Synthesis and Compaction of Al-based Nanopowders by Pulsed Discharge Method

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Abstract Synthesis and compaction of Al-base nano powders by pulsed discharge method were investigated. The aluminum based powders with 50 to 200 nm of diameter were produced by pulsed wire evaporation method. The powders were covered with very thin oxide layer. The perspective process for the compaction and sintering of nanostructured metal-based materials stable in a wide temperature range can be seen in the densification of nano-sized metal powders with uniformly distributed hard ceramic particles. The promising approach lies in utilization of natural uniform mixtures of metal and ceramic phases, e.g. partially oxidized metal powders as fabricated in our synthesis method. Their particles consist of metal grains coated with oxide films. To construct a metal-matrix material from such powder, it is necessary to destroy the hard oxide coatings of particles during the compaction process. This goal was realized in our experiments with intensive magnetic pulsed compaction of aluminum nanopowders passivated in air.

Keywords: Aluminium nano powder, Pulsed wire evaporation, Magnetic pulsed compaction

1. Introduction

Synthesis of nano metallic powders from atomic or molecular sources depends on the control of a variety of nanoscale attributes desired in the final product. In general, there are basically two broad areas of synthetic techniques for nano metallic powders, namely, physical methods[1] and chemical methods.[2] Several different physical methods are currently in use for the synthesis and commercial production of nano powders. The most widely used technique involves the synthesis of single-phase metals by the inert-gas evaporation technique.[3] The generation of atom clusters by gas phase condensation proceeds by evaporating a precursor material, either a single metal or a compound, in a gas maintained at a low pressure.

In this study, we used the pulsed wire evaporation (PWE) method for the synthesis of metallic Al nanopowder. The PWE method, which is a kind of inert gas phase condensation (IGC) method, is one of the most promising methods for the production of low-cost nanopowders. This method consists of dispersing a thin metallic wire as a high-power current pulse is passed through it.[4] When the high current passed

through the metal wire, it was heated up, over its boiling temperature, in a very short time of several microseconds and exploded. After it vaporized and met the surrounding gases like Ar, N_2, etc., the metal vapors condensed and formed powders with nano size. The brief sequence of this process is drawn in Fig. 1. It was recognized that a major factor determining the particle size after the PWE is superheating of the evaporated material.[5] When an energy in the order of or higher than binding energies is injected into the metal, all particles are formed from the vapor phase. It is possible to synthesize the nano metals,[6] oxides, nitrides, carbides and even alloy powders by controlling the atmosphere in the reaction chamber. The typical particle size of metal powders produced by the PWE method reduces substantially with increasing superheat of the metal, K = W/Ws (where W is the energy injected into the evaporating wire and Ws is the wire sublimation energy),[7] diminishes inconsiderable with decreasing wire diameter,[7] and decreases as the surrounding gas pressure is raised.[8] After synthesis of Al nanopowder by the PWE method, we characterize the size, shape of nanopowders with several methods.
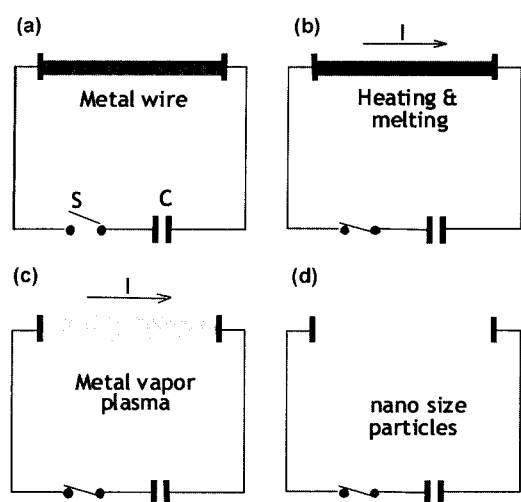
On the other hand, the interest to compact the

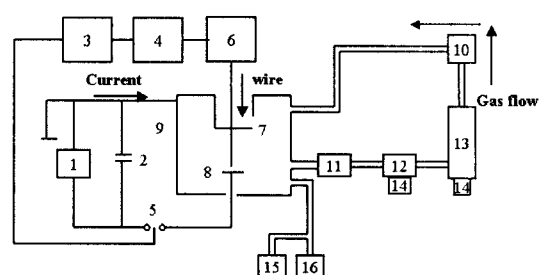Fig. 1. A brief mechanism of Pulsed Wire Evaporation (PWE) method.

Fig. 2. A schematic diagram of the PWE experimental setup. 1) power supply system, 2) capacitor battery, 3) trigger pulse, 4) control unit, 5) triggered switch, 6) wire feed unit, 7) exploding wire, 8) high voltage electrode, 9) explosion chamber 10) fan, 11) separator, 12) cyclone, 13) electrical filter, 14) hopper, 15) vacuum system, and 16) gas supply system.

nanostructured metal materials by pressing methods is increased because of attractive opportunities to create more stable structures, using nano-sized powders. The extensive researches in this direction were carried out with application of different methods of pressing.[9,10] The important aspect in the compaction for nanostructured materials is how to achieve full densification while simultaneously retaining a nanoscale microstructure. The relaxation of defective structure and grain growth under mechanical loading is probable, and resultantly, that is no more nanostructure. Therefore, the process to compact the nano powder with retaining the nano structure has been required strongly. The short duration time of high-pressure action realized in the pulsed compaction methods, allow to keep non-equilibrium nanostructured states and to apply considerably higher pressures. The known data to pressing nano-sized powders by high pulsed pressure testify an opportunity of getting extremely dense compacts with nanostructure and high mechanical properties.[11,12]

In this study, we prepared compacts of nano Al powders by magnetic pulsed compaction (MPC) method, and investigated the effect of the compacting temperature on the compressibility, microstructure, and mechanical properties.

2. Experiments

2.1. Synthesis of Al nano powders

The experimental setup shown in Fig. 2 consists of

a pulse power generator, reaction chamber, wire feeding system, electrical filter, gas supply system, blower, and so on. The starting material was pure Al wire (>99.9%) with the diameter of 0.45 mm. The feeding length of Al wire into the reaction chamber was 88 mm and the induced voltage was 26 kV.[13] A high purity (99.99%) of Ar gas of 4 bar filled the chamber to prevent oxidation of the powder. After synthesis, Al nano powders were collected through the cyclone and mechanic filter. A passivation of oxide coating was carried out to stabilize the powders. The passivation was done by slow oxygen filling with flow rate of 3 mL/min for 30 min.

Nano aluminum powders with micro-sized Al-P1 and nano sized Al-P2 contained oxide only in amorphous state, mainly as a film of about 2.5 nm in thickness, covering the metal particle.

2.2. Characterizations of nano-powders

The size and shape of the nano powders (Al-P2) were investigated by scanning electron microscopy (SEM, JEOL 6300) and transmission electron microscopy (TEM, JEOL 2000). X-ray diffraction (XRD, Rigaku D/MAX-3C) was conducted for phase analysis and grain size determination. We used the Hall-Williamson equation like equation (1) to determine the grain size of powder from the full width half maximum (FWHM) obtained from X-ray diffraction,

$$\beta cos\theta = \frac{k\lambda}{\delta + \epsilon\theta} \quad (1)$$

where, k is the Scherrer constant 0.94, β is the

FWHM, θ is the Bragg angle, λ is the wave length of X-ray, ε is the internal strain, and δ is the grain size.

X-ray photoelectron spectrometer (XPS, ESCA LAD 220I) and Brunauer-Emmett-Teller (BET, Micrometitics ASAP 2000) analyses were conducted for the investigation of the oxide layer on the Al powder and specific surface area, respectively. The average size of powder from the BET result, d_{BET}, was determined by equation (2) like below,

$$d_{BET} = \frac{6}{S_s \rho} \tag{2}$$

where S_s is the specific surface area of powder resulted from the BET measurement, and ρ is the density of powder. And we used the laser particle size analyzer (LPSA, BIC 90Plus) to determine the size distribution of nanopowders and compared each results.

2.3. Magnetic pulsed compaction and Characterization

A schematic diagram of the uniaxial magnetic pulsed compaction setup is shown in Fig. 3. Major components of the magnetic pulsed press include a flat helical inductor and a mechanical concentrator,

Fig. 3. A schematic diagram of the magnetic pulsed compaction equipment.

which are enclosed in a rigid O-shaped frame.[14] The pulsed force that compresses the powder inside the mold is generated as a result of the interaction between the pulsed magnetic field of the inductor and the concentrator's current-conducting surface. High-power current pulses to power the inductor are generated by discharging the energy storage capacitor with controlled triggering of the spark gap.

The amplitude of compaction pressure was about 1.5 GPa. With the purpose of removal of porous gases and adsorbed substances from a particles surface, the mold with the powder passed a degassing procedure with uninterrupted evacuation up to pressure 1 Pa, accompanied with a heating up to given temperature from the range of 20 to 400°C with a holding time within 1 to 4 hours. The pressed samples had mainly the form of a disk by a diameter of 15 mm and height about 2.5 mm. The X-ray structural analysis of compacts and powders was carried out. A grain size was determined using the Scherrer method. The microhardness was measured on the PMT-3 device under 40 g loading, with an accuracy of about 10%. Density of samples was measured by a standard Archimedes method of immersing.

3. Results and Discussion

3.1. Synthesis and characterization of Al nano powders

The sublimation energy of Al is 33 J/mm³. The length of Al wire was 88 mm, and input voltage was 26 kV. According to this experimental condition, the K (=W/W_s) value of our experiment was 2. The shape of Al powders synthesized by the PWE method in a given condition was spherical with size distribution of 80 to 120 nm as shown in Fig. 4. It was easily thought that as the Al wire was exploded, it was dispersed to a vapor phase. The Al vapors met the Ar gas in chamber and condensed to sphere with nano size to minimize the surface energy. Whether a liquid phase or semi solid phase was condensed, it became a relatively larger particle like A or B than others in Fig. 4.[15,16]

The result of the phase analysis of passivated Al nano powder by XRD is shown in Fig. 5. It shows that the only pure Al peaks were observed without any peak of the passivated oxide layer. However, from Fig. 6 we can see the oxide layer on the surface of Al powder. It was considered amorphous state from the high resolution TEM view in Fig. 6(c). Because the
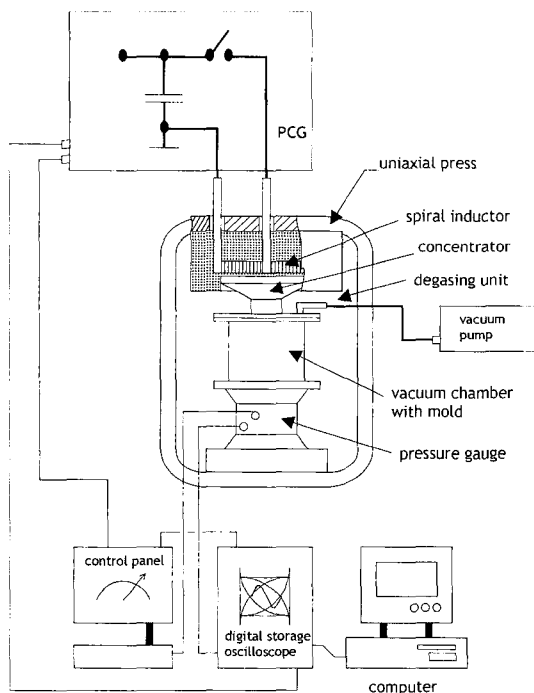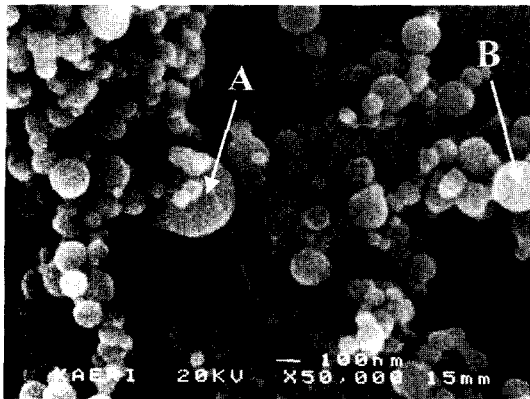
Fig. 4. SEM view of Al nanopowders synthesized by the PWE method.
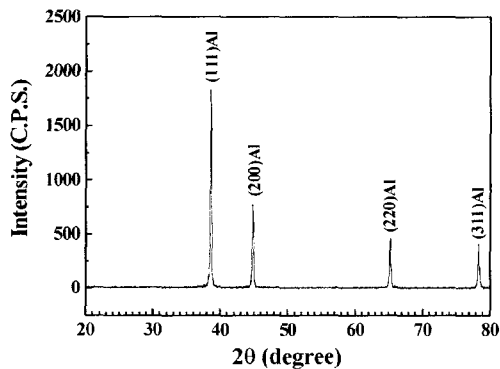
Fig. 5. XRD pattern of Al nanopowders synthesized by the PWE method.

Fig. 6. TEM view shows particle size and thickness of passivated oxide layer on the surface of Al nanopowder.

oxide phase was very thin and not a crystalline state, it was hardly detected by X-ray diffraction method. The size of the Al powder was about 100 nm having passivated oxide of 2.5 nm thicknesses. The crystalline Al phase showed the FCC structure. The comparative characteristics of powders are summarized in the Table 1.

By XPS for the measurement of binding energy between elements, it is possible to verify the phase as shown in Fig. 7. The Al^{3+} at 75.00 eV means passi-
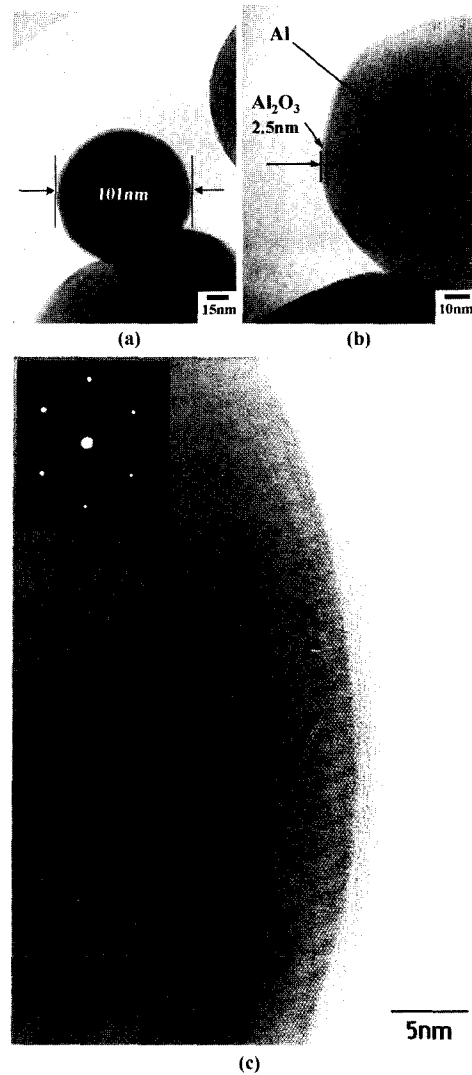
vated Al^{3+} oxide on the surface. Al^0 at 77.73 eV shows the pure metallic Al. The Pt is from the specimen holder. Because the peak was broad and the thickness of the passivated layer was so thin, it was hard to observe the oxide layer in Fig. 5 as same explanation

Table 1. Characteristics of powders

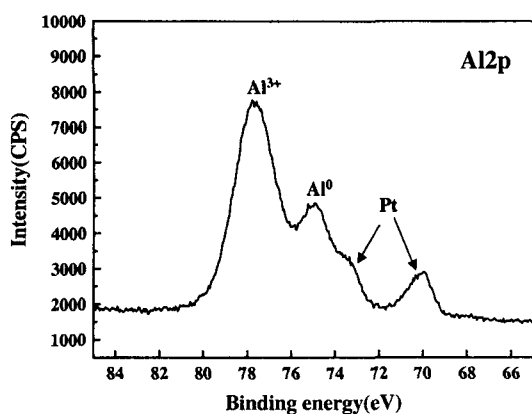| Powder	Phase composition, wt.%		Diameter, nm		S_{BET}, m^2/g
	Metal	Oxides	Metal	Oxides	
Al-P1	88-Al	12-Al_2O_3	>100 nm	Amorphous	6
Al-P2	85-Al	15-Al_2O_3	~ 80	Amorphous	15

Fig. 7. XPS pattern of Al nanopowders synthesized by the PWE method.

from the TEM analysis.[17]

3.2. Comparison of grain and powder size by different analysis

From Fig. 4, the average powder size was 80~120 nm by direct observation. The relative surface area was 20.4 m^2/g from the results of the BET measurement. It can convert to particle size, d_{BET}, of 109 nm by the equation (2). By the laser particle size analysis, the average particle size was about 87.7 nm, which was similar with the result from direct observation. On the other hand the average grain size was obtained as about 28 nm from XRD analysis. Therefore each particle may not be single crystal but poly crystal, which have several grains in the particle. Particle sizes measured by each analysis were summarized in Table 2.

3.3. Compaction conditions and characterization

Aluminum-based compacts of powders, Al-P1 and Al-P2, have been prepared. Data on density, microhardness and average grain size of samples are plotted in a Fig. 8(a) to (c). The monotonous growth of compacts density with increase of initial temperature of a powder finds a logical explanation in increase of a material plasticity. The maximal density of samples 2.76 g/cm^3 exceeds a little the normal density of pure aluminum, as the pressed material contains a significant amount of more dense oxide. This value should be a full density
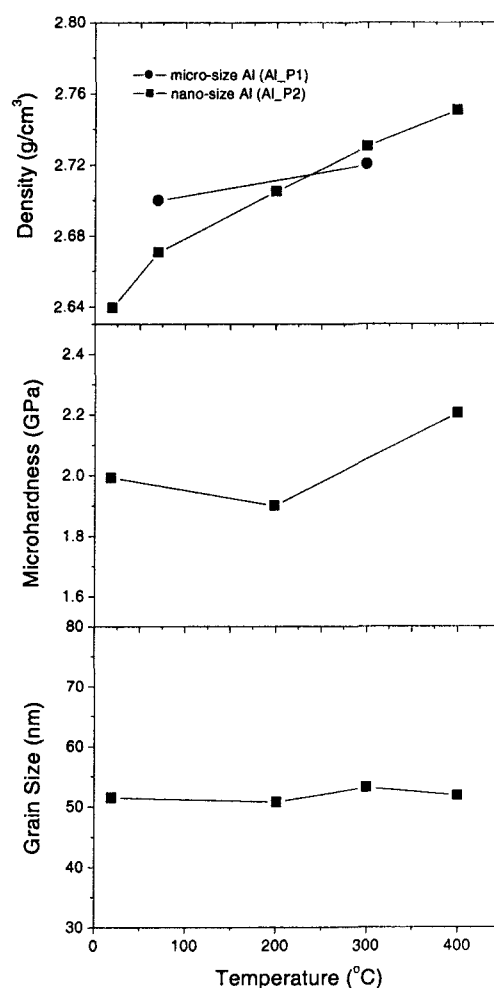

Fig. 8. The characteristics of the pressed samples from aluminum nanopowders depending on compaction temperature : (a) compact density, (b) microhardness, (c) average grain size.

of Al-P2 powder under assumption that the density of amorphous alumina is equal to 3.1 g/cm^3. The behavior of microhardness and grain size with increasing sample temperature is very unusual for metal nanostructured aluminum. The microhardness (Fig. 8(b)) even grows at increase of temperature up to 400°C a little. And, the average level of microhardness, 2.2 GPa, in a wide range of temperature on the order of size surpasses microhardness of microcrystal aluminum at a room

Table 2. Particle and grain size of Al nano powder synthesized by PEW method

Material	SEM & TEM	BET	LPSA	XRD
Al-P2	80 ~ 120 nm	20.4 m^2/g, 108.9 nm	87.7 nm	28 nm

temperature. The average grain size of the pressed aluminum samples (Fig. 8(c)) in the investigated range of temperatures practically is constant and approximately equal to the size of particles of an initial powder Al-P2. Probable explanation for stabilization in a wide range of temperatures at an unusual level of micro-hardness and grain size can be fine distribution of small alumina particles in a metal matrix. The realized processes of pulse pressing are characterized by severe constraints, at which it is possible to expect intensive destruction of oxide shells around of starting particles of a passivated aluminum powder. It is interesting to compare our results to the data of other work,[18] where the pressing of similar passivated aluminum powders by static pressure up to 0.6 GPa was studied. The density and hardness of compacts achieved did not exceed 2.3 g/cm^3 and 0.6 GPa, respectively, which are much lower than our data.

With the purpose of thermal stability study of structure and properties of nano-composite Al + Al$_2$O$_3$ the pressed samples of Al-P2 have been subjected to additional annealing at 400°C within 3 hours. In result of the annealing the phase states of components were kept, which meant the metal aluminum has remained in a crystal state, and alumina in amorphous state. The absolute values of the crystallite sizes have not

exceeded 65 nm. On all samples, the change in structure and hardness after annealing are insignificant. It means that the material keeps at such processing the nanostructured state and properties, inherent in it.

3.4. Microscopic characterization of compacts

The microscopic research of the given composite of Al-P2 composition with use of SEM, device LEO 982, and TEM, device JEOL 200, has been executed. Both methods confirm values of the average size of crystals measured on line broadening of X-ray patterns at a level of 50-70 nm. Fig. 9 represents a characteristic view of SEM of a sample compacted by pulsed pressure of 1.5 GPa at different compaction temperature. In Fig. 10 the typical compact structure pressed at temperature of 20 and 400°C is given. In the whole structure of samples is homogeneous enough with the average size of grains about 100 nm. On electron diffraction patterns taken from such places only pure aluminum dotted rings consisting of the large number of dotted reflexes were observed. The boundaries between grains are well expressed and grains have net fashion structure of boundaries. On electron diffraction patterns practically there are no additional reflexes showing the presence in a structure of Al$_2$O$_3$. In rare cases under small angles it is possible to find out the separate dots,
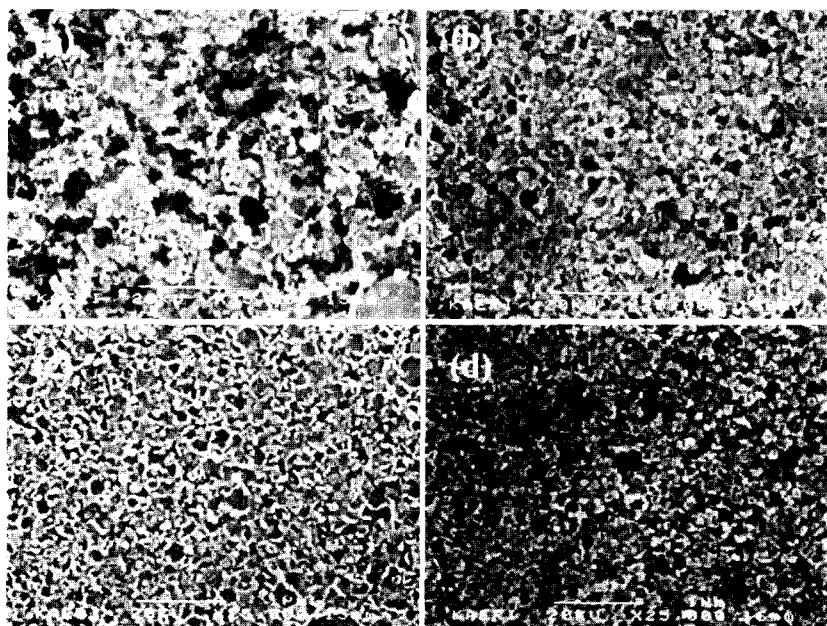

Fig. 9. SEM views of nano Al compacted by the MPC method at (a) 200°C, (b) 300°C of Al-P1 and (c) 200°C (d) 300°C of Al-P2.
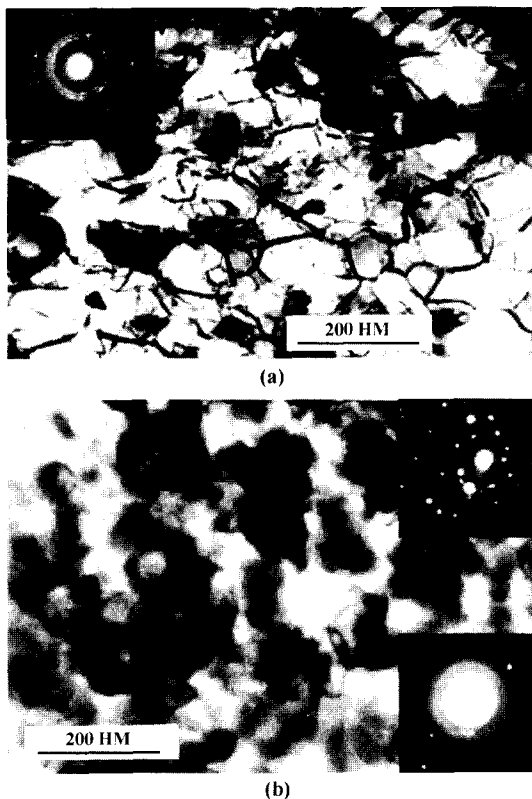
Fig. 10. TEM pictures of compact structure pressed at (a) 20°C, and (b) 400°C.

which cannot be connected with aluminum, and, probably, it is possible to consider as an attribute of presence in structure of small alumina particles.

The microstructure of a sample compacted at 400°C essentially differs from sample structure made at a low temperature. The average grain size inside compacts remains practically without change and is at the level of 100 m. However, net fashion structure of borders completely disappears. In a structure the plenty dark allocations are observed. It is possible to assume that it is the oxide particles. At structure of this sample the re-crystallized grains also are present inside which at the center the allocations are visible. Besides such allocations settle down by chains on borders of aluminum grains. On electron diffraction patterns from this sample are observed the same diffraction rings as well as low temperature sample. However alongside with them on diffraction patterns there are other diffraction effects as, for example, diffuse halo testifies about presence at structure of amorphous alumina.

4. Conclusions

From the synthesis and compaction of Al nanopowders, the following conclusions were obtained:

1. The Al nano powder was polycrystalline with an average grain size of 28 nm. The particle was about 80 to 120 nm in size from the LPSA and SEM results.

2. The layer on the surface for the passivation and stabilization of Al powder was Al_2O_3 with 2 to 3 nm of thickness. It was very stable in air. This oxide layer was an amorphous state as observed by TEM and XPS analysis but it was hard to detect by XRD method. On the other hand the Al was crystalline with FCC structure.

3. The MPC of passivated nano Al powder leads to formation of metal-matrix composite $Al-Al_2O_3$ with thermally stable nanostructure and high microhardness at the level of 2.2 GPa. This compact can be a new light material with nanosized structure capable for many applications to replace known aluminum alloys.

Acknowledgement

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