Journal of Molecular Structure 1160 (2018) 360–367

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Investigation of the influence of pretreatment parameters on the surface characteristics of amorphous metal for use in power industry

Jolanta Nieroda [a, *], Andrzej Rybak [b], Grzegorz Kmita [b], Maciej Sitarz [a]

[a] AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Department of Silicate Chemistry and Macromolecular Compounds, al. Mickiewicza 30, 30-059 Krakow, Poland
[b] ABB Corporate Research Center, ul. Starowislna 13A, 31-038 Krakow, Poland

ARTICLE INFO

Article history:
Received 19 December 2017
Received in revised form
29 January 2018
Accepted 29 January 2018
Available online 3 February 2018

Keywords:
Amorphous metal
Surface degreasing
Annealing
Plasma treatment

ABSTRACT

Metallic glasses are metallic materials, which exhibit an amorphous structure. These are mostly three or more component alloys, and some of them are magnetic metals. Materials of this kind are characterized by high electrical resistivity and at the same time exhibit very good magnetic properties (e.g. low-magnetization loss). The above mentioned properties are very useful in electrical engineering industry and this material is more and more popular as a substance for high-efficiency electrical devices production. This industry area is still evolving, and thus even higher efficiency of apparatus based on amorphous material is expected. A raw material must be carefully investigated and characterized before the main production process is started.

Presented work contains results of complementary examination of amorphous metal Metglas 2605. Studies involve two ways to obtain clean and oxidized surface with high reactivity, namely degreasing followed by annealing process and plasma treatment. The amorphous metal parameters were examined by means of several techniques: surface free energy (SFE) measurements by sessile drop method, X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), and both ex situ and in situ Raman spectroscopy. Additionally, influence of plasma parameters on wetting properties were optimized in systematic way with Design of Experiments (DOE) method.

A wide range of used methods allow to fully investigate the amorphous metal material during preliminary preparation of surface. Obtained results provide information about appropriate parameters that should be applied in order to obtain highly reactive surface with functional oxide layer on it.

1. Introduction

As a daily requirements for electrical energy are higher and higher, the electrical engineering industry is still evolving. Due to economic and environmental aspects, a low cost production and high-efficiency of electrical devices is mandatory, therefore a new kind of materials and design solutions are applied to e.g. production of transformers among others. Nowadays, an amorphous metal, made by rapid cooling of melted alloy, is a very popular material for transformer core production [1]. Such a material is characterized by a lack of long-range crystalline order and thus it is called also metallic glass [2]. From application point of view as a transformer core material, it exhibits easy magnetization and high electrical resistivity [1,2]. In order to obtain the best magnetic properties of transformer core the amorphous metal is used in a shape of thin ribbon, like the Metglas foil [3]. It is characterized with ductility, flexibility and high magnetic permeability [4], and it is widely used as core material in distribution and special transformers in both oil-immersed and dry types [5]. When amorphous core is compared with standard silicon steel core, it can be found that amorphous core has lower saturation induction [1] and much lower losses, for example reduced core loss up to 70% [5]. Lower losses cause higher efficiency of working transformer and provides money saving. Besides economic benefits, it is also obvious, that amorphous metal-based transformers are environmentally friendly and allow to reducing carbon dioxide emission, due to much lower no-load losses in the power grid [5,6]. It was found, that the environmental impact of amorphous metal distribution transformers is only 40% of impact of standard transformer [1]. In order to achieve useful transformer core made of amorphous metal, the metal has to

* Corresponding author.
E-mail address: jolanta.nieroda@agh.edu.pl (J. Nieroda).

https://doi.org/10.1016/j.molstruc.2018.01.081
0022-2860/

be annealed in the presence of external magnetic field, which eventually reducing the quenching stresses created during casting of the alloy and induce the magnetic anisotropy along the desired direction of magnetisation [2,7,8]. As the heat treatment is an obligatory step, numerous research has been done in order to determine the influence of temperature, time and magnetic field on the final properties of amorphous core made of e.g. Fe-Si-B alloys manufactured by Metglas. Some of them concerned the aging of amorphous material [9–11], others studied the crystallization process [12–14], and all of them examined a variation of the magnetic properties of amorphous core after heat and thermo-magnetic treatment.

The presented work is focused on examination of the surface of amorphous metal ribbon Metglas 2605, which followed degreasing process, oxidizing during the annealing as well as plasma treatment. All these operations aimed at obtaining cleaned, oxidized surface with high reactivity and wettability, and the presented approach is novel since other published literature data do not provide such detailed information on the surface characterization of the Metglas 2605 ribbon. It is however critical, from the perspective of other technological operations, which relays on the state of surface, e.g. consolidation of amorphous metal, similarly to the one presented in Ref. [15]. Therefore it is necessary to have an effective pretreatment method to control it.

2. Materials and methods

The examined material was an amorphous, iron-based metal ribbon Metglas 2605, supplied by Metglas® Inc. It is a 23 μm thin foil with one glossy and one mat side, and chemical composition of it is as follows: 85–95% of iron, 5–10% of silicon and 1–5% of boron by weight [3]. The samples were degreased, annealed (oxidized) and plasma treated. Degreasing process was carried out using the two types of ultrasonic cleaners, namely Elmasonic S 30 (H) (Elma Schmidbauer GmbH), with 37 kHz frequency and 320 W power, and Emmi 40 HC (EMAG Polska), with 45 kHz frequency and 250 W power. The latter one had additionally a possibility to adjust 50%, 75% and 100% of the power. Two types of cleaning solvents were used, namely: ethanol 96% (POCH) and acetone analytical grade (POCH).

Both degreasing and plasma treatment were controlled by SFE measurements based on sessile drop technique, using a Drop Shape Analyzer – DSA 25 (Kruss) and the Owens-Wendt-Rabel-Kaelble (OWRK) method. SFE values provided information about enhancement in reactivity of the surface, which was desirable as high as possible. Samples of 3 μl of liquids were used for testing and the dosing rate was 100 μl/min [16].

Samples were annealed in air at 300 °C at different times: 2 h, 24 h, 72 h and 7 days, and then were analyzed by XPS, SEM and Raman spectroscopy. The selected temperature was high enough to obtain a useful oxide layer on the surface while being lower than the Curie temperature.

Surface analysis by XPS method was done using a Vacuum Systems Workshop spectrometer with Mg anode and 12 V applied voltage. The penetration depth was approximately 5 nm, and the spectral lines were matched with the use of XPSPEAK 4.1 program.

SEM observations were carried out using the NOVA NANO SEM 200 scanning electron microscope (FEI EUROPE COMPANY) coupled to the EDS detector (EDAX). As the samples were conductive, they were tested without additional preparation.

Amorphous structure of tested material after the annealing process was controlled with PANalytical diffractometer using K_α radiation from Cu anode. Bragg-Brentano setup was used and all measurements were carried out at room temperature, with the 0.007° step size at 2θ scanning range and the 145 s of measurement time for each step.

Raman spectroscopy was performed with the use of both ex- and in situ method. Ex situ Raman characterization was made using a LABRAM 800HR spectrometer equipped with an Nd-YAG laser of 532 nm wavelength. The used range was 50–1400 cm^{-1} with acquisition time of 30s and 1800 grooves/mm. In situ measurements were done for 2 h annealing at room temperature, 150 °C, 200 °C and 300 °C. Analysis was carried in the TS1500 stage from Linkam, placed in Jobinn-Yvonne's Labram HR confocal micro-Raman unit based on Czerny-Turner's monochromator. Long distance optical objective (50×, NA = 0.5), 532 nm laser and Synapse CCD detector (1024) were used with the grating rate of 1800 [grooves/mm]. Samples of amorphous metal ribbon were mounted on a ceramic wool filter placed inside the ceramic heating element in TS1500 cell. Reaction cell's parameters such as: temperature, rate of heating and cooling were controlled with Linksys program, whereas Labram HR was managed by Labspec 6.

Surface activation by plasma treatment was done using a PlasmaActivate 50 plasma chamber (Plasma technology GmbH) equipped with oxygen generator and argon gas. Tests were performed according to Design of Experiments (DOE) method [17], and the influence of four factors, namely: time, power, pressure and gas combination, were examined for wetting properties with polar solvent. Tested parameters were as follows: 1 min and 5 min of plasma treatment, 10% or 80% of maximum available plasma power (2 kV), 0.1 mbar and 0.4 mbar working pressure and gas combinations 90% of argon with 10% of oxygen or 10% of argon and 90% of oxygen.

All measurements, except for XRD measurements, were performed at both glossy and mat side of the amorphous ribbon.

3. Results and discussion

3.1. Degreasing process

The amorphous ribbon samples were cleaned with two types of solvent, namely ethanol and acetone, in the preliminary step. No positive effect was observed, when surface free energy of the cleaned samples was compared to the reference sample (Table 1). However, the average SFE value at both sides was slightly higher for acetone, therefore this kind of solvent was eventually chosen for further cleaning process. In the next step, the two types of ultrasonic cleaners were used and samples were degreased in acetone for 5 min in both of them. Additionally, 50%, 75% and 100% power of Emmi cleaner was also checked. After 5 min of ultrasonic cleaning it can be found (Table 1.), that only the Elmasonic device provided the enhancement of SFE for both sides of sample.

The time of degreasing was prolonged to 15 min and after this, about 40% relative increase of SFE for glossy and 35% for mat side was obtained (Table 2).

Additionally, polar and dispersive components of SFE were obtained and their percentage of SFE was calculated (Table 3). When we compare presented results, we can observe that after 15 min degreasing in Elmasonic cleaner, polar to dispersive ratio is almost the same for both sides. In a consequence the difference between glossy and mat sides was reduced, what allow to choose 15 min as the appropriate time for cleaning process. Another important information is wetting properties of polar solvent, because this kind of solution will be usually used in the future examinations. After degreasing, water contact angle was 55.04°(±2.65) for glossy side, while 50.42°(±1.03) was obtained for the mat side of the sample.

3.2. Oxidiation process

The surface of the amorphous metal is full of oxides and