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Research Article

Experimental Study of the Al-Mg-Sr Phase Diagram at 400°C

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The Al-Mg-Sr system is experimentally studied at 400°C using EPMA and XRD techniques. It was determined that the intermetallic phases in the Al-Mg-Sr system have a tendency to form extended substitutional solid solutions. Two ternary phases were found in this system. Solubility limits of binary and ternary phases were determined and the phase equilibria among phases were established. The isothermal section of the Al-Mg-Sr system at 400°C has been constructed using results of the phase analysis and experimental literature data.

1. Introduction

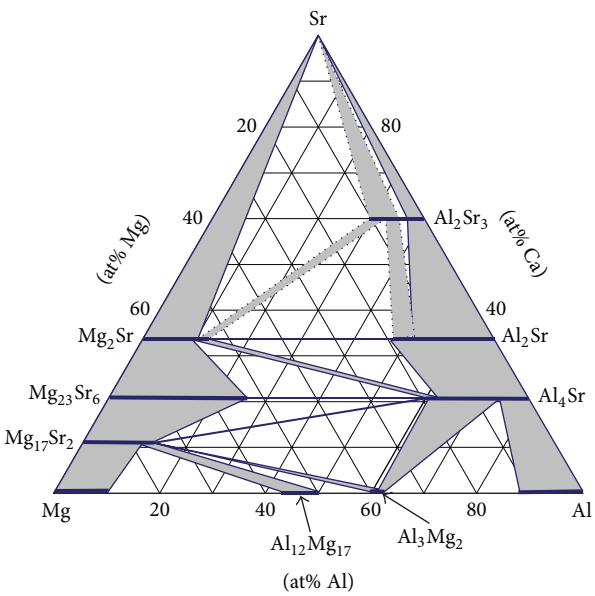
The growing demand for light-weight alloys in automotive and aerospace industries determines the continuously increasing interest in magnesium-based alloys. The most common commercial magnesium alloys are Mg-Al-based alloys, especially the AZ and AM series. Unfortunately, they are not appropriate for the special automotive applications, such as powertrain components or engine blocks that require sufficient creep resistance at elevated temperatures. For these elevated temperature applications, new alloys are being developed through additions of rare earth (RE) elements or Ca and Sr [1]. Since Sr additions significantly improve creep resistance of Mg-Al-based alloys, Al-Mg-Sr phase diagram attracted attention of researchers. Several experimental studies and thermodynamic models of this system were reported in the literature [1–4]. However, numerous discrepancies could be found in these publications as will be discussed below.

In this study, the isothermal section of the Al-Mg-Sr phase diagram has been experimentally studied between 0 and 35 at% Sr. The aim of the present work is to determine the compositions and solubility ranges of the binary and ternary phases in the Al-Mg-Sr system at 400°C, to analyze the phase equilibria, and to construct the isothermal section of the Al-Mg-Sr phase diagram at 400°C. Alloys with various compositions were cast, annealed, and analyzed in order to establish phase relations and phase stability under given conditions. Microstructural characterization using optical microscopy, scanning electron microscopy (SEM), electron probe microanalysis (EPMA), and X-ray powder diffraction (XRD) was used to determine the composition of phases and the microstructure of the alloys.

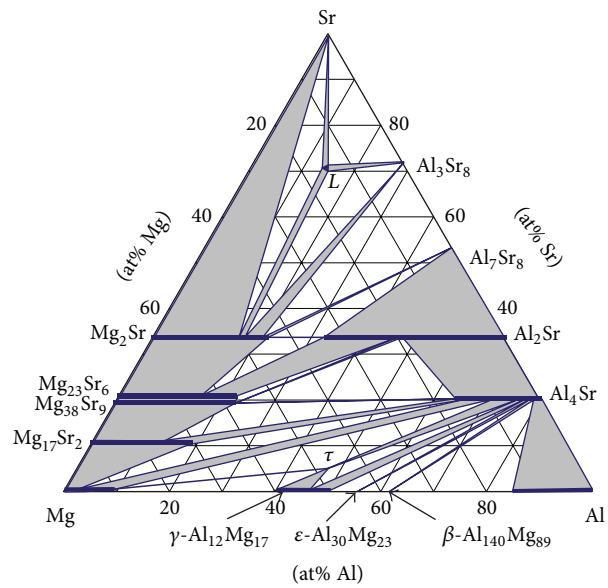
2. Literature Review

A detailed experimental study of the ternary Al-Mg-Sr system was carried out by the group of Makhmudov [5–9], who studied the liquidus of the Al-Mg-Sr phase diagram [5, 6], quasibinary sections [7], and the isothermal section at 400°C [8]. Their isothermal section is presented in Figure 1.

Makhmudov et al. [8] investigated the isothermal section using XRD and microhardness measurements. According to their work, the ternary solubilities of the binary phases were found to be 12 at% Al in $SrMg_2$, 13 at% Al in Sr_2Mg_{17},



Figur e 1: Experimental isothermal section of the Al-Mg-Sr ternary system at 400°C redrawn from [8].



Figur e 2: Calculated isothermal section of the Al-Mg-Sr ternary system at 400°C redrawn from [1].

27 at% Al in Sr_6Mg_{23}, 25 at % Mg in Al_4Sr, and 19 at% Mg in Al_2Sr. Further, the ternary solubilities of the Mg_2Al_3, $Mg_{17}Al_{12}$, and Al_2Sr_3 binary phases were reported to be below 5 at%. They also reported a ternary compound with an approximate composition of Al_6MgSr_{10} and close to Al_2Sr_3 binary compound [8], but its crystal structure was not determined. The existence of ternary Al_6MgSr_{10} and the binary Al_2Sr_3 compounds was not confirmed in later studies and, therefore, their stability is questionable.

A critical evaluation and thermodynamic modeling of the binary subsystems and ternary phase diagram of the Al-Mg-Sr were reported by [2]. The ternary phase diagram was extrapolated from binary data using the quasichemical model for the liquid phase without considering any extended solubilities of the binary compounds nor the existence of ternary compounds.

Thorough experimental investigation of this system was reported by Parvez et al. [10]. The liquidus surface was studied by DSC and the phase relations in the ternary alloys were investigated by XRD. Their experimental results were compared with thermodynamic modeling of Chartrand and Pelton [2] and reported substantial discrepancies.

The phase equilibria in the Mg-Al-Sr system were studied by Aljarrah et al. [3] using EMPA, DSC, XRD, and SEM. The investigated samples were annealed at 400°C for 48 h. They found that there are extended solubilities of the binary compounds in the ternary system (23.2 at % Mg in Al_4Sr, 21.3 at% Al in $Mg_{17}Sr_2$, and 12.5 at% Al in $Mg_{38}Sr_9$).

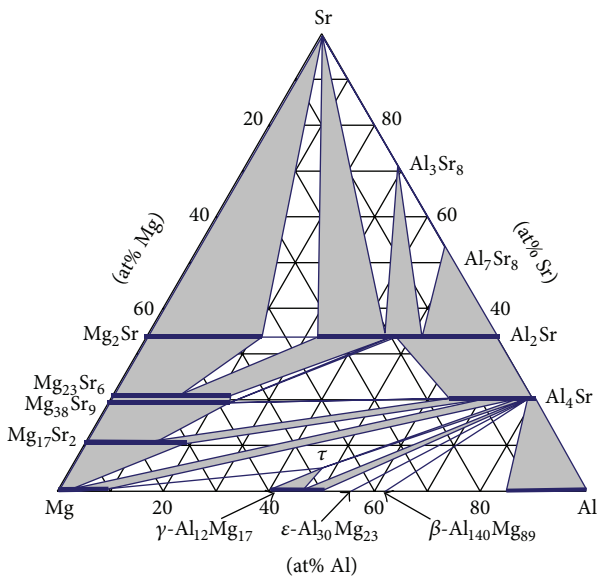
Baril et al. [11] reported the formation of the ternary phase with unclear stoichiometry in the commercial AJ52x alloys. The approximate composition of the phase is $Mg_{13}Al_3Sr$ which is different from that reported by [8]. The later work of Medraj et al. [12] reported a new ternary compound with a chemical composition of $Mg_{69.9\pm1.5}\,Al_{19.3\pm2.0}\,Sr_{8.7\pm0.6}$. The composition of this phase was determined by EPMA analysis of three different alloys.

Another thermodynamic model of the system was constructed based on literature data and own experiments by [1]. The calculated isothermal section of the Al-Mg-Sr system at 400°C is drawn in Figure 2. A stoichiometric ternary compound with a composition $Al_{38}Mg_{58}Sr_4$ was reported. The ternary solubilities of binary phases were reported to be 16.5 at% Al in $Mg_{17}Sr_2$, 16.8 at% Al in $Mg_{38}Sr_9$, 15.9 at% Al in $Mg_{23}Sr_6$, 12.9 at % Al in Mg_2Sr, 10.2 at% Mg in Al_4Sr, and 17.9 at% Mg in Al_2Sr. The ternary solubility of other binary phases was considered to be below 1 at%.

Zhang and Akiba [13] reported the existence of the ternary C36 phase between Al_2Sr and Mg_2Sr. The C36-type Laves phase $Sr(Al_{1-x}Mg_x)_2$ was found as a structural intermediate between the Zintl phase (Al_2Sr) and the C14 Laves phase (Mg_2Sr). The single-phase regions for the Al_2Sr, C36, and Mg_2Sr phases on the $Sr(Al_{1-x}Mg_x)_2$ section were determined to be $x = 0$–0.10, 0.45–0.68, and 0.80–1, respectively. This phase was not previously reported and its existence was verified in this work.

A recent study of the Al-Mg-Sr system was reported by Aljarrah et al. [4] as a part of the quaternary Al-Mg-Ca-Sr system. The extended solubilities of binary compounds [4] correspond well with the data reported by [1]. The isothermal section of the Al-Mg-Sr system at 400°C reported by [4] is shown in Figure 3. The main difference in the phase diagrams, comparing with the data of [1], is the directions of the tie-lines in the Sr-rich corner.

The formation of the Mg_9Al_3Sr ternary phase in AJ62 Mg alloys with a high Sr content was reported by L'Espérance et al. [14]. It was found in as-cast alloys that also contained Mg, Mg_9Al_3Sr, and Al_4Sr phases. They [14] reported that Mg_9Al_3Sr phase decomposes after the heat treatment of



Figur e 3: Calculated isothermal section of the Al-Mg-Sr ternary system at 400°C redrawn from [4].

alloys. The authors associated this phase with the Mg_8Al_2Sr phase reported by Medraj et al. [12]. On the other hand, it could be associated with the $Mg_{13}Al_3Sr$ phase found in AJ52x alloys by Baril et al. [11]. The decomposition of this phase could be a sign that it is metastable. The TEM study of the Mg_9Al_3Sr ternary phase showed that it has a tetragonal structure with the following lattice parameters: $a = 1012$ pm and $c = 1169$ pm.

The aforementioned results will be compared with the current work in the Discussion section.

3. Experimental

Two sets of samples were prepared; the first set was prepared at CANMET using the following procedure: pure aluminium and magnesium (Mg-99.8 wt.%, Al-99.9 wt.%) of proper ratios were charged into a graphite crucible, which has 150-gram capacity. The crucible was then placed inside an induction furnace. Gas cover of argon with 1% SF_6 was used throughout the melting process. After the metals were molten in the crucible, strontium (Sr-99 wt.%) was plunged in with a graphite rod, followed by stirring. The chemical compositions of the as-cast alloys were analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) method. The as-cast alloys were annealed at 400°C under constant flow of protective Ar gas for 48 hours and quenched in water.

The second set of samples was prepared at Concordia University. The pure metals (Mg-99.8 wt.%, Al-99.9 wt.%, and Sr-99 wt.%, Alfa Aesar) were molten using an arc-melting furnace equipped with water cooled copper crucible under protective Ar atmosphere. The prepared samples were sealed in quartz tubes filled with Ar. Annealing was performed at 400°C for 15 days followed by quenching in water.

All samples were experimentally studied using optical microscopy, SEM, EPMA, and XRD. EPMA was used to determine the compositions of the phases and phase boundaries of the solid solutions. XRD was used for the phase analysis of the alloys.

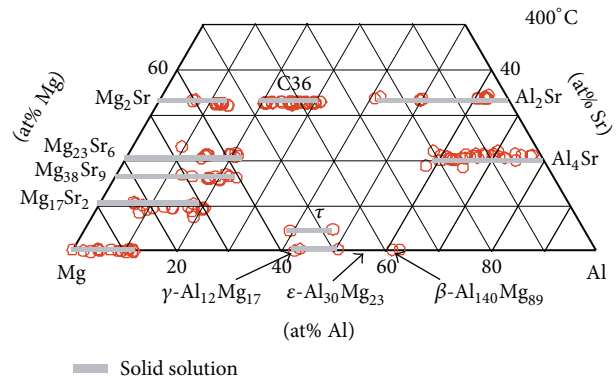


Figure 4: Homogeneity ranges of the solid solutions in the ternary Al-Mg-Sr system at 400°C.

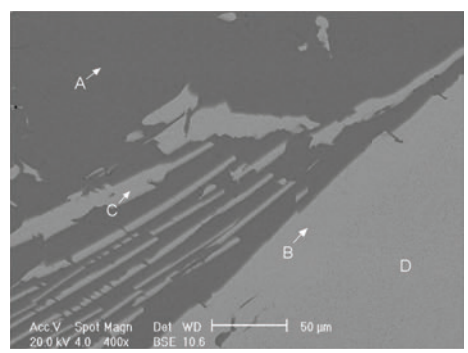


Figure 5: Microstructure of Al-Mg-Sr ternary alloy with C36 phase (B, C, and D regions) and Mg_2Sr phase in region A.

4. Results

In this work, we present results of experimental investigation of 37 ternary alloys studied by EPMA and XRD. The compositions of all the phases in the Mg-Al-rich side have been determined as presented in Figure 4.

In the investigated samples, annealing time has a small effect on the solubility of the phases. For example, the difference in the solubility ranges between 48-hour annealing and 2-week annealing is below 2 at%. Since the estimated error of the EPMA measurements was 2 at%, we suggest that such differences are negligible. This means that our samples reached equilibrium and they do not require additional annealing.

The extended solubility of the binary compounds in the ternary system has been found to be 20.3 at% Al in $Mg_{17}Sr_2$, 23.1 at% Al in $Mg_{38}Sr_9$, 21.0 at% Al in $Mg_{23}Sr_6$, 13.1 at% Al in Mg_2Sr, 21.0 at % Mg in Al_4Sr, and 25.4 at % Mg in Al_2Sr. The extended solubility of the other binary compounds has been found to be below 1 at%. The error of measurement was estimated to be ±2 at%. Surprisingly, the Sr content in the $Mg_{38}Sr_9$ phase was found to be 16.4 ± 0.2 at % Sr.

Table 1: Ternary solid solubilities of the Al-Mg-Sr binary compounds.

Phase	[1] experimental	[8] experimental	[3] experimental	[13] experimental	[4] calculated	[4] experimental	This work
$Mg_{17}Sr_2$	16.5 at% Al	13 at% Al	21.3 at% Al		20.0 at% Al	13.1 at% Al	20.3 at% Al
$Mg_{38}Sr_9$	16.8 at% Al		12.5 at% Al		20.3 at% Al	23.1 at% Al	23.1 at% Al
$Mg_{23}Sr_6$	15.9 at% Al	27 at% Al				21.9 at% Al	21.0 at% Al
Mg_2Sr	12.9 at% Al	12 at% Al		13.3 at% Al	26.1 at% Al	18.6 at% Al	13.1 at% Al
Al_4Sr	10.2 at% Mg	25 at% Mg	23.2 at% Mg		19.9 at% Mg	15.9 at% Mg	21.0 at% Mg
Al_2Sr	17.9 at% Mg	19 at% Mg		6.7 at% Mg	26.1 at% Mg	30.8 at% Mg	25.4 at% Mg

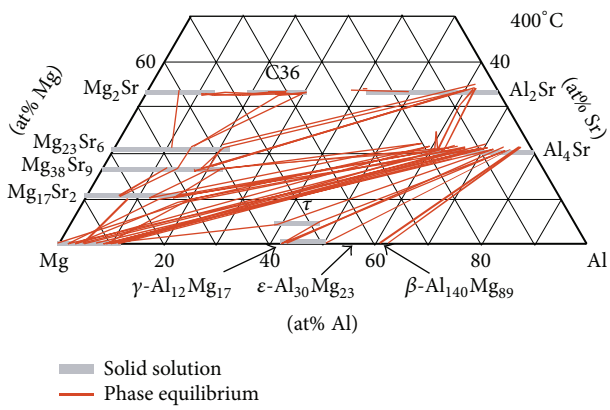


Figure 6: Experimental phase equilibria in the Al-Mg-Sr system at 400°C.

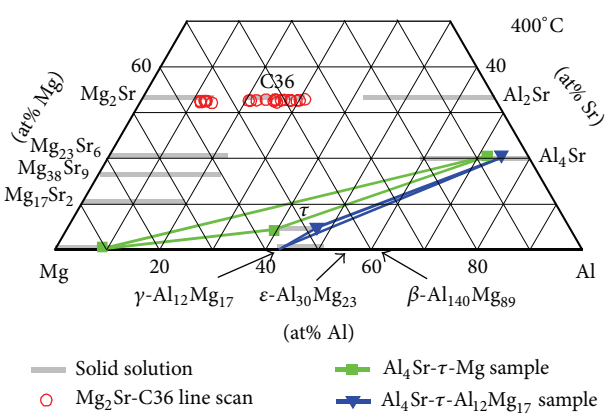


Figure 7: Determination of solubility ranges of the Al-Mg-Sr ternary compounds.

This value is an average of 15 EPMA point measurements in 5 independent alloys. According to the formula, Sr content in the $Mg_{38}Sr_9$ should be 19.1 at% Sr. This difference of the Sr content in binary $Mg_{38}Sr_9$ phase and $(Mg,Al)_{38}Sr_9$ solid solution cannot be explained by the systematic error of the EPMA measurement because in all the other 5 binary compounds, the Sr content perfectly corresponds to the stoichiometric compositions. Such deviation could be explained by a possible homogeneity range of $Mg_{38}Sr_9$ compound in the binary Mg-Sr system. This solubility will cause a shift in the Sr content in the $(Mg,Al)_{38}Sr_9$ solid solution.

Two ternary phases with wide homogeneity ranges were found in this system. The $(Al,Mg)_2Sr$ phase with C36 crystal structure has a solubility from 19.5 to 31.5 at% Al. The τ phase with the composition $(Al,Mg)_{20}Sr$ has a solubility from 39.3 to 47.3 at% Al. The Sr content was found to be constant at 4.7 at% Sr. An example of the C36 containing alloy is presented in Figure 5. The regions denoted on the micrograph as B, C, and D correspond to the C36 phase.

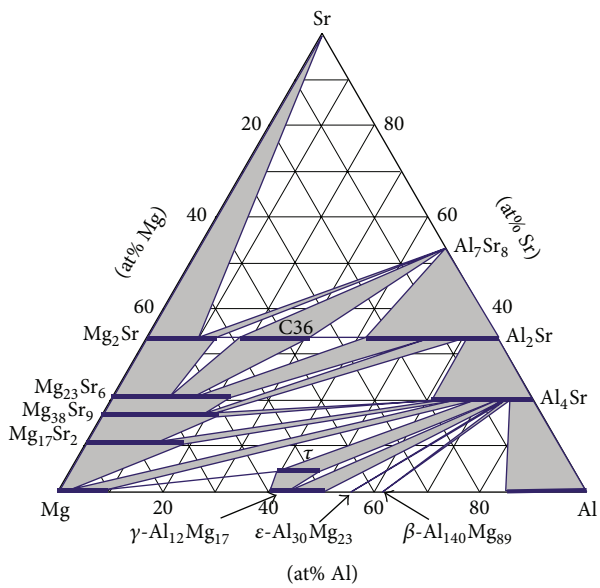
The phase equilibrium relationships among the different phases in this system were determined using EPMA and XRD analysis. The experimental tie-lines obtained from the EPMA measurements are illustrated in Figure 6.

5. Discussion

As a result of this study, we have obtained the experimental data on solid solubilities and phase relations in the Mg-Al-rich side of the Al-Mg-Sr system at 400°C. The ternary solid solubilities of the $Mg_{17}Sr_2$, $Mg_{38}Sr_9$, $Mg_{23}Sr_6$, Mg_2Sr, Al_4Sr, and Al_2Sr binary compounds are determined and compared with the literature data in Table 1. The ternary solubilities of the Al-Mg binary phases were found to be below 1 at%. Since it is lower than the estimated experimental error (2 at%), the solubility of these phases is considered as negligible.

The Al-Mg-Sr system clearly shows the trend to form extended solid solutions, where Al and Mg substitute each other. As shown in Table 1, the solubility ranges of Al-Sr and Mg-Sr binary phases exceed 20 at% in most cases. The relatively low solubility range of the Mg_2Sr compound may be explained by the formation of the C36 ternary compound close to it. The C36 phase and the Mg_2Sr belong to the Laves phases. They have similar crystal structures and therefore are energetically close to each other. The location of the C36 phase near the Mg_2Sr and small two-phase region between them indicates that the formation of a ternary C36 phase is energetically more favorable than further extension of the Mg_2Sr solid solution. No extended solubility was detected for the Al-Mg binary phases.

Two ternary compounds with wide homogeneity ranges were found in this system. They are denoted by C36 and τ in Figure 7. The solubility range of the C36 phase was determined by the EPMA line scan. The obtained solubility of the C36-$(Al,Mg)_2Sr$ phase (19.5–31.5 at% Al) is in a good agreement with the C36 solubility reported by [13] (21.3–36.7 at% Al). The solubility range of the τ phase was detected by EPMA point analysis in two ternary alloys as shown in Figure 7. These alloys are located in the three-phase regions



Figur e 8: Experimental isothermal section of the Al-Mg-Sr system at 400°C.

on both sides of the τ phase. Therefore, the compositions of the τ phase in these samples correspond to the solubility limits of this phase. This intermetallic compound has solubility from 39.3 to 47.3 at% Al at 400°C and could be associated with the stoichiometric $Al_{38}Mg_{58}Sr_4$ ternary compound reported by [1]. If the τ phase is associated with the Mg_9Al_3Sr ternary phase reported by [14] in the as-cast alloy, one should expect substantial extension of its solubility towards Mg at elevated temperatures.

Based on the current experiments and literature data, the isothermal section of the Al-Mg-Sr phase diagram at 400°C has been constructed and presented in Figure 8. As can be seen in this figure, the general direction of the tie-lines is from binary Al-Sr system towards Mg corner which is in good agreement with the literature data. Most of the authors report the same direction of the phase equilibria. Not only does the Mg_2Sr-Al_4Sr tie-line reported by [8] contradict our findings, but it contradicts other literature data as well.

The Al_4Sr and Al_2Sr phases are dominating in this system because of their high melting temperatures and stability. Al_4Sr phase dominates the isothermal section below 20 at% Sr and in equilibrium with all phases in that region.

6. Conclusion

The isothermal section of the Al-Mg-Sr phase diagram at 400°C is experimentally studied and constructed in this work. Two ternary compounds C36 and τ with wide homogeneity ranges have been found in this system. Their solubility ranges are determined by EPMA analysis. The ternary solid solubilities of the $Mg_{17}Sr_2$, $Mg_{38}Sr_9$, $Mg_{23}Sr_6$, Mg_2Sr, Al_4Sr, and Al_2Sr binary compounds are also determined. No ternary solubility was detected for Al-Mg binary phases. This study substantially modified and enhanced the description of the ternary Al-Mg-Sr phase diagram at 400°C.

Conflict of Interests

The authors of the paper declare that there is no conflict of interests of any sort that might have influenced the data, results, discussions, or conclusions of this paper.

Acknowledgments

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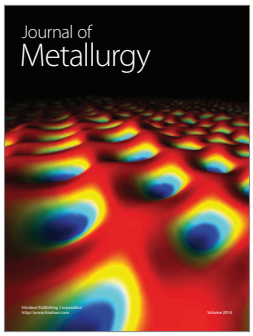

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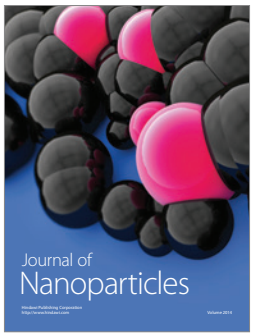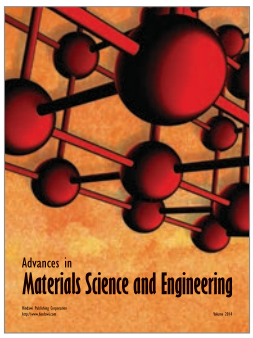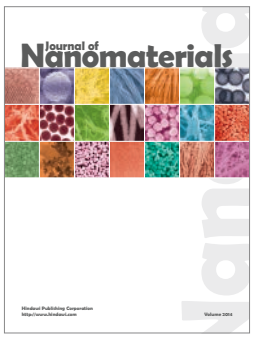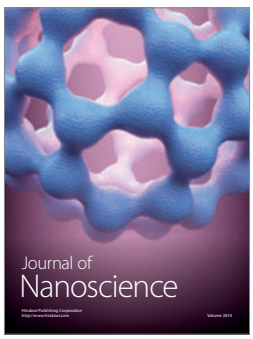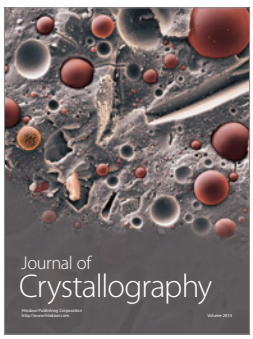
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