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Effects of Sb, Sm, and Sn additions on the microstructure and mechanical properties of Mg-6Al-1.2Y-0.9Nd alloy

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Abstract

The microstructure and mechanical properties of Mg-6Al-1.2Y-0.9Nd magnesium alloy with Sb, Sm, or Sn addition were investigated through X-ray diffraction (XRD), optical microscopy (OM), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). The results show that small amounts of Sb, Sm, and especially Sn can refine the grains of the alloy. High melting point Sb_3Y_5, Al_2Sm, and Nd_5Sn_3 intermetallic compounds can be formed respectively when Sb, Sm, and Sn are added to the alloy. Sb and Sm can improve the tensile strength of the alloy at ambient and elevated temperatures. The tensile strength of the alloy with Sm addition is the highest at 293 and 423 K. However, the tensile strength of the alloy with Sn addition is the highest at 448 K.

Keywords: magnesium alloys; mechanical properties; microstructure; Sb; Sm; Sn

1. Introduction

The magnesium alloy is the lightest metal structural material. It has good properties such as low density, high specific strength and specific stiffness, good cast characteristics and electric conductivity and thermal conductivity, and it has been widely applied in the automobile industry, electron industry, and 3C products. It is a critical factor to improve the strength and other related properties of the magnesium alloy for its expanding application. Currently, about 70% of the magnesium alloy castings are made for the automotive industry. Lowering car mass by 100 kg makes it possible to save 0.5 L of petrol per 100 km. The application of magnesium alloy in the automobile industry has a strong influence on the reduction of fuel consumption [1-2]. Although the magnesium alloy has many advantages mentioned above, its application is limited for lower heat resistant performance at elevated temperatures. Alloying is an effective way to improve the mechanical properties of the magnesium alloy at elevated temperatures.

The addition of rare earth to the magnesium alloy is an effective way to refine grain and improve the mechanical properties of the alloy at ambient and elevated temperatures, and improve the anti-oxidation capacity and casting characteristics. Sm has a unique orthorhombic structure than other rare earth elements. However, only a few research literatures about the microstructure and mechanical properties of the Sm-containing Mg-Al alloy has been found. Only a small number of reports describe the Mg-Al-Sm phase diagram, so the effect of Sm on the microstructure and mechanical properties of the Mg-Al alloy needs further research. Sb is one of the beneficial elements for the magnesium alloy because it can improve mechanical properties and increase the surface activity of the magnesium alloy. A few reports exhibit that [3-4] when a proper content of cheaper Sb element is added to AZ magnesium alloy, high heat stability Mg_3Sb_2 phases precipitated are dispersed in the alloy and act as the substrate of heterogeneous nucleation of the α-Mg. This promotes the precipitation of fine and continuous $Mg_{17}(A1,Sb)_{12}$ phases which distribute in the grain interior and coherent with the α-Mg base. Therefore, the mechanical properties of the magnesium alloy can be improved at ambient and elevated temperatures. Currently, there are only a few reports about Mg-Al alloys added with Sb containing rare earth elements (commonly is mischmetal, and the content of rare earth is low (≤ 1.5%)). Sn modifies the microstructure of a magnesium ingot and causes the formation of Mg_2Sn precipitates with high hardness and melting point (t_m =1043 K), and it increases the strength at ambient and elevated temperatures [5]. Sm and Sn can improve the strength of magnesium alloys by solution strengthening mechanism (the solid solubility of Sm in Mg: 813 K, 5.7 wt.%; 473 K,

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0.4 wt.%. The solid solubility of Sn in Mg: 834 K, 14.48 wt.%; 473 K, 0.65 wt.% [1]). The Mg-6Al-1.2Y-0.9Nd alloy has higher mechanical properties at ambient and elevated temperatures [6]. Due to the above-mentioned reasons, the effects of Sb, Sm, and Sn on the microstructure and mechanical properties of the Mg-6Al-1.2Y-0.9Nd alloy are emphatically studied.

2. Experimental

The chemical composition of the studied alloys is listed in Table 1. Alloy ingots were then prepared from high purity Mg (99.95%), Al (99.98%), Sb (99.95%), Sn (99.95%), and Mg-18wt.%Y, Mg-18wt.%Nd, Mg-24wt.%Sm master alloys in an induction melting furnace under a mixed atmosphere of CO_2 and SF_6 at a volume ratio of 100:1. The alloys were held for 15 min at 963 K, and then poured into a metallic mold which was preheated to 523 K. Samples machined out from the casting covered with MgO powders were heated for solution treatment at 693 K for 20 h and then water quenched. Artificial aging treatments were performed at 473 K for 10 h.

The tensile tests were carried out at a strain rate of 1 mm/min in an AG-I250kN precision universal material test machine at room temperature (written as 293 K), 423 K, and 448 K. The microstructure and composition of the alloys were analyzed using optical microscopy and scanning electron microscopy (JSM-5610LV) with energy dispersive spectroscopy (EDS). Phase analyses were performed with an X'pertmpdpro X-ray diffractometer (XRD). The grain size was determined using a linear intercept method from a large number of non-overlapping measurements. Microhardness measurements of the aged alloys were carried out with a Vickers microhardness tester, using a test load and application time of 0.98 N and 10 s, respectively.

Table 1. Chemical composition of the alloys investigated wt.%

Alloy	Al	Y	Nd	Sb	Sm	Sn	Mg
MA	6	1.2	0.9	—	—	—	Bal.
MSB	6	1.2	0.9	0.5	—	—	Bal.
MSM	6	1.2	0.9	—	0.5	—	Bal.
MSN	6	1.2	0.9	—	—	0.5	Bal.

3. Results and analysis

3.1. Effects of Sm, Sn, and Sb on the microstructure of the Mg-6Al-1.2Y-0.9Nd alloy

The microstructure of the experimental alloy after T6 treatment is shown in Fig. 1, and the results of EDS and XRD analyses are shown in Figs. 2 and 3.

Combining the EDS and XRD results (shown in Figs. 2 and 3), it can be seen that Al_2Y and Al_3Nd phases distribute in the MA alloy in blocky or island-like shape, and a small amount of Mg_2Al_3 phase are formed. The aggregation of Al_2Y and Al_3Nd phases in the alloys with Sb and Sn addition decreases. In the MSM alloy, the Al-Nd phase is defined as AlNd phase through XRD analysis, and its shape and distribution changes compared with the Al_3Nd phase in the MSB alloy. In the MSB alloy, Al_2Y and Al_3Nd phases (shown in Fig. 1(b)) disperse in blocks and granules (small amount), the quantity of rod-like Mg_2Al_3 phase increases, and the granular hexagonal Sb_3Y_5 phase is formed. In the MSM and MSN alloys, Al_2Y phases and AlNd (MSM alloy)/Al_3Nd (MSN alloy) (shown in Figs. 2(c) and 2(d)) disperse in blocks (small amount) or granules, and rod-like Mg_2Al_3 phases disappear. Granular cubic structure Al_2Sm phase in the MSM alloy and rod-like hexagonal Nd_5Sn_3 phase in the MSN alloy are formed.

It is essential for grain refinement to possess high-segregation-ability solute atoms and effective nucleation sites. The segregation of the solute onto the dendritic solidification fronts leads to constitutional supercooling, and hinders the growth of dendrite and provides the driving force for nucleation in the constitutional supercooling region. The quantity of valid nuclei is determined by the nucleation ability of nucleation sites in the constitutional supercooling region during alloy solidification. According to phases present in binary Mg-Sb, Mg-Sm, and Mg-Sn alloys, when the content of Sb, Sm, and Sn is 0.5%, the solute equilibrium partition coefficient of Sb, Sm, and Sn in magnesium is as follows:

$$k_0 = C_s / C_L < 1,$$

where C_S and C_L are the equilibrium concentrations of solid and liquid phases, respectively. Therefore, Sb, Sm, and Sn atoms are squeezed into the solid-liquid interface during solidification, which leads to constitutional supercooling, promotes nucleus forming, and hinders the growth of Al-RE phases. Otherwise, the high melting point compounds (Sb_3Y_5, Al_2Sm, or Nd_5Sn_3 phase) are formed between inter-dendritic α phase and can mechanically hinder the growth of α-Mg grains.

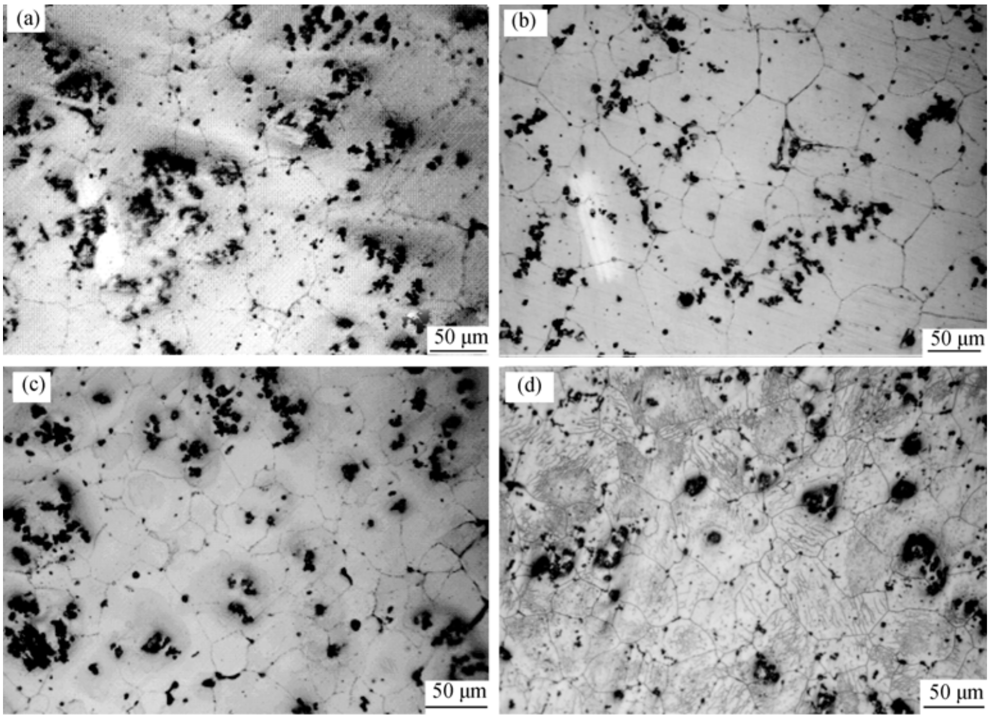

Fig. 1. OM micrographs of the aged alloys: (a) MA; (b) MSB; (c) MSM; (d) MSN.

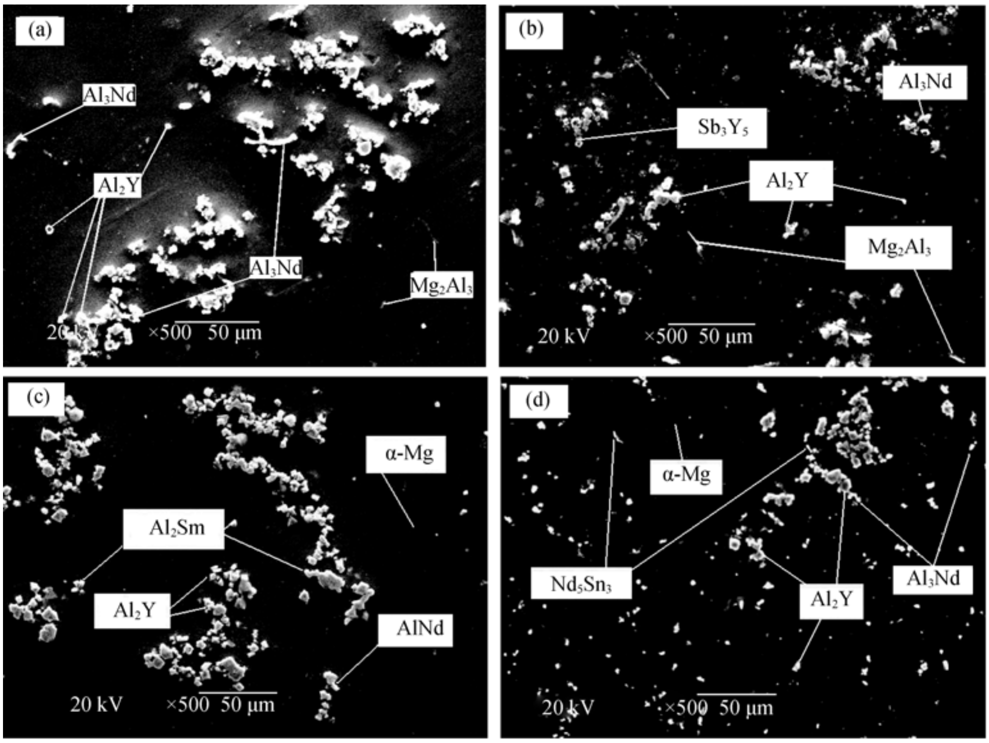

Fig. 2. EDS analysis results of the aged alloys: (a) MA; (b) MSB; (c) MSM; (d) MSN.

The effect of solute element is explained in terms of growth restriction factor [7]:

$$\mathrm{GRF} = \sum m_i c_{0i}(k_i - 1),$$

where m_i is the slope of the liquidus line, k_i is the partition coefficient, and c_{0i} is the initial concentration of element i. The larger the growth restriction factor, the better the refining efficiency of the grain. It has been calculated that the GRF of MA, MSB, MSM, and MSN is 33.71, 33.97, 35.27, and 34.44, respectively (Fig. 4). With the addition of Sb, Sm and Sn, the grain is refined to some degree. The grain size of

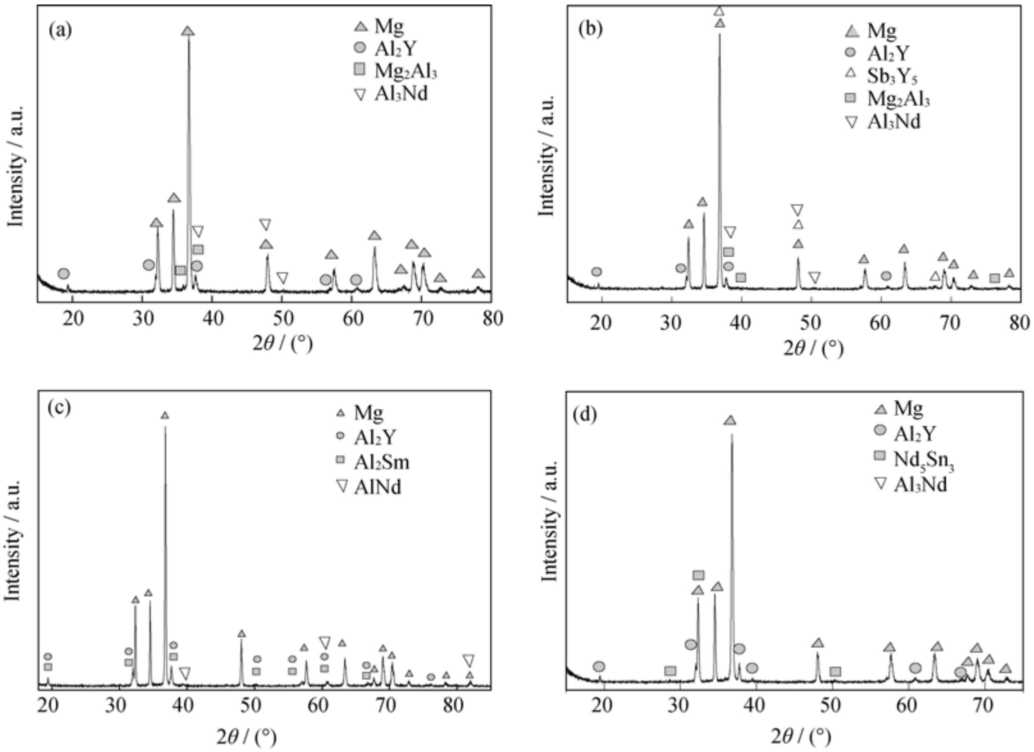

Fig. 3. XRD patterns of the aged alloys: (a) MA; (b) MSB; (c) MSM; (d) MSN.

MA, MSB, MSM, and MSN is 56.8, 50.4, 43.5, and 47.2 µm, respectively. GRFs correspond well to the changes of grain size.

The Miedema's model is a simple semi-empirical scheme for predicting the enthalpy of formation of binary metallic alloys; it should be simplified for predicting the multi-component alloy system [8-10]. Based on the solvent of Mg/Al/Y/Nd, and disregarding the interactions of solutes, the predicted enthalpies of formation in alloys using Miedema's model is shown in Table 2. Therefore, according to the solidification thermodynamics of metallic melt, Al-Sm, Sb(Sn)-Y, and Sb(Sn)-Nd compounds can be formed preferentially. Al atoms attract RE more strongly than Mg in the Mg-Al alloy and ordered phase tends to form in clusters [11-12]. When Sb/Sn is added to the Mg-6Al-1.2Y-0.9Nd alloy, Sb-Y or Sn-Nd compounds are formed, then Al_2Y, Al_3Nd phases decrease in amount and disperse in the alloy, and Al-RE phases tend to disperse in granules. Only a small amount of Al-RE phases have been formed in clusters. Similarly, because the formation enthalpy between Sm and Al is larger than that between Mg and Sm, the Sm-Al compound can be formed preferentially. In the MSB alloy, the reason why the Sb_3Y_5 phase rather than the Nd-Sb phase is formed needs further research.

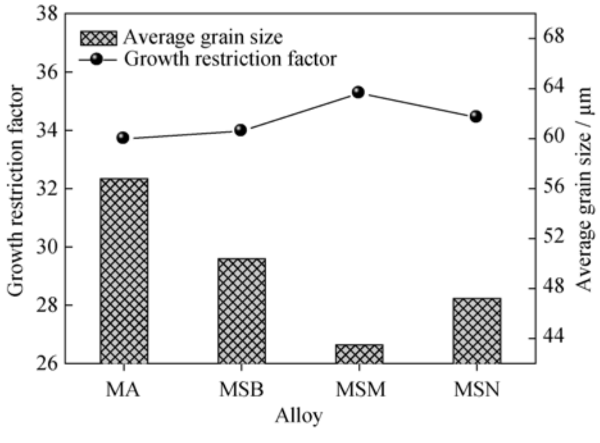

Fig. 4. GRF and average grain size of the aged alloys.

Table 2. Predicted enthalpies of formation in alloys kJ/mol

Solvent	Mg	Al	Y	Nd	Sm	Sn	Sb
Mg	—	−0.2535	−0.0127	−0.0075	−0.0032	−0.0209	−0.0601
Al	−0.2357	—	−2.7632	−1.4026	−0.7294	−0.0601	−0.1711
Y	−0.0116	−2.6234	—	−0.6409	−0.4151	−13.2809	−20.5401
Nd	−0.0068	−1.2714	−0.6415	—	−0.6823	−21.4797	−33.2230

Table 3 shows the α-Mg lattice constant of the alloys. With the addition of Sm or Sn, the α-Mg lattice constants increase respectively, which indicates that a small amount of Sm or Sn is dissolved in the Mg-matrix. Sm and Sn atoms have larger atomic radii than Mg ($R_{Mg} = 0.1598$ nm, $R_{Sm} = 0.259$ nm, $R_{Sn} = 0.172$ nm) and form substitution solid solution and increase the lattice constant around Sm and Sn atoms. The larger the difference of atomic radius between solute atoms and the matrix alloy, the better the strengthening effect of the alloy, and Sm and Sn can enhance the strength of MSM and MSN alloys by solid solution strengthening. The lattice constant of α-Mg in the MSB alloy changes very little, which is attributed to the lower solid solubility of Sb in the Mg-matrix. The effects of Sb, Sm, and Sn on the Vickers hardness of the MA alloy are shown in Fig. 5. The hardness values of MA, MSB, MSM, and MSN are 74, 75, 78, and 80, respectively. Minor differences in hardness are caused by different solid solution quantities of Sb, Sm, and Sn in the alloy.

Table 3. Lattice constants of α-Mg in the aged alloys

Alloy	a / μm	c / μm
MA	0.3192	0.5182
MSB	0.3191	0.5182
MSM	0.3194	0.5189
MSN	0.3204	0.5196

3.2. Effect of Sm, Sn, and Sb on the mechanical properties of the Mg-6Al-1.2Y-0.9Nd alloy

Fig. 6 shows the mechanical properties of experimental alloys at ambient and elevated temperatures after T6 treatment. Compared with the MA alloy, the strength of MSB, MSM, and MSN alloy increases at ambient and elevated temperatures except for MSN alloy at 293 K. The tensile strength of MSM is the highest (251 and 186 MPa, respectively) at 293 and 423 K, and the tensile strength of MSN is the highest (251 MPa) at 448 K. The tensile strength of MSN decreases slowly with the increase of temperature. The elongation of MSM has a little increase at ambient and elevated temperatures. The elongation of MSN decreases obviously compared with MA at ambient and elevated temperatures. As for the MSB alloy, its elongation decreases in some degree at 293 and 423 K and increases a little at 448 K.

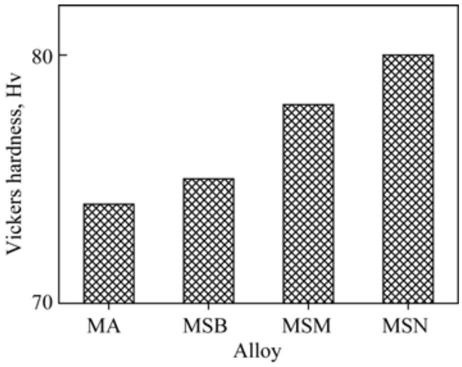

Fig. 5. Microhardness of the aged alloys.

Blocky phases are harmful to the mechanical properties of the alloy. The mechanical condition of second phase particles escaping from the alloy matrix is $\sigma \propto d^{-1}$, where σ is the stress that particles required to escape from the matrix, and d is the diameter of second phase particles. It means that bulky second phase particles easily escape from the alloy matrix and micro-pores are formed, then cracks generate easily around the micro-pores. On the other hand, massive second phase particles easily produce stress concentration and intergranular cracks are formed easily when the alloy is loaded. Cracks propagate preferentially along the interface of the second phase particles and alloy matrix and decrease the mechanical properties of the alloy [13].

The mechanical properties of MA added with Sm, Sb, or Sn have been influenced by the multi-strengthening mechanism as shown below.

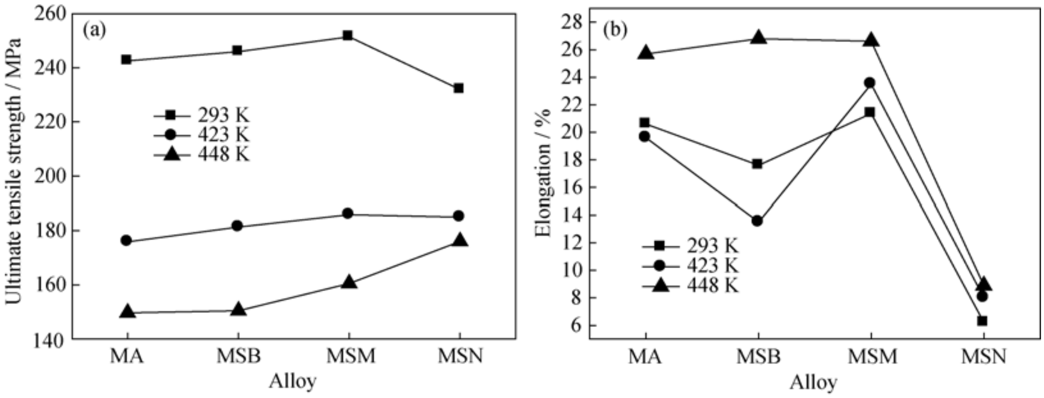

Fig. 6. Tensile properties of the aged alloys: (a) ultimate tensile strength; (b) elongation.

(1) Grain refinement strengthening. According to the Hall-Petch relationship, grain size has a great effect on mechanical properties. The decrease of grain size results in the increase of the ratio of grain surface area to volume, so the surface tension increases. The increase of surface tension and the interaction of neighboring grains result in lattice deformation of the grain surface layers; therefore, a hard deformation area near grain boundaries is formed. The smaller the polycrystalline size, the larger the deformation resistance, and the larger the value of the alloy's strength and hardness at the same time [14-15].

(2) Solid solution strengthening. Solid solution strengthening results from the combined effect of elastic interaction, chemical interaction, and electrostatic interaction between dislocation and solute atoms. When the solid solution develops plastic deformation, the movements of dislocation change the distribution of solute atoms in the solid solution, which has the distribution of short range order or segregation before plastic deformation, leading to the increase of system energy. Therefore, the resistances of dislocation slip and deformation increase. Sm and Sn can enhance the strength of MSM and MSN alloys by solid solution strengthening mechanism [16].

(3) Second phase strengthening. The heat resistance of the magnesium alloy is determined by the softening resistance of the Mg-matrix, and the physical properties, morphology, size, and distribution of second phases in the alloy. The Sb element has poor solubility; it improves the strength of the alloy by forming the second phase particles. The high melting point dispersoid phases (Sb_3Y_5, t_m = 1963 K) formed during solidification have a higher thermodynamic stability, which can effectively improve the mechanical properties of the alloy at elevated temperatures. At elevated temperatures, the dissolvable precipitated phases prefer to coarsen and soften and are unable to strengthen the alloys, while dispersoid phases with a higher thermodynamic stability can hinder the dislocation slip and strengthen the alloy [17]. The granular Al_2Sm phases in the MSM alloy have a high melting point (t_m = 773 K) and disperse in the alloy, and Al_2Y, Al_2Nd, or AlNd phases in MSB, MSM, and MSN alloys tend to disperse in the alloy. The above mentioned phases can effectively hinder dislocation movement and crystal boundary sliding by the Orowan strengthening mechanism. The rod-like Nd_5Sn_3 phases (t_m = 1933 K) disperse in MSN alloy. It can effectively pin dislocations and hinder the deformation of the alloy, but microcracks form easily when distortion of the crystal lattice becomes more serious to some degree. Under tensile stress, microcracks propagate along the interface between Nd_5Sn_3 phase and α-Mg, which finally leads to fracture [18]. This is the reason that MSN alloy has a lower elongation than the other alloys.

Due to the above-mentioned reasons, the multi-strengthening mechanism of the magnesium alloy needs further research, and developing a new type of heat resistant magnesium alloy is one of the research emphases for scientific workers henceforth.

4. Conclusions

(1) The elements Sb, Sm, and especially Sn can refine the grains of the Mg-6Al-1.2Y-0.9Nd alloy. MSM alloy has the smallest average grain size. When Sb, Sm, and Sn are added to the Mg-6Al-1.2Y-0.9Nd alloy, the high melting point Sb_3Y_5, Al_2Sm, and Nd_5Sn_3 intermetallic compounds can be formed as granular, blocky, and rod-like shape, respectively.

(2) Compared with MA alloy, the tensile strength of MSB, MSM, and MSN alloys increases at ambient and elevated temperatures except for MSN alloy at 293 K. The tensile strength of MSM is the highest (251 and 186 Mpa, respectively) at 293 and 423 K, while the tensile strength of MSN is the highest (176 MPa) at 448 K.

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