The influence of nanoprecipitates on Al-Mg-Nb alloy processed by powder metallurgy after special thermomechanical treatments

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Abstract. Al-Mg based alloys have special attention due to the lightness of the material and certain mechanical properties and recyclability. Normally classified as non-heat-treatable these alloys obtain higher strength either by strain-hardening or by solid solution. The powder metallurgy (P/M) process in the Al-Mg alloys in study leading to fine grain structure after the thermal treatment. The direct observations were made in optical and electron microscopes (BX 60M; Philips XL30 SEM; JEM200C; JEM2010) combined with mechanical characterization utilizing Vickers hardness and also electrical resistivity measurements. All samples preparation followed the usual route of metallographic specimen preparation. The understanding of the observed phenomena is dependent on materials produced by powder metallurgy due to complex interface reactions in a great amount of nucleation sites and a subtle change in the structure of the material causes an important variation in your properties. The alloys in study offered interesting values of specific properties with evident technological potential.

Introduction

Light materials have been studied thoroughly and used in components of pieces in the automobile, naval and aerospace industries in the last decade. Their application makes possible: to reduce the mass, to increase the load capacity, increase of the speed and improvement in the mechanical properties when it is possible. Al-Mg alloys have special attention due to the lightness of the material and certain mechanical properties; their application is in a range from components of pieces in the automobile up to that in the naval and aerospace industries. Some of the criteria for selection of those materials for structural applications are: specific mechanical resistance

(resistance-weight ratio) and the specific rigidity, which differs among the several materials of light alloys. The recyclability of the aluminum alloys is one factor of special interest nowadays [1-5]

The work hardening has limited applications in view of the loss of ductility, with such alloys are typically used in annealed condition. Usually the annealing temperatures situate in the range of 493K – 693K. High concentrations of magnesium involve larger concentrations of phase Mg_2Al_3, increasing the mechanical strength of 110 MPa (Al-Mg) to 340 MPa (Al-Mg), but detected a decrease in relative elongation of 25% [6, 7].

The interaction processes among crystalline and precipitate defects are of fundamental interest in the recovery and recrystallization processes in metallic alloys. Materials, such the aluminum alloys, when at high deformation degrees, create an amount of crystalline defects that provide them certain mechanical properties. The analysis of the degree of crystalline defects is, in many cases, indirectly observed, through mechanical test, such as microhardness analysis.

However the production of such alloys by P/M technique lead to fine grain structure and the understanding of the some observed phenomena during the processes of recovery and recrystallization depends, mainly, to the fact that those materials present complex interface in a great amount of nucleation sites and a subtle change in the structure of materials will cause important variation in their properties [8, 9].

The principal criteria for selection of those materials for structural applications are: specific mechanical resistance (resistance-weight ratio) and the specific rigidity that differs among the several materials of light alloys. Among those materials, the aluminum-magnesium alloys have special attention due, not only to the lightness of the material, but also to certain mechanical properties and recyclability [1, 2].

The aluminum has CFC structure, lattice parameter of 0.4041 nm; show low density, high values of thermal and electric conductivity, ductility and corrosion resistance. The common impurities found in the aluminum are: Fe, Si, Ti, Cu and Zn; in general, they deteriorate the physical properties previously mentioned. However, the inclusion of certain concentrations of impurities and mechanical treatments (plastic deformation, for instance) can improve the mechanical resistance and the hardness of the aluminum and their alloys [10-14].

The magnesium, with HCP structure, lattice parameter of 0.5199 nm, shows good machinability and capacity of absorbing mechanical loads (impact and vibration, for example). Compared to the aluminum, has inferior values of thermal conductivity (33% of that), electric (50%), elastic module (33%), but practically the same specific rigidity, and ductility and corrosion resistance decreases much more than for the aluminum, in presence of the same type of impurities. In pure form, the magnesium oxidizes intensely when warm, what takes to problems in the fusion and moulding of their alloys. In the powder form, it can begin ignition in to the air in usual temperatures (300K) [2].

Several properties of the materials are strongly dependent of microstructure, such as: resistance limit, elongation, toughness, ductile - fragile transition temperature, resistance to the impact and wear resistance. Plastic deformations introduced during the processes of mechanical conformation promote dimensional alterations and modifications in the mechanical properties of the material. Those properties are also influenced by the temperature, deformation rate in the processing and the way as the material is deformed [6, 7, 10 - 15].

It is known that most of the metallic materials in some stage of their production were submitted to cold or hot deformation processes to obtain products as foils, wires, tubes, etc. In some of these processes, occur simultaneous microstructural alterations as hardening, recovery and recrystallization [11 - 14].

The above-mentioned phenomena take place simultaneously to the deformation when the material is under a field of tensions and, sometimes, at high temperature, leading to differentiations in the materials regarding, without a doubt, of their own melting temperature.

The addition of these phenomena is accomplished in an indirect way, that is, through stress-strength curve obtained during hot mechanical testing (tension, compression and torsion). It is known that several properties are strongly dependent of the microstructure, such as: flow strength; elongation; tenacity; temperature of transition ductile-fragile; impact resistance and wear resistance.

The plastic deformations introduced during the mechanical processes (cold work) promote as dimensional alterations as modifications in the mechanical properties of the material. Those properties are also influenced by the temperature, deformation rate in the processing and how the material is deformed.

The solution and precipitation of the kinetics of second phase is dependent of the temperature and time, being also influenced by deformation. Different results are obtained in a given metallic alloy, depending on their thermal-mechanics history and the consequence of that is a variety of microstructures that can be favorable to studies by electron microscopy, because it is a technique that determines the local crystallographic orientation with larger precision implicating in an analysis related with the local heterogeneity of the plastic deformation and the correspondent microstructure induced by crystal defects, of great value in recrystallization studies [11-14].

Additions of elements in metals provide three types of alloys, of the point of view of the recrystallization: a) the alloying elements are in solid solution; b) the alloying elements are in the form precipitate of second phase; c) the alloying elements are in the form of a second phase and the volumetric fraction of this second phase is high [3].

The effects of such second phase elements on the recrystallization can be as to stimulate as to delay the recrystallization phenomena, depending in the way as the particle interacts with the microstructure during the thermal-mechanic processing [11 – 14].
Some alloys with dispersion of second phases show the delay of the recrystallization process. Such particles act as barriers for the movement of the boundaries of high angle due to the dragging force exercised by the particles at grain boundaries. If this force grows more than the force for boundaries movement, there won't be migration and consequently the recrystallization nucleus cannot grow, impeding the recrystallization [11 – 13].
The alloys produced by P/M are generated by compacting (compact pressure of 400 MPa for aluminum alloys) of particles at high solidification rates and temperatures range from 673 to 723 K being the diameter of the compacting particles in the range from some micrometers to millimeters, and the final products have microstructures of fine grains and low segregation degree, that can be eliminated by conventional thermal treatments.
It is verified that the precipitation of intermetallics phases during the compacting stage has important place over all the phase transformations, because it provides alloys with differentiated physical properties, such as increase of the recrystallization temperature and of the mechanical resistance of the alloy to usual and high temperatures.

Experimental Procedure

The material in study, bars of Al-2%Mg-1%Nb (weight %) was obtained by the technique of processing (powder metallurgy) of the material in form of particles in high energy mill (by two hours in recipient of Polyethylene of the type UHMW - Ultra-High Molecular Weight) together with steel spheres followed by uniaxial compression in vacuum and hot extrusion (with temperature for both processes of 723 K; the pressures were 400 MPa in hot compressed process and 60 MPa in extrusion process). Aluminum powder was supplied with medium granulometry of 25 μm. The magnesium and niobium powders were obtained by crushing small pieces of them until the size turn into the order of tenth of millimeters.
These processes were made in the Powder Metallurgy Laboratory of the Materials Science and Technology Center of IPEN/USP. After the process of compacting and extrusion, the alloy was 89% cold worked and annealed at the range of 473 - 623 K, up to 6000 s of time treatment.
Following the process of analysis, Vickers hardness measurements were made in a Fischerscope H100 to verify possible mechanical enhancements (Table 1).

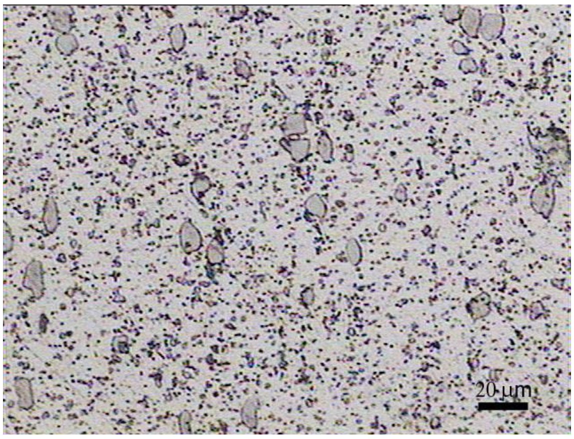
Table 1. Parameters utilized in Vickers hardness measurements.

Applied Load	100 mN
Loading velocity	3,33 mN/s
Loading time	20 s
Unloading rate	2 mN/s
Indentation number per sample	15

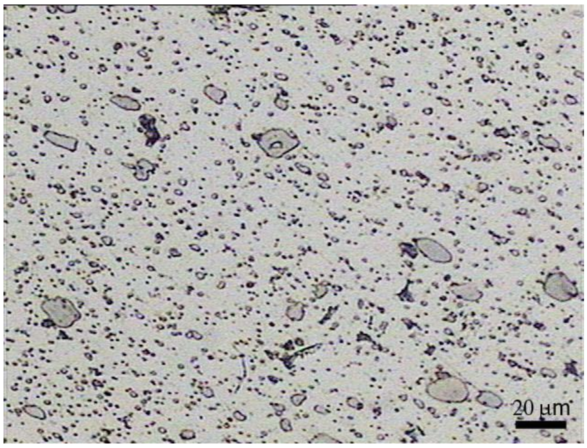
Samples were prepared for microstructural observation (optical and electron microscopy), which process of preparation followed the usual route.

Results and Discussion

The Figs. 1(a) and 1(b) show the evolution on the microstructure (optical microscopy) in heat treated Al-2%Mg-1%Nb alloys where it is not possible to clearly observe the grain formation due to a very intense and regularly precipitation distributed by the entire microstructure. The precipitates are of in large range of size always smaller than 15 μm.



(a)



(b)

Fig. 1 Optical micrograph of the alloy Al-2%Mg-1%Nb heat treated during 3600s at: (a) 373 K; (b) 773 K.

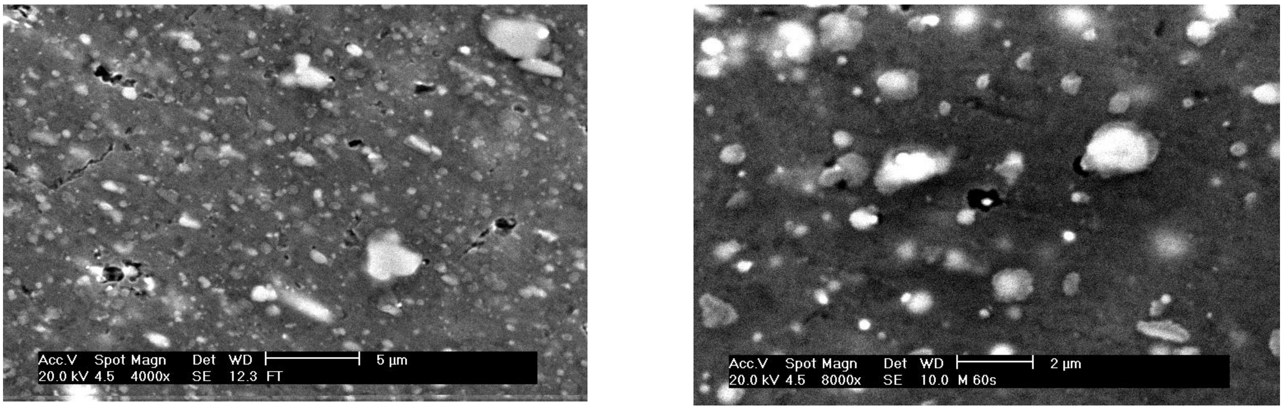
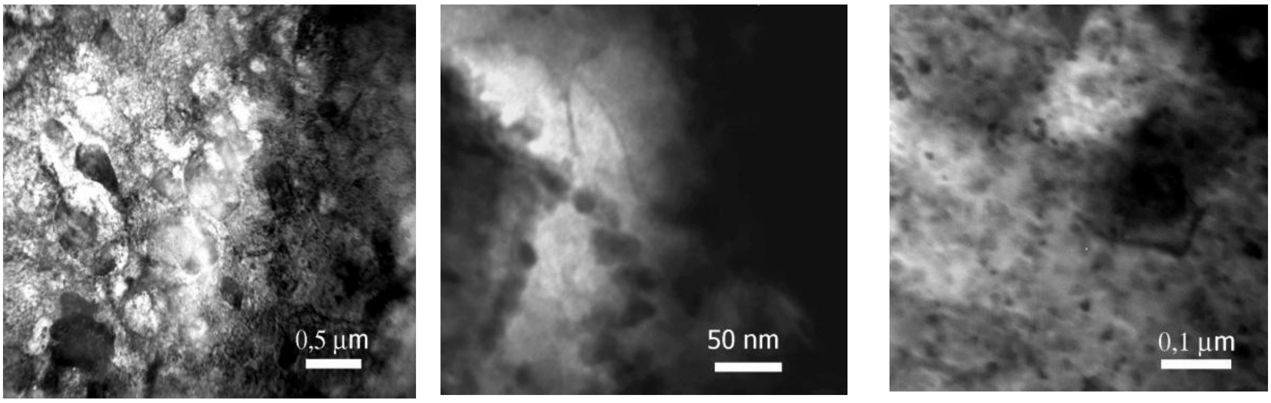


Fig. 2 SEM micrographs of the alloy Al-2%Mg-1%Nb heat treated during 3600s at: (a) 373 K; (b) 773 K.

The Figs. 2(a) and 2(b) show a wide dispersion of precipitates during the observation with SEM in the alloys Al-2%Mg-1%Nb heat treated during 3600s at 373 K and 773 K, respectively. Analysis by EDS of several precipitates shows the small presence of niobium in them, because niobium present in a very thin precipitation around the larger precipitates seen in Figs. 3(b) and 3(c) by TEM observations.



(a) **(b)** **(c)**

Fig. 3 Transmission electron microscopy of Al-2Mg-1Nb (weight values) alloy, produced by powder metallurgy (hot compacting and extrusion technique), 89% cold worked, and annealed, show at: (a) 373 K (60 s) fine precipitates inside the grains and high degree of crystalline defects, (b) 373 K (600 s) bands of dislocations interacting both with each other and precipitates, (c) 673 K (6000 s) precipitates with round format, with very different dimensions to each other.

The transmission electron microscopy observations show an evolution on the microstructure of the samples in study. The Fig. 3 show a great dispersion of fine precipitates, little influence of the treatment temperature in the structural condition in the Al-Mg-Nb alloy.
The precipitates present in the Al-Mg-Nb alloy show round format, with very different dimensions to each other, not presenting appreciable amounts of niobium. The occurrence of this phenomenon is owed to a very fine precipitation of $NbAl_3$ (in order of 20 nm) in the contour of these larger precipitates. It is also observed an evolution on the shape and grain size of the precipitates.
The Fig. 4 shows microhardness graphic of the Al-Mg-Nb samples in study after 6000 s of time of treatment at several temperatures, which show a loss of hardness with the increase of temperature of thermal treatment.

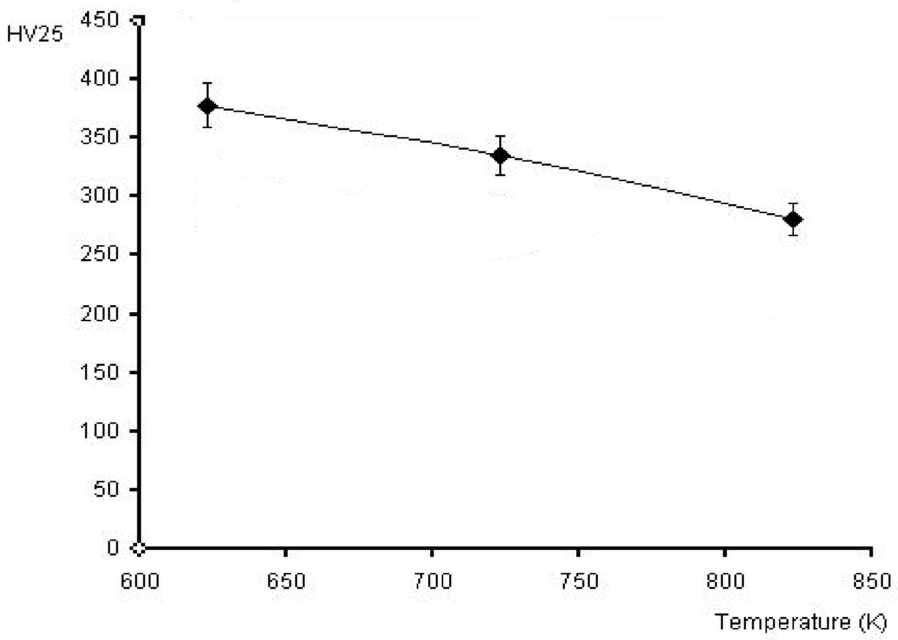


Fig. 4 Curve of microhardness analysis of samples of the Al-2%Mg-1%Nb alloy (weight percent), produced by powder metallurgy (hot compacting and extrusion technique), 89% cold worked, and then annealed for 6000 s at three different temperatures.

The Fig. 5 shows the estimated Young's modulus profile for Al-2%Mg-1%Nb alloys samples heat treated between 373K and 773K.

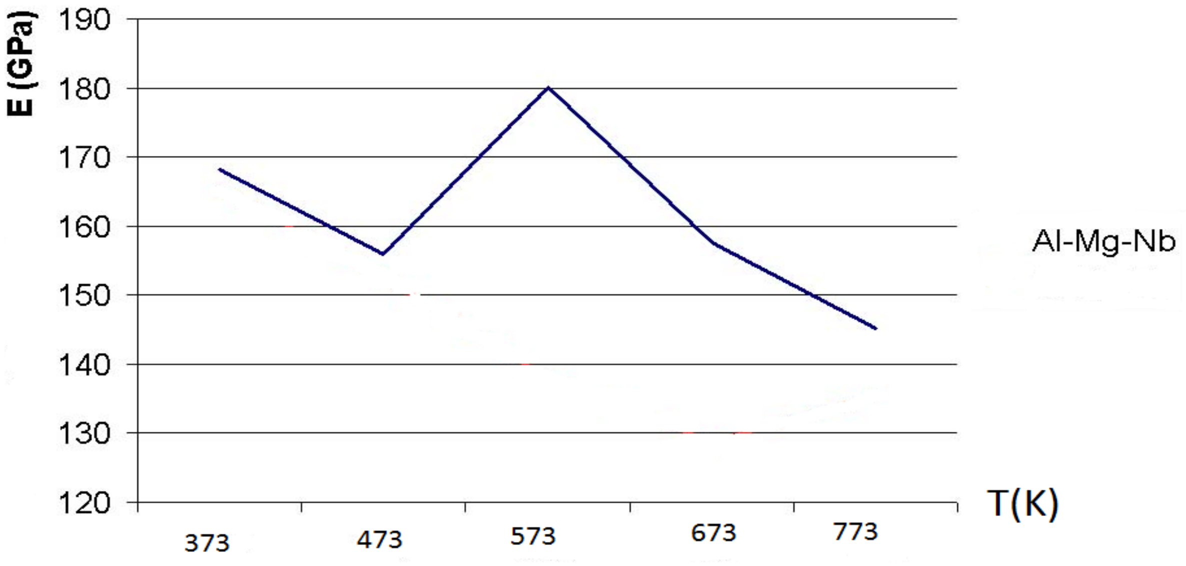


Fig. 5 Young Modulus graphic of Al-2%Mg-1%Nb alloys after thermal treatments.

The Fig. 6 shows the DSC thermal analysis on the no previous heat treated Al-2%Mg-1%Nb alloy who presents a stable behavior until 503K where occurs a endothermic peak due to the precipitation of intermetallic $NbAl_3$

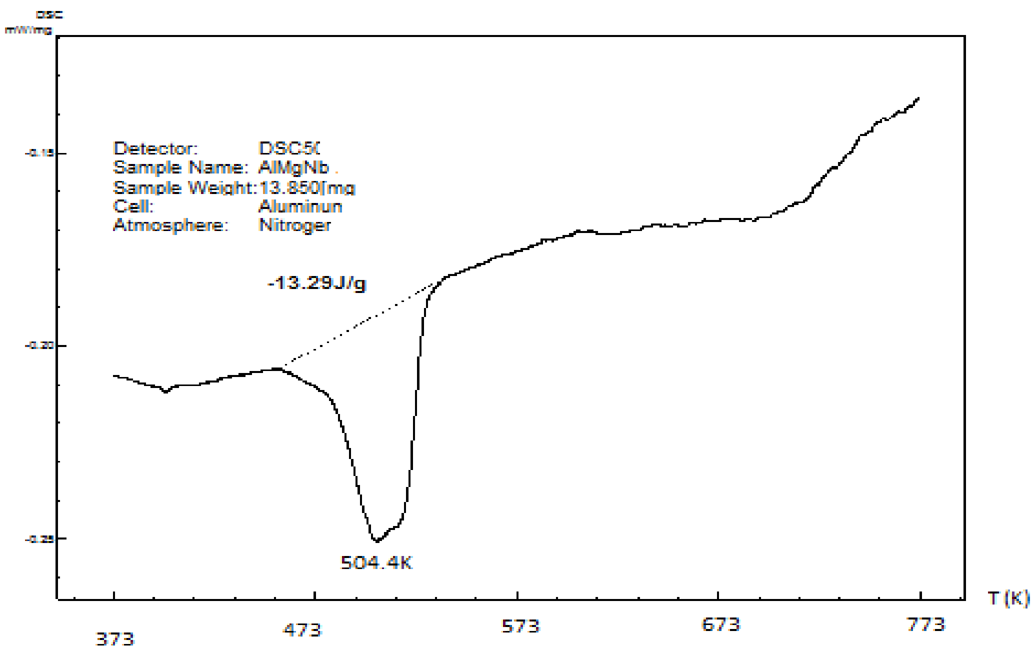


Fig. 6 Differential scanning calorimetry (DSC) analysis on sample of Al-2%Mg-1%Nb alloy without heat treatment.

The Fig. 7 shows the variation of the electrical resistivity of Al-2%Mg-1%Nb alloys after a few heat treatments. There is a small drop on the values of electrical resistivity of Al-2%Mg-1%Nb with increasing temperature until 673 K, after this take place a rapid increase on electrical resistivity (773 K) due to structural changing in alloys (dissolution of precipitates on the matrix).

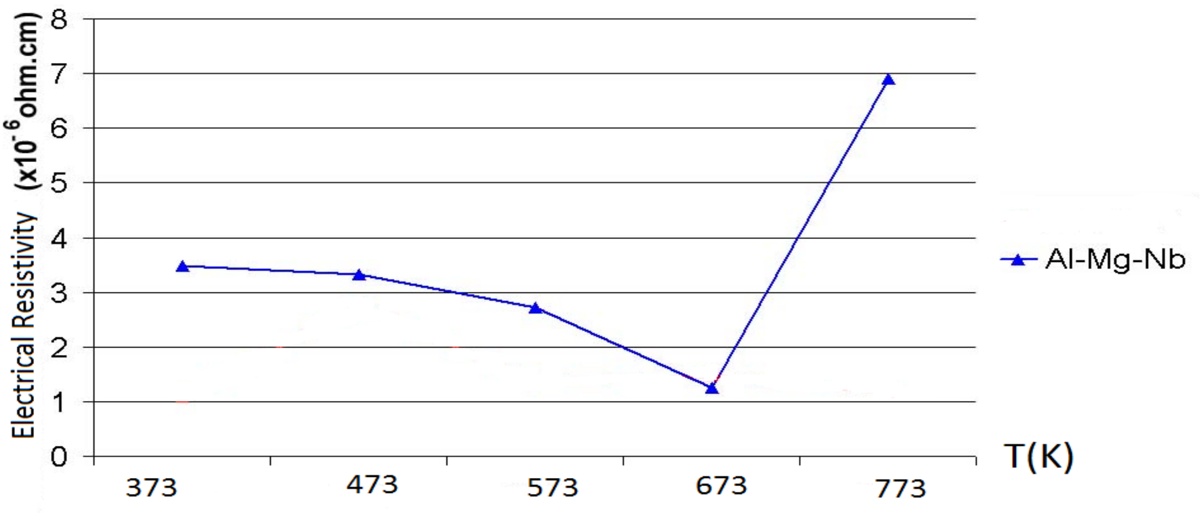


Fig. 7 Influence of heat treatment in electrical resistivity of Al-2%Mg-1%Nb alloys.

Conclusions

The understanding of the observed phenomena is dependent on materials produced by powder metallurgy who exhibit complex interface reactions in a large amount of nucleation sites, with a subtle change in the structure of the material that causes a significant change in their properties. The small size of the grain in alloys normally occurs with materials produced by powder metallurgy, that makes limited use of optical microscopy (normally by this analysis is possible to evaluate the distribution of precipitates). The nature and the morphology of precipitates (second phases) can be determined with scanning electron microscopy, most of these phases has a polygonal shape, with their chemical composition-dependent of thermal treatment.

The precipitates on Al-2%Mg-1%Nb exhibit rounded form, with different dimensions, not showing appreciable levels of niobium. The occurrence of this phenomenon is due to a very fine precipitation of $NbAl_3$ (around 20 nm) on the around these precipitates. The mechanical properties are much higher than those reported in the literature for most aluminum alloys. This detail is due to large mechanical deformation imposed on samples, causing great work hardening, and the existence of niobium-containing fine precipitates, dispersed by metal matrix.

When samples of these alloys are heat treated, there is a special hardness decrease on it. The niobium participates in the formation of a very large quantity of precipitates with very small dimensions and low mobility in the matrix, the predominant hardening mechanism of the material. At 773 K occurs an abrupt drop in the hardness value who indicates that should be indicated the recrystallization process at this temperature.

The estimate of the modulus of elasticity should be analyzed with prudence, since it is obtained by indirect method from a superficial measure. The Nb presence has a drop on modulus of elasticity at the beginning of the process, then showing an increase when the treatment temperature reaches 573 K. Considering the existence of an intense precipitation of $NbAl_3$ at 504.4 K, one can attribute to this intermetallic the effect of increasing on the modulus of elasticity.

It can observe during in situ heat treatment observation in transmission electron microscope the phenomena related to recovery processes, with the movement of dislocations and precipitates during heating. A structure composed of a dislocations tangle does not change until the temperature of 773 K, indicating a much slower recovery process at this temperature.

As commented before, precipitates of niobium in Al-2%Mg-1%Nb have small dimensions (between 10 nm, 20 nm), grouping together around the precipitates containing only aluminum and magnesium. The values of electric resistivity of Al-2%Mg-1%Nb alloys showed a different behavior between themselves. The condition of heat treatment carried out large change in resistivity values, occurrence which is not the case in conventional alloys produced by powder metallurgy; for Al-Mg-Nb alloys it is considered valid the Matthiessen's rule, in which the electrical resistivity of the alloy depends only on its chemical composition and temperature, the effect of the structure would have negligible influence (on the order of 3 % in value of resistivity).

When the amount of crystalline defects decreases, take place a decrease in electrical resistivity due to this reduction that provides a greater "scattering" of electrons, enhancing the self mobility of electrons when the electric field is applied. In Al-Mg-Nb alloy there is a drop in the resistivity value greater than would be expected, due to subtle structural transformations that have occurred. At the temperature of 773 K (heat treatment), a sharp increase in the value of resistivity occurs due to the sudden structural changes with the beginning of the recrystallization process.

The relative density measured in this alloy was equal to the theoretical value, indicating a densification of 100% ($2{,}77 \times 10^3$ kg/m^3), according to previous work [16]. Finally, the alloys in this study indicated interesting values of properties, with obvious technological potential. The relation between physical characteristics and thermal treatments in all measures, suggests that materials produced by powder metallurgy exhibit significant changes in its properties with minimal changes in its structural conditions.

In this study, were observed decreases of hardness with the increase of the treatment temperature, with final experimental hardness, after 6000 s of time of treatment in temperature of 823 K, around 300 HV25 for the alloy Al-2%Mg-1%Nb. The variation among the parameters of this kinetics is due to the differences of chemical composition, since the other processing parameters were maintained.

The TEM analysis could contribute to understand some important aspects of the phase transformations, which leads to the processes of recovery and/or recrystallization. However, in the alloys produced by P/M in study, shows interactions between fine precipitates and crystal defects, precipitate distributions interacting with dislocations, annihilation of dislocation and the evolution in the form and size of the grains indicating that the processes of recovery and/or recrystallization of the alloys in study highly depends on the fact that those materials present complex interface reactions in a great amount of nucleation sites and changes in the structure of the material causes an important variation in your properties as observed in the hardness.

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References

[1] Miska, K. H. Aluminium P/M parts are strong, economical and they save weight, Source Book on P/M - ASM, pp 74-78, (1979).

[2] Buso, S.J. and Monteiro, W.A. Characterisation of a P/M Al-Mg-Zr alloy after thermal treatments by TEM. Proceedings of the International Conference on Advanced Materials Processing Technologies (AMPT'01). Leganés, Madrid, Spain (2001).

[3] Arzamasov, B. N. et allii. Materials Science, cap. 12. Mir Publishers Moscow, Moscow (1989).

[4] Sistiaga, J. M., Aleaciones de Alumínio y de Magnésio, cap. II-III, Ed. Montecorvo, Madrid, 1963.

[5] Hatch, J. E., Aluminum Properties and Physical Metallurgy, ASM, USA, 1984.

[6] Mcnelley, T.R., Crooks, R., Kalu, P.N., Rogers, S.A., Precipitation and recrystallization during processing of a superplastic Al-10Mg-0.1Zr Alloy. Materials Science and Engineering, A166, pp. 135-143, USA, 1993.

[7] Wang, J.; Iwahashi, Y.; Horita, Z., Furukawa, M., Nemoto, M., Valiev, R.Z., Langdon, T.G., An investigation of microstructural stability in an Al-Mg alloy with submicrometer grain size. Acta Mater. Vol.44. n.7. pp. 2973-2982, 1996.

[8] Buso, S. J. and Monteiro, W. A. Characterisation by TEM of a supersaturate P/M Al-Mg-Zr alloy after thermal treatments In: International Conference on Processing & Manufacturing of Advanced Materials (Thermec'2003). Leganés, Madrid, Spain (2003).

[9] Monteiro, W. A.; Buso, S. J.; Almeida Filho, A.; Ferrari, R. B. Comparison of microstructural aspects by electron microscopy observed in Al-Mg based alloys obtained by conventional and p/m processes after thermomechanical treatments In. 5th International Conference on Physical and Numerical Simulation of Materials Processing. China (2007)

[10] Cahn, R.W., Recrystallization, Grain Growth and Textures, Ed. H. Margolin, ASM, Metals Park, Ohio, 1966.

[11] Bourname, M.; Nedjar, M.; Sirenko, A.F.; Precipitation in solid solutions of Al-Mg. Scripta Materialia, vol. 40, n.3, pp. 375-382, 1999.

[12]. Humphreys, F.J.; Haterly, M. Recrystallization and Related Annealing Phenomena, Elsevier, 1996.

[13]. Dimitrov, O. Recrystallization of Metallic Materials, ed. Haessner, 1978.

[14]. Lücke, K.; Stüwe, H. P. Recovery and Recrystallization in Metals, ed. L. Himmel, 1962.

[15]. Buso, S. J. PhD thesis, USP, 2004 (in Portuguese).

[16] Almeida Filho, A. PhD thesis, USP, 2005 (in Portuguese).