Structural relaxation of Al–W amorphous thin films

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Abstract

The pronounced variation of the electrical resistivity of the amorphous Al–W thin films observed during initial heating above room temperature was examined. Both isochronal and isothermal treatments were performed in order to investigate the effects of the film composition, substrate material, and substrate temperature, on the magnitude of the relaxation phenomena. Regarding the isochronal heating, it was observed that the relaxation effects decreased with an increase of the heating rate, and decreased with the aluminum content in the film. The Al78W22 amorphous thin films were subjected to isothermal annealing for 6 h at a temperature of 515 °C. The effects of the substrate material (alumina ceramic, glass and sapphire), and the deposition temperature (LNT, RT, 200 and 400 °C) were examined. The relaxation decreased in a sequence of: alumina ceramic–glass–sapphire substrates, as well as with an increase of the substrate temperature. An assumed dominant role of the aluminum in the effects observed, was tested by the corresponding investigation of Al–Ti and Cu–Ti amorphous thin films.

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1. Introduction

The amorphous alloys of highly electrically conductive metals and refractory transition metals, such as the Al–W alloys, are very interesting as to their practical application to modern technology [1]. These alloys can be used as a diffusion barriers [2], and they exhibit very good corrosion properties [3,4].

From a scientific point of view, the investigation of the properties of these alloys is of general interest because their composition is close to the widely investigated early transition–late transition metal (TE–TL or simply TM) based amorphous alloys.

For the application of these alloys, it is important to investigate their thermal stability. The best method for the investigation of the changes of the structure in these alloys, is a monitoring of the changes of the electrical resistance R (i.e. the resistivity $\rho$) upon heating [5,6]. The resistivity measurement results, correlated with the structural changes obtained by an X-ray diffraction (XRD)
investigation, allow a fairly comprehensive insight into the heat-induced structural transformations.

The crystallization kinetics of the amorphous Al\textsubscript{100-x}W\textsubscript{x} films (75 < x < 80) upon isochronal heating were reported elsewhere [7]. The onset of the dynamical crystallization of these alloys was observed at temperatures $T_x$ well above 500 °C, which indicates that the amorphous structure of the Al–W films is rather stable in the concentration range investigated.

However, a rather high and irreversible rise of the resistivity in the amorphous Al–W films upon the first heating cycle below $T_x$, was observed. The effect was attributed to the relaxation of the amorphous structure. This paper shows that, below $T_x$, the resistivity depends on the heating rates upon the isochronal heating, the film composition, the duration of isothermal heating, the temperature of the substrate during the deposition of the films, and the surface quality of the substrate.

Detailed results for the temperature dependence of the resistivity of the amorphous Al–W films below room temperature (RT) were published elsewhere [8]. The resistivity in the Al–W films is rather high, ranging from about 200 $\mu\Omega$cm in the Al\textsubscript{80}W\textsubscript{20} alloy, to about 400 $\mu\Omega$cm in the Al\textsubscript{72}W\textsubscript{28} alloy. The temperature coefficient of the resistivity at room temperature, $d\rho/dT$, is negative, and of the order of magnitude of $10^{-4}$ K\textsuperscript{-1}. High values of the resistivity, and a negative $d\rho/dT$, are in accordance with the Mooij correlation [9], which is characteristic for the amorphous alloys. Furthermore, the temperature dependence of the resistivity of the amorphous AlW alloys from 20 K to RT, can be expressed [8] in terms of a weak localisation of electrons, which is characteristic for a highly resistive TE–TL amorphous alloys [10].

In what follows, the values of resistivity are normalized to the values obtained at room temperature (prior to the heating cycle).

The observed difference in the temperature dependence of the resistivity in a TM-based alloys, and the Al-based films, upon the initial heating, can be attributed to the effects of the Al sp- and TM d-electron interactions. In order to confirm such an assumption, the results obtained were compared with the results of the investigation of Al–Ti and Cu–Ti amorphous films.

2. Experimental

The amorphous Al–W thin films were prepared using a simultaneous d.c. sputtering of both pure components in a multiple source sputtering apparatus described elsewhere [11,12]. In case of the Al–W alloys, the entirely amorphous films were prepared in the composition range between Al\textsubscript{80}W\textsubscript{20} and Al\textsubscript{80}W\textsubscript{30}. For the isochronal heating, the films were produced by the deposition onto the alumina ceramic maintained at the liquid nitrogen temperature (LNT). For the isothermal heating, the Al\textsubscript{78}W\textsubscript{22} films were prepared on the alumina ceramics, sapphire and glass substrates at the LNT, while on the substrates kept at the room temperature, 200 and 400 °C, respectively, the films were prepared on the alumina ceramic, only. The substrates were of a disk shape with the diameter of 1 cm, and about 0.3 mm thick. In order to ensure the lateral homogeneity of the deposited films, the substrate holder rotated during the deposition. The temperature variation of the resistivity of the samples prepared in such a manner, below RT, does not depend on the arbitrary position of the current or voltage contacts, which is an indication of their macroscopic lateral homogeneity. The thickness of the films was in the 1–3 $\mu$m range. The composition of the alloys was estimated from the measurements of the deposition rates and, for the Al–W alloys, it was tested on several samples using a proton induced X-ray emission (PIXE) method. The estimated uncertainty of the film composition is about 10% relative to the minor component. The structure of the as-deposited films, as well as of the annealed ones, was determined by the X-ray diffraction method using a Philips PW 1820 vertical goniometer with a mono-chromatized CuK\textsubscript{α}-radiation.

The resistivity measurements were performed using the four-probe method and the standard ac technique, and the electrical noise was <1 part in $10^4$. For the high temperature measurements, the contacts were a tungsten rods spring-loaded directly onto the films. The distance between the voltage contacts was 2 mm and the backlash of each rod was about 50 $\mu$m. Thus, an intermittent noise, which was due to the mechanical displacement of the spring-loaded contacts during
heating-cooling cycle was a greatest source of measurement error. The maximum possible error from the contact displacements was 5% (as is indicated in the figures). The exact thickness of the films investigated is of no importance, since all the results obtained were normalized to the electrical resistance at the room temperature.

In case of the isochronal heating, the measurements were performed in a vacuum chamber at the pressure of about $10^{-3}$ Pa. The samples were radiatively heated.

For the isothermal measurements, a tubular furnace heater (40 cm in length) through which a quartz tube (150 cm in length) was inserted, was used. The sample was initially placed as far as possible from the heated region. The tube was filled with a continuous flow of the Ar gas. The sample was inserted in the center of the furnace after the desired temperature was obtained. Because of a rather high mass of the substrates, a time interval of $\approx$1 min was required to obtain equilibrium, and a stable temperature of the films. The temperature difference between the centre of the film and its edges was found to be about 0.5 °C at 500 °C.

After either isochronal or isothermal heating of the samples, no traces of the oxidation of the films were detected by the subsequent X-ray diffraction examination.

3. Results

3.1. The relaxation effects during the isochronal heating

A characteristic dependence of the resistivity on temperature during the isochronal heating and cooling of the as-deposited amorphous Al$_{80}$W$_{20}$ films, is illustrated in Fig. 1. The approximate value of the temperature at the onset of the dynamical crystallization of the Al–W film is marked by $T_x$. As seen, the resistivity of the Al–W amorphous film increases upon crystallization.

In order to compare the temperature dependence of the electrical resistivity $\rho$ in the Al–W films and the TM-based amorphous alloys, the temperature dependence of $\rho$ in the as-quenched Ni$_{80}$B$_{18}$Si$_{12}$ amorphous alloy, was added in Fig. 1. The Ni$_{80}$B$_{18}$Si$_{12}$ alloy has been prepared by a standard rapid quenching from the melt. In such an alloy, the expected drop of the resistivity upon crystallization, was observed. At the same time, no significant influence of the relaxation effects upon resistivity in the amorphous phase, was observed. Such a general behaviour of the resistivity upon heating is characteristic for the TE–TL or the TM-metalloid alloys [5,13,14], and is quite different from the resistivity behaviour in the Al–W based alloys.

Fig. 1 shows that the resistivity in the Al–W film initially decreases with the increase of temperature, which usually occurs below room temperature [8]. At a somewhat higher temperature, the dependence of the resistivity is influenced by the interplay of the relaxation of the amorphous structure and the temperature dependence of the resistivity of this changing structure. Therefore, $d\rho/dT$ could be either positive or negative.

Fig. 2 illustrates the temperature dependence of the resistivity in the as-deposited Al$_{80}$W$_{20}$ alloys on the isochronal heating, for three heating rates. It was observed that, for slower heating rates, i.e., when there was time enough for a more complete relaxation, the resistivity continuously increased.
with the increase of temperature up to \( T_x \). This indicates that, for low heating rates, the relaxation effects govern the changes of the resistivity. For higher heating rates, the relaxation effects are somewhat delayed, and the temperature dependence of the resistivity resumes the low temperature behaviour, i.e., \( d\rho/\rho dT \) turns negative once again. The above-named temperature dependence of the resistivity is irreversible, as expected.

The dependence of the resistivity on temperature during the isochronal heating (with the same heating rate \( dT/dr = 4 \text{ K/min} \)) in three Al–W films of a different composition, is shown in Fig. 3. The corresponding XRD patterns of the as-deposited films are given in Fig. 4. It is evident that the relaxation effects influencing the resistivity, strongly depend on the film composition, and decrease with a decrease of the aluminum content. However, the initial structure of all three films seems to be fairly similar, exhibiting a very broad diffraction maxima (at \( 2\theta \approx 40^\circ \)) with an effective grain size below 4 nm. However, the pre-peak growth (at about \( 2\theta \approx 24^\circ \)) with an increase of the Al content, was observed. Its origin is unclear to us for the time being.

The dependence of the temperature variations of the resistivity on the maximum temperature in the heating cycle, for the Al\(_{75}\)W\(_{25}\) alloy, is shown in Fig. 5. The sample film was heated successively during the three heating cycles (with \( dT/dr = 2 \text{ K/min} \)) with the increasing maximum temperatures of 300, 420, 520 °C, respectively. At the fourth step, the sample was heated up to 730 °C, i.e.,
above $T_c$. The film structure was tested after heating up to 520 and 730 °C, respectively. The corresponding XRD-patterns are given in Fig. 6. Following each heating cycle, the room temperature value of the resistivity was higher than the preceding one. Furthermore, the temperature dependence of the resistivity on the subsequent heating cycle initially followed the temperature dependence of the resistivity during the cooling in the preceding cycle. At 520 °C, the XRD pattern still showed a broad, but somewhat narrower maximum (Fig. 6(b)). After the heating at 730 °C, the sample crystallized (Fig. 6(c)).

3.2. The effects of the isothermal heating

The $\text{Al}_{78}\text{W}_{22}$ films were isothermally annealed for 6 h at a temperature of 515 °C, which was slightly lower than the temperature at which the onset of the dynamical crystallization was observed ($\approx 550$ °C). After cooling to the room temperature, the amorphicity of the films was tested by the XRD, and no traces of the crystalline phases were observed.

A characteristic dependence of the resistivity on temperature and time in the $\text{Al}_{78}\text{W}_{22}$ films upon the annealing, is presented in Fig. 7. The time dependence of the film temperature was determined by the experimental set up and the substrate thickness. Therefore, the behaviour of $\rho$ up
to 200 °C was affected by a period of time necessary to obtain a selected temperature in the center of the furnace, i.e., by the heating of the sample at the end of the furnace. The temperature dependence of \( \rho \) in the range of temperatures between 200 and 515 °C, was induced by the mass of the substrate, i.e., the time-period which is necessary for the film to reach the equilibrium temperature.

The time dependence of the resistivity of two \( \text{Al}_{78}\text{W}_{22} \) films during the annealing for 6 h, at a temperature of 515 °C, is presented in an insertion to Fig. 7. An arbitrary physical quantity \( p \) in the amorphous materials during the relaxation, usually follows the empirical equation

\[
p - p_0 = (p_0 - p_s) \exp\left[-\left(\frac{t}{\tau}\right)^n\right]
\]

[15], where \( p_0 \) is the value at the time = 0, \( p_s \) is the saturation value at the infinite time, and \( 0 < n < 1 \). The results for the time dependence of the resistivity of the Al–W films upon the isothermal annealing (Fig. 7), are in a qualitative agreement with the above equation with \( 0.5 < n < 0.7 \). However, the values for \( \tau \) strongly depend on the fitting procedure. This could be explained by the uncertainty in the initial conditions. Otherwise, a more detailed analyses ought to be performed within the framework of a distribution in the relaxation times [15].

3.3. The effects of substrate temperature

The observation that the annealing of the Al–W films, at somewhat high temperatures, results in the stabilization of the amorphous structure, leads to further investigations of the dependence of films properties on the substrate temperature during the film deposition. The resistivity changes upon the heating in three \( \text{Al}_{78}\text{W}_{22} \) films deposited at LNT and temperatures of 200 and 400 °C are illustrated in Fig. 8. The films were deposited onto alumina ceramic substrates of the same surface quality. They were all annealed for 6 h at a temperature of 515 °C. The annealing effects, as observed by the resistivity measurements, decreased with the increase of substrate temperature during the deposition of the films, and in the film deposited at 400 °C, the relaxation effects on \( \text{d} \rho/\text{d}T \) become evident only close to that temperature. Such results are to be expected, since the higher the substrate temperature, the stronger the relaxation of the amorphous alloy during the production.

Fig. 8 shows that a rather stable amorphous Al–W alloys can be prepared by codeposition onto the substrate maintained at the elevated temperature. The additional stability of the amorphous structure can be improved by the subsequent annealing of the samples at higher temperatures.

3.4. The effects of substrate material

The relaxation effects in the films deposited on the three alumina ceramic, two sapphire and one glass substrate, are illustrated in Figs. 9 and 10. The representative XRD patterns of the as-deposited films onto different substrates are given in Fig. 11, exhibiting the same feature, a very broad maximum. After the films reached the temperature of 515 °C, they were annealed for 6 h at that temperature. From the increase of the resistivity during the annealing, it can tentatively be concluded that the relaxation effects decrease in a sequence of alumina ceramic–glass–sapphire substrates, which is apparently related to the deposition surface roughness and/or thermal coefficient of the substrate expansion (through the stress induced...
relaxation). The effects of the substrate material needs to be investigated further.

3.5. The isochronal heating of Al–Ti and Cu–Ti amorphous films

In order to test the influence of the aluminum content on the resistivity in the Al-transition metal alloys, the temperature dependence of the resistivity on the isochronal heating in the as-deposited amorphous Al–Ti and Cu–Ti films, was studied. The films were deposited onto alumina ceramic substrates at the LN temperature using the same method as for the Al–W films. For these films, only the ratio of the cathodic currents during the deposition was denoted, which indicated a relative concentration of the alloy components.

The temperature dependence of the resistivity of three amorphous Al–Ti, and three amorphous Cu–Ti films, is shown in Fig. 12. At lower temperatures, $\frac{d\rho}{dT}$ is negative for all the samples. At a temperature of $\approx200 \, ^\circ C$, the resistivity in the Al–Ti films begins to increase with the increase of the temperature. As in case of the Al–W films (Fig. 3), the increase of $\rho$ with $T$, increases with the Al content. However, the resistivity of the Al–Ti films decreases during the crystallization, which is in contrast to the behaviour observed in the Al–W films.

At the same time, the resistivity of the as-deposited Cu–Ti films decreases rapidly and continuously with the temperature increase (with the exception of a kink, at about $500 \, ^\circ C$, in the film with the cathodic current densities 1:3.5).
4. Discussion

A possible explanation for the large increase of resistivity in the Al–W films during the initial heating, as well as the comparison of the results obtained for the Al–W films with those usually observed in the TM based amorphous alloys, is given below. It is known that Al can form quasicrystals with transition metals, as well as the decagonal approximants, in which the resistivity may be very high, and even of a non-metallic type. Therefore, in such alloys, the increase in the structural order (from amorphous to quasicrystalline alloys or decagonal approximants) may result in a major increase of the resistivity [16–18]. In the amorphous alloys, the structural relaxation increases the short range order, which is generally reflected in the increase of the density of the alloys. At the same time, the electronic structure of the Al–TM alloys, and their electronic transport properties, are strongly influenced by the sp–d electronic interaction [19,20], where the d-electron wave functions have strongly varying radial component. Therefore, a small changes in the interatomic distances and the increase in both topological and chemical short range order during the process of the relaxation, may seriously affect the changes in the transport properties.

Concerning the alloy composition, Fig. 3 shows that the relaxation effects influencing the resistivity strongly depend on the film composition and decrease with the decrease of the aluminum content. At the same time, the initial structures of the alloys (apart from the pre-peak at 2θ ≈ 24°) seem to be fairly similar. At present, we are not prepared to correlate the relaxation effects observed through the resistivity results to the structure of the alloys. We can only speculate that, for the tungsten content high enough, when the sp–d hybridization is well-established throughout the alloy, the electronic properties become less sensitive to small structural changes which occur during the relaxation.

Finally, the results for the isochronal heating of Al–Ti and Cu–Ti alloys (Fig. 12) suggest that the relaxation effects (observed by the resistivity changes in the Al–W films) are characteristic for the Al-based amorphous alloys, i.e., that the variation of the sp- and d-electron interactions is the cause of the large resistivity change on the relaxation of the amorphous structure.

5. Conclusions

Amorphous Al–W thin films prepared by a co-sputtering technique exhibit a pronounced irreversible variation of the electrical resistivity (due to the structural relaxation) upon initial heating above room temperature. It was found that the relaxation effects, obtained by resistivity measurements, and observed during the isochronal heating, decreased with an increase of the heating rate. For the slow heating rates, the temperature coefficient of the resistivity, after turning positive, may remain positive up to the crystallization temperature. However, for the fast heating rates, the relaxation could be delayed, so that dρ/dT remained negative up to Tc. The relaxation effects also decreased with a decrease of the Al concentration.

Following the isothermal annealing of the Al78W22 films (prepared on different substrates and at different substrate temperatures) for 6 h at the
temperature of 515 °C, the films were still XRD-amorphous, i.e., with no traces of crystallinity. It was observed that the relaxation effects significantly decreased with an increase of the substrate temperature during the deposition of the films, and that rather stable films could be prepared at higher temperatures requiring no subsequent annealing. Concerning the substrates, the decrease of the relaxation effects in the sequence alumina ceramic–glass–sapphire substrates, could be related to the deposition surface roughness (and related film in-homogeneity), and to the substrate thermal expansion properties.

A strong influence of the structure relaxation on the resistivity in the Al–W films might be due to the aluminum component. The relaxation of the amorphous structure generally results in a change of the interatomic distances and increase of the chemical short range order. These two parameters strongly determine the sp–d electron interaction, and subsequently the electronic structure and electrical resistivity in the Al–TM alloys. The preliminary results obtained for Al–Ti and Cu–Ti amorphous films support the above-mentioned suggestion.

References