DEVELOPMENT OF NOVEL Mg-Ca-Sc ALLOYS AS POTENTIAL BIODEGRADABLE IMPLANT MATERIAL

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by

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CERTIFICATE

This is to certify that the thesis entitled "**DEVELOPMENT OF NOVEL Mg-Ca-Sc ALLOYS AS POTENTIAL BIODEGRADABLE IMPLANT MATERIAL**" is being submitted by **Mr. CHETAN SINGH** to the Indian Institute of Technology Delhi for the award of the degree of **DOCTOR OF PHILOSOPHY**. This is a record of bonafide research work carried out by him under our supervision and guidance. The matter presented in this thesis has not been submitted, in part or in full to any other University or Institute for the award of any degree or diploma.

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Abstract

Magnesium (Mg) based alloys have attracted significant attention as potential biodegradable implant materials owing to their good biocompatibility, superior osteogenesis ability and admissible biodegradability. However, their higher corrosion rate limits widespread applicability, which degrades the mechanical integrity of the magnesium implant even before the damaged tissue has healed. Therefore, it is necessary to design and develop an Mg-based alloy with improved corrosion resistance having acceptable mechanical and tribological properties. The drawbacks mentioned above can be overcome by effective alloying and thermomechanical processing. However, the alloying addition in the case of biomaterials should be chosen such that the byproducts of the alloy degradation should not be toxic so that the biocompatibility of Mg is not compromised. Among alloying elements, rare-earth (RE) elements enhance corrosion resistance by preferentially forming an impermeable protective layer, grain refinement and removing impurity elements via the scavenger effect. Scandium (Sc) is the most promising RE alloying addition as it unprecedently enhances the biocompatibility and corrosion resistance of the Mg alloy.

However, the high cost of RE elements limits their addition in significant quantity. Thus, to develop a cost-effective implant material, the addition of calcium (Ca) as an alternate alloying element to Mg alloys has been considered as Ca provides all the specified biomedical benefits. However, the concentration of Ca was restricted at 0.6 wt. % to avoid a higher volume fraction of detrimental intermetallic Mg_2Ca phase. Therefore, Sc as a ternary addition to the binary Mg-0.6Ca alloy was explored. First, a pseudo-binary Mg-0.6Ca-xSc phase diagram was developed using ThermoCalc, which exhibited enhanced solubility on simultaneous addition. Then Mg-0.6Ca-xSc alloys were developed through a die casting process. In the current dissertation, the influence of Sc as a ternary addition on the deformation, corrosion, mechanical, and wear behaviour is investigated to evaluate the potential of the developed novel alloy compositions.

The produced alloys were thermomechanically processed to achieve desired microstructural features, for instance, finer grain size and strong basal texture. During thermomechanical processing, the effect of simultaneous addition of non-rare-earth (Ca) and rare-earth (Sc) elements on the hot-rolled deformation behaviour, recrystallization and texture evolution of Mg alloys is evaluated. The simultaneous addition of Ca and Sc resulted in the desired microstructural features. Based on the results of thermomechanical processing, the Sc concentration was restricted to 0.5 wt. % as the gains on further Sc addition was not cost-effective.

The influence of Sc as a ternary addition and thermomechanical processing on the corrosion behaviour of Mg-0.6Ca binary alloy was explored. The Sc addition resulted in improved corrosion resistance. *In-situ* corrosion study was performed on an as-cast Mg-0.6Ca binary alloy to develop an understanding of the activated corrosion mechanism. Additionally, the cytotoxicity of the developed novel composition was studied, where the developed Mg-0.6Ca-xSc alloys exhibited negligible cytotoxicity.

Further, the influence of Sc addition on the mechanical viz tensile and compression behaviour was studied. The Sc addition up to 0.5 wt. % did not significantly affect the mechanical properties, as compared to other RE additions. *In-situ* tensile study was performed on recrystallized Mg-0.6Ca binary alloy to develop an understanding of the deformation and fracture behaviour. The tensile testing was done at multiple strain rates to explore the strain rate sensitivity as Ca addition is known to increase the strain rate sensitivity.

The stress corrosion cracking (SCC) and wear behaviour of the developed novel alloys were studied in 0.9 wt. % NaCl to study the influence of the combined effect of corrosive media and mechanical strain. The SCC behaviour was studied using the slow strain rate testing method under tensile strain. The wear experimentation utilised a ball-on-disc tribometer with the countersurface as an alumina ball. The analysis of the wear track was performed using field emission scanning electron microscopy (FESEM) and a 3D profilometer to understand the underlying wear mechanisms and calculate the wear rate. The Sc containing alloys exhibited reduced susceptibility to SCC and improved wear resistance.

In summary, the present study reports a systematic study starting from the development of Mg-0.6Ca-xSc alloys to exploring the mechanical, electrochemical, tribological and cytotoxic behaviour to develop a comprehensive understanding of the developed alloy compositions.

सार

मैग्नीशियम (Mg) आधारित मिश्र धातुओं ने अपनी अच्छी जैव-अनुकूलता, बेहतर अस्थिजनन क्षमता और स्वीकार्य जैवअवक्रमण क्षमता के कारण संभावित जैव-अवक्रमणीय प्रत्यारोपण सामग्री के रूप में महत्वपूर्ण ध्यान आकर्षित किया है। हालांकि, उनकी उच्च संक्षारण दर व्यापक प्रयोज्यता को सीमित करती है, जो क्षतिग्रस्त ऊतक के ठीक होने से पहले ही मैग्नीशियम प्रत्यारोपण की यांत्रिक अखंडता को कम कर देती है। इसलिए, स्वीकार्य यांत्रिक और ट्राइबोलॉजी गुणों वाले बेहतर संक्षारण प्रतिरोध के साथ मैग्नीशियम -आधारित मिश्र धातु को डिजाइन और विकसित करना आवश्यक है। ऊपर वर्णित कमियों को प्रभावी मिश्र धातु और थर्मोमेकेनिकल प्रसंस्करण द्वारा दूर किया जा सकता है। हालांकि, बायोमैटिरियल्स के मामले में मिश्र धातु को इस तरह से चुना जाना चाहिए कि मिश्र धातु के बायप्रोडक्ट्स जहरीले न हों ताकि मैग्नीशियम की बायोकम्पैटिबिलिटी से समझौता न हो। मिश्र धातु तत्वों में, दुर्लभ-पृथ्वी तत्व अधिमानतः एक अभेद्य सुरक्षात्मक परत बनाकर, ग्रेन शोधन और मेहतर प्रभाव के माध्यम से अशुद्धता तत्वों को हटाकर संक्षारण प्रतिरोध को बढ़ाते हैं। स्कैंडियम (Sc) सबसे आशाजनक दुर्लभ-पृथ्वी मिश्रधातु है क्योंकि यह अभूतपूर्व रूप से मैग्नीशियम मिश्र धातु की जैव-अनुकूलता और संक्षारण प्रतिरोध को बढ़ाता है।

हालांकि, दुर्लभ-पृथ्वी तत्वों की उच्च लागत महत्वपूर्ण मात्रा में उनके अतिरिक्त योग को सीमित करती है। इस प्रकार, एक लागत प्रभावी प्रत्यारोपण सामग्री विकसित करने के लिए, कैल्शियम (Ca) को वैकल्पिक मिश्र धातु तत्व के रूप में मैग्नीशियम मिश्र धातु के रूप में जोड़ने पर विचार किया गया है क्योंकि कैल्शियम सभी निर्दिष्ट जैव चिकित्सा लाभ प्रदान करता है। हालाँकि, कैल्शियम की सांद्रता 0.६ प्रतिशत वजन पर प्रतिबंधित है हानिकारक इंटरमेटेलिक $Mg_२Ca$ के उच्च मात्रा अंश से बचने के लिए। इसलिए, बाइनरी Mg-0.६Ca मिश्र धातु के लिए एक टर्नरी जोड़ के रूप में स्कैंडियम का

उपयोग किया गया। सबसे पहले, थर्मोकैल्क का उपयोग करके एक छद्म-बाइनरी Mg-0.६Ca-xSc चरण आरेख विकसित किया गया था, जो एक साथ जोड़ पर बढ़ी हुई घुलनशीलता का प्रदर्शन करता था। फिर Mg-0.६Ca-xSc मिश्र धातुओं को डाई ढलाई प्रक्रिया के माध्यम से विकसित किया गया। वर्तमान शोध प्रबंध में, विकसित उपन्यास मिश्र धातु रचनाओं की क्षमता का मूल्यांकन करने के लिए विरूपण, जंग, यांत्रिक और घिसाव के व्यवहार पर एक त्रिगुट जोड़ के रूप में स्कैंडियम के प्रभाव की जांच की गई है।

उत्पादित मिश्र धातुओं को वांछित सूक्ष्म संरचनात्मक विशेषताओं को प्राप्त करने के लिए थर्मोमेकेनिकल रूप से संसाधित किया गया था, उदाहरण के लिए, महीन ग्रेन का आकार और मजबूत बेसल बनावट। थर्मोमेकेनिकल प्रोसेसिंग के दौरान, गैर-दुर्लभ-पृथ्वी (कैल्शियम) और दुर्लभ-पृथ्वी (स्कैंडियम) तत्वों के साथ-साथ हॉट-रोल्ड विरूपण व्यवहार, मैग्नीशियम मिश्र धातुओं के पुन: क्रिस्टलीकरण और बनावट विकास पर प्रभाव का मूल्यांकन किया जाता है। कैल्शियम और स्कैंडियम के एक साथ जोड़ के परिणामस्वरूप वांछित सूक्ष्म संरचनात्मक विशेषताएं हुईं। थर्मोमेकेनिकल प्रोसेसिंग के परिणामों के आधार पर, स्कैंडियम एकाग्रता 0.५ प्रतिशत वजन तक सीमित थी क्योंकि प्रतिशत वजन योग के रूप में आगे स्कैंडियम जोड़ पर लाभ लागत प्रभावी नहीं था।

Mg-0.६Ca बाइनरी मिश्र धातु के जंग व्यवहार पर टर्नरी जोड़ और थर्मोमेकेनिकल प्रसंस्करण के रूप में स्कैंडियम के प्रभाव का पता लगाया गया था। स्कैंडियम जोड़ के परिणामस्वरूप संक्षारण प्रतिरोध में सुधार हुआ। सक्रिय जंग तंत्र की समझ विकसित करने के लिए इन-सीटू जंग अध्ययन एक कास्ट Mg-0.६Ca बाइनरी मिश्र धातु पर किया गया था। इसके अतिरिक्त, विकसित उपन्यास रचना की साइटोटोक्सिसिटी का अध्ययन किया गया, जहां विकसित Mg-0.६Ca-xSc मिश्र धातुओं ने नगण्य साइटोटोक्सिसिटी का प्रदर्शन किया।

इसके अलावा, यांत्रिक जैसे तन्यता और संपीड़न व्यवहार पर स्कैंडियम जोड़ के प्रभाव का अध्ययन किया गया था। अतिरिक्त 0.५ तक अन्य दुर्लभ-पृथ्वी तत्वों परिवर्धन की तुलना में स्कैंडियम ने यांत्रिक गुणों को महत्वपूर्ण रूप से प्रभावित नहीं किया। विरूपण और फ्रैक्चर व्यवहार की समझ विकसित करने के लिए पुन: क्रिस्टलीकृत Mg-0.६Ca बाइनरी मिश्र धातु पर इन-सीटू तन्यता अध्ययन किया गया था। तनाव दर संवेदनशीलता का पता लगाने के लिए तन्यता परीक्षण कई तनाव दरों पर किया गया था क्योंकि कैल्शियम अतिरिक्त तनाव दर संवेदनशीलता को बढ़ाने के लिए जाना जाता है।

तनाव जंग क्रैकिंग और विकसित उपन्यास मिश्र धातुओं के घिसाव के व्यवहार का 0. ९ प्रतिशत सोडियम क्लोराइड घोल में अध्ययन किया गया था, संक्षारक मीडिया और यांत्रिक तनाव के संयुक्त प्रभाव के प्रभाव का अध्ययन करने के लिए । तनाव जंग क्रैकिंग व्यवहार का अध्ययन तन्यता तनाव के तहत धीमी गति दर परीक्षण पद्धति का उपयोग करके किया गया था। घिसाव के प्रयोग में एल्यूमिना बॉल के रूप में काउंटर-सतह के साथ एक बॉल-ऑन-डिस्क ट्राइबोमीटर का उपयोग किया। घिसाव के ट्रैक का विश्लेषण क्षेत्र उत्सर्जन स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी और एक ३डी प्रोफिलोमीटर का उपयोग करके अंतर्निहित घिसाव के तंत्र को समझने और घिसाव की दर की गणना करने के लिए किया गया था। स्कैंडियम युक्त मिश्र धातुओं ने तनाव जंग क्रैकिंग के प्रति कम संवेदनशीलता और बेहतर घिसाव के प्रतिरोध का प्रदर्शन किया।

संक्षेप में, वर्तमान अध्ययन एक व्यवस्थित अध्ययन की रिपोर्ट करता है जो Mg-0.६Ca-xSc मिश्र धातुओं के विकास से शुरू होकर विकसित मिश्र धातु रचनाओं की व्यापक समझ विकसित करने के लिए यांत्रिक, विद्युत रासायनिक, ट्राइबोलॉजी और साइटोटोक्सिक व्यवहार की खोज करता है।

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