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IDENTIFICATION OF NANOSTRUCTURE IN ALUMINIUM ALLOYS BY X-RAY DIFFRACTION

IDENTYFIKACJA NANOSTRUKTURY W STOPACH ALUMINIUM Z UŻYCIEM DYFRAKCJI PROMIENIOWANIA RENTGENOWSKIEGO

A number of physical properties of polycrystalline materials, including the mechanical properties, greatly depend on grain size and therefore grain size is a very important parameter in the technology of modern structural materials. Adaptation of optical microscopy in evaluation of crystallite size is frequently limited by basic parameters of this technique, and the result represents only a small area of the specimen surface. Therefore, it has been decided to use an alternative method in evaluation of the crystallites size. The method determines the width of the X-ray diffraction reflections according to a relationship expressed by Scherrer's formula. Easy analysis of the large material volume seems to be significant advantage of this method. The size of the crystallites was calculated by mathematical modelling of the profiles of small-angle diffraction reflections obtained by the Bragg-Brentano technique. The applicability range of this method was established along with the conditions indispensable for its correct application. The described method was used to determine the size of crystallites in the selected aluminium products, in ribbons made by the process of rapid solidification, and in nanometric materials prepared from commercial aluminium alloys. The results obtained were compared with optical microscopy and transmission electron microscopy, and showed enough by the X-ray measurement satisfactory consistency of the measured quantities.

Keywords: X-ray diffraction, nanometric materials, size of crystallites, Scherrer's formula

Wiele właściwości fizycznych, w tym właściwości mechaniczne materiałów polikrystalicznych w istotny sposób zależą od wielkości ziarna i dlatego rozmiar ziarna jest znaczącym parametrem w technologii nowoczesnych materiałów konstrukcyjnych. Zastosowanie mikroskopii świetlnej do oceny wielkości krystalitów jest ograniczone możliwościami technicznymi, a wynik uzyskiwany jest z niewielkiego obszaru powierzchni próbki. Do oceny wielkości krystalitów przyjęto metodę alternatywną, poddająca analizie szerokość rentgenowskich refleksów dyfrakcyjnych zgodnie z zależnością wyrażoną wzorem Scherrera. Niekwestionowaną zaletą metody dyfrakcyjnej jest łatwość analizy znacznej objętości materiału. Pomiar wielkości krystalitów zrealizowano przy użyciu modelowania matematycznego profili niskokątowych refleksów dyfrakcyjnych {111} uzyskanych w technice Bragg-Brentano. Określono również zakres stosowalności metody i warunki niezbędne do prawidłowego jej użycia. Opisaną metodą oznaczono wielkość krystalitów w wybranych wyrobach aluminiowych, w taśmach wytwarzanych metodą szybkiej krystalizacji oraz w nanometrycznych preparatach sporządzonych z komercyjnych stopów aluminium. Uzyskane wyniki zweryfikowano przy użyciu mikroskopii świetlnej i elektronowej wykazując zadowalającą zgodność oceny mierzonych wielkości.

1. Introduction

The significant progress in technology of modern engineering materials has been observed since many years. Considerably reduced grain size, which often does not exceed even 100 nm [1–4], that is up to about 250 layers of the elementary cells in a crystal lattice of aluminium, has improved materials properties. The size of grains in modern technology is an important parameter affecting the value of lower yield point (the yield stress) R_{eL} [5] in a manner expressed by the Hall-Petch formula [6–8] (equation 1).

$$R_{eL}(d) = \sigma_i + \frac{k}{\sqrt{d}} \quad , \tag{1}$$

where: R_{eL} – lower yield point [MPa], k – a materials constant for given temperature and deformation rate (the resistance of grain boundaries), d – average size (the mean diameter) of a grain or subgrain, σ_i – the yield

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stress (the starting stress for dislocation movement, the friction stress of active dislocations).

The effective use of metallographic methods for the grain size evaluation is often difficult due to the insufficient magnification of optical microscopes when examining the structure of some ultra-fine grain materials. An alternative technique to estimate the size of the crystallites is the X-ray diffraction method, based on an analysis of the diffraction patterns. The X-ray method is suitable for estimation of the size of crystallites of any arbitrary dimensions from glass to monocrystals.

2. The description of a method for estimation of the crystallite size

The X-ray technique for estimation of the crystallite size consists in interpretation of the intensity distribution of diffraction reflections. The width of a diffraction reflection originating from an arbitrary $\{hkl\}$ planes depends on the crystallite size in exposed polycrystalline material according to a relationship expressed by Scherrer's formula [9–11] (equation 2).

$$B_{0.5} = \sqrt{B_m^2 - B_a^2} = \frac{k \cdot \lambda}{D_{hkl} \cdot \cos\theta} \quad , \tag{2}$$

where: $B_{0.5}$ – the width of a reflection, $FWHM$ [rad], B_m – the measured width of a reflection, $FWHM$ [rad], B_a – constant reflection broadening due to diffraction geometry [rad], k – Scherrer's constant, $k \in [0.85 \div 0.99]$, λ – the length of X-ray wave [nm], D_{hkl} – an average size of crystallites in direction normal to the specimen surface [nm], $2 \cdot \theta$ – the diffraction angle of X-ray wave [°].

From Scherrer's formula it follows that large crystallites give diffraction reflections characterised by small half-width. The reflections become broader when the diffraction takes place in refined crystallites. In crystallites of the size not much larger than that of an elementary cell, broad reflections of small amplitude are formed, which makes their identification very difficult.

3. The results of the estimation of an average crystallite size

The size of crystallites was estimated on a number of samples taken from different products made from aluminium and its alloys (Table 1). Subsequently the distribution of $\{111\}_{Al}$ diffraction reflection intensities was measured using a D8 Advance (Bruker) X-ray diffractometer. The examinations of the obtained diffraction patterns led to a conclusion that crystallites of the largest size are formed in products extruded on presses. In 10 μm thick aluminium foil, the crystallites size was 8 μm, while in a H19 cold-rolled strip, the crystallites had the size from 1.7 μm to 3.7 μm, depending on the specimen section selected for analysis. Crystallites of even smaller size (from 250 nm to 600 nm) were found in a fine-grain slurry of alloy 7475 and in the layers of pure aluminium (150 nm) applied in vacuum onto substrates activated by the technique of corona discharge.

TABLE 1

The results of estimation of an average crystallite size

No.	Name of product	Alloy grade	Examined plane	Approximate average crystallite size
1.	Rod 6082 ⌀ 21.5 mm	AlMgSi1Mn	cross-section	20.8 μm
2.	Rod 7475 ⌀ 6 mm (RS extruded)	AlZn5.5MgCu	cross-section	17.8 μm
3.	Aluminium foil 0.010 mm	Al99.5	different sections	8.0 μm
4.	Rod 7475 ⌀ 20 mm	AlZn5.5MgCu	cross-section	6.0 μm
5.	Strip 3104 H19 0.3 mm	AlMn1Mg1Cu	strip surface ND	3.7 μm
6.	Strip 3104 H19 0.3 mm	AlMn1Mg1Cu	longitudinal section TD	3.3 μm
7.	Strip 3104 H19 0.3 mm	AlMn1Mg1Cu	cross-section RD	1.7 μm
8.	Chips 7475 (RS processing)	AlZn5.5MgCu	surface	2.3 μm
9.	Slurry 7475	AlZn5.5MgCu	layer of sediment	600 nm
10.	Slurry 7475 (Al_2O_3 contaminated)	AlZn5.5MgCu	layer of sediment	250 nm
11.	Coating on polyester foil 0.2 μmAl/25 μm	pure Al*	metal-coated surface	150 nm

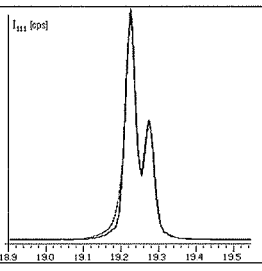
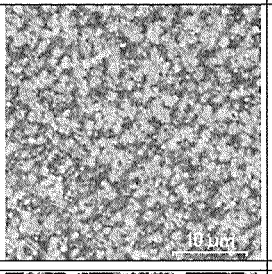
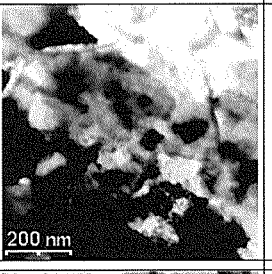
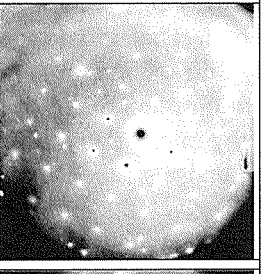
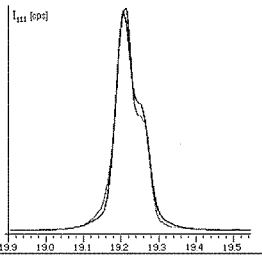
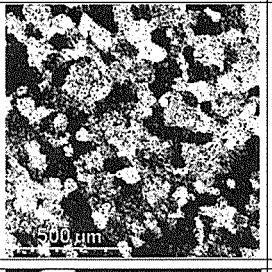
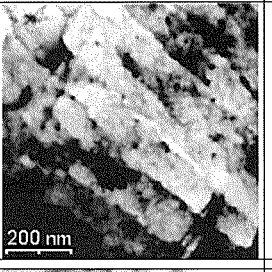
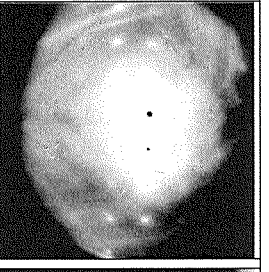
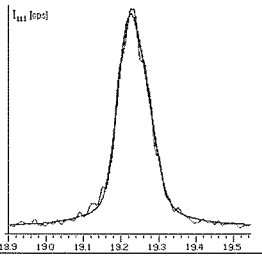
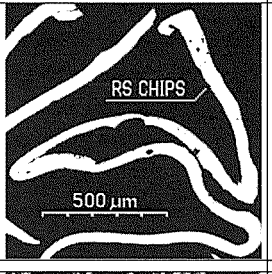
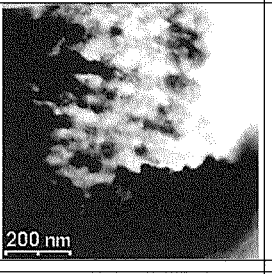
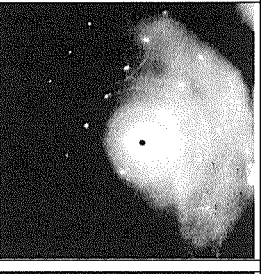
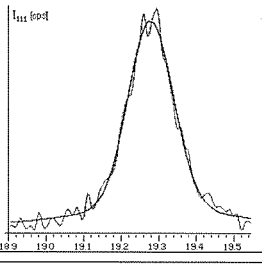
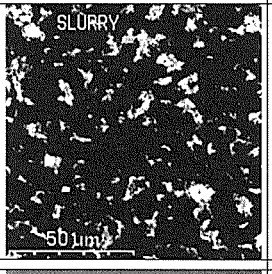
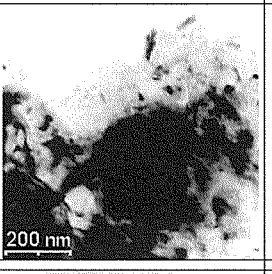
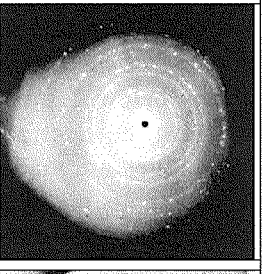
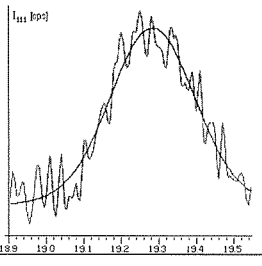
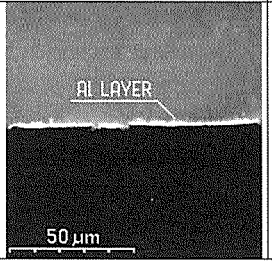
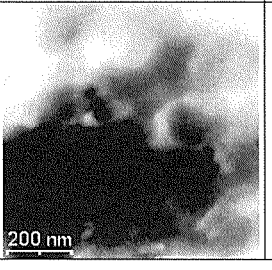
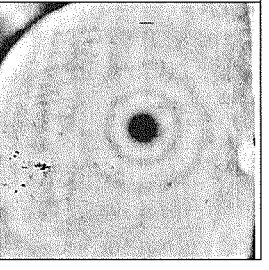
* Notes: The purest, commercially available, aluminium grade containing 99.98% Al is designated as 1098. The domestic industry produces aluminium containing 99.7% Al, and it is designated as 1070.

4. Comparison of the results of crystallite size estimation

The selected results of the X-ray estimation of the crystallite size were compared with the results obtained by two independent research methods. The first one was the metallographic method, where the average size of grains was measured by means of the OLYMPUS GX71 optical microscope. The second method, that is transmission electron microscope, included the microstructure and electron diffraction analysis using a TESLA BS 500 microscope (Table 2).

TABLE 2

A comparison of the results obtained in determine of an average crystallite size D

	D	Technique			
		X-ray diffraction	Optical microscopy	Electron microscopy	Electron diffraction
Rod 7475 made RS	17.8 µm				
Std. rod 7475	6.0 µm				
Chips 7475 RS	2.3 µm				
Slurry 7475	600 nm				
Pure Al coating	150 nm				

5. Summary

Using three independent research methods, the size of the crystallites was examined in specimens of the selected aluminium products, with satisfactory consistency obtained between the individual results. Using an optical or electron microscope, it is possible to examine the structure on a surface area of 100 μm^2 or even smaller one, receiving images of much higher resolution with electron microscope. The results of the crystallite size estimation by the method of the X-ray diffraction analysis are obtained from an area of about 100 mm^2 with an effective X-ray penetration into the specimen to a depth of 0.01 mm. That is why, an undeniable advantage of the X-ray diffraction method is the analysis material surface about 6 orders of magnitude larger than the surface available by microscopy methods. This makes the results of X-ray analysis much more representative, especially the method gives results from the significant volume of the examined material. A special case of error in an interpretation of the grain or crystallite size is the grain morphology or dendritic structure of products subject to plastic working, where the result of the grain size evaluation depends on a section of the examined specimen. In products rolled or extruded, the grains of the smallest surfaces were observed on the cross-sections, perpendicular to the direction of plastic working.

As a result of the studies carried out so far it has been observed that with increasing magnification of the microstructure images the difficulty in distinguishing the grain or crystallite boundaries increases. This difficulty often results in erroneous distinction of the grain boundaries within strongly defected areas of high dislocation density.

The application of diffraction technique in estimation of the crystallite size gives the results leaving no room for misinterpretation as there is a considerable broadening of the diffraction reflection in crystals of dimensions below 1 μm. During the studies it has been proved that the electron diffraction patterns of the 150 nm crystallites are made up of a extremely spread reflection leading to broad and continuous rings. The electron diffraction patterns of the 1 μm crystallites are composed of the diffraction patterns rings with an effect of fragmentation or with a discrete spots, while the electron diffraction patterns of the 10 μm crystallites are no longer composed of the rings but always comprise a discrete spots. The difficulty in producing and keeping the nanostructure in products fabricated from commercial aluminium alloys is mainly due to the high stacking fault energy in aluminium and its alloys [12]. Refining of granular structure increases the total surface of the grain boundaries as well as the total energy of the lattice defects. Additionally, the local accumulation of dislocations results in local high concentration of energy, and hence activation of recovery and recrystallisation processes within selected areas. An example of the described phenomenon is alloy 7475 (AlZn5.5MgCu), in which the crystallites of about 2 μm are formed due to rapid solidification. However the dimensions of crystallites are reaching 17 μm (Table 1). According to the theory discussed in [13], the formation and preservation of nanostructure in pure aluminium could have taken place only when the activation energy of a recrystallisation process would have been reduced, e.g. by reducing the internal energy on grain boundaries. In practice of nanomaterials fabrication using aluminium as a base product, a few percent alloying addition of the rare earth metals (lanthanum, ytterbium, neodymium, samarium, gadolinium, cerium) is usually introduced along with a few percent alloying addition of transition metals (the families of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel or copper) [14–17].

To verify the definition of grain, subgrain and crystallite used in metals science, an attempt has been made to identify these objects by means of different research methods. Consequently, it has been stated that the single grain observed at a small optical magnification may comprise as many as even 10000 subgrains. In this situation a question must arise if a grain, or a subgrain rather, is the object of measurements described by Scherrer's formula. The results of the measurements of the crystallite size in the examined specimens indicate that the size of crystallites is comparable with the size of subgrains, and under these circumstances the term "crystallite" can stand for the term "subgrain". Hence it has been concluded that the method based on Scherrer's equation serves for the measurement of the crystallite or subgrain size, in spite of the fact that various descriptions of this method use the "grain size measurement" formulation. It seems that this misunderstanding results from some drawbacks of the methods used in microstructure evaluation. The term "grain" denotes an object perceived by the examiner under some specific conditions. At a predetermined optical magnification, only the grain section in a strictly determined class of sizes can be seen. Moreover, the results of two-dimensional metallographic examinations made on a three-dimensional grain must unavoidably mean a significant simplification. An examination like this is disregarding some important stereological parameters, as well as the grain morphology. The size of the grains is commonly described by various stereological parameters, like grain diameter, mean grain diameter, or average grain diameter, or average grain volume, or average weighted volume. The parameter as such is called grain size or grain dimension.

The plastic deformation of true materials, is inseparably connected with the existence of dislocations and can be expressed as a function of dislocations density by the equation 3.

$$\tau = \tau_0 + \alpha G b \sqrt{\rho}\,, \tag{3}$$

where: τ – the stress of plastic deformation, τ_o – the stress of friction in a crystal lattice, α – a constant (0.05–1.5) depending on the hardening mechanism and lattice type, G – the modulus of shape elasticity, b – Burgers vector, ρ – the density of dislocations.

From a comparison of the Hall-Petch relationship (equation 1), with the formula expressed by equation 3 it follows that under the conditions of plastic deformation, a product of the grain diameter and dislocations density is constant for a given material. This can justify the application of dislocations density parameter for describing the grain size in a structure of nano- or ultra-fine grained materials.

6. Conclusions

1. The size of crystallites was determined in selected aluminium products, in strips made by Rapid Solidification, and in special fine-grained materials prepared from commercial aluminium alloys using the X-ray diffraction method. The results were compared with those obtained using optical microscopy and transmission electron microscopy, with satisfactory consistency between the values of the estimated quantities.
2. The X-ray diffraction method may be applied for estimation of crystallite size in aluminium products and in the case of optimisation of fabrication process of modern fine-grain alloys. The results of the crystallite size estimation conducted by the technique of the X-ray diffraction analysis valid for an area of about 100 mm^2, with radiation penetrating to a depth of 0.01 mm.

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