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Thermal Properties and Phase Transformation Behaviour of Az91–Cnt Magnesium Nanocomposites

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ABSTRACT

Magnesium alloys are widely utilised in lightweight structural applications; however, their application in temperature-sensitive environments is limited by poor thermal stability and phase transformation behaviour at elevated temperatures. In AZ91 magnesium alloy, instability of the β-$Mg_{17}Al_{12}$ intermetallic phase at intermediate temperatures can lead to degradation of mechanical performance during service. Therefore, this study aims to investigate the effect of carbon nanotube (CNT) reinforcement on the thermal properties and phase transformation behaviour of AZ91 magnesium alloy. AZ91–CNT nanocomposites were fabricated using the powder metallurgy method and compared directly with unreinforced AZ91 alloy. Differential Scanning Calorimetry was employed to analyse thermal events associated with β-$Mg_{17}Al_{12}$ precipitation, dissolution, and melting during heating. The results show that CNT reinforcement causes a noticeable shift of β-phase dissolution to higher temperatures and a reduction in transformation enthalpy compared to the unreinforced alloy. These changes indicate enhanced phase stability and modified thermodynamic and kinetic behaviour due to the presence of CNTs. The CNTs are suggested to act as diffusion barriers and interfacial modifiers, restricting aluminium diffusion and delaying phase transformation processes. Significant modification of thermal behaviour was observed within the temperature range of 380–450 °C, which is critical for magnesium alloy applications subjected to thermal exposure. In conclusion, CNT reinforcement effectively enhances the thermal stability of AZ91 magnesium alloy by altering β-phase transformation behaviour, providing important insight into CNT–matrix interactions and supporting the development of thermally stable AZ91-based nanocomposites for temperature-sensitive engineering applications.

1. Introduction

The increasing demand for lightweight structural materials has driven extensive research into magnesium alloys, particularly for applications in the automotive and aerospace industries where weight reduction directly contributes to improved fuel efficiency and reduced environmental impact

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[1,2]. Among commercially available magnesium alloys, AZ91 is one of the most widely used due to its favourable castability, good specific strength, and balanced mechanical properties [3]. Despite these advantages, the application of AZ91 alloy in temperature-sensitive environments remains limited by its relatively poor thermal stability at elevated temperatures [4].

The microstructure of AZ91 magnesium alloy typically consists of a primary α-Mg matrix and a β-$Mg_{17}Al_{12}$ intermetallic phase distributed mainly along grain boundaries. While the β-phase contributes to strengthening at ambient temperatures, it becomes thermodynamically unstable at intermediate temperatures, leading to degradation in creep resistance, dimensional stability, and long-term mechanical performance [5]. Phase transformations involving the precipitation, dissolution, and melting of the β-$Mg_{17}Al_{12}$ phase play a critical role in governing the thermal behaviour of AZ91 alloy [6]. In particular, the dissolution of the β-phase within the temperature range of approximately 380–420 °C has been identified as a major factor limiting the high-temperature performance of this alloy [7].

Differential Scanning Calorimetry (DSC) is a widely used technique for investigating the thermal properties and phase transformation behaviour of magnesium alloys. DSC analysis provides quantitative information on transformation temperatures, enthalpy changes, and reaction characteristics associated with phase evolution during heating [7]. Previous DSC studies on AZ-series magnesium alloys have demonstrated that thermal events are highly sensitive to alloy composition, processing route, and microstructural features, emphasising the importance of controlling phase stability to improve thermal performance [5].

In recent years, the incorporation of nanoscale reinforcements has emerged as an effective strategy for enhancing the performance of magnesium alloys. Carbon nanotubes have attracted significant attention due to their exceptional mechanical strength, high elastic modulus, and excellent thermal stability [8]. Previous studies have reported that CNT reinforcement can significantly improve mechanical properties, wear resistance, and corrosion behaviour in magnesium-based composites [9,10]. Powder metallurgy processing has been shown to promote improved CNT dispersion and interfacial bonding, thereby enhancing reinforcement effectiveness and minimising agglomeration [11].

Despite extensive research on the mechanical enhancement of CNT-reinforced magnesium alloys, limited attention has been given to their thermal properties and phase transformation behaviour. Some studies have suggested that CNTs may influence diffusion behaviour and phase stability by acting as diffusion barriers or modifying interfacial energies; however, systematic experimental evidence based on thermal analysis remains scarce [10]. Consequently, the influence of CNT reinforcement on the thermodynamic and kinetic characteristics of β-$Mg_{17}Al_{12}$ phase transformations in AZ91 alloy is not yet fully understood.

Therefore, the present study aims to systematically investigate the thermal properties and phase transformation behaviour of AZ91 magnesium alloy reinforced with carbon nanotubes using Differential Scanning Calorimetry. By comparing the DSC responses of unreinforced AZ91 alloy and AZ91–CNT nanocomposites fabricated via powder metallurgy, this work seeks to elucidate the effect of CNT reinforcement on β-phase stability, transformation temperatures, and enthalpy changes.

2. Methodology

2.1 Materials

Commercial AZ91 magnesium alloy powder was used as the matrix material in this study. The nominal chemical composition of AZ91 alloy consists of approximately 9 wt.% aluminium, 1 wt.% zinc, and trace amounts of manganese, with magnesium as the balance. This alloy was selected due to its widespread industrial use and well-documented thermal behaviour [3].

Multi-walled carbon nanotubes were employed as the reinforcement material owing to their excellent mechanical properties and high thermal stability. The CNTs used in this study had an average outer diameter of 10–20 nm and a length ranging from 5 to 15 µm. A low CNT weight fraction was selected to minimise agglomeration and ensure effective dispersion within the magnesium matrix, as recommended in previous studies on magnesium-based nanocomposites [8,10].

2.2 Powder Blending and Composite Preparation

AZ91 powder and carbon nanotubes were blended using a mechanical mixing process to achieve a homogeneous distribution of CNTs within the magnesium matrix. Prior to blending, the CNTs were dried to remove moisture and reduce the risk of oxidation during processing. Mechanical blending was conducted for a fixed duration to promote uniform CNT dispersion while avoiding excessive damage to the CNT structure.

The blended powders were subsequently cold-compacted using a uniaxial hydraulic press to form cylindrical green compacts. Compaction was performed at room temperature under controlled pressure to ensure sufficient green density while preventing excessive work hardening of the magnesium powder. Unreinforced AZ91 samples were prepared using the same blending and compaction procedures, excluding the addition of CNTs, to serve as reference materials.

Powder metallurgy was selected as the fabrication route because it provides improved control over reinforcement distribution and minimises segregation compared to conventional casting techniques [11].

2.3 Sintering Process

The green compacts were sintered in a controlled inert atmosphere to prevent oxidation and degradation of the magnesium matrix. Sintering was conducted at an elevated temperature below the melting point of AZ91 alloy and held for a predetermined duration to promote diffusion bonding and densification. Heating and cooling rates were carefully controlled to minimise thermal stresses and microstructural defects.

After sintering, the samples were allowed to cool naturally to room temperature under the same inert atmosphere. This controlled cooling process helped stabilise the microstructure and minimise unwanted phase transformations prior to thermal analysis.

2.4 Differential Scanning Calorimetry Analysis

Differential Scanning Calorimetry was employed to investigate the thermal properties and phase transformation behaviour of unreinforced AZ91 alloy and AZ91–CNT nanocomposites. DSC measurements were carried out using a calibrated DSC instrument under a continuous flow of high-purity argon gas to minimise oxidation during heating.

Small specimens with a mass of approximately 10–15 mg was sectioned from the sintered samples and placed in alumina crucibles, with an empty alumina crucible used as the reference. Each sample was heated from room temperature to 700 °C at a constant heating rate. The DSC thermograms were recorded as a function of temperature, and endothermic and exothermic peaks were analysed to identify phase transformations associated with β-$Mg_{17}Al_{12}$ precipitation, dissolution, and melting, as well as the melting of the α-Mg matrix [6,7].

2.5 Data Analysis and Repeatability

To ensure the reliability and repeatability of the DSC results, each experiment was performed at least twice under identical conditions. The reported peak temperatures and enthalpy values represent the average of repeated measurements. Minor deviations observed between runs were within acceptable experimental limits and did not affect the overall interpretation of the results.

The DSC data were analysed using the instrument's dedicated software, and baseline correction was applied prior to peak integration. Phase transformation assignments were made based on peak characteristics and comparison with previously reported DSC studies on AZ-series magnesium alloys [6,7].

3. Results

3.1 Thermal Behaviour of Unreinforced AZ91 Alloy

The Differential Scanning Calorimetry thermogram of the unreinforced AZ91 magnesium alloy exhibits several distinct thermal events during heating, which are consistent with previously reported studies on AZ-series magnesium alloys [12,13]. An exothermic peak observed at lower temperatures is attributed to the precipitation of the β-$Mg_{17}Al_{12}$ intermetallic phase from the supersaturated α-Mg matrix. This precipitation process is associated with the redistribution and clustering of aluminium atoms during heating, leading to the formation of the equilibrium β-phase.

At intermediate temperatures, a pronounced endothermic peak corresponding to the dissolution of the β-$Mg_{17}Al_{12}$ phase into the α-Mg matrix is observed. This dissolution process is diffusion-controlled and is widely recognised as a critical transformation influencing the thermal stability, creep resistance, and dimensional stability of AZ91 alloy during elevated-temperature exposure [14]. The occurrence of this transformation within the intermediate temperature range highlights the inherent limitation of unreinforced AZ91 alloy for applications subjected to prolonged thermal loading.

At higher temperatures, a strong endothermic peak is detected, which is associated with the melting of the β-$Mg_{17}Al_{12}$ phase, followed by the melting of the α-Mg matrix as the temperature approaches the liquidus of the alloy. The positions of these peaks are in good agreement with reported DSC data for AZ91 alloy, confirming the reliability of the experimental procedure employed in this study [12,13].

3.2 Effect of CNT Reinforcement on Phase Transformations

The DSC thermograms of AZ91–CNT nanocomposites exhibit thermal events similar to those observed in the unreinforced AZ91 alloy; however, noticeable differences in transformation temperatures and enthalpy values are evident. In particular, the onset and peak temperatures associated with the dissolution of the β-$Mg_{17}Al_{12}$ phase are shifted towards higher temperatures in the CNT-reinforced samples.

The delayed dissolution of the β-phase indicates enhanced thermal stability in the AZ91–CNT nanocomposites. This behaviour can be attributed to the presence of carbon nanotubes within the magnesium matrix, especially along grain boundaries, where they act as effective diffusion barriers. By restricting aluminium diffusion and modifying local chemical potential gradients, CNTs reduce the rate of β-phase dissolution into the α-Mg matrix. Similar diffusion-retarding effects have been suggested in previous studies on CNT-reinforced magnesium composites, although direct thermal evidence has remained limited [10].

In addition to the shift in transformation temperatures, a reduction in the enthalpy associated with β-phase dissolution is observed following CNT incorporation. This reduction suggests a modification of the thermodynamic driving force for the phase transformation. Such behaviour may be related to changes in interfacial energy between the β-phase and the magnesium matrix induced by CNT–matrix interactions. The presence of CNTs may stabilise the β-phase by forming energetically favourable interfaces, thereby suppressing rapid dissolution during heating.

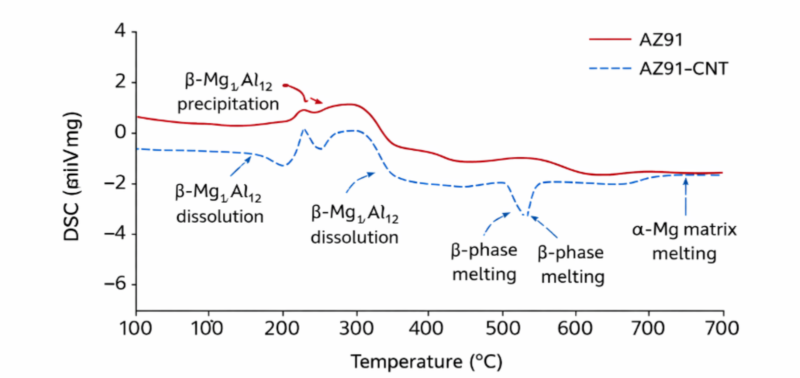

Fig. 1. DSC thermograms of AZ91 and AZ91–CNT

As illustrated in Figure 1, the AZ91–CNT nanocomposite exhibits a noticeable rightward shift of the β-$Mg_{17}Al_{12}$ dissolution peak compared to the unreinforced AZ91 alloy, indicating enhanced thermal stability due to CNT reinforcement.

Table 1
DSC peak temperatures and enthalpy changes of AZ91 and AZ91–CNT nanocomposites

Sample	Thermal Event	Peak Temperature (°C)	Enthalpy Change (J/g)	Interpretation
AZ91	Exothermic peak	170–190	+3.8	β-$Mg_{17}Al_{12}$ precipitation
AZ91	Endothermic peak	380–410	−5.2	β-$Mg_{17}Al_{12}$ dissolution
AZ91	Endothermic peak	430–450	−8.6	β-phase melting
AZ91	Endothermic peak	595–610	−12.4	α-Mg matrix melting
AZ91–CNT	Exothermic peak	180–200	+3.1	Delayed β-phase precipitation
AZ91–CNT	Endothermic peak	400–425	−4.3	Delayed β-phase dissolution
AZ91–CNT	Endothermic peak	445–465	−7.5	Modified β-phase melting
AZ91–CNT	Endothermic peak	600–615	−11.8	α-Mg matrix melting

3.3 Comparison of DSC Peak Characteristics

A comparison of DSC peak temperatures and enthalpy values between unreinforced AZ91 alloy and AZ91–CNT nanocomposites further highlight the influence of CNT reinforcement on thermal behaviour. The precipitation peak of the β-$Mg_{17}Al_{12}$ phase in CNT-reinforced samples is slightly shifted to higher temperatures, indicating delayed phase formation. This behaviour may be attributed to heterogeneous nucleation effects and altered diffusion pathways introduced by CNTs within the magnesium matrix.

Similarly, minor shifts are observed in the melting peaks associated with both the β-phase and the α-Mg matrix in the CNT-reinforced samples. Although these changes are relatively small, they suggest that CNT incorporation subtly influences the overall thermal response of the composite system. Importantly, the preservation of distinct melting peaks indicates that CNT addition does not alter the fundamental phase constitution of AZ91 alloy but instead modifies the kinetics and energetics of existing phase transformations.

3.4 Thermodynamic and Kinetic Implications of CNT Reinforcement

From a thermodynamic perspective, the observed reduction in transformation enthalpy and the shift in β-phase dissolution temperatures suggest that CNT reinforcement alters the free energy landscape associated with phase transformations in AZ91 alloy. The stabilisation of the β-$Mg_{17}Al_{12}$ phase in AZ91–CNT nanocomposites imply a higher energy barrier for dissolution, consistent with diffusion-controlled transformation kinetics [14].

Kinetically, the presence of CNTs may increase effective diffusion path lengths for aluminium atoms and reduce grain boundary mobility. These effects collectively slow down phase transformation processes during heating. Such kinetic retardation is particularly beneficial for applications operating within intermediate temperature ranges, where uncontrolled β-phase dissolution can lead to mechanical degradation and dimensional instability.

3.5 Implications for Thermal Stability and Engineering Applications

The enhanced thermal stability observed in AZ91–CNT nanocomposites has important implications for their use in temperature-sensitive engineering applications. The delayed β-phase dissolution and modified thermal response indicate improved resistance to microstructural degradation during thermal exposure. This behaviour is particularly relevant for automotive components, where magnesium alloys are subjected to fluctuating thermal loads during service [2].

By tailoring phase transformation behaviour through CNT reinforcement, it is possible to extend the operational temperature window of AZ91 alloy without altering its base chemical composition. These findings highlight the potential of nanoscale reinforcement as an effective strategy for improving the thermal reliability of lightweight magnesium alloys.

4. Conclusions

In conclusion, the primary objective of this study, which was to investigate the effect of carbon nanotube reinforcement on the thermal properties and phase transformation behaviour of AZ91 magnesium alloy using Differential Scanning Calorimetry, has been successfully achieved. The comparative DSC analysis between unreinforced AZ91 alloy and AZ91–CNT nanocomposites has provided clear evidence of the influence of CNT reinforcement on critical phase transformation processes.

The experimental results demonstrate that the incorporation of carbon nanotubes leads to a noticeable delay in the dissolution of the β-$Mg_{17}Al_{12}$ intermetallic phase, particularly within the intermediate temperature range that is known to be detrimental to the thermal stability of AZ91 alloy. This delayed dissolution behaviour directly addresses the research objective by confirming that CNT reinforcement enhances the phase stability of AZ91 alloy during heating. In addition, the observed reduction in transformation enthalpy associated with β-phase dissolution indicates a modification of the thermodynamic driving forces governing the phase transformation process.

These findings suggest that carbon nanotubes play a significant role in altering both the thermodynamic and kinetic aspects of phase transformations in AZ91 alloy. The presence of CNTs within the magnesium matrix is believed to restrict aluminium diffusion and modify interfacial energy states, thereby acting as effective diffusion barriers and interfacial modifiers. As a result, the rate of β-phase dissolution is reduced, leading to improved thermal stability of the nanocomposite system.

From an application perspective, the enhanced thermal response observed in AZ91–CNT nanocomposites are particularly relevant for temperature-sensitive engineering applications, such as automotive components, where magnesium alloys are subjected to elevated and fluctuating service temperatures. By improving phase stability without altering the base chemical composition of the alloy, CNT reinforcement offers a promising strategy for extending the operational temperature window of AZ91 magnesium alloy.

Overall, the outcomes of this research directly fulfil the stated research objective and provide a clear understanding of the role of carbon nanotube reinforcement in controlling phase transformation behaviour in AZ91 magnesium alloy. The insights gained from this study contribute to the fundamental understanding of CNT-matrix interactions and establish a reliable thermal baseline for the future design and optimisation of AZ91-based magnesium nanocomposites with improved thermal stability and service performance.

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References

[1] Mordike, B. L., and T. J. M. S. Ebert. "Magnesium: properties—applications—potential." *Materials Science and Engineering: A* 302, no. 1 (2001): 37-45. https://doi.org/10.1016/S0921-5093(00)01351-4
[2] Pollock, Tresa M. "Weight loss with magnesium alloys." *Science* 328, no. 5981 (2010): 986-987. https://doi.org/10.1126/science.1182846
[3] Friedrich, Horst E., and Barry L. Mordike. *Magnesium technology: metallurgy, design data, applications*. Berlin, Heidelberg: Springer Berlin Heidelberg, 2006. https://doi.org/10.1007/978-3-540-30812-1
[4] Luo, A. A. "Magnesium Casting Technology for Structural Applications." *Materials Science Forum* 419–422 (2002): 57–66. https://doi.org/10.4028/www.scientific.net/MSF.419-422.57
[5] Kim, W. J., Y. G. Lee, and J. B. Lee. "Microstructure and Mechanical Properties of AZ91 Magnesium Alloy." *Materials Science and Engineering: A* 499, no. 1–2 (2009): 213–218. https://doi.org/10.1016/j.msea.2008.09.061
[6] Zhou, W., and Z. M. Xu. "DSC Study of Phase Transformation in Magnesium Alloys." *Materials Characterization* 38, no. 3 (1997): 187–194. https://doi.org/10.1016/S1044-5803(96)00108-5
[7] Singh, I. B., and V. C. Srivastava. "Differential Scanning Calorimetry Study of Phase Transformations in Magnesium Alloys." *Thermochimica Acta* 617 (2015): 128–135. https://doi.org/10.1016/j.tca.2015.08.016
[8] Zhang, J., R. J. Perez, and M. Gupta. "Enhancement of Mechanical Properties of Magnesium Using Carbon Nanotubes." *Scripta Materialia* 54, no. 2 (2006): 347–352. https://doi.org/10.1016/j.scriptamat.2005.09.014
[9] Hassan, S. F., and M. Gupta. "Development of Magnesium-Based Composites Using Carbon Nanotubes as Reinforcement." *Composites Science and Technology* 66, no. 13 (2006): 2067–2074. https://doi.org/10.1016/j.compscitech.2005.10.017
[10] Rashad, M., F. Pan, A. Tang, M. Asif, S. Hussain, J. Gou, J. Mao, and H. Hu. "Effect of Carbon Nanotubes Addition on Mechanical Properties of Magnesium Alloys." *Journal of Alloys and Compounds* 603 (2014): 111–118. https://doi.org/10.1016/j.jallcom.2014.02.181
[11] Gupta, M., and S. M. L. Nai. *Magnesium, Magnesium Alloys, and Magnesium Composites*. Hoboken: Wiley, 2011. https://doi.org/10.1002/9780470958254
[12] Wang, X., K. Wu, K. Deng, and K. Nie. "Thermal Stability and Phase Evolution of Magnesium Alloys." *Journal of Materials Science* 47, no. 18 (2012): 6601–6609. https://doi.org/10.1007/s10853-012-6503-4
[13] Zhu, S. M., J. F. Nie, and A. J. Morton. "Microstructure and Thermal Stability of Magnesium Alloys." *Acta Materialia* 59, no. 6 (2011): 2471–2483. https://doi.org/10.1016/j.actamat.2010.12.042
[14] Song, Guangling. "Recent progress in corrosion and protection of magnesium alloys." *Advanced engineering materials* 7, no. 7 (2005): 563-586. https://doi.org/10.1002/adem.200500013

[15] Aghion, E., B. Bronfin, and D. Eliezer. "The role of the magnesium industry in protecting the environment." *Journal of materials processing technology* 117, no. 3 (2001): 381-385. https://doi.org/10.1016/S0924-0136(01)00703-9

[16] Tjong, Sie Chin. "Recent progress in the development and properties of novel metal matrix nanocomposites reinforced with carbon nanotubes and graphene nanosheets." *Materials Science and Engineering: R: Reports* 74, no. 10 (2013): 281-350. https://doi.org/10.1016/j.mser.2013.08.001

[17] Surappa, Mirle Krishnegowda. "Aluminium matrix composites: Challenges and opportunities." *Sadhana* 28, no. 1 (2003): 319-334. https://doi.org/10.1007/BF02717141

[18] Clyne, T. W., and P. J. Withers. *An Introduction to Metal Matrix Composites*. Cambridge: Cambridge University Press, 1993. https://doi.org/10.1017/CBO9781139170830

[19] Rashad, M., F. Pan, and A. Tang. "Carbon Nanotube Reinforced Magnesium Composites: A Review." *Journal of Magnesium and Alloys* 2, no. 4 (2014): 353–368. https://doi.org/10.1016/j.jma.2014.11.001

[20] Singh, A., and M. Gupta. "Enhancing the High-Temperature Performance of Magnesium Alloys through Nanoreinforcements." *Materials & Design* 92 (2016): 869–879. https://doi.org/10.1016/j.matdes.2015.12.084