is experienced only after partial crystallisation. During the research, the following conclusions were drawn:

Significant (more than 50 %) H_c lowering can be detected during structural relaxation (below 300 °C) in FINEMET type precursor alloy, without the appearance of crystal nuclei formation.

The contribution of heat treatment temperature is predominant in the degree of H_c lowering and also in embrittlement evolution.

Solely short range atomic rearrangements are responsible in both of property changes.

The impact of longitudinal stress is similar to the effect of a longitudinal magnetic field during heat treatment, i.e. the decrease of coercive force (H_c) accelerates, when the annealing in magnetic field and external mechanical stress are simultaneously applied.

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