Crystal Diffraction Techniques Were Used to Investigate the Structural Properties of Some Aluminum Alloys.

Sukaina Iskandar Yusuf 1, Mohammed Muhana Meteab 2, Abdulkader Ahmed Annaz3

1. Department of Physical, Science college, Tikrit University
2, 3 Department of Mechanical, Engineering college, Tikrit University

Abstract: Due to the importance of these alloys in the manufacture of aircraft, coatings, radiation shields, and electronic circuits, the study's objectives include investigating previously unstudied structural properties of some aluminum alloys, alloy A (Al-Zn-Mg-Ti) and alloy B (Al-Zn-Mg-Mn) were prepared using the casting method, and their structural properties were studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques (granular size and theoretical density). The results of analyzing the X-ray diffraction data and determining the phases formed on the two alloys after matching them with the international standard cards (JCPDS) revealed that it is polycrystalline, with structures (cubic and hexagonal) on alloy A and structures (cube, hexagonal, and anorthic) on alloy B. The results revealed that the average grain size estimated by the Debye-Scherer method is less than that estimated by the Williamson-Hall method, and that the grain size of alloy A is less than that of alloy B due to the presence of titanium in alloy A's composition, which works to reduce particle size. The theoretical density of Alloy A and B that was used in X-ray diffraction was calculated. SEM analysis of the spherical shape of the grains on the surfaces of alloys A and B revealed that the average grain size on the surface of alloy A is smaller than on the surface of alloy B, which is consistent with the results of XRD analyses.

Keywords: X-ray diffraction (XRD), scanning electron microscopy (SEM), crystal structure, grain size, theoretical density.

1. Introduction:
Many times, especially in metals, the attributes of a solid substance are defined by the properties of the atom or atoms of the components that make up the material. As a result of the study of this system, a lot may be learned about the properties of matter in general. Aluminum alloys combine the features of the alloy's constituents, such as copper, zinc, magnesium, silicon, lithium, manganese, and others, to produce new structural, mechanical, and physical properties. Using crystal diffraction, it is possible to analyze the structural qualities and microscopic properties of these alloys, allowing them to be used in a variety of applications, such as aircraft and ships, coatings, protective barriers against electromagnetic radiation, and many more [1,2].

X-ray diffraction (XRD) is a powerful tool for studying and analyzing crystalline and amorphous materials. According to Bragg's Law, the wavelength of X-rays (λ) is equal to the distance between the atomic levels (d). The peaks that appear as a result of Bragg's reflections from parallel crystal surfaces are subject to Bragg's law, as shown below [3,4]:

\[ 2d \sin\theta = n\lambda \] .......(1)
2. Experimental procedures

2.1 Alloy preparation

After using a digital balance to determine the weight ratios of the elements included in the preparation of alloy A and B, which are shown in Table (1) the aluminum was first placed in the boat and entered the furnace at a temperature of 700°C. After its complete melting, the rest of the alloying elements were added after each element was coated with pure aluminum foil to isolate it from oxygen. and avoid combustion or oxidation) and dipped successively by tongs. The molten was mixed with an electric mixer at a speed (150 radian/min.) to ensure the homogeneity of the mixture. A carbon mold was heated to (250°C) and filled with the molten metal, which was then allowed to cool slowly. Both alloys were prepared using this process. There were (1 cm) diameter and (10 cm) height cylindrical samples obtained.

2.2 X-ray diffraction and microstructure:

In the Ministry of Industry and Minerals - Geological Survey and Mining, the prepared alloys were examined to determine the phases formed using a Japanese made X-ray diffraction device (XRD-7000) with voltage (40 Kv) and current (30 mA). All tests were conducted at room temperature and with angles ranging from 10 to 80 degrees. The obtained results and data were compared to the international standard cards (JCPDS).

Following the determination of the unit cell's lattice parameters (a, b, c), the volume of the unit cell for the crystal phases inferred from X-ray diffraction (XRD) was calculated using the following relationships [5,6,7,8]:

| Cubic : | \( V = a^3 \) ............... (2) |
| Hexagonal | \( V = \frac{\sqrt{3}}{2} a^2 c \) .............(3) |
| Anorthic | \( V = abc \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2\cos \alpha \cos \beta \cos \gamma} \) ...........(4) |

Furthermore, we investigated the surface formation of the samples using an electron diffraction technique with a scanning electron microscope (SEM) and estimated the grain size with a computer program (Image-J).

The following are some of the most essential traits that have been researched:

**First: calculate the theoretical density** (\( \rho_{x-ray} \)) for the phases inferred from the X-ray diffraction spectrum using the relationship [8]:

\[ \rho_{x-ray} = \frac{Z M_{\text{at}}}{N_a V} \] ...........(5)

Whereas:

- \( Z \): The number of atoms in a unit cell
- \( M_{\text{at}} \): molar mass
- \( N_a \): Avogadro's number
Second: Estimation of Grain size ($D_{sh}$) using the Debye-Scherer equation [5,8,9]:

$$D_{sh} = \frac{K\lambda}{\beta_r \cos \theta}$$  

Whereas:
- $K$: A constant value of about 0.9
- $\lambda$: The wavelength is 0.15406 nm.
- $\beta_r$: FWHM (Full width at half maximum) is a radian measurement
- $\theta$: X-ray angle of incidence in degree

Third: Estimation of the micro-strain of the crystal lattice by applying the Williamson-Hall equation [6,10]:

$$\beta_r \cos \theta = \frac{KA}{D_{WH}} + 4\varepsilon \sin \theta$$

Whereas:
- $\varepsilon$: the micro-strain of the crystal lattice

3. Results and discussion:

First. Phase properties: The structural properties of alloy A and B were studied using X-ray diffraction (XRD).

Figures (1) and (2) depict the X-ray diffraction patterns of alloys A and B, respectively, as the figure depicts the presence of four peaks for each alloy, indicating that it is polycrystalline (Hexagonal, cubic) for alloy A and (Hexagonal, Anorthic, cubic) for alloy B, and after matching the measured XRD examination values with the international standard cards (JCPDS), the phases whose characteristics were deduced in Tables (2) and (3) for alloy A and B, respectively.
The degree of crystallinity for alloys A and B was estimated to be (65.25) and (68.45), respectively, implying an increase in the regular arrangement of the atoms within the crystal structure, resulting in an increase in the X-rays reflected from the crystal levels and thus the rise of Bragg's peaks [11].

Second. Theoretical density (ρx-ray): The theoretical density was calculated from the X-ray diffraction spectrum of alloys A and B using equation (5), where we noticed a difference in the theoretical density of the phases due to differences in their structural properties from the molar mass (which depends on the atomic mass and atomic number of the elements constituting the single phase) and the size of unit cell. Tables (4) and (5) show the calculated values for the theoretical density.
The crystal structure of the phases formed in alloy A and B was drawn using the computer program (VESTA), as shown in the figure (3), after determining the crystal lattice parameters a, b, and c, knowing the crystal angles $\alpha$, $\beta$ and $\gamma$ from X-ray diffraction (XRD), and knowing the distance between the atomic levels.

**Table (4)**: Phase structural properties and theoretical density of alloy A

| Constituent phase | a (Å) | b (Å) | c (Å) | $\alpha$ (°) | $\beta$ (°) | $\gamma$ (°) | V (Å³) | Z | $\rho_{\text{x-ray}}$ (gm/cm³) |
|-------------------|-------|-------|-------|--------------|------------|-------------|--------|---|-------------------------------|
| AlMg$_2$Zn$_{11}$ | 4.96  | 4.96  | 14.02 | 90           | 90         | 120         | 298.70 | 1 | 4.69                          |
| TiO               | 3.031 | 3.031 | 3.2377| 90           | 90         | 120         | 25.76  | 1 | 4.12                          |
| Al$_{12}$Mg$_{17}$| 10.5438| 10.5438| 10.5438| 90           | 90         | 90          | 1172.17| 2 | 2.09                          |
| AlTi$_3$          | 5.77  | 5.77  | 4.62  | 90           | 90         | 120         | 133.21 | 2 | 3.06                          |

**Table (5)**: Phase structural properties and theoretical density of alloy B

| Constituent phase | a (Å) | b (Å) | c (Å) | $\alpha$ (°) | $\beta$ (°) | $\gamma$ (°) | V (Å³) | Z | $\rho_{\text{x-ray}}$ (gm/cm³) |
|-------------------|-------|-------|-------|--------------|------------|-------------|--------|---|-------------------------------|
| Mn$_2$O$_3$       | 9.4146| 9.4146| 9.4146| 90           | 90         | 90          | 834.46 | 16| 5.03                          |
| MgAl$_2$O$_4$     | 8.174 | 8.174 | 8.174 | 90           | 90         | 90          | 8.174  | 8 | 3.46                          |
| Al$_{11}$Mn$_4$   | 5.052 | 8.873 | 5.034 | 89.7         | 99.8       | 104.9       | 214.71 | 1 | 3.567                         |
| AlMg$_2$Zn$_{11}$ | 4.96  | 4.96  | 14.02 | 90           | 90         | 120         | 298.70 | 1 | 4.69                          |

The crystal structure of the phases formed in alloy A and B was drawn using the computer program (VESTA), as shown in the figure (3), after determining the crystal lattice parameters a, b, and c, knowing the crystal angles $\alpha$, $\beta$ and $\gamma$ from X-ray diffraction (XRD), and knowing the distance between the atomic levels.

**Fig. (3)** Phase crystal structure from X-ray diffraction (XRD)
Third grain size:
The grain size was estimated in the nanosize range of the phases resulting from X-ray diffraction of alloy A and B, respectively, using equation (6), and the results were included in the table (6) and (7), it was also estimated using equation (7), which takes into account the microscopic strain of the crystal lattice, as shown in the figure (4) and (5). When the results of the two methods were compared, it was discovered that the average grain size estimated by the Debye-Scherer equation is less than that estimated by the Williamson-Hall equation.

When the results of the two methods were compared, it was discovered that the average grain size estimated from the Debye-Scherer equation is less than that estimated from the Williamson-Hall equation. The reason for this is that the Williamson-Hall equation takes into account the effect of the microscopic strain of the lattice, which causes the locations of the peaks to shift to greater degrees from their original positions for the Bragg diffraction angles (2θ) in the standard card [10]. We also notice that the average grain size of alloy A is smaller than that of alloy B, which is due to the addition of titanium, which resulted in an improvement in atomic sizes (reducing the grain size of alloy A)

| 2θ (degree) | FWHM (βr) (degree) | Br, cosθ | D_{Sh.} (nm) |
|-------------|--------------------|----------|--------------|
| 38.0189     | 0.31293            | 0.29586432 | 0.418756368  |
| 44.26974    | 0.32271            | 0.298926109 | 0.397834308  |
| 64.65947    | 0.36386            | 0.307456025 | 0.321867857  |
| 77.81677    | 0.4517             | 0.351490915 | 0.238768567  |

\[ D_{ave.} = 0.344306775 \]

| 2θ (degree) | FWHM (βr) (degree) | Br, cosθ | D_{Sh.} (nm) |
|-------------|--------------------|----------|--------------|
| 38.06532    | 0.29619            | 0.279998134 | 0.442361767  |
| 44.30687    | 0.31782            | 0.294357687 | 0.40390215   |
| 64.09638    | 0.36704            | 0.311103873 | 0.320067705  |
| 77.8633     | 0.43444            | 0.337949201 | 0.248173294  |

\[ D_{ave.} = 0.353626229 \]
Fig. (4) Microscopic lattice strain of alloy A and average grain size estimated from the Williamson-Hall equation

The surface of alloys A and B was imaged using (SEM), as shown in Figures (6) and (7), as the images showed the spherical shape of the grains on their surfaces, and the computer program (Image-J) was used to analyze the images, providing us with a summary that includes the average area of the existing particles.

The average particle size (D) was obtained from the image, and the Gaussian distribution polygon was drawn, and a statistic of the rate of the particle size of the crystals on the surface of alloys A and B was made, and the results were included in the tables (8) and (9), respectively.

It was discovered that the grain size rate on the surface of alloy A is lower than the grain size rate on the surface of alloy B, which corresponds to the results of the XRD examination and for the same reasons stated previously.

Fig. (5) SEM image of alloy A with the frequency polygon plot of the Gauss distribution
**Table (8)**: shows the statistics of the average grain size of the crystals on the surface of the alloy A

| Diameter (nm) |
|---------------|
| Maximum | Median | Minimum | Sum | Standard Deviation | Mean | N total |
| 58.23 | 37.305 | 16.63 | 149.47 | 17.90495 | 37.3675 | 25 |

**Table (9)**: shows the statistics of the average grain size of the crystals on the surface of the alloy B

| Diameter (nm) |
|---------------|
| Maximum | Median | Minimum | Sum | Standard Deviation | Mean | N total |
| 85.67 | 37.38 | 24.78 | 185.2 | 27.03293 | 46.302 | 25 |

4. **Conclusions:**
X-ray diffraction (XRD) analysis of the structural properties of alloys A and B revealed that the alloy has a polycrystalline structure. Because the molar masses of the phases differ, there is a difference in the theoretical density of the phases produced by alloys A and B. Because of the presence of titanium in alloy A's composition, which reduces grain size, the rate of grain size is lower than that of alloy B. The average grain size estimated by the Debye-Scherer equation is smaller than the average grain size estimated by the Williamson-Hall equation. The reason for this is that the Williamson-Hall equation accounts for the effect of microscopic strain in the lattice, which causes the locations of the peaks to shift to greater degrees from their original locations for the Bragg diffraction angles (2θ) in the standard card. It was discovered that the grain size rate on the surface of alloy A is lower than the grain size rate on the surface of alloy B, which corresponds to the results of the XRD examination.

**References:**

1. Muhammad Salah al-Din Abbas Hamid, Ibrahim Musa Ibrahim, “Production and Manufacturing Technology”, Vol. 1, Third Edition, Scientific Books House for Publishing and Distribution, 2000.
2. Jaafar Taher Al-Haidari, "Engineering materials - an introduction to their properties and applications" University of Technology, 1995.
3. N. Fourikis, "5 - Beamformers," in Advanced Array Systems, Applications and RF Technologies, N. Fourikis, Ed., ed London: Academic Press, , pp. 325-353 , 2000.
4. Esraa Ahmed Mohammed, " A comparative study of the method of Williamson Hall and the pattern of cadmium oxide nanoparticles for X-rays " , Turkish Journal of Computer and Mathematics Education, Vol.12 No. 4, pp.881-889 , 2021.
5. M. Augustin and T. Balu, "Estimation of Lattice Stress and Strain in Zinc and Manganese Ferrite Nanoparticles by Williamson-Hall and Size-Strain Plot Methods", International Journal of Nanoscience, Vol. 16 , No. 03, 2017.
6. Yendrapati Taraka Prabhu," X-Ray Analysis by Williamson-Hall and Size-Strain Plot Methods of ZnO Nanoparticles with Fuel Variation" , World Journal of Nano Science and Engineering, Vol. 4 , No. 3 , pp 21-28 , 2013.
7. C. Kittel ," Introduction to Solid State Physics" , 8 th Edition , John Wiley &Sons , Inc., ISBN: 978-0-471-41526-8 , USA , 2004.
8. Christopher Hammond " The Basic of Crystallography and Diffraction", 3rd edition, International union of Crystallography. Oxford science publication, 2009.

9. Vinila V. S. " XRD Studies on Nano Crystalline Ceramic Superconductor PbSrCaCuO at Different Treating Temperatures", Crystal Structure Theory and Applications, Vol. 3, pp 1-9 , 2014.

10. Yendra pati Taraka Prabhu," X-Ray Analysis by Williamson-Hall and Size-Strain Plot Methods of ZnO Nanoparticles with Fuel Variation", World Journal of Nano Science and Engineering, Vol. 4, No.3, pp. 21-28, 2013.

11. O.G Senatorova," Influence of different minor additions on structure and properties of high-strength Al alloys", Materials Science and Engineering, Vol.331-337, 2000.

12. Nath, D.; Singh, F.; Das, R. ," X-ray diffraction analysis by Williamson-Hall, Halder-Wagner and size-strain plot methods of CdSe nanoparticles - a comparative study". Mater Chem. Phys., Vol.239, pp.1-9, 2020.

13. Sharma, G., Kumar, J., Sharma, S., Singh, G., Singh, J., Sharma, A., . . . Obaid, A. J. (2021). Performance of diesel engine having waste heat recovery system fixed on stainless steel made exhaust gas pipe. Materials Today: Proceedings.

14. F. Findik and K. Ermiş, “Thermal energy storage”, Sustainable Engineering and Innovation, vol. 2, no. 2, pp. 66-88, Jul. 2020.