

**PROCESSING, STRUCTURE AND MECHANICAL
CHARACTERISATION STUDIES FOR OPTIMISED
DESIGN OF COPPER AND NITINOL BASED POROUS
METALLIC FIBROUS MATERIALS**

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For Abu and Mamma

Certificate

This is to certify that the thesis entitled “**PROCESSING, STRUCTURE AND MECHANICAL CHARACTERISATION STUDIES FOR OPTIMISED DESIGN OF COPPER AND NITINOL BASED POROUS METALLIC FIBROUS MATERIALS**” is being submitted by **Ms ARAVI MUZAFFAR** 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 her 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

Traditionally metallic porous materials are made by binding metallic powders together or foaming liquid melt. The porosity and its distribution obtained from these processes cannot be accurately controlled, and the compositional inhomogeneities in their structure make them prone to brittle failure. Another distinct way of making porous materials is using metal fibres and arranging them, in random or ordered orientation, to create a network. These are called porous metallic fibre networks. The low relative density (controllable), lesser compositional inhomogeneities, higher specific strength, transverse isotropy and high open porosity are some of the unique characteristics of these fibre networks. Apart from porosity, the material specific characteristics (such as microstructure and composition) of the individual fibre, and the architectural aspects of the fibre networks significantly influence their properties. The present work thus deals with understanding the respective effect of the material and structural parameters on the mechanical properties of porous metallic fibrous materials.

To study the effect of fibre material on the mechanical properties of porous metallic fibre networks, two different materials, pure Copper (Cu) and Nitinol (50 at. % Nickel (Ni) + 50 at. % Titanium (Ti)), have been selected for the present work. Cu doesn't show any phase transformation (i.e., non-transforming fibre material), whereas Nitinol undergoes a phase transformation both as a function of stress and temperature (i.e., transforming fibre material). Upon loading, Cu, as a non-transforming fibre, deforms in a ductile manner, wherein elastic deformation is followed by yielding and strain hardening before fracture. In contrast, Nitinol, as a transforming fibre, undergoes solid-state phase transformation (within elastic range) prior to strain hardening and failure. The structural parameters of the fibre networks, on the other hand, include porosity, fibre geometry, fibre aspect ratio as well as the inclination of the fibre with respect to the loading axis. Amongst these, fibre inclination is a critical parameter, which is investigated by considering the Cu single fibres, oriented in different angles (in the range of

0° - 45°) with respect to the loading axis, and pulled till failure. This systematically exhibits the influence of varying fibre inclination angles on the Cu fibre mechanical response, representing the deformation behaviour of fibres aligned in random orientations in the porous fibre network structure. It is observed that the yield and fracture forces decrease with increase in fibre inclination angle, whereas the displacement at yielding and failure increases. The Euler-Bernoulli approach is used to identify the forces acting on an inclined fibre when subjected to tensile deformation in the vertical direction, by considering a 1D model of the inclined fibre. The axial-, shear-force, and bending moment acting on the inclined fibre are seen to increase with the fibre inclination angle. As obtained from the model, the respective deformation mechanics has also been correlated with the experimental results.

Further, to demonstrate the effect of structural parameters on a transforming fibre material, equiatomic Nitinol was considered. The as-received cold deformed SMA fibre does not show any reversible transformation, as confirmed through differential scanning calorimetry (DSC), and thus the optimization of its superelastic properties is required. This is achieved by annealing at different temperatures in the range of 400 °C to 600 °C for a specific time. At lower annealing temperatures, a two-stage transformation due to presence of R-phase (B19), while at recrystallisation temperature (~ 600 °C), a single-stage austenite (B2) to martensite (B19') phase transformation has been observed in the DSC thermogram. The respective changes in the superelastic properties (plateau stress and strain and recovery strain etc.) upon deformation due to change in annealing conditions are also reported. With the increase in annealing temperature, the transformation stress decreases and the plateau strain increases. In contrast, the recovery strain is lowest for the completely recrystallized sample. The optimized annealing condition of 450 °C – 1h has been selected considering its transformation and superelastic behaviour. Further, the optimized Nitinol fibre is used to determine the structural parameter effect – mainly fibre inclination angle. With the increase in the fibre inclination

angle, a delay in the transformation is evident (i.e., an increase in the strain value). The recovery strain is lower when the fibre is inclined at 45° , but the plateau strain is higher. It thus establishes that apart from the structural aspects, the processing parameters of the fibre also define the observed properties.

Further, single-layer fibre networks of Cu and Nitinol are separately made with the vertical and inclined orientation of fibres, and their tensile properties are evaluated. It is observed that for both the networks, the vertical fibre fails initially, after which the inclined fibre takes up the load before finally failing. Also, the yield and the fracture force of the Cu network are higher than the respective single fibre values. For the Nitinol network, the recovery strain is lower than the single fibre, but the strain to failure is higher. The effect of network architecture is also studied by considering all the design parameters in the single-layer network. It is observed that porosity, fibre inclination angle and segment length (i.e., distance between two fibre-fibre bonds) broadly influence behaviour of the single-layer fibre network. Different single-layer Nitinol networks with varied network parameters are thus modelled to analyse their effect. The superelastic behaviour of these networks is simulated using the Finite Element Method (FEM), where the maximum load before unloading and load hysteresis is determined. An increase in porosity and hence inclined segment length results in lower transformation load and hysteresis. The results also depend on the fibre inclination angle, wherein lower inclination at higher vertical segment length resulted in higher load-bearing capacity of the network. The single-layer fibre network behaviour provides an insight into the deformation behaviour of the multilayer network, wherein the interaction of fibres is of prime importance.

The study thus highlights the material, processing, structural and architectural aspects of the porous metallic fibre networks and may be beneficial in delineating their deformation behaviour for enhanced use in targeted applications.

सार

परंपरागत रूप से धात्विक झरझरा सामग्री धात्विक चूर्णों को एक साथ बांधकर या तरल पदार्थ को पिघलाकर बनाया जाता है। इन प्रक्रियाओं से प्राप्त सरंध्रता और इसके वितरण को सटीक रूप से नियंत्रित नहीं किया जा सकता है, और उनकी संरचना में संरचनात्मक असमानताएं उन्हें भंगुर विफलता के लिए प्रवण बनाती हैं। झरझरा सामग्री बनाने का एक और अलग तरीका धातु के तंतुओं का उपयोग करना और उन्हें एक नेटवर्क बनाने के लिए क्रम रहित या आदेशित अभिविन्यास में व्यवस्थित करना है। इन्हें झरझरा धात्विक फाइबर नेटवर्क कहा जाता है। कम आपेक्षिक घनत्व (नियंत्रणीय), कम संरचनात्मक असमरूपता, उच्च विशिष्ट शक्ति, अनुप्रस्थ आइसोट्रॉपी और उच्च खुले सरंध्रता इन फाइबर नेटवर्क की कुछ अनूठी विशेषताएं हैं। सरंध्रता के अलावा, व्यक्तिगत फाइबर की भौतिक विशिष्ट विशेषताएं (जैसे कि माइक्रोस्ट्रक्चर और संरचना), और फाइबर नेटवर्क के वास्तुशिल्प पहलू उनके गुणों को महत्वपूर्ण रूप से प्रभावित करते हैं। वर्तमान कार्य इस प्रकार झरझरा धातु रेशेदार सामग्री के यांत्रिक गुणों पर सामग्री और संरचनात्मक मापदंडों के संबंधित प्रभाव को समझने से संबंधित है।

वर्तमान कार्य के लिए झरझरा धातु फाइबर नेटवर्क के यांत्रिक गुणों पर फाइबर सामग्री के प्रभाव का अध्ययन करने के लिए, दो अलग-अलग सामग्री, शुद्ध कॉपर (Cu) और नितिनोल (50 % निकेल (Ni) + 50 % टाइटेनियम (Ti) (परमाणु %)) पर का चयन किया गया है। Cu किसी भी चरण परिवर्तन (यानी, गैर-रूपांतरित फाइबर सामग्री) को नहीं दिखाता है, जबकि नितिनोल तनाव और तापमान (यानी, रूपांतरित फाइबर सामग्री) दोनों के कार्य के रूप में एक चरण परिवर्तन से गुजरता है। लोड करने पर, Cu, एक गैर-रूपांतरित फाइबर के रूप में, एक नमनीय तरीके से विकृत होता है, जिसमें फ्रैक्चर से पहले उपज और तनाव सख्त होने के बाद लोचदार विरूपण होता है। इसके विपरीत, नितिनोल, एक रूपांतरित फाइबर के रूप में, तनाव सख्त और विफलता से पहले ठोस-अवस्था चरण परिवर्तन (लोचदार सीमा के भीतर) से गुजरता है। दूसरी ओर, फाइबर नेटवर्क के संरचनात्मक मापदंडों में सरंध्रता, फाइबर ज्यामिति, फाइबर पहलू अनुपात के साथ-साथ लोडिंग अक्ष के संबंध में फाइबर का झुकाव शामिल है। इनमें से,

फाइबर झुकाव एक महत्वपूर्ण पैरामीटर है, जिसकी लोडिंग अक्ष के संबंध में विभिन्न कोणों ($0^\circ - 45^\circ$ की सीमा में) में उन्मुख घन एकल फाइबर पर विचार करके जांच की जाती है, और विफलता तक खींची जाती है। यह झरझरा फाइबर नेटवर्क संरचना में यादृच्छिक झुकाव में संरेखित फाइबर के विरूपण व्यवहार का प्रतिनिधित्व करते हुए, Cu फाइबर यांत्रिक प्रतिक्रिया पर अलग-अलग फाइबर झुकाव कोणों के प्रभाव को व्यवस्थित रूप से प्रदर्शित करता है। यह देखा गया है कि फाइबर झुकाव कोण में वृद्धि के साथ उपज और फ्रैक्चर बल घटते हैं, जबकि उपज और विफलता में विस्थापन बढ़ता है। यूलर-बर्नौली दृष्टिकोण का उपयोग झुके हुए फाइबर के १-डी मॉडल पर विचार करके ऊर्ध्वाधर दिशा में तन्यता विरूपण के अधीन होने पर एक झुके हुए फाइबर पर कार्य करने वाली शक्तियों की पहचान करने के लिए किया जाता है। झुकाव वाले फाइबर पर काम करने वाले अक्षीय, कतरनी-बल और झुकने का क्षण फाइबर झुकाव कोण के साथ बढ़ता हुआ देखा जाता है। जैसा कि मॉडल से प्राप्त किया गया है, संबंधित विरूपण यांत्रिकी को भी प्रायोगिक परिणामों के साथ सहसंबद्ध किया गया है।

इसके अलावा, एक परिवर्तित फाइबर सामग्री पर संरचनात्मक मापदंडों के प्रभाव को प्रदर्शित करने के लिए, समपरमाणुक नितिनोल पर विचार किया गया था। प्राप्त शीत विकृत एसएमए फाइबर कोई प्रतिवर्ती परिवर्तन नहीं दिखाता है, जैसा कि विभेदक स्कैनिंग कैलोरीमेट्री (डीएससी) के माध्यम से पुष्टि की जाती है, और इस प्रकार इसके सुपरलेस्टिक गुणों का अनुकूलन आवश्यक है। यह एक विशिष्ट समय के लिए ५०० डिग्री सेल्सियस से ६०० डिग्री सेल्सियस की सीमा में विभिन्न तापमानों पर एनीलिंग द्वारा प्राप्त किया जाता है। कम एनीलिंग तापमान पर, आर-चरण (बी१९) की उपस्थिति के कारण दो-चरण परिवर्तन, जबकि पुनर्क्रिस्टलीकरण तापमान (~ 600 डिग्री सेल्सियस) पर, एकल-चरण ऑस्टेनाइट (बी२) से मार्टेंसाइट (बी१९') चरण परिवर्तन डीएससी थर्मोग्राम द्वारा देखा गया है। एनीलिंग स्थितियों में परिवर्तन के कारण विरूपण पर सुपररेलास्टिक गुणों (पठार तनाव और तनाव और पुनर्प्राप्ति तनाव इत्यादि) में संबंधित परिवर्तन भी रिपोर्ट किए जाते हैं। एनीलिंग तापमान में वृद्धि के साथ परिवर्तन तनाव कम हो जाता है और पठार का तनाव बढ़ जाता है। इसके विपरीत, पूरी तरह से पुनः क्रिस्टलीकृत नमूने

के लिए रिकवरी स्ट्रेन सबसे कम है। ४५० °C – १ घंटा अनुकूलित एनीलिंग स्थिति को इसके रूपांतरण और सुपररेलास्टिक व्यवहार को देखते हुए चुना गया है। इसके अलावा, अनुकूलित नितिनोल फाइबर का उपयोग संरचनात्मक पैरामीटर प्रभाव - मुख्य रूप से फाइबर झुकाव कोण को निर्धारित करने के लिए किया जाता है। फाइबर झुकाव कोण में वृद्धि के साथ, परिवर्तन में देरी स्पष्ट है (यानी, तनाव मूल्य में वृद्धि)। जब फाइबर ४५° पर झुका होता है तो रिकवरी स्ट्रेन कम होता है, लेकिन पठारी स्ट्रेन अधिक होता है। इस प्रकार यह स्थापित करता है कि संरचनात्मक पहलुओं के अलावा, फाइबर के प्रसंस्करण पैरामीटर भी देखे गए गुणों को परिभाषित करते हैं।

इसके अलावा, Cu और नितिनोल के सिंगल-लेयर फाइबर नेटवर्क को अलग-अलग फाइबर के वर्तिकल और इंक्लाइन्ड ओरिएंटेशन के साथ बनाया जाता है, और उनके तन्य गुणों का मूल्यांकन किया जाता है। यह देखा गया है कि दोनों नेटवर्क के लिए, लंबवत फाइबर प्रारंभ में विफल रहता है, जिसके बाद झुका हुआ फाइबर अंत में असफल होने से पहले लोड लेता है। इसके अलावा, Cu नेटवर्क की उपज और फ्रैक्चर बल संबंधित एकल फाइबर मूल्यों से अधिक है। नितिनोल नेटवर्क के लिए, रिकवरी स्ट्रेन सिंगल फाइबर की तुलना में कम है, लेकिन असफलता के लिए तनाव अधिक है। सिंगल-लेयर नेटवर्क में सभी डिज़ाइन मापदंडों पर विचार करके नेटवर्क आर्किटेक्चर के प्रभाव का भी अध्ययन किया जाता है। यह देखा गया है कि सरंध्रता, फाइबर झुकाव कोण और खंड की लंबाई (यानी, दो फाइबर-फाइबर बॉन्ड के बीच की दूरी) एकल-परत फाइबर नेटवर्क के व्यवहार को व्यापक रूप से प्रभावित करती है। विभिन्न नेटवर्क मापदंडों के साथ अलग-अलग सिंगल-लेयर नितिनोल नेटवर्क इस प्रकार उनके प्रभाव का विश्लेषण करने के लिए तैयार किए गए हैं। इन नेटवर्कों के सुपररेलास्टिक व्यवहार को परिमित तत्व विधि (FEM) का उपयोग करके अनुकरण किया जाता है, जहां अनलोडिंग और लोड हिस्टैरिसिस से पहले अधिकतम भार निर्धारित किया जाता है। सरंध्रता में वृद्धि और इसलिए झुके हुए खंड की लंबाई के परिणामस्वरूप कम परिवर्तन भार और हिस्टैरिसिस होता है। परिणाम फाइबर झुकाव कोण पर भी निर्भर करते हैं, जिसमें उच्च ऊर्ध्वाधर खंड लंबाई पर कम झुकाव के परिणामस्वरूप नेटवर्क की उच्च भार वहन

क्षमता होती है। सिंगल-लेयर फाइबर नेटवर्क व्यवहार बहुपरत नेटवर्क के विरूपण व्यवहार में एक अंतर्दृष्टि प्रदान करता है, जिसमें फाइबर की परस्पर क्रिया प्रमुख महत्व रखती है।

अध्ययन इस प्रकार झरझरा धातु फाइबर नेटवर्क की सामग्री, प्रसंस्करण, संरचनात्मक और वास्तुशिल्प पहलुओं पर प्रकाश डालता है और लक्षित अनुप्रयोगों में उपयोग के लिए उनके विरूपण व्यवहार को चित्रित करने में फायदेमंद हो सकता है।

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Glossary

Austenite: High-temperature stable phase of Nitinol.

Austenitic finish temperature, A_f : Temperature during heating at which austenite formation is complete.

Austenitic start temperature, A_s : Temperature during heating at which austenite formation starts.

Axial force, F_a : Force acting along the axis of an inclined fibre.

B2 phase: CsCl structure of austenite in Nitinol.

B19 phase: Trigonal structure of R-phase in Nitinol.

B19' phase: Monoclinic martensitic phase in Nitinol.

Fibre inclination angle, θ : Inclination angle of the metallic fibre with respect to the loading axis.

Fibre aspect ratio, l/d : Ratio of length of the metal fibre to its diameter.

Hysteresis: Difference between the upper and lower plateau stress/load.

Inclined fibre: Metal fibre inclined at an angle with respect to the loading axis/vertical fibre.

Inclined segment length, l_{IS} : Length of inclined fibre between two joints/bonds.

Length at the bottom, l_b : Length of the vertical fibre of the network at the bottom after laying the inclined fibres.

Length at the top, l_t : Length of the vertical fibre of the network at the top before laying the inclined fibres.

Martensite: Low-temperature stable phase of Nitinol.

Martensitic finish temperature, M_f : Temperature during cooling at which martensitic formation is complete.

Martensitic start temperature, M_s : Temperature during cooling at which martensite formation starts.

Nitinol: Alloy of 50 at. % Nickel (Ni) and 50 at. % Titanium (Ti).

Number of inclined fibres, n_i : Number of non-vertical fibres used in the formation of a single-layer network.

Number of straight fibres, n_s : Number of vertical fibres used in the formation of a single-layer network.

Paper-tab: Gripping set-up for thin metal fibres.

Plateau strain, ϵ_p : Transformation strain for austenite to martensite transformation during loading.

Plateau stress, σ_p : Transformation stress for austenite to martensite transformation during loading.

Plateau stress, Lower, σ_{LPS} : Plateau stress for martensite to austenite transformation during unloading.

Plateau stress, Upper, σ_{UPS} : Plateau stress for austenite to martensite transformation in Nitinol during loading.

Recovery strain, ϵ_R : Strain recovered by unloading Nitinol fibre after loading it to some specified elongation.

R-phase: Pre-martensitic phase in Nitinol present in the cold deformed alloy.

R-phase finish temperature, R_f : Temperature during cooling at which R-phase formation is complete.

R-phase start temperature, R_s : Temperature during cooling at which R-phase formation starts.

Shear force, F_s : Force acting perpendicular to the axial force on an inclined metal fibre.

Stress-induced martensitic transformation (SIMT): Transformation of austenite (B2) to martensite (B19) due to the application of load/stress.

Total inclined length, l_{TI} : Length of the inclined fibre between two extreme vertical fibres in a single-layer network.

Transformation force, F_{Tr} : Force at which austenite to martensite transformation takes place during loading.

Transformation stress, σ_{Tr} : Stress at which austenite to martensite transformation takes place during loading.

Uniform elongation: Fracture strain of the Nitinol fibre during tensile loading.

Vertical fibre: Metallic fibre inclined along the loading axis.

Vertical segment length, l_{VS} : Length of the vertical fibre between two consecutively placed inclined fibres in a single-layer network.

Yield force, F_{yield}^θ : Force required for yielding of a metal fibre inclined at an angle θ to the loading axis.

Note: Porous metal fibrous networks, porous metallic fibre materials, metallic fibrous networks, metallic fibre networks, porous networks, fibre networks, metallic fibrous materials,

and metallic networks are used synonymously to define the porous materials made from metallic fibres.