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Synthesis and characterization of single-phase nanocrystalline Ag_2Al particles

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Abstract: Single-phase Ag_2Al intermetallic nanoparticles, and Ag and Al metallic nanoparticles were synthesized by the flow-levitation (FL) method. Measurements of *d*-spacings from X-ray diffraction and electron diffraction confirmed that the intermetallic nanoparticles had the hexagonal Ag_2Al structure. The morphology, crystal structure and chemical composition of Ag_2Al nanoparticles were investigated by transmission electron microscopy, X-ray diffraction and induction-coupled plasma spectroscopy. A thin amorphous coating was formed around the particles when exposed to air. Based on the XPS measurements, the surface coating of the Ag_2Al nanoparticles could most likely be aluminum oxide or silver aluminum oxide. Therefore, the single-phase nanocrystalline Ag_2Al intermetallic compound particles can be produced by adjusting some experimental parameters in FL method.
Key words: intermetallics; Ag_2Al nanoparticles; Ag_2Al-oxide ($AgAlO_2$); flow-levitation method

1 Introduction

It is now well established that nanoparticles (1−100 nm) exhibit unique chemical and physical properties different from the corresponding bulk materials. The characterization of these properties can ultimately lead to identifying many potential applications, such as catalysis, ceramics, microelectronics, sensors, pigments, magnetic storage to drug delivery and biomedical applications. Recently, the study of bimetallic alloy nanoparticles has gained significant interest due to new properties that arise from the combination of different compositions of metals on the nanoscale. Their unique properties have been utilized in the field of electronic, optical, and catalysis applications [1]. Intermetallics represent a unique type of materials that retain ordered atomic structure up to melting point. Intermetallic compounds are the potential candidates for structural and non-structural applications including high temperature gas turbine hardware, corrosion resistant materials, heat treatment fixtures, magnetic materials and hydrogen storage materials [2].

Many different techniques have been developed to synthesize the intermetallic nanoparticles. CHOPKAR et al [3] synthesized the Ag_2Al intermetallic nanoparticles by mechanical alloying (MA). But the particle size of the nanoparticles was larger than 100 nm (the final grain size was 18 nm). LIU et al [4, 5] produced Fe_3Al and Ti−Fe nanoparticles by hydrogen plasma−metal reaction. But the phase composition of the nanoparticles was very difficult to control, and the particle size distribution of them was also very wide. PITHAWALLA et al [6, 7] synthesized the FeAl nanoparticles by laser-vaporization-controlled condensation, and the nanoparticles had an average particle diameter between 6 and 9 nm. But the yield of them is not high.

In this work, we present a simple and novel approach to synthesize intermetallic nanoparticles using the flow-levitation (FL) method [8−12]. The flow-levitation (FL) method is an advanced technology to synthesize intermetallic nanoparticles by the principle of condensation of physical gas phase. The size distribution and phase composition of nanoparticles synthesized by the FL method are determined by several factors such as the electrical power for the electromagnetic induction,

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the velocity of supplying resource materials, the diameter of the metal droplet, the flow velocity and pressure of the inert gas [13, 14].

Many studies have been performed on aluminum alloys as lightweight materials, especially on strengthening via precipitation. The Al−Ag system has received considerable attention both in science and technology. From a technological perspective, several Al alloys contain Ag due to its beneficial effects on strength and microstructure control in precipitation reactions (Al−Li−Mg−Cu−Ag Ω-phase is just one example). From a scientific standpoint, Al–Ag alloys are of interest because they represent one of the simplest cases of a phase transformation involving a change in crystal structure, namely fcc→hcp. Al-rich Al−Ag alloys may be heat-treated to produce metastable γ' and equilibrium γ hcp precipitates, both of which were reported to be stoichiometric Ag_2Al [15].

2 Experimental

The Ag_2Al intermetallic nanoparticles were produced by the FL method. The scheme diagram of the double metal wire supply is shown in Fig. 1. In principle, the two solid metal wires were firstly heated by a high-frequency electromagnetic induction coil so that a metal liquid droplet was formed. The droplet was levitated and heated continuously under its interaction with the magnetic field generated by another reverse electromagnetic induction coil. Atoms on the surface of the droplet were evaporated when a high enough temperature reached. These evaporated atoms were quickly cooled through their collision with the inert gas and formed nanoparticles. When the inert gas with a special gradient pressure was imposed in the vapour environment, metal atoms and resultant nanoparticles can flow in a definite direction in no contact with the reactor wall and finally enter the collector [14]. Consequently,

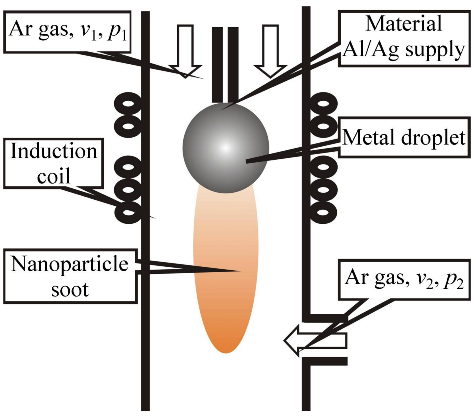

Fig. 1 Scheme diagram of double metal wire supply by flow-levitation method (v_1, v_2 are flow velocity; p_1, p_2 are pressure of inert gas)

both high yield and high purity of nanoparticles are expected. During synthesizing nanoparticles by the FL method, the aerosol was rapidly cooled and diluted to prevent extensive sintering and coalescence growth for maintaining nanosized particles and weak agglomeration. In the present experiments, these synthesized nanoparticles were taken out of the collector and were immediately placed into ethanol to reduce oxidation and coalescence and to improve their dispersion.

3 Results and discussion

3.1 TEM analyses

Figure 2 shows a set of bright-field TEM images of Ag_2Al nanoparticles synthesized by the FL method. Statistically, Ag_2Al nanoparticles are spherical but not very well defined. The range of particle size is 10−90 nm in diameter. And some particles have coalesced with each other. Our additional experiments showed that a lower temperature for evaporation, a slower velocity of supplying resource materials, a larger flow-velocity ratio (i.e., v_2:v_1) of the inert gas, or a higher pressure gradient (i.e., p_2:p_1) led to smaller nanoparticles and a narrower size distribution. For synthesizing Ag_2Al nanoparticles, the temperature for evaporation was 1360 °C, the resource materials of Al and Ag were supplied at a rate of 20 Hz and 38.9 Hz, and v_1 and v_2 are equal to 0.4 and 0.8 m^3/h, respectively. The pressure of Ar is 9.69×10^4 Pa for p_1 and 1.02×10^5 Pa for p_2. Assuming that nanoparticles are in well defined spheres and those coalescing with others are neglected, the size distribution of Ag_2Al nanoparticles was estimated from TEM images (see Fig. 3). The diameter of a nanoparticle was obtained by averaging its diameters measured along several directions in the TEM images. Figure 3 shows that Ag_2Al nanoparticles centre around 34 nm in diameter.

3.2 Component and phase composition analyses

3.2.1 Component analyses

The compositions of the intermetallic Ag_2Al nanoparticles were examined by using the ICP and EDS techniques. There are 67.58% (molar fraction) Ag and 32.42% Al in the nanoparticles as determined by the ICP analyses. The EDS results show that there are 65.43% Ag and 34.57% Al in the nanoparticles. The similar results were obtained by using the two different techniques. The result of component analyses indicates that the molar ratio of Ag and Al is almost homogeneous throughout the nanoparticle sample prepared in the vapor phase.

3.2.2 XRD analyses

In order to compare the properties of Ag_2Al nanoparticles with those of Ag and Al nanoparticles, we

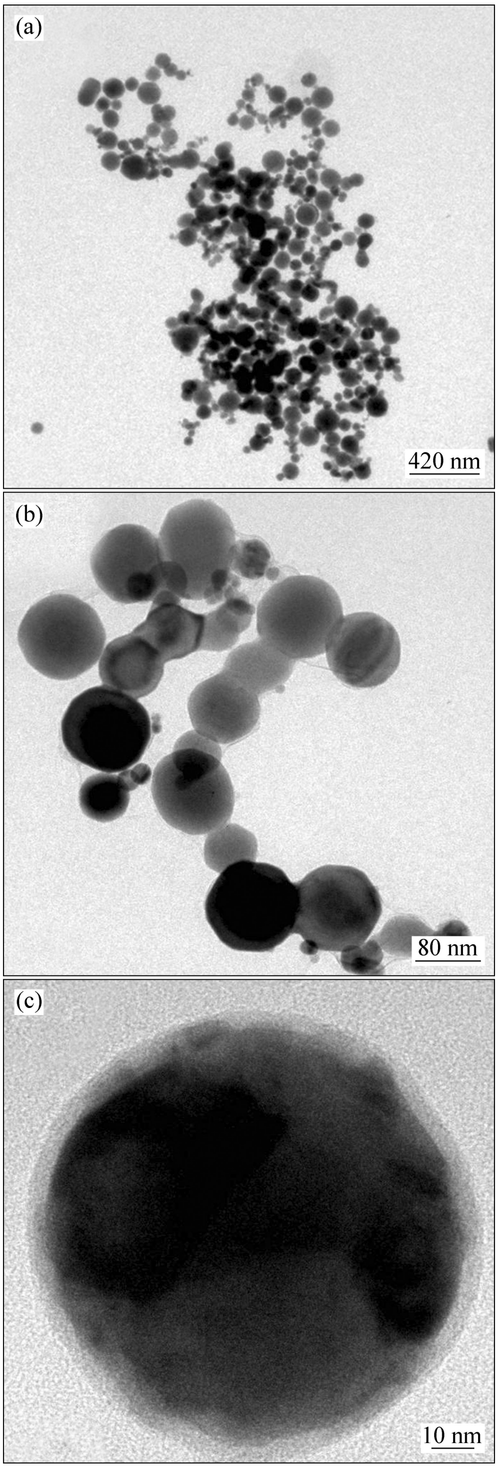

Fig. 2 TEM images of Ag−Al nanoparticles with low (a) and high (b, c) amplification factors for sample Ag_2Al

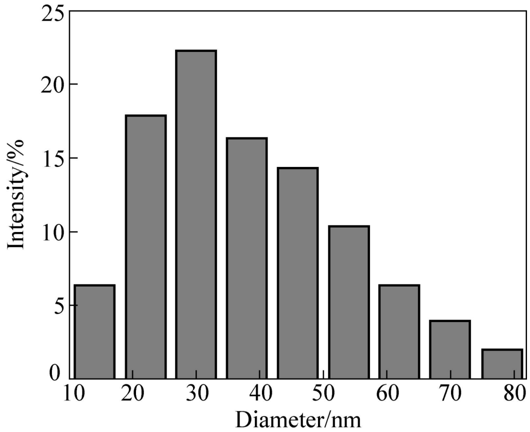

Fig. 3 Size distribution of Ag_2Al nanoparticles estimated from TEM image

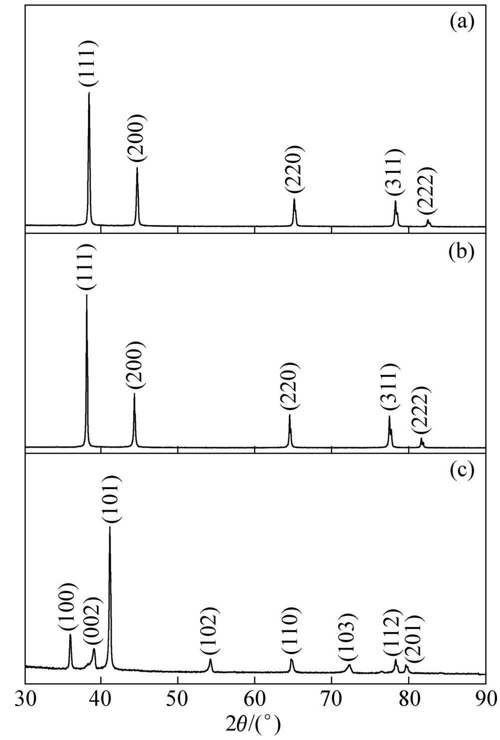

Fig. 4 XRD patterns of nanoparticles of Al (a), Ag (b) and Ag_2Al (c) prepared FL method

also produced the pure metallic Al and Ag nanoparticles by the FL method. The XRD results of the nanocrystalline Al and Ag samples are presented in Figs. 4 (a) and (b), respectively. The XRD spectrum of Al nanoparticles exhibits four strong peaks at scattering angles 2θ of 38.49°, 44.73°, 65.07° and 78.19°, which can be assigned to the crystalline Al lines (111), (200), (220) and (311), respectively. The XRD spectrum of the Ag nanoparticles shows peaks at 2θ values of 37.81°, 44.37°, 64.43° and 77.37°, which can be assigned to the four strongest crystalline Ag lines of (111), (200), (220) and (311) planes, respectively. The lattice parameters for the unit cells of Al and Ag nanoparticle were calculated by assuming cubic symmetry in both cases. The calculated lattice parameters for Al and Ag nanoparticle are 4.05 nm and 4.085 nm, respectively, which are in good agreement with the known lattice parameters for bulk Al and bulk Ag (4.049 nm and 4.086 nm, respectively) [16, 17].

The crystallinity of the Ag_2Al nanoparticles obtained by the FL method is verified in Fig. 4(c). It is evident that the XRD pattern matches neither that of Al nor that of Ag. The strong diffraction peaks at the scattering angles of 36.00°, 39.11°, 41.13°, 72.26°, 78.23° and 79.54° can be assigned to the (100), (002), (101), (103), (112) and (201) planes, respectively, of the Ag_2Al crystal lattice. The calculated lattice parameter (2.835 nm×2.885 nm×4.618 nm) of Ag_2Al nanoparticles is in good agreement with the bulk lattice parameter (2.885 nm×2.885 nm×4.624 nm) [18].

3.2.3 SAED and surface composition analyses

Figure 5 displays a TEM image of the Ag_2Al nanoparticles along with the associated selected area electron diffraction (SAED) pattern. The observation of multiple rings indicates no preferential orientation within the nanoparticle sample. The *d*-spacing values calculated from the SAED pattern match the *d*-spacing values reported for bulk Ag_2Al [18], confirming the intermetallic nature of the nanosize silver aluminium powers. The population size distribution calculated from several TEM images shows the average particle diameter to be about 33 nm. A few of larger particles which are approximately 85 nm in diameter are also observed. The Ag_2Al particles are found to have an amorphous coating surrounding the crystalline core. It is clear that the Ag_2Al particle is coated with a uniform amorphous layer of about 3.5 nm thickness for the 85 nm particles.

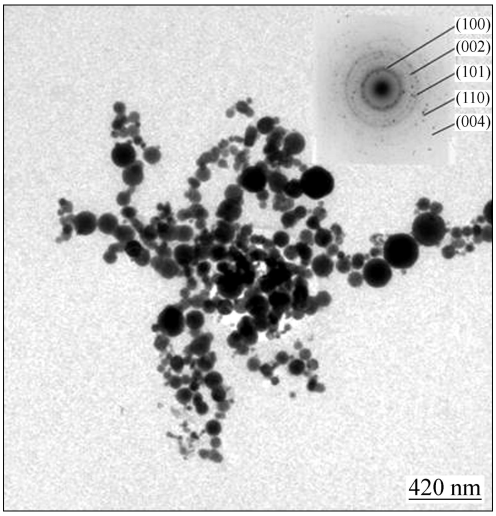

Fig. 5 TEM image of Ag_2Al nanoparticles (Insert shows SAED pattern from nanoparticles)

We also attempted to characterize the amorphous coating using X-ray photoelectron spectroscopy (XPS) measurements. Figure 6 displays XPS spectrum of the Ag_2Al nanoparticles. To compensate for sample charging, binding energy was referenced to that of the adventitious C 1s peak at 285.0 eV. The O 1s peak then appears at 530.5 eV, whereas the Al 2p peak appears at a binding energy of 73.6 eV. It is known that the binding energies of Al 2p peak are in a range of 72.4−73.1 eV for Al and in a range of 73.5−76.6 eV for oxidized Al [19, 20]. Therefore, the Al 2p peak at 73.6 eV is presumably from oxidized Al. Characteristic binding energy (BE) values of 368.1 eV for Ag $3d_{5/2}$ and 374.1 eV for Ag $3d_{3/2}$ are observed for Ag_2Al nanoparticles, indicating that Ag in the sample exists as Ag^+ [21, 22]. The result confirms that the surface coating of the Ag_2Al nanoparticles could most likely be aluminum oxide or silver aluminum oxide.

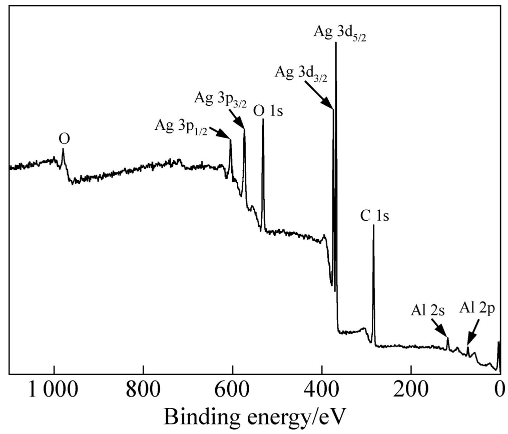

Fig. 6 XPS spectrum of Ag_2Al nanoparticles

4 Conclusions

1) The flow-levitation method was developed to synthesize single-phase Ag_2Al nanoparticles. The TEM result shows that their average diameter is 33 nm. The XRD and SAED measurements confirm that the silver aluminum nanoparticles have the same hexagonal Ag_2Al structure as the bulk material.

2) The nanoparticles acquire a thin amorphous coating layer upon exposure to air. Results from XPS measurement show that the amorphous layer of the Ag_2Al nanoparticles could most likely be aluminum oxide or silver aluminum oxide.

3) The single-phase nanocrystalline Ag_2Al intermetallic compound particles can be produced by adjusting some experimental parameters in FL method.

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References

[1] EDELSTEIN A S, CAMMARATA R C. Nanomaterials: Synthesis, properties and applications [M]. Philadelphia: Institute of Physics, 1996: 55−71.

[2] STOLOFF N S, LIU C T, DEEVI S C. Emerging applications of intermetallics [J]. Intermetallics, 2008, 8: 1313−1320.
[3] CHOPKAR M, KUMAR S, BHANDARI D R, DAS P K, MANNA I. Development and characterization of Al_2Cu and Ag_2Al nanoparticle disperser water and ethylene glycol based nanofluid [J]. Materials Science and Engineering B, 2007, 139: 141−148.
[4] LIU T, LENG Y, LI X. Preparation and characteristics of Fe_3Al nanoparticles by hydrogen plasma-metal reaction [J]. Solid State Comminications, 2003, 125: 391−394.
[5] LIU T, LI X. Synthesis and characteristics of Ti−Fe nanoparticles by hydrogen plasma-metal reaction [J]. Intermetallics, 2004, 12: 97−102.
[6] PITHAWALLA Y B, EL-SHALL M S, DEEVI S C. Synthesis and characterization of nanocrystalline iron aluminide particles [J]. Intermetallics, 2000, 8: 1225−1231.
[7] PITHAWALLA Y B, DEEVI S C, EL-SHALL M S. Preparation of ultrafine and nanocrystalline FeAl powders [J]. Materials Science and Engineering A, 2002, 329: 92−98.
[8] LI C M, LEI H, TANG Y J, LUO J S, LIU W, CHEN Z M. Production of copper nanoparticles by the flow-levitation method [J]. Nanotechnology, 2004, 15: 1866−1869.
[9] CHU Guang, XIONG Zhi-qun, LIU Wei, WEI Jian-jun. Microstructure and properties of nano-copper powders prepared by flow-levitation method [J]. The Chinese Journal of Nonferrous Metals, 2007, 17(4): 623−628. (in Chinese)
[10] CHU Guang, LIU Wei, YANG Tian-zu, TANG Yong-jian, Properties of nanocrystalline copper prepared by vacuum-warm-compaction method [J]. Transactions of Nonferrous Metals Society of China, 2009, 19: 394−398.
[11] LIU Wei, YANG Tian-zu, CHU Guang, LUO Jiang-shan, TANG Yong-jian. Synthesis and properties of nanocrystalline nonferrous metals prepared by flow-levitation-molding method [J]. Transactions of Nonferrous Metals Society of China, 2007, 17: 1347−1351.
[12] WEI Jian-jun, WU Dong, TANG Yong-jian, WU Wei-dong, LEI Hai-le. Synthesis and characterization of single-phase nanocrystalline intermetallic compound AlNi [J]. Atomic Energy Science and Technology, 2008, 42(11): 965−968. (in Chinese)
[13] WEI Jian-jun, TANG Yang-jian, WU Wei-dong, WEI Sheng, LI Chao-yang, YANG Xiang-dong. Preparation and granularity control of nanosized copper particles by flow-levitation method [J]. High Powder Laser and Particle beams, 2003, 15(9): 869−872. (in Chinese)
[14] TANG Yong-jian, WEI Jian-jun, LI Chao-yang, WU Wei-dong, WANG Chao-yang. Theoretical simulations of preparation of nanometal particles by flow-levitation method [J]. Acta Physica Sinica, 2003, 52(9): 2331−2336. (in Chinese)
[15] HOWE J M, DAHMEN U, GRONSKY R. Atomic mechanisms of precipitate plate growth [J]. Philos Mag A, 1987, 56: 31−61.
[16] SWANSON H E, TATGE E. Standard X-ray diffraction powder patterns [M]. Circular: National Bureau of Standards (U.S.), 1953, 539(1): 1−95.
[17] SPREADBOROUGH J, CHRISTIAN J W. High-temperature X-ray diffractometer [J]. Metallurgical Transactions, 1970, 1: 1961−1971.
[18] NEUMANN J P, CHANG Y A. The influence of temperature on the lattice parameters of the intermetallic compound Ag_2Al [J]. Transactions of the Metallurgical Society of AIME, 1968, 242: 700−702.
[19] MOULDER J F, STICKLE W F, SOBOL P E, BOMBEN K D. Handbook of X-ray photoelectron spectroscopy [M]. CHASTAN J, KING R C. Eden Prairie, Minnesota: Physical Electronics, 1995.
[20] VINCENT CRIST B. Handbook of monochromatic XPS spectra: the elements and native oxides [M]. New York: Wiley, 2000.
[21] MUÑOZ-ROJAS D, SUBÍAS G, FRAXEDAS J, GÓMEZ-ROMERO P, CASAÑPASTOR N. Electronnic stucture of $Ag_2Cu_2O_4$.evidence of oxidized sliver and copper and internal charge delocalization [J]. The Journal of Physical B, 2005, 109(13): 6193−6203.
[22] MUÑOZ-ROJAS D, SUBÍAS G, ORÓ-SOLÉJ, FRAXEDAS J, MARTÍNEZ B, CASAS-CABANAS M, CANALES-VÁZQUEZ J, GONZALEZ-CALBET J, GARCÍA-GONZÁLEZ E, WALTON R, CASAÑPASTOR N. Ag_2CuMnO_4: A new silver copper oxide with delafossite structure [J]. Journal of Solid State Chemistry, 2006, 179(12): 3883−3892.

单相纳米晶 Ag_2Al 颗粒的制备及表征

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摘 要：采用自悬浮定向流法制备单相 Ag_2Al 金属间化合物纳米颗粒及 Ag 和 Al 纳米颗粒；利用透射电镜、X 射线衍射、X 射线光电子能谱分析、电感耦合等离子体发射光谱等对纳米 Ag_2Al 微晶的形貌、粒度、相组成、成分及微结构进行表征。研究表明：所制备的金属间化合物纳米粒子为球形的六边形结构，其平均粒径为 33 μm，样品中 Ag 和 Al 的摩尔比非常接近标准配比 2:1，颗粒由单相的 Ag_2Al 组成。对放置在空气中的 Ag_2Al 纳米颗粒表面成分进行分析，XPS 测试结果表明：在 Ag_2Al 微晶表面形成了一层很薄的氧化物膜，可能是铝的氧化物或银铝氧化物。实验证实，通过控制气相反应的工艺条件可以制备出粒径很小的单相 Ag_2Al 纳米晶。

关键词：金属间化合物；Ag_2Al 纳米颗粒；银铝氧化物；自悬浮定向流法

(Edited by YANG Hua)