Creep and Corrosion Behavior of SiC Nanoparticles Dispersed Squeeze-cast Mg-5.0Al-2.0Ca-0.3Mn Alloy

Dissertation submitted in partial fulfilment
of the requirement of the degree of
Doctor of Philosophy

in

Metallurgical Engineering

by

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CERTIFICATE

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Contents

List of Figures xi

List of Tables xviii

List of Abbreviations xix

List of Symbols xx

Abstract xxi

Chapter 1 1

1.1 Introduction 1

1.2 Objective of the present thesis 4

1.3 Organization of the thesis 5

Chapter 2 6

2.1 Designation of magnesium (Mg) alloys 6

2.2 Role of selected alloying elements in Mg alloys 6

2.3 Mg-Al-Ca alloys 7

2.4 Creep 11

  2.4.1 Classification of creep mechanisms 13
    2.4.1.1 Diffusion creep (p = 2 to 3, n = 1) 13
    2.4.1.2 Grain boundary sliding (p = 2 to 3, n = 2) 13
    2.4.1.3 Dislocation creep (p = 0, n = 3 to 7) 15
  2.4.2 Impression creep 15
  2.4.3 Creep behavior of pure Mg- and Mg alloy-based nanocomposites 17

2.5 Tensile and compression properties 18

  2.5.1 Tensile and compression behavior of Mg- and Mg alloy-based nanocomposites 19

2.6 Corrosion 22

  2.6.1 Galvanic corrosion 23

2.6.2 Pitting corrosion 23
2.6.3 Intergranular corrosion 23
2.6.4 Stress corrosion cracking 23
2.6.5 Corrosion at elevated temperature 24
2.6.6 Corrosion behavior of Mg- and Mg alloy-based nanocomposites 24
2.7 Motivation for the thesis 25

Chapter 3 26

3.1 Fabrication of alloy and nanocomposites 26

3.2 Microstructural characterization of alloy and nanocomposites 27

3.2.1 X-ray Diffraction (XRD) 27
3.2.2 Optical Microscopy (OM) and Scanning Electron Microscopy (SEM) 27
3.2.3 Fractal analysis 27
3.2.4 Transmission Electron Microscopy (TEM) analysis 28
3.3 Mechanical characterization of alloy and nanocomposites 28

3.3.1 Tensile and compressive tests 28
3.3.2 Impression creep tests 28
3.3.3 Post-creep microstructural study 29
3.4 Corrosion tests of alloy and nanocomposites 29

3.4.1 Hydrogen evolution and immersion tests 29
3.4.2 Electrochemical corrosion tests 31
3.4.3 Measurement of volta potential 31
3.4.4 Analysis of corrosion products 31
3.5 Heat treatment of alloy and nanocomposites 32

3.6 Designations of aged alloy and nanocomposites 32

3.7 Hardness measurement 32

Chapter 4 33

4.1 X-ray diffraction analysis 33

4.2 Optical and SEM micrographs 35

4.3 Fractal analysis of SEM micrographs 39

4.4 TEM analysis.. 42

4.5 Summary of chapter 4 47

Chapter 5 48

5.1 Evaluation of mechanical properties 48

  5.1.1 Tensile Yield Strength, Ultimate Tensile Strength, and % Elongation...... 48
  5.1.2 Compressive Yield Strength and Ultimate Compressive Strength............ 49
  5.1.3 Strain-hardening responses 49
5.2 Theoretical prediction of strength and analyses of strengthening mechanisms… 53

5.3 Observation of dislocations in post-tensile samples 57

5.4 Analyses of fracture surfaces 60

5.5 Summary of chapter 5 62

Chapter 6 63

6.1 Creep behavior 63

  6.1.1 Nature of creep curves and comparison of creep responses 63
  6.1.2 Assessment of creep mechanism 65
6.2 Post-creep microstructural analysis 68

  6.2.1 Observation of sub-surfaces 68
  6.2.2 Observation of dislocations 73
6.3 Summary of chapter 6 76

Chapter 7 77

7.1 Hydrogen evolution and immersion tests 77

7.2 Open circuit potential (OCP) 79

7.3 EIS studies 81

7.4 Potentiodynamic polarization test 84

7.5 Volta potential measurement 86

7.6 Characterization of corrosion film 88

  7.6.1 SEM micrographs of corroded film 88
  7.6.2 XRD and FTIR analysis of the corroded products 88
  7.6.3 XPS analysis 93

7.7 Characterization of corroded surfaces 95

7.8 Summary of chapter 7 100

Chapter 8 101

8.1 Hardness response of aged AXM520 alloy and NCs 101

8.2 Microstructural characterization of aged AXM520 and NCs 102

8.3 Creep behavior 105

  8.3.1 Creep response and creep mechanism 105
  8.3.2 Construction of creep mechanism map 110

8.4 Microstructural analyses of creep-tested specimens 111

  8.4.1 Observation of deformed region 111
  8.4.2 Characterization of twinning and dislocations 115

8.5 Summary of chapter 8 121

Chapter 9 122

Conclusions and Scope for Future Research 122

9.1 Conclusions 122

9.2 Scope for future research 125

References 126

Dissemination 139

List of Figures

Figure 2.1 Illustration of coordination polyhedras centered by atoms at non-equivalent occupation sites in crystalline phases, including (a) C15-Al_2Ca, (b) C14-Mg_2Ca, and (c) C36-$(Mg,Al)_2Ca$. The number and type of constituent atoms in each coordination polyhedras are also shown. Wyckoff positions are shown with polyhedra. The light green, cyan, and blue spheres stand for Mg, Al, and Ca atoms, respectively [55] 9

Figure 2.2 SEM micrographs of the as-cast Mg-Al-Ca-Mn alloys: (a, d) AXM530; (b, e) AXM630; (c, f) AXM730 [59]. 10

Figure 2.3 Precipitation of Al_2Ca phase in the die-cast AXJ530 alloy aged at 573 K. TEM bright-field images of the specimens aged for (a)10 s, (b) 30 s, (c) 100 s, (d) 600 s, (e) 3.6 ks and (f) 36 ks. These images were taken with B = $11\bar{2}0$ α, and **g**= 0002α. Precipitates are marked with arrows in (b) and (c) [60]. 10

Figure 2.4 (a) Energy states of a dislocation motion while encountering an energy barrier, which interrupts its motion [63]; (b) a typical tensile creep curve showing different stages of creep; and (c) strain rate in creep test as a function of total strain [64]. 12

Figure 2.5 Vacancy and atom diffusion direction during (a) Nabarro-Herring, (b) Coble creep; and (c) Grain boundary sliding to accommodate the applied strain at high temperature. [63] 14

Figure 2.6 (a) A schematic exhibiting dislocation climb assisted by vacancy diffusion, and (b) a typical impression creep curve. 16

Figure 2.7 A typical engineering stress-strain curve exhibiting 0.2% yield strength, ultimate tensile strength, and fracture strength [64]. 20

Figure 3.1 Schematic portraying the region of post-creep microstructural analysis below indentation after creep test. 30

Figure 4.1 (a) XRD patterns obtained from the as-cast AXM520 alloy and all the nanocomposites; (b) magnified view of the XRD patterns obtained from the AXM520 alloy and NC3.0SiC in the 2θ range from 30 to 50 °; and (c) magnified view of the 2θ range from 36.0 to 37.5 ° confirming the shift of the high-intensity peak of the α-Mg phase..................34

Figure 4.2 Optical micrographs with the corresponding grain size distribution of the (a) AXM520 alloy, (b) NC0.5SiC, (c) NC1.0SiC, (d) NC2.0SiC, and (e) NC3.0SiC nanocomposites...37

Figure 4.3 (a) SEM micrograph of as-cast AXM520 alloy; (b) a magnified view of ‘a’; (c) X-ray elemental mapping of Mg, Al, Ca and Mn corresponding to ‘b’; (d) another magnified view of ‘a’ indicating the regions of EDS analysis; EDS spectra taken from (e) spot 1 confirming α-Mg phase, (f) spot 2 confirming C36 phase, and (g) spot 3 confirming Al_8Mn_5 phase. 38

Figure 4.4 SEM micrographs of the as-cast (a) NC0.5SiC, (b) NC1.0SiC, (c) NC2.0SiC, and (d) NC3.0SiC nanocomposites..40

Figure 4.5 Fractal analyses of the (a) AXM520, (b) NC0.5SiC, and (c) NC3.0SiC exhibiting the maximum connected C36 phase extracted from the respective binary SEM images; and (d) to (f) exhibit the fractal dimension (D_f) plots obtained from the respective images fractal dimension (D_f) plots obtained from the respective images from ‘a’ to ‘c’. 41

Figure 4.6 (a) TEM BF image taken from the C36 phase of AXM520 alloy, and (b) SAED pattern corresponding to ‘a’ with beam direction B = [0001]; (c) TEM BF image taken from the C36 phase of NC3.0SiC, and (d) SAED pattern corresponding to ‘c’ with beam direction B =$[2\bar{4}23]$; (e) TEM BF image taken from the matrix of NC2.0SiC exhibiting the distribution of SiC nanoparticles, and (f) SAED pattern corresponding to ‘e’; (g) TEM BF image taken from the matrix of NC3.0SiC exhibiting the agglomeration of SiC nanoparticles, and (h) SAED pattern corresponding to ‘g’..45

Figure 4.7 (a) HR-TEM image of the SiC_{np} present in α-Mg of NC3.0SiC; (b) FFT corresponding to ‘a’; (c) distribution of SiC_{np} close to the C36 phase at the intergranular region of the NC3.0SiC; and (d) SAED pattern corresponding to ‘c’ 46

Figure 5.1 (a) Typical engineering stress-strain curves obtained from tensile tests of the AXM520 alloy and NCs, and (b) tensile properties calculated from ‘a’; (c) typical engineering stress-strain curves obtained from compression tests of the AXM520 alloy and NCs, and (d) compressive properties calculated from ‘c’. 50

Figure 5.2 Log-log plots of true stress-strain curves for the alloy and NCs displaying the strain hardening exponent (n) calculated from the tensile tests (a) and compression tests (b); variation of strain-hardening rate ($d\sigma/d\varepsilon$) vs. true plastic strain (ε) for the alloy and NCs corresponding to the tensile tests (c), and compression tests (d). 52

Figure 5.3 (a) Contribution of different strengthening mechanisms to the tensile yield strength (TYS) of the NCs;(b) magnified view of 'a' depicting the load-bearing effect; (c) comparison of the calculated and experimentally determined values of TYS of the NCs; (d) variation of agglomeration factor (φ), inter-particle distance (λ) and '$\varphi\lambda$' with volume fraction (V_p) of the nanoparticles; (e) agglomeration factor (φ) vs. V_p of the nanoparticles with curve fitting; (f) comparison of the experimental and predicted values of TYS. 55

Figure 5.4 (a) TEM bright-field image exhibiting dense dislocation forest inside α-Mg grain in the AXM520 alloy; (b) weak beam diffraction pattern acquired from the region shown in 'a'; (c and d) TEM dark-field images exhibiting dense dislocation tangles [corresponding to spot $g_{10\bar{1}1}$ and $-g_{10\bar{1}1}$indicated in 'b', respectively.] 58

Figure 5.5 (a) TEM BF image exhibiting the dislocation pile-ups at the interface of α-Mg and C36 phases in the AXM520 alloy, and (b) SAED pattern corresponding to 'a' exhibiting two beam condition; (c) interaction of dislocations with the SiC nanoparticles in the NC2.0SiC, and (d) SAED corresponding to 'c'. 59

Figure 5.6 Fracture surfaces of the tensile tested (a) AXM520 alloy, and (b) NC2.0SiC; fracture surfaces of the compression tested (c) AXM520 alloy, and (d) NC2.0SiC ('SD' shear direction). 61

Figure 6.1 (a) Impression depth vs. time plots for the AXM520 alloy and nanocomposites nanocomposite creep tested at 498 K and 435 MPa; (b) impression velocity vs. time plots based on 'a'; and (c) steady-state impression velocities estimated from 'a'; and (d) steady-state impression velocities estimated from 'a', as well as previously reported nanocomposites, and alloy [30,34]. 64

Figure 6.2 Stress dependence of the steady-state impression velocities at different temperatures for the (a) AXM520 alloy and (b) NC2.0SiC; temperature dependence of the steady-state impression velocities at different stresses for the (c) AXM520 alloy and (d) NC2.0SiC. 66

Figure 6.3 EBSD map of the creep tested samples showing grain orientation map under the punch for (a) AXM520 alloy, and (b) NC2.0SiC creep tested at 498 K and 435 MPa; corresponding grain boundary maps (c and d) and KAM maps (e and f) for the AXM520 alloy (from a) and NC2.0SiC (from b)......71

Figure 6.4 SEM micrographs displaying flow configuration underneath the indentations for the (a) AXM520 alloy, and (b) NC2.0SiC nanocomposite creep tested at 498 K and 435 MPa. 72

Figure 6.5 Bright Field (BF) TEM micrographs of the AXM520 alloy creep tested at 498 K and 435 MPa showing the (a) dislocation forest, (b) planner defect, (c) dislocation cell in the α-Mg matrix, and (d) dislocation pile-ups around the C36 phase; (e) BF TEM micrograph micrographs of the NC2.0SiC nanocomposite creep tested at 498 K and 435 MPa showing the dislocation pile-ups near the nanoparticles, and (f) SAED pattern taken from ‘e’.......74

Figure 6.6 BF (a) and DF (b) TEM micrographs taken with B = $[1\bar{2}1\bar{1}]$ from the grain interior (i.e., α-Mg phase) of the AXM520 alloy creep tested at 498 K and 435 MPa depicting the dislocations; BF (c) and DF (d) TEM micrographs taken with g$[0002]$ reveal the presence of <c> type dislocation in ‘a’; BF (e) and DF (f) TEM micrographs taken with g$[10\bar{1}0]$ reveal the presence of <a> type dislocation in ‘a’.......75

Figure 7.1 (a) Hydrogen evolution as a function of time, (b) corrosion rate calculated from 'a’ for AXM520 and NCs, (c) weight loss of the alloy and NCs as a function of time, and (d) corrosion rates calculated from ‘c’. 78

Figure 7.2 Variation of OCP recorded as a function of time for all the materials tested........80

Figure 7.3 Presentation of (a) Nyquist plots, (b) impedance vs. frequency, and (c) phase angle vs. frequency Bode plots for AXM520 alloy and NCs; and (d) equivalent circuit for the observed EIS response. 83

Figure 7.4 (a) Potentiodynamic polarization curves; (b) the variation of calculated Icorr, $E_{corr,}$ and corrosion rates with SiC_{np} concentration for the AXM520 alloy and NCs. 85

Figure 7.5 Volta potential maps for (a) AXM520 and (c) NC3.0SiC; the variation of volta potential (b and d) across the lines marked in ‘a’ and ‘c’ exhibiting the potential difference between α-Mg and $(Mg,Al)_2Ca$ (C36) phases. 87

Figure 7.6 SEM images of the corrosion films formed on the surfaces of AXM520 (a) and NCs (b to e). 89

Figure 7.7 EDS results obtained from the corroded films of the AXM520 alloy (a and b) and NC3.0SiC (c and d) confirming the higher Al content on the corrosion film of the NC3.0SiC. 90

Figure 7.8 (a) XRD and (b) FTIR profiles recorded from the corroded films of all the materials tested. 92

Figure 7.9 XPS spectra acquired from the corroded films of AXM520 (a, c, e) and NC3.0SiC (b, d, f). 94

Figure 7.10 3D presentation of corrosion products free surface morphologies of AXM520 (a) and NCs (b to e); summary of surface roughness values (f). 96

Figure 7.11 SEM micrographs of corrosion products free surfaces of AXM520 with elemental mapping (a and b), and NCs (c to f). 97

Figure 7.12 Cross-sectional micrographs of the corroded surfaces of the (a) AXM520 alloy and (b) NC3.0SiC depicting the extent of corrosion. 98

Figure 7.13 Schematic representation showing the different stages of corrosion mechanism took place in (a) AXM520, and (b) NC3.0SiC. 99

Figure 8.1 (a) Variation of hardness values with aging time for AXM520HT and NCs; (b) XRD pattern acquired from the peak-aged AXM520HT and NCs; (c) magnified view of the 2θ range from 30 to 50 ° for the XRD patterns shown in 'b' for AXM520HT and NC2.0SiCHT. 103

Figure 8.2 (a) SEM micrograph of the aged AXM520HT; enlarged view of 'a' showing the (b) morphologies of C36 and Al_8Mn_5 phases, and (c) regions of elemental mapping and EDS analyses; (d) elemental maps corresponding to 'c'; EDS results from (e) spectrum 1 corresponding to α-Mg, (f) spectrum 2 corresponding to C36, and (g) spectrum 3 corresponding to Al_8Mn_5; (h) SEM micrograph of the aged NC2.0SiCHT; (i) enlarged view of 'h' showing the morphology of C36 phase. 104

Figure 8.3 (a) TEM image (BF) revealing the precipitates formed in the α-Mg grain interior of AXM520HT; (b) enlarged view of ‘a’ showing two precipitates with rod and planner-like morphologies, (c) SAED pattern captured from ‘a’; (d) TEM image (BF) exhibiting the presence of precipitates and SiC_{np} in the α-Mg grain interior of NC2.0SiCHT; (e) enlarged view of ‘d’ showing the morphologies of precipitates and dispersed SiC_{np} phase, (f) SAED pattern captured from ‘c’ 106

Figure 8.4 (a) Impression depth vs. time plots obtained at 435 MPa and 498 K for the aged AXM520HT and NCs; (b) steady-state impression velocity vs. time plot for AXM520HT and NCs corresponding to ‘a’; representative plots showing (c and d) stress and (e and f) temperature dependence of steady-state impression velocities for AXM520HT and NC2.0SiCHT 108

Figure 8.5 Diffusion coefficient normalized steady-state strain rate vs. shear modulus normalized applied stress plot exhibiting various deformation mechanisms in Mg-Al-Ca (AX) alloys (a) D_L- and D_p -controlled dislocation creep; (b) D_{gb}- and D_p -controlled grain boundary sliding creep; (c) grain size vs. shear-modulus normalized applied stress plot exhibiting dislocation mechanism map of Mg-Al-Ca (AX) alloys and their nanocomposites at 473 K, and (d) shear modulus normalized applied stress vs. homologous temperature plot for NC2.0SiCHT with grain size of 33 μm. 113

Figure 8.6 SEM micrographs exhibiting the deformation flow pattern in different regions under impressions on the creep-tested (T = 498 K, σ = 435 MPa) specimens of (a) AXM520HT, as well as (b) NC2.0SiCHT. 116

Figure 8.7 EBSD GB maps captured from the highly deformed corner regions of (a) AXM520HT and (b) NC2.0SiCHT; (c) and (d) misorientation map corresponding to ‘a’ and ‘b’, respectively; (e) IPF maps for the twins observed in AXM520HT and NC2.0SiCHT; and (f) comparison of twin fractions in creep-tested (T = 498 K, σ = 435 MPa) AXM520HT and NC2.0SiCHT 117

Figure 8.8 (a) BF image exhibiting an extension twin of type $\{10\bar{1}2\}<10\bar{1}1>$ taken from creep-tested NC2.0SiCHT; (b) SAED pattern corresponds to ‘a’; (c) BF image exhibiting a double twin of type $\{10\bar{1}1\}$-$\{10\bar{1}2\}$ taken from creep-tested AXM520HT; (d) SAED pattern corresponds to ‘c’ 119

Figure 8.9 (a) and (c) BF and DF images of the <c+a> and <a> type dislocations while **g**= $10\bar{1}0$; (b) and (d) BF and DF images of the <c+a> and <a> type dislocations while **g**= 0002 in the same location taken from creep-tested NC2.0SiCHT; (e) schematic exhibiting <c+a> dislocation's dissociation into <a> and <c> type dislocations;(f) and (g) BF and DF image of the dislocation interaction with SiC_{np} in NC2.0SiCHT creep teste at 435 MPa and 473 K. 120

List of Tables

Table 2.1 Abbreviations used for the alloying elements added to Mg [50]. 7

Table 3.1 The sample designations and compositions of the alloy and nanocomposites. 26

Table 4.1 Summary of the phases formed in the Mg-Al-Ca-Mn alloys reported in the literature. 35

Table 4.2 The calculated grain size, volume fraction, and fractal dimension of the C36 phase in the alloy and nanocomposites. 36

Table 5.1 A summary of the parameters used to calculate the strength of the nanocomposites. 54

Table 6.1 Definitions of the parameters used in the equations. 67

Table 6.2 Summary of the n values obtained from the creep tests at different temperature levels. 68

Table 6.3 Summary of the Q values obtained from the creep tests at different stress levels. 68

Table 7.1 A comparison of corrosion rates evaluated from H_2 evaluation tests in the present study with that obtained on various Mg-Al-based alloys and their composites. 79

Table 7.2 Summary of the elements obtained from the equivalent circuit fitted with the experimental EIS data. 84

Table 7.3 Summary of the area percentage data evaluated from the XPS peaks of AXM520 and NC3.0SiC after deconvoluting. 93

Table 8.1 Summary of the n values obtained from the creep tests at different temperature levels. 109

Table 8.2 Summary of the Q values obtained from the creep tests at different stress levels. 110

Table 8.3 List of equations with constant values employed to construct the creep deformation mechanism maps of the Mg-Al-Ca-based alloys and their nanocomposites. 112

List of Abbreviations

BF	:	**B**right **F**ield
CYS	:	**C**ompressive **Y**ield **S**trength
DF	:	**D**ark Fild
FWHM	:	**F**ull **W**idth **H**alf **M**axima
GB	:	**G**rain **B**oundary
GBMS	:	**G**rain **B**oundary **M**isorientation **S**train
GNP	:	**G**raphene **N**ano **P**articles
HAGB	:	**H**igh **A**ngle **G**rain **B**oundary
KAM	:	**K**ernel **A**verage **M**isorientation
LAGB	:	**L**ow **A**ngle **G**rain **B**oundary
NCs	:	**N**anocomposites
OCP	:	**O**pen **C**ircuit **P**otential
SHE	:	**S**train **H**ardening **E**xponent
SHR	:	**S**train **H**ardening **R**ate
TB	:	**T**win **B**oundary
TYS	:	**T**ensile **Y**ield **S**trength
UTS	:	**U**ltimate **T**ensile **S**trength
UCS	:	**U**ltimate **C**ompressive **S**trength
XRD	:	**X**-ray **D**iffraction

List of Symbols

T : Absolute temperature

σ : Applied stress

K : Boltzmann's constant

b : Burgers vector

Q : Creep activation energy

A : Diameter of the indenter

D_0 : Coefficient of self-diffusion

%El : %Elongation

D : Grain size

p : Inverse grain size exponent

P_m : Mean pressure

$\dot{\epsilon}$: Steady-state creep rate

G : Shear modulus

n : Stress exponent

R : Universal gas constant

V_{imp} : Impression velocity

σ_{imp} : Stress in impression creep

Abstract

The influences of the SiC nanoparticles (SiC_{np}) dispersion on the microstructural modification, tensile, compression, creep, and corrosion behavior of the squeeze-cast Mg-5.0Al-2.0Ca-0.3Mn (AXM520) (wt.%) alloy have been investigated. The concentrations of the SiC_{np} are varied from 0.5 to 3.0 (wt.%), and the squeeze-cast nanocomposites (NCs) are abbreviated as NC0.5SiC, NC1.0SiC, NC2.0SiC and NC3.0SiC. A detailed microstructural characterization of the AXM520 alloy and NCs has been carried out. The as-cast microstructures of the AXM520 alloy and NCs consist of a primary solid solution (α-Mg), a eutectic of α-Mg and $(Mg,Al)_2Ca$ (C36) phases, and an Al_8Mn_5 phase. Additionally, the SiC phase is also present in the NCs. The continuous network of the C36 phase is fragmented and becomes discontinuous as the content of the SiC_{np} increases in the NCs.

The ambient temperature tensile and compressive properties of the AXM520 alloy and NCs have been evaluated. All the NCs exhibit superior tensile and compressive properties to the AXM520 alloy. The NC2.0SiC exhibits the best tensile properties among the NCs employed. The YS of the NCs improves with the increase in the SiC_{np} content up to 3.0 (wt.%). The UTS and %El of the NCs increase up to $2.0SiC_{np}$ (wt.%), and beyond that, the same declines owing to the agglomeration of the nanoparticles. The discontinuous network of the C36 phase in the NCs inhibits crack propagation, leading to their improved %El. All the NCs exhibit a higher strain-hardening exponent (n) and strain-hardening rate (SHR) compared to the AXM520 alloy. The superior 'n' and SHR exhibited by the NCs are attributed to the grain refinement and dislocations generation. The strengthening from CTE mismatch contributes the most to the overall strengthening of the NCs. The 'Zhang and Chen' model is modified by introducing an agglomeration factor, and the predicted YS of the NCs matches pretty well with the experimentally obtained values.

The creep behavior of the AXM520 alloy and NCs has been examined using impression creep tests in the temperature range from 448 K to 523 K and stress range from 390 to 490 MPa. All the NCs reveal improved creep performance compared to the AXM520 alloy. The creep rate of the NCs decreases with the increase in the SiC_{np} content. The NC2.0SiC exhibits an improvement in creep resistance by 73.2% compared to the alloy. However, the creep resistance deteriorates since the amount of the nanoparticles is further increased in the

NC3.0SiC, leading to agglomeration. The stress exponents vary from 5.0 to 6.7, and activation energies vary from 89.8 to 101.8 kJ/mol, implying that the creep in the materials is controlled by the climb of dislocation assisted by the pipe diffusion. The pile-ups of dislocations take place around the C36 phase and near the SiC_{np}. The additional strengthening owing to the presence of the SiC_{np} in the NCs is responsible for their improved creep performance compared to the AXM520 alloy.

The corrosion behavior of the AXM520 alloy and NCs has been investigated in a 3.5 (wt.%) NaCl solution at a pH of 7.0. The corrosion resistance of the NCs measured in the hydrogen evolution test is superior to the AXM520 alloy, and the improvement is 91.1% in the NC3.0SiC. The polarization resistance determined from the EIS increases with the increase in the SiC_{np} content in the NCs. The potentiodynamic polarization scans further confirm the superior corrosion resistance of the NCs to the AXM520 alloy. Among the fabricated NCs, NC3.0SiC exhibits the highest corrosion resistance, and it is 91.3% lower in comparison to the AXM520 alloy. The corrosion products predominantly consist of $Mg(OH)_2$. The addition of SiC_{np} reduces the formation of $Mg(OH)_2$ and increases the content of the $Al(OH)_3$ in the NCs, leading to the higher stability of the corroded film formed on them. The α-Mg phase is severely damaged owing to the galvanic corrosion between the α-Mg and C36 phases. However, the same is reduced due to a decrease in the volta potential between α-Mg and C36 phases in the NCs, resulting in their superior corrosion resistance.

The squeeze-cast AXM520 alloy and NCs are further subjected to age-hardening. The alloy and NCs are homogenized at 773 K and artificially aged at 523 K. The aged alloy is designated as AXM520HT, and the nanocomposites containing 1.0 and 2.0 (wt.%) of SiC_{np} are designated as NC1.0SiCHT and NC2.0SiCHT, respectively. The microstructural evolution and creep characteristics of the squeeze-cast age-hardened alloy and NCs have been investigated. The age-hardened alloy and NCs contain primary α-Mg grains, $(Mg, Al)_2Ca$ (C36), Al_2Ca (C15), and Al_8Mn_5 phases. The SiC phase is additionally identified in the NCs. The NCs reveal superior creep resistance compared to AXM520HT, and it is the best in the NC2.0SiCHT. The creep resistance of the NC2.0SiCHT surpasses AXM520HT by 76%. Dislocation climb, facilitated by pipe diffusion, emerges as the mechanism governing creep deformation in the alloy and NCs. The creep deformation mechanism maps for the Mg-Al-Ca-based alloys and NCs are successfully constructed. The microstructural observation of the creep-tested specimens under the indenter concludes that the C36 phase is utterly broken in the

AXM520HT, whereas the same remains intact in the NC2.0SiCHT. The percentage of twins in the creep-tested specimen of NC2.0SiCHT is lower than in the AXM520HT alloy. Two different types of twins, i.e., extension twin $\{10\bar{1}2\}<10\bar{1}1>$, and double twin $\{10\bar{1}1\}$-$\{10\bar{1}2\}$ are observed in the NCs. The density of the <c> type dislocations is much higher than that of the <a> type dislocations in the NCs. The presence of SiC nanoparticles impedes the dislocation motion. The significant improvement in creep resistance of all the NCs over the AXM520HT alloy is attributed to the age-hardening as well as dispersion strengthening from the presence of the SiC nanoparticles.

To conclude, the tensile, compression, creep, and corrosion behavior of the squeeze-cast NC0.5SiC, NC1.0SiC, NC2.0SiC, and NC3.0SiC are superior to that of the AXM520 alloy. Thus, the use of NCs is beneficial over the AXM520 alloy. Among the as-cast NCs, NC2.0SiC is the best, considering the mechanical properties and corrosion behavior. In addition, the creep behavior of the age-hardened NC1.0SiCHT and NC2.0SiCHT is superior to that of the AXM520HT alloy. Among the aged alloy and NCs, the NC2.0SiCHT is the best considering the creep behavior.

Keywords: Magnesium alloy; Nanocomposite; Squeeze-cast; Microstructure; Creep; Corrosion