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Potential and perspectives on additive manufacturing of high-entropy alloys for ballistic impact applications

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Abstract

While the design of complex shaped parts is enabled using additive manufacturing (AM) techniques, the need for tailoring microstructures catering to the requirements of specific applications must not be neglected. Considering the level of design complexity involved in the design of parts for ballistic applications, AM techniques may be envisaged to be employed in their design. On the other hand, there are innumerous reports, especially since the last decade, on a new class of metallic materials known as high-entropy alloys (HEAs) or multicomponent alloys, extensively investigated for their microstructure-property relation for a number of different applications. However, it may be noted that such studies are mainly limited to fundamental research and have not systematically focussed on correlating the findings of fundamental research with real-time applications. Therefore, considering that both AM and HEAs are relatively "new" and "booming" areas of research, the present book chapter provides a review on the development of AM HEAs towards designing components (e.g. armors) with high resistance to dynamic impact applications, in order to qualify themselves as alternatives and even superior to conventional materials (such as steels) for high-end ballistic applications. Additionally, this chapter will also focus on the challenges associated with employing AM HEAs for these applications and provide a roadmap for both fundamental and industrial research through strategies to design AM HEAs.

Keywords Additive Manufacturing, High-entropy alloys, Microstructure-property correlation, ballistic applications.

9.1 Introduction

AM has recently emerged as a critical enabler in the design and fabrication of next-generation HEAs, especially for demanding applications such as ballistic protection and defence [1–3]. In sharp to the conventional fabrication methods, the flexibility of AM allows precise control over both (i) material shapes and (ii) microstructural features [4–6]. While design of complex-shaped parts are essential from the industrial point of view [7–9], especially when considering the intricacies required for designing parts such as armors etc., it is also to be noted that precise control of microstructural aspects such as phase distribution, grain size, defect populations etc. are highly important for engineering the response of these components towards extreme dynamic loading [5]. HEAs, or debatably, multi-component alloys, characterized by their multi-principal element compositions (both equiatomic and non-equiatomic), present unique deformation mechanisms, high toughness, and exceptional strain-hardening capabilities [5,10–24], positioning them as potential advanced alternatives to conventional armor steels or lightweight alloys in impact engineering [3,25]. It is noteworthy to mention that one of the strategies to design HEAs for extreme dynamic loading is to design impact-resistant HEAs through control of deformation twins in their microstructures [3]. Apart from investigating the impact resistance, it is also important to examine the spall strength of HEAs for rendering them shock-resistant for dynamic loading conditions [25]. This book chapter aims to present a review of the advancements in the design of HEAs for potential applications in ballistic impact applications. It initially begins with an elucidation of layer-wise AM fabrication techniques (e.g., powder-bed fusion (PBF), directed energy deposition (DED) etc.) that enable engineering of complex architectures and tailored microstructures. In the subsequent sections, recent advances and current limitations in the AM of HEAs are highlighted, with an emphasis on the structural performance and dynamic mechanical properties. Metallic compositions with multiple principal elements (with number of elements $\geq$ 5), designed to maximize configurational entropy and exploit synergetic effects for enhanced strength, ductility, and phase stability are emphasized. Relationship between microstructure (including defects, grain size, and phase distribution) and mechanical response of AMed HEAs under ballistic and impact loading are elucidated with primary focus on high-velocity impact, including energy dissipation, deformation, crack initiation, and resistance to penetration or fracture. Further, prominent gaps towards fabricating HEAs through AM and directions for future research aimed at overcoming persistent challenges in this swiftly evolving field are discussed.

By bridging foundational concepts with current research challenges, this chapter aims to equip readers with both the theoretical grounding and practical insights necessary for advancing AM strategies and HEA design, particularly where high dynamic performance is essential. The chapter is structured as follows:

- In the first section, i.e. section 9.1, the requirement for switching to AM (in terms of HEA fabrication) will be discussed. Following that, key challenges involved in AM of HEAs and the current knowledge gaps will be highlighted.
- Sections 9.2 through 9.4 will discuss on recent AM research in general and in ballistic protection and high-energy applications respectively.
- Sections 9.5 and 9.6 will highlight on the fundamentals of finite element modelling (FEM) to engineer the lattice structures and defects and the applications of FEM in the avenue of dynamic/ballistic loading respectively.
- Section 9.7 will discuss on the challenges and future perspectives of AMed HEAs for ballistic applications.
- Finally, the chapter is summarized in section 9.8.

9.1.1 Why Focus on AM and HEAs?

Traditional alloy development has for long relied on selecting a primary element and incrementally adding alloying elements to enhance specific properties. However, this approach can restrict the compositional landscape and often leads to inherent trade-offs between strength, ductility, processability, and cost [14,23]. HEAs represent a paradigm shift, employing multiple principal elements in near-equimolar ratios to maximize configurational entropy, stabilize novel phases, and unlock exceptional properties - including enhanced strength-ductility synergy (**Fig. 9.1**), toughness, and corrosion resistance [5,11,17,21]. The integration of AM processes, such as laser powder bed fusion (L-PBF), further expands the design space by enabling the fabrication of complex geometries, customized microstructures, and component-specific property gradients that are unattainable through conventional manufacturing [1,2,18,22,26].

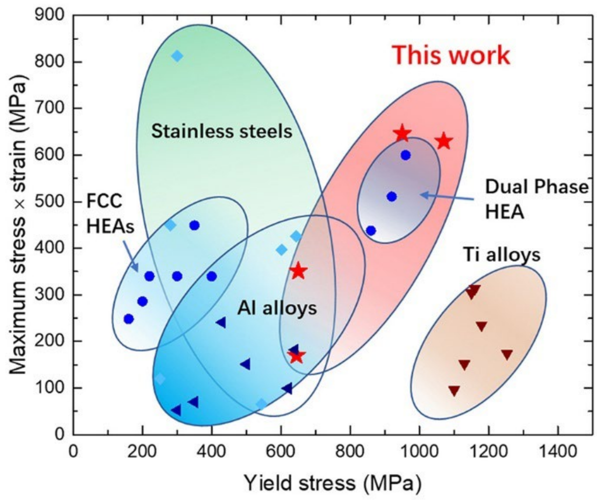

Fig. 9.1 Ashby plot showing the enhanced strength-ductility synergy of additively manufactured HEAs in comparison with conventionally fabricated FCC HEAs, dual-phase FCC+BCC HEAs, Al and Ti-alloys and stainless steels (Reproduced with permission from Ref. [2]). Note that the term "this work" in the figure refers to selectively laser melted (SLM) HEA with a single-phase FCC crystal structure.

9.1.2 Initial Design Hurdles

While the promise of HEAs and AM is immense, several scientific and technological hurdles remain. Firstly, the relationships between rapid solidification, microstructural evolution, and resultant mechanical or functional performance during AM are far from fully understood. Unique features such as non-equilibrium solidification, residual stresses, and hierarchical microstructures often emerge, which can either enhance or limit performance depending on their nature and distribution [2,26,27]. Secondly, AMed materials are prone to defects such as porosity, unmelted particles, and composition segregation. These issues are largely amplified in multicomponent HEAs and can adversely affect fatigue resistance, ductility, and fracture toughness, which are essential for high-strain-rate or ballistic applications [2,3,27]. Besides, for ballistic and impact-resistant applications, understanding the dynamic mechanical response (including strain-rate sensitivity, microband formation, and twinning behaviour) is crucial, but currently under-reported for many AM HEA systems [2]. There is also a lack of comprehensive predictive tools that can bridge the gap between alloy design, AM process parameters, and final part i.e. material performance. The complexity of multicomponent phase equilibria and deformation mechanisms complicates both modeling and experimental assessment [2].

9.1.3 Knowledge Gaps and Research Drivers

Despite the proliferation of literatures on HEAs and AM, several areas remain insufficiently addressed. The primary question remains as how do AM-induced rapid cooling rates and repeated thermal cycling influence phase stability, grain size, and defect population in HEAs? and most importantly, how do the aforementioned microstructural changes translate into macroscopic properties under realistic service conditions, particularly under dynamic loading? Although most studies attempt to address the first question by proposing optimization or tailoring of process design parameters, in practical scenarios the intrinsic quality of the starting feedstock - particularly metal powders - plays a dominant role in governing subsequent microstructural evolution and ultimately the mechanical performance of AM-produced components. Variations in powder characteristics such as particle size distribution, morphology, flowability, surface oxidation, moisture content, and internal defects directly influence melt pool dynamics, solidification rates, porosity formation, and phase stability during printing. Consequently, it is not uncommon to find reports in the literature where components made from nominally identical alloy compositions, processed using the same AM technology and even similar synthesis parameters, exhibit significantly different mechanical properties. These inconsistencies can often be traced back to differences in the quality, history, or handling of the raw powder, highlighting that feedstock attributes are as critical as process parameter selection in achieving reproducible material performance. This point is extensively discussed in Ref. [28]. Most conventional alloys exhibit well-studied dislocation slip and twinning mechanisms, but HEAs often introduce synergistic interactions among slip, twinning, micro banding, and phase transformation - especially under high strain rates. **Fig. 9.2** illustrates a complex interplay of different deformation mechanisms involved during plastic deformation of a single-phase $Cr_{26}Mn_{20}Fe_{20}Co_{20}Ni_{14}$ HEA. The interplay of these mechanisms, and their sensitivity to AM-specific microstructures, needs further investigation [2,3,26]. The effect of intentional or process-induced heterogeneities (such as dual-phase structures or compositional gradients) on impact behaviour, energy absorption, and fracture characteristics is still unclear for many HEA systems fabricated by AM [27,29]. There is limited data on the long-term reliability, fatigue, and ballistic performance of AM-fabricated HEAs under realistic operational environments, which impedes technology adoption in safety-critical applications [1,2,29].

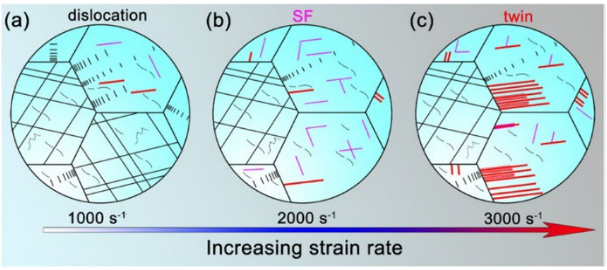

Fig. 9.2 Strain-rate dependence of different deformation mechanisms involved during plastic deformation of a single-phase $Cr_{26}Mn_{20}Fe_{20}Co_{20}Ni_{14}$ HEA (Reproduced with permission from Ref. [30]).

9.2 Recent AM Research

9.2.1 Latest AM Techniques for HEAs in Ballistic Contexts

Recent progress has focused on adapting and refining AM techniques - particularly laser (L)-PBF, SLM, and DED to HEA systems suitable for impact resistance [2]. These methods facilitate the fabrication of fully dense, tailored microstructures with hierarchical features such as sub-micron dislocation cells, cellular solidification arrangements, and refined grain structures that are difficult to achieve with conventional fabrication routes [2,29]. PBF has proven to produce single-phase solid-solution HEAs with outstanding properties, such as FeCoCrNi and CoCrFeNiMn compositions with exceptional ductility and strain hardening [2]. DED is another technique which allows for compositionally graded structures and in situ alloying, enabling the design of location-specific mechanical responses within lattice architectures [1,2]. Studies have reported that AM-processed HEAs demonstrate higher strain-rate sensitivity, improved work-hardening rates, and tailored microband and twin densities, all of which contribute to superior performance under dynamic and ballistic loads [2,26,30]. Notably, AM enables not only structural densification but also the introduction of engineered porosities and hierarchical lattices for energy absorption.

9.3 AM in Ballistic Protection Applications

9.3.1 Experimental Studies and Real-World Context

Ballistic testing of AM-built HEA plates and lattices has revealed critical advantages when compared to both conventional rolled or cast metallic armours and commercially used steels [1,3,26]. Studies on ballistic experiments - including gas gun and bullet penetration tests on AM-fabricated $Fe_{40}Mn_{20}Cr_{20}Ni_{20}$ and related systems indicated that AM HEA targets display good ductility, exhibit stable crater formation under impact, and high resistance to crack propagation, even at high impact velocities (≈ 930 m/s) [1,3]. Besides, dense dislocation/twin structures and microbands, promoted by AM processing, underlie significant strain hardening and delayed failure [1,2]. Therefore, when benchmarked against sophisticated high-manganese steels and traditional armours, AM HEAs (such as $Fe_{40}Mn_{20}Cr_{20}Ni_{20}$ and FeCoCrNi) demonstrate competitive or superior resistance to penetration and lower tendency toward brittle fracture [26,27]. Additionally, AM enables the construction of lattice structures and multi-material designs, improving ballistic performance through controlled deformation paths and compartmentalized energy dissipation.

9.4 <u>AM HEAs for High-Energy Absorption</u>

9.4.1 Mechanical Properties, Microstructure, and Strain-Rate Response

AM-processed HEAs exhibit advanced mechanical behaviour under quasi-static and dynamic loading that is directly linked to their engineered microstructures [2,26,29]. In terms of microstructure, AM HEAs have high densities of cellular dislocation structures (typ. 500–2000 nm cell size), refined grains, and phase homogeneity or tailored multiphase distributions [2,26]. AM FeCoCrNi alloys maintained stable yield stress and exceptional toughness upto strain rates up to 10,000 s^{-1} due to collective dislocation nucleation and extensive twin formation [2,25]. Dual-phase HEAs (e.g., $Fe_{50}Mn_{30}Co_{10}Cr_{10}$) fabricated via AM or forging show a combination of high tensile strength (800–820 MPa), elongation (up to 50%), and impact energy (>140 J at room temperature), surpassing many conventional alloys [26]. **Fig. 9.3** shows a comparison of Charpy impact energies for a wide range of metals and alloys (including as-cast and forged $Fe_{50}Mn_{30}Co_{10}Cr_{10}$ HEA). Strain-rate sensitivity, activation volumes, and transition in deformation mechanisms (from dislocation glide to twinning to phase transformation) all contribute to the outstanding impact resistance and energy-absorbing capacity of HEAs, especially when processed via AM [2,25,31].

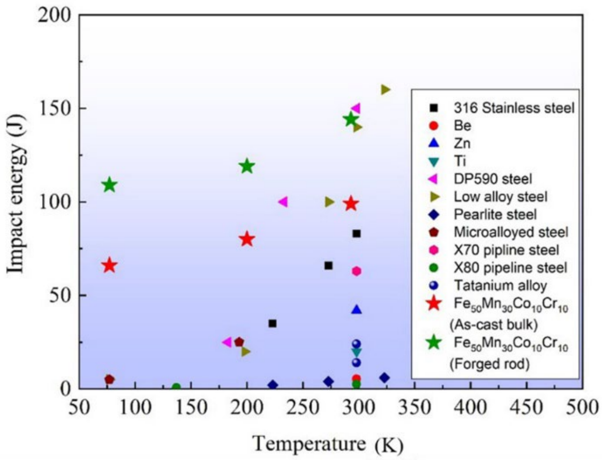

Fig. 9.3 Comparison of Charpy impact energies for a wide range of metals and alloys (Reproduced with permission from [26]).

9.5 FEM of AM Lattice Structures and Defects

9.5.1 Predictive Modelling of Porosity, Anisotropy, and Tolerance

FEM is pivotal in predicting and optimizing the mechanical performance of AM HEA structures subjected to ballistic and impact loading. FEM allows quantification of the effects of built-in porosity and AM-induced defects on stress distributions, failure modes, and residual strength. Lattice topologies and defect clusters can be explicitly modelled to evaluate their impact on energy dissipation and crack arrest behaviours [1,2,25]. AM introduces anisotropic properties due to directional solidification; FEM incorporates realistic anisotropic constitutive equations, often extending the Johnson-Cook or visco-plastic models with microstructure-based hardening terms [3]. For example, yield stress as a function of strain rate and temperature is modelled by the Johnson-Cook model predicts the flow stress (σ) of a metal during plastic deformation: [32] (See Appendix 9.9 for the representation of symbols used in Equation (9.1))

$$\sigma = (A + B\varepsilon^n)\left[1 + c\ln\left(1 + \frac{\varepsilon}{\varepsilon^\circ}\right)\right]\left[1 - \left(\frac{T - T_r}{T_m - T_r}\right)^m\right] \qquad (9.1)$$

However, it may be noted that the following are the effects which are taken into account by the model.

- Strain hardening - Strain hardening represents the increase in flow stress of a material as it undergoes plastic deformation. In the Johnson-Cook model, this effect is captured through a power-law relationship between stress and equivalent plastic strain. The underlying mechanism arises from the multiplication and interaction of dislocations within the metal lattice during deformation. As plastic strain increases, dislocation density increases, making further movement of dislocations progressively more difficult. Consequently, the material requires higher stress to sustain additional plastic flow. This phenomenon is particularly significant in metals subjected to large deformations such as machining, forming, or ballistic impact. Equation (9.1) accounts for this behaviour through the strain hardening term $(A + B\varepsilon^n)$, where A denotes the yield stress under reference conditions, B quantifies the contribution of strain hardening, and n is the strain hardening exponent that governs how rapidly strength increases with deformation. A higher value of n suggests a stronger dependence on strain, indicative of materials that exhibit pronounced work hardening.

- Strain-rate sensitivity - Strain-rate sensitivity describes the material's response to different deformation rates. Many metals demonstrate increased flow stress when deformed rapidly, due to limited time for thermally activated dislocation processes. In high strain-rate events such as impact loading, crash scenarios, and explosive forming, this sensitivity becomes crucial for accurately predicting material behavior. A logarithmic strain-rate term $[1 + C\ln(\frac{\dot{\varepsilon}}{\dot{\varepsilon}_0})]$ in equation (9.1) accounts for this effect. Here, C is an empirical constant representing the sensitivity level, and $\dot{\varepsilon}_0$is a reference strain rate. When the strain rate increases above $\dot{\varepsilon}_0$, the multiplicative term increases the flow stress, reflecting material strengthening at high deformation speeds. Conversely, when strain rates are lower, the contribution diminishes. This term allows the JC model to capture dynamic loading responses across several orders of magnitude in strain rate, making it particularly useful in simulations involving shock, penetration, and adiabatic shear localization.
- Thermal softening - Thermal softening refers to the reduction in flow stress as temperature increases during deformation. Under severe plastic deformation, a significant fraction of mechanical work converts into heat, elevating the material's temperature. Increased temperature accelerates dislocation recovery mechanisms and enhances atomic mobility, reducing the resistance to slip. This effect is incorporated using a temperature-dependent term $[1 - (\frac{T - T_{\text{room}}}{T_{\text{melt}} - T_{\text{room}}})^m]$, where T is the current temperature, T_{room} is the reference room temperature, and T_{melt} is the melting temperature. The exponent m governs sensitivity to thermal effects. As temperature approaches T_{melt}, the softening term tends toward zero, indicating loss of load-bearing capacity. This temperature dependence is vital when modeling processes such as high-

speed machining, welding, and impact events where substantial thermal rise occurs. Equation (9.1) thus enables realistic prediction of flow stress reduction under adiabatic conditions and helps in assessing the onset of thermal failure mechanisms including melting and shear band formation.

Nevertheless, predictive models are routinely validated using microstructural data from AM specimens, such as cell size, twin density, and defect distributions, linking them directly to macroscopic impact resilience [2,30]. That means a thorough understanding of the microstructure is highly necessitated to be able to predict the mechanical response using FEM-based modelling.

9.6 FEM for Dynamic/Ballistic Loading on AM Structures

9.6.1 Impact, Penetration, and Energy Dissipation Simulations

FEM simulations of ballistic loading provide deep insights into the failure and energy-dissipation mechanisms of AM HEA structures. Simulations replicate gas-gun and bullet tests, predicting crater size, depth, and plug formation as functions of impact velocity, alloy composition, and microstructure [1,25]. Lattice models demonstrate that strategic architectures, including gradient porosity and hierarchical cell sizes, increase energy absorption and delay catastrophic failure, as confirmed by both simulation and experiments [1,26]. High-speed imaging and post-mortem microscopy confirm FEM predictions of shear band formation, twin nucleation, and crack deflection paths, thereby enabling the rational design of AM HEA armours, optimizing both mass efficiency and protection levels for specific threat profiles [25,33].

9.7 Technological and Industrialization Challenges

9.7.1 Technical Limitations, Cost, and Certification

Despite the promise of AM HEAs for ballistic protection, several challenges remain to be addressed. Most importantly, control over residual porosity, phase homogeneity, and defect mitigation remains a challenge, affecting both consistency and reliability in high-strain-rate applications [2,25]. Besides, the high cost of both AM processes and constituent high-purity elements (e.g., Co, Ni) currently limits widespread field implementation, motivating the search for more abundant element substitutions and improved AM efficiency [29]. There are few established industrial standards for AM HEAs in defence; robust certification protocols for AM processing, in situ monitoring, and post-process quality assurance are required [1].

9.7.2 Roadmap for Research and Industry

Microstructure-property databases are currently required to expand material informatics and high-throughput frameworks for correlating AM process parameters, microstructure, and ballistic performance. Although there are a number of Calculation of Phase Diagrams (CALPHAD) based tools to optimize alloy compositions based on prediction of phase evolution and mechanical response (primarily, tensile properties), however, to design alloys (especially HEAs) for ballistic applications, these databases also need to account for the impact properties and spallation responses. Besides, considering that the impact properties are also largely dependent on the defect distribution in the microstructure, kinetic databases need to account for such effects. Hydrogen embittlement (HE) is one of the phenomenon which can severely affect the lifetime of components designed for ballistic applications. As Hydrogen (H) is omnipresent and therefore, is always trapped in metallic materials (including AM HEAs), methods to mitigate HE-induced damage needs to be devised, for which a detailed understanding of HE mechanisms is indispensable. Currently, one of the ways to understand HE mechanisms is through identification of defects serving as strong H-trapping sites which may be expected to prevent the accumulation of H at potential crack-initiation sites. Since the last few decades, a series of studies have attempted to study strong H-trapping sites by charging deuterium (H-isotope) to samples and analyzing the distribution of deuterium in near-atomic scale using 3D atom probe [34–38]. However, there seems to be a dearth of studies showing the presence of strong H-trapping sites in AMed materials (especially HEAs). These studies are expected to aid in the design of HE-resistant AM HEAs for ballistic applications. Besides, leveraging of AM for architected protection materials (e.g. hybrid lattices or gradients) is required to tailor mechanical impedance and energy dispersal. In addition, development and systematic implementation of standard test protocols for AM HEAs in ballistic and dynamic impact regimes is a necessity. As modeling and in situ monitoring tools mature, and rapid certification methods are developed, AM HEAs are likely to become foundational materials for future armor, vehicle, and critical infrastructure applications.

9.8 **Summary**

AM is fundamentally transforming the engineering and deployment of HEAs for use in ballistic protection and dynamic impact scenarios. AM enables the precise control of alloy composition and microstructure, allowing alloys with complex atomic interactions (such as HEAs) to be processed into net-shape components with tailored, site-specific properties. The rapid solidification dynamics unique to AM support the stabilization of multiple phases and complex defect architectures, endowing AM HEAs with superior energy absorption, exceptional work hardening capability, and notably high resistance to crack initiation and propagation under extreme loading conditions. Experimental results repeatedly show that AM HEAs, particularly those based on FCC or dual-phase microstructures, outperform many conventional steels and Ni-based alloys in dynamic impact and ballistic penetration tests, making them compelling candidates for advanced military, aerospace, and protective technologies [2,33]. The synergy between AM and HEA design enables a new paradigm for armor development, ushering in systems that can be optimized at both the microstructural and macroscopic levels. Advanced modeling, informed by detailed microstructural and mechanical characterization, accelerates the discovery of new alloy chemistries and AM process parameters that maximize impact resistance, strength-ductility synergy, and damage tolerance. As a result, AM HEAs are not only structurally robust but also offer customizable performance profiles for next-generation armors and protective systems. However, key challenges remain, including scale-up of AM processing, reduction of residual stresses and anisotropy, design of HE-resistant alloy microstructures and standardization for certification and deployment in mission-critical applications. Nevertheless, ongoing research in process monitoring, hybrid manufacturing, and property optimization signals strong prospects for the adoption of AM HEAs, positioning them at the heart of future high-performance defence platforms and protective technologies.

9.9 Appendix

List of symbols used in equation (9.1):

Symbol	What it represents?
σ	Flow (yield) stress of the material
ε	Equivalent plastic strain
$\dot{\varepsilon}$	Plastic strain rate (rate of deformation)
$\dot{\varepsilon}_0$	Reference strain rate (a constant, often 1 s^{-1})
T	Current (absolute) temperature of the material
T_r	Reference temperature (usually room temperature)
T_m	Melting temperature of the material

A	Initial yield stress at reference conditions (baseline strength)
B	Hardening modulus
n	Strain-hardening exponent
c	Strain-rate sensitivity coefficient
m	Thermal softening exponent

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