ARCHIVES OF METALLURGY
Volume 48 2003 Issue 1

TOMASZ WEJRZANOWSKI*, WITOLD ZIELIŃSKI*, JERZY LATUCH*,
KRZYSZTOF J. KURZYDŁOWSKI*

A QUANTITATIVE DESCRIPTION OF CRYSTALLIZATION OF AlY AMORPHOUS ALLOY

ANALIZA ILOŚCIOWA KRYSTALIZACJI AMORFICZNEGO STOPU AlY

Transmission Electron Microscopy is an essential technique for imaging the microstructures at the nanometer scale. However, quantitative analysis of such images is not easy due to the nature of TEM contrast based on diffraction phenomena.

A quantitative description of the microstructure of melt-spun AlY ribbons has been carried out in the present work. TEM observations have revealed randomly distributed and oriented spherical nanometer crystals. In order to describe quantitatively their size and shape, images under different diffraction conditions were recorded.

These images have been analyzed using software for image analysis. The data have been compared to the results obtained by other techniques, such as *X*-ray diffractometry and differential scanning calorimetry.

Transmisyjna Mikroskopia Elektronowa jest podstawową techniką obrazowania mikrostruktury materiałów w skali nanometrycznej. Jednakże analiza ilościowa obrazów jest trudna ze względu na naturę kontrastu mikroskopowego opierającego się na zjawisku dyfrakcji elektronów w sieci krystalicznej materiału.

W niniejszej pracy przedstawione są wyniki analizy ilościowej mikrostruktury stopu AlY w postaci taśmy otrzymanej na drodze przechłodzenia ze stanu ciekłego. Obserwacje przeprowadzone za pomocą transmisyjnego mikroskopu elektronowego ujawniły przypadkowo rozmieszczone i zorientowane kryształy o wymiarach nanometrycznych. W celu ich ilościowego opisu zarejestrowano obrazy mikrostruktury przy różnych orientacjach preparatu względem wiązki elektronów. Analizę obrazów przeprowadzono za pomocą specjalnego programu komputerowego.

Wyniki przeprowadzonych pomiarów porównano z wynikami otrzymanymi za pomocą dyfraktometru rentgenowskiego oraz kalorymetru różnicowego.

Key words: Nanocrystallization; TEM; Quantitative description

* WYDZIAŁ INŻYNIERII MATERIAŁOWEJ, POLITECHNIKA WARSZAWSKA, 02-507 WARSZAWA, UL. WOŁOWSKA 141

1. Introduction

Increasing demand for high performance engineering components drives the development of advanced materials such as amorphous and nanocrystalline alloys. Al-based amorphous alloys containing lanthanide and transition metals [1] have been reported to exhibit tensile strengths in excess of 1 GPa [2]. This is about two times higher than the values for conventional crystalline Al-alloys. Research on these materials has found further stimulus from the finding that partially crystallized amorphous alloys, which contain nanocrystals in amorphous matrix, may display outstanding mechanical properties [3]. High cooling rates are needed for amorphisation of Al rich alloys due to a high tendency for crystallization. This can be exploited for obtaining partially crystallized materials directly from melt quenching [4]. Alternatively the glass is annealed to induce nanocrystalization [5].

In this investigation the computer image analysis, calorimetric and *X*-ray diffraction methods have been used for quantitative description of microstructure of nanocrystal-amorphous matrix composites (NCAMCs). The effect of annealing temperature on number, size, and volume fraction of Al nanocrystals that form during primary crystallization has been studied.

2. Experimental methods

Ingots of quaternary $Al_{85}Y_8Ni_5Cu_2$ alloys were prepared from a high purity elements by arc melting in an argon atmosphere. During melt spinning, the melt was ejected from the crucible on to a rotating copper wheel with peripheral speeds of from 25 to 40 m s^{-1}. This technique, allows quenching the melt with a rate of 10^5–10^6 K s^{-1}. The resulting ribbons were typically 2 mm wide and 28–40 μm thick. The microstructures of the ribbons were studied by X-ray diffraction (XRD) using CuK_α radiation and by transmission electron microscopy (TEM). Crystallization temperatures and released energy were determined using differential scanning calorimetry (DSC) working in continuous and isothermal heating modes. The volume fraction, V_V, of α-Al nanocrystals was estimated by the method described by Inoue et al [6]. TEM specimens were prepared by ion beam milling technique. The microstructure imaging has been conducted in STEM JEOL 1210 at 100 kV accelerating voltage.

The quantitative description of ribbons microstructures was performed using a special computer software. The stereological methods [7] (taking into account the special character of TEM images) were used to obtain volume fraction, V_V, number per volume unit, N_V, and average of equivalent diameter of α-Al nanocrystals, $E(d_3)$. Particles spatial arrangement was also quantified using linear covariance technique [8]. The foil thickness (needed to obtain N_V parameter) was estimated using the method of contamination cones built-up by the locked electron beam [9].

3. Results and discussion

Figure 1a illustrates XRD pattern obtained for the as-melt spun alloy. The pattern shows a broad diffused peak, which is typical of amorphous alloys. Figure 2a shows DSC curve for studied amorphous alloy. The curve reveals that the first peak is very broad and separated from the others. The process of nanocrystallization was carried out by an indirect method, i.e. by isothermal annealing of initially fully amorphous alloys at temperatures below the temperature of the onset of crystallization. The annealed samples retain the amorphous state and change into α-Al + amorphous composites. Figure 1b shows XRD pattern indicating the presence of some Al nanocrystals in the annealed ribbon. This was confirmed by microstructure examination using dark field TEM. Maximum value of V_V (~ 10%) was calculated from the DSC curve for samples annealed at 230°C for 30 min presented in Figure 2b. The lattice parameter of the Al phase obtained from XRD was 0.4053 nm. This value is larger than that of pure Al (0.4047 nm) indicating supersaturated solid solution state.

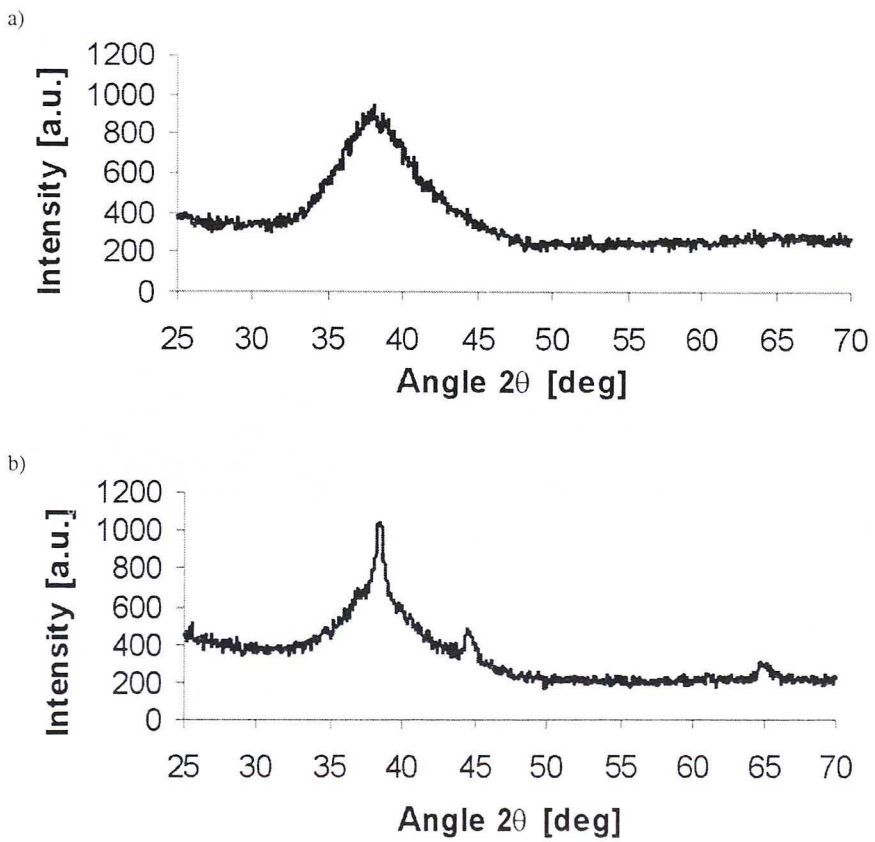

Fig. 1. XRD patterns of melt spun (a) and isothermally annealed (b) ribbons

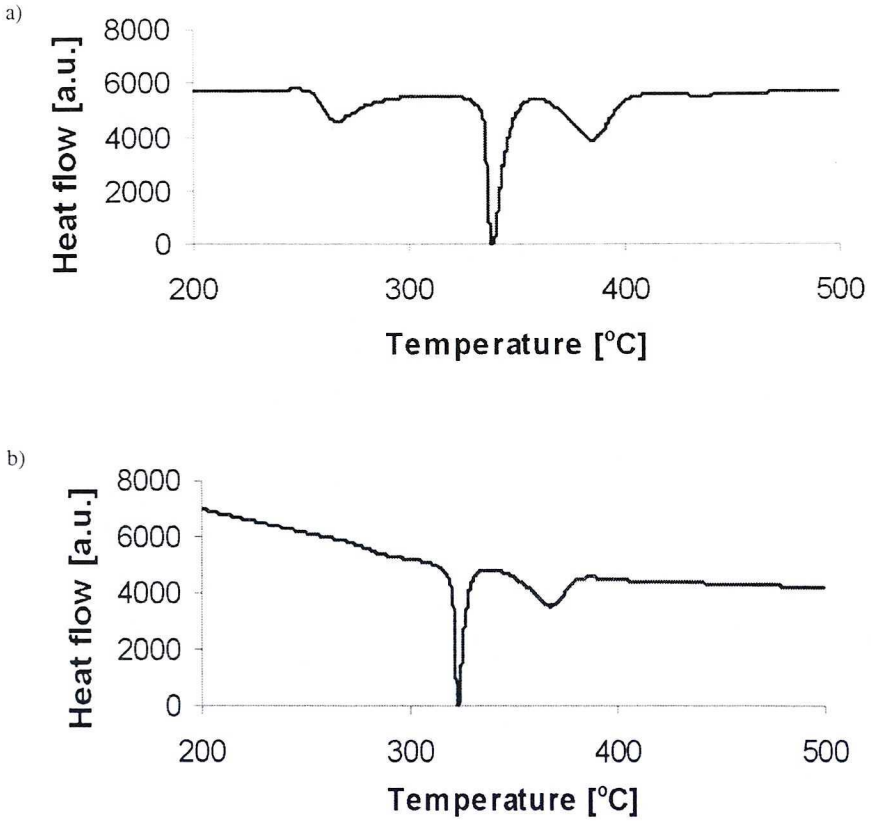

Fig. 2. DSC curves of melt spun (a) ribbons and isothermally annealed (b) ribbons

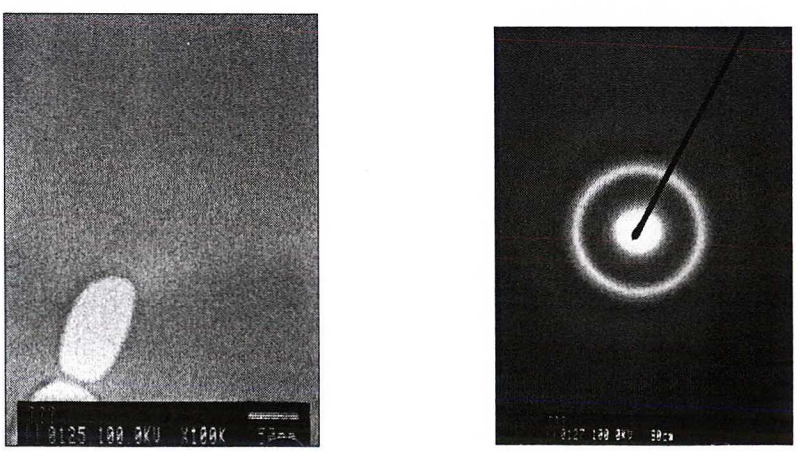

Fig. 3. TEM images of the microstructure of as melt-spun $Al_{85}Y_8Ni_5Cu_2$ ribbon. a) image of amorphous microstructure. b) diffraction pattern

Figure 3a, b presents a TEM image of the microstructure and the corresponding diffraction pattern of the as melt-spun $Al_{85}Y_8Ni_5Cu_2$ ribbon. A characteristic feature of the TEM contrast of amorphous structure and the diffused diffraction rings are present. Figure 4a, b shows a TEM bright field image and the diffraction pattern of the microstructure of as-annealed ribbon. Figure 4c shows a dark field image of the microstructure obtained

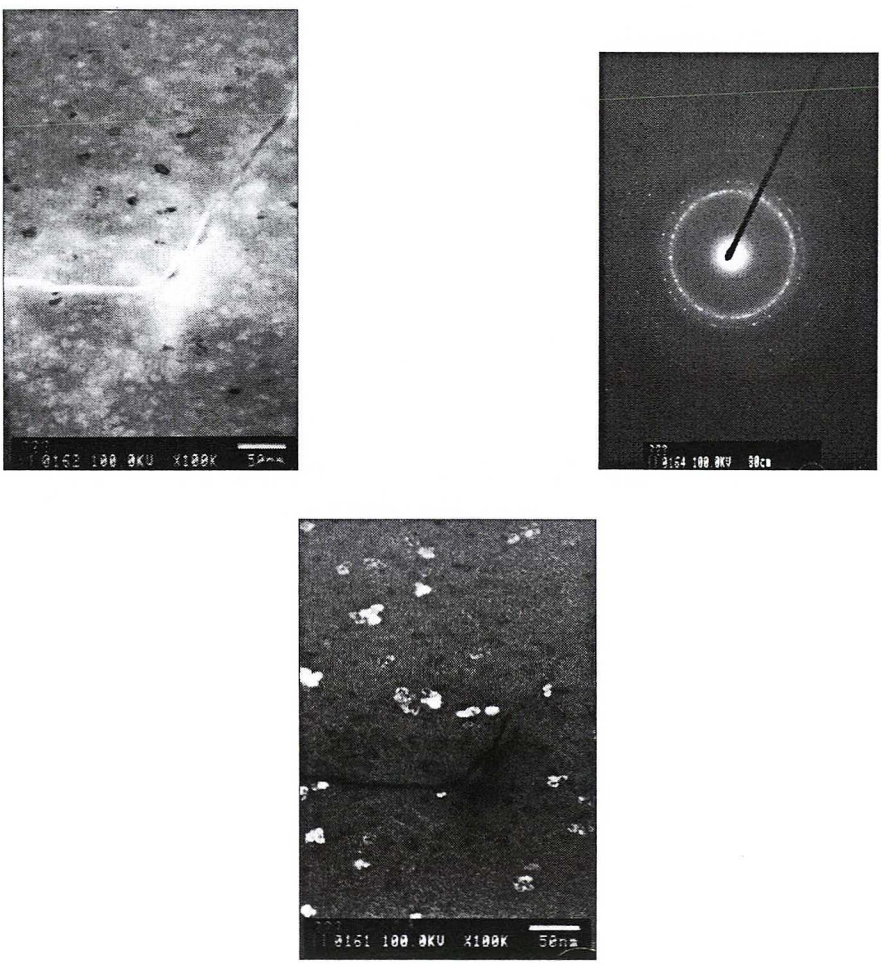

Fig. 4. TEM images of the as-annealed $Al_{85}Y_8Ni_5Cu_2$ ribbon. a) bright field image. b) diffraction pattern. c) dark field image

with use of the strongest ring in the diffraction pattern. Randomly oriented crystals are visible in amorphous matrix (in the center of the image a fracture in the TEM foil is present). Individual as well as clustered crystals are observed.

TABLE

V_V [%]	N_V [μm^{-1}]	$E(d_3)$ [nm]	$CV(d_3)$ [%]
~ 8	$2{,}2 \cdot 10^3$	~ 7	27

The image analysis results presented in Table show that the α-Al nanocrystals occupy about 8% of the whole volume of material and are very dispersed (high number of nanocrystals per unit volume, N_V). Nanocrystals have a small size (average of equivalent diameter, $E(d_3) \approx 7$ nm). The size distribution of α-Al particles presented in Fig. 5. shows that the size distribution of nanocrystals is relatively narrow.

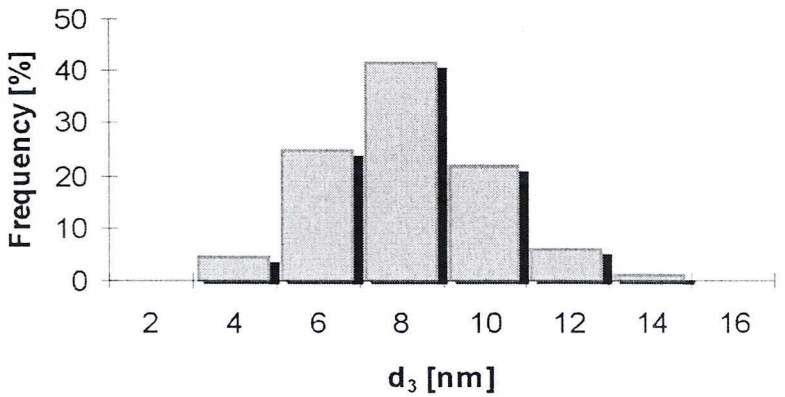

Fig. 5. Distribution of equivalent diameter of α-Al nanocrystals

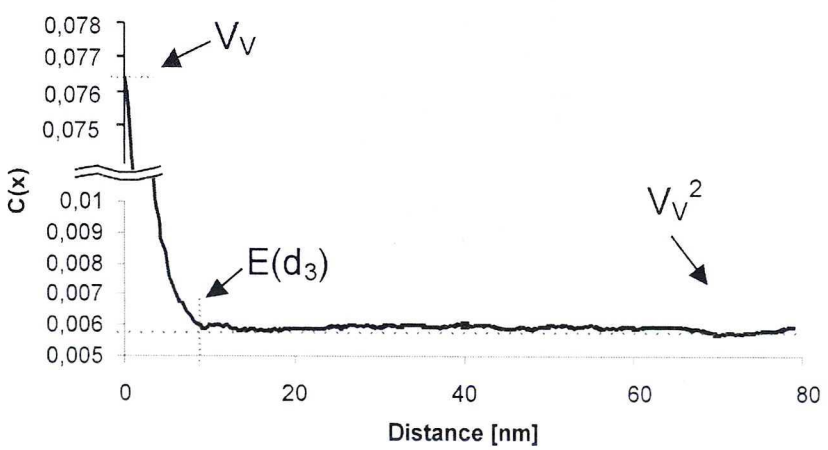

Fig. 6. Covariogram obtained for studied material

Figure 6 presents the covariogram for spatial position of nanocrystals of Al in amorphous matrix. The width of first height peak is determined by nanocrystals size and it confirms that the average size is about 7 nm. The height of this peak refers to the volume fraction of the α-Al nanocrystals and it is about 8%. The next part of curve is very smooth. It is typical of random spatial distribution of particles.

4. Conclusions

Quantitative analysis of TEM images analysis method, *X*-ray diffractometry and differential scanning calorimetry of the $Al_{85}Y_8Ni_5Cu_2$ microstructure after crystallization from amorphous state parameters have been obtained which are useful in the studies of the quantitative relation between structure and properties of the material in question.

Isothermal annealing of amorphous $Al_{85}Y_8Ni_5Cu_2$ alloy produced nanocomposite like structure consisting of a fine dispersion of α-Al crystallites in an amorphous matrix. It has been shown that nanocrystals of α-Al have an average size of 7 nm and random spatial arrangement.

Acknowledgements

The work has been supported by the Foundation for Polish Science under Scholar Grant Program and Polish State Committee for Scientific Research under contract 512G/1090/5150. Professor Jan Kozubowski is acknowledged for valuable remarks.

REFERENCES

[1] A. Inoue, Prog. Mater. Sci. **43**, 365 (1998).
[2] A. Inoue, M. Yamamoto, H.M. Kimura, T. Masumoto, J. Mater. Sci. Lett. **6**, 194 (1987).
[3] Y.H. Kim, A. Inoue, T. Masumoto, Mater. Trans. JIM **31**, 747 (1990).
[4] Z.C. Zhong, A.L. Greer, Int. J. Non-Equilibrium Process **11**, 35 (1998).
[5] J. Latuch, A. Kokoszkiewicz, H. Matyja, Mat. Sci. Eng. A **226–228**, 809 (1997).
[6] A. Inoue, H. Tomioka, T. Masumoto, J. Mater. Sci. **18**, 153 (1983).
[7] J. Ryś, Stereologia Materiałów 1995.
[8] T. Wejrzanowski, K. Rożniatowski, K.J. Kurzydłowski, 8th Congress for Stereology and Image Analysis. Bordeaux (2001).
[9] D.A. Rae, V.D. Scott, G. Love, The Metal Society, 57 (1981).

REVIEWED BY: JAN DUTKIEWICZ
Received: 17 November 2002.