University of Belgrade
Technical Faculty in Bor,
Mining and Metallurgy
Institute Bor

54th International October Conference on Mining and Metallurgy

PROCEEDINGS

Editors:
Ljubiša Balanović
Dejan Tanikić

18-21 October 2023, Bor Lake, Serbia

PROCEEDINGS,

54th INTERNATIONAL OCTOBER CONFERNCE

on Mining and Metallurgy

Editors:

Prof. dr Ljubiša Balanović

Prof. dr Dejan Tanikić

University of Belgrade, Technical Faculty in Bor

Technical Editor:

M. Sc. Miljan Marković

University of Belgrade, Technical Faculty in Bor

Publisher: University of Belgrade, Technical Faculty in Bor

For the publisher: Dean Prof. dr Dejan Tanikić

Circulation: 200 copies

CIP - Каталогизација у публикацији Народна библиотека Србије, Београд

622(082)(0.034.2)
669(082)(0.034.2)

INTERNATIONAL October Conference on Mining and Metallurgy (54 ; 2023 ; Borsko jezero)
Proceedings [Elektronski izvor] / 54th International October Conference on Mining and Metallurgy - IOC 2023, 18-21 October 2023, Bor Lake, Serbia ; [organized by] University of Belgrade, Technical Faculty in Bor and Mining and Metallurgy Institute Bor ; editors Ljubiša Balanović, Dejan Tanikić. - Bor : University of Belgrade, Technical Faculty, 2023 (Niš : Grafika Galeb). - 1 USB fleš memorija ; 1 x 1 x 5 cm

Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Tiraž 200. - Preface / Ljubiša Balanović. - Bibliografija uz svaki rad.

ISBN 978-86-6305-140-9

a) Рударство -- Зборници b) Металургија -- Зборници

COBISS.SR-ID 126659849

Bor Lake, Serbia, October 18-21, 2023

Conference is financially supported by
The Ministry of Science, Technological
Development and Inovation
of the Republic of Serbia

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DESIGNING BIOCOMPATIBLE HIGH ENTROPY ALLOYS USING MONTE CARLO SIMULATIONS

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Abstract

This study examines the potential of high-entropy alloys (HEAs) as promising biomaterials, with a specific focus on the development of alloys with a low Young's modulus. Utilizing Monte Carlo simulations coupled with machine learning techniques, the research identifies critical variables that significantly influence the Young's modulus, uncovering a notable correlation between specific heat and the elastic properties of the alloys. The validation of the Extra Trees Regressor as a reliable predictive model in this study, furthermore, facilitates the identification of promising HEAs with tailored properties. These findings provide significant insights that are expected to guide future progresses in the development of HEAs as advanced biomaterials.

***Keywords**: (HEA, Monte Carlo simulations, Young's modulus)*

5. INTRODUCTION

Biomaterials made from titanium alloys have been successful for decades as substitutes for hard tissues in the human body [1]. This popularity stems from their exceptional combination of properties: high strength, resistance to corrosion and wear, low Young's modulus, and biocompatibility. Among these titanium alloys, special mention is made of titanium β alloys, which show extremely low values of Young's modulus. These alloys have proven to be advantageous in the field of implantology due to their ability to improve load transfer characteristics, thereby reducing the risk of premature implant failure and preserving the vitality of the surrounding bone tissue. Moreover, the implantation of such materials is associated with significant improvements in bone tissue rehabilitation, affecting cell adhesion and accelerating the healing process [2]. The most traditional alloy used for this purpose, Ti-6Al-4V, has been questioned because of its Young's modulus (>100 GPa), which compared to the Young's modulus of bone (up to 35 GPa) is a big difference. Also, Al and V were declared cytotoxic and emphasis was placed on some other elements such as Ni, Mo, Fe, Zr, whose presence does not leave harmful effects on the human body [3,4].

However, in the last two decades, a new class of biomaterials called high entropy alloys (HEAs) has emerged. This group of materials fundamentally deviates from traditional alloys. In contrast to conventional alloys, in which the desirable properties of a single element predominate, HAE contains at least five primary elements in similar proportions. This unique composition leads to an increase in mixing entropy, resulting in the formation of a single-phase solid solution, predominantly adopting cubic (BCC) and face-centered cubic (FCC) crystal lattices. As a result, these alloys exhibit an extensive range of exceptional properties [2, 5].

Although the potential applications of HEAs in the field of biomaterials are still under active investigation, they promise to be an ideal choice where no compromises need to be made between material properties [5]. This paper presents an innovative approach to the design of HEAs without the presence of cytotoxic elements, with Young's modulus below 70 GPa. The Monte Carlo

simulation and machine learning techniques are used to identify and analyze key variables that significantly affect Young's modulus.

6. METHODS

The principle of machine learning was applied to a database of biocompatible titanium alloys with a low value of Young's modulus, precisely defined in the Ref. [6, 7]. Thanks to the ability to decipher complex patterns in the data, it was possible to determine the most important features that affect Young's modulus [8].

Our dataset [6] is divided into a training set (65%) and a test set (35%). The Extra Trees Regressor prediction model was used to display predicted and actual Young's modulus values. In addition, a Monte Carlo simulation was conducted to explore a wide range of random compositions. This simulation involved randomly generating compositions with weighted proportions of alloying elements and impurities within predefined ranges. The aim was to evaluate Young's modulus and different compositions of HEA. This method, and software is given in reference [9].

7. RESULTS AND DISSCUSION

The observation that the coefficient of determination (R^2) for the test set is ~0.7 is a positive indicator of the validity of the model. Figure 1 represents the relationships between actual and predicted values of Young's modulus based on the number of samples tested, provides additional support for the validity of the model. It is possible to see that the largest deviations between the predicted and actual values occurred at the extremes.

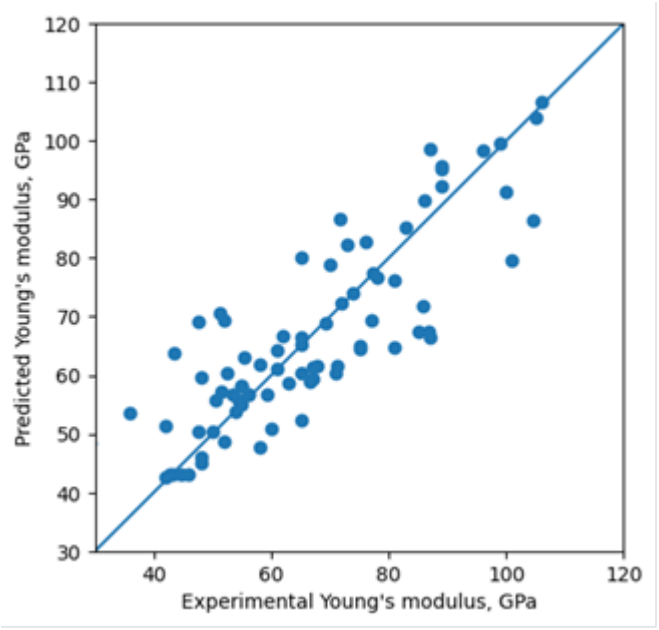

Figure 1- Experimental and predicted value of Young's modulus using machine learning method

The analysis identifies the specific heat as the primary parameter influencing the predictive accuracy of the machine learning model [8, 9]. Theoretical support can be derived from both the Einstein and Debye models, as they provide insights into the quantum mechanical foundations of the changes in molar heat capacity resulting from temperature fluctuations. Consequently, these models establish an important but indirect relationship between specific heat and Young's modulus (E). The aforementioned models serve to encapsulate the fundamental nature of atomic vibrations occurring within a given material, which plays an important part in the determination of its elastic properties. Einstein's model provides an initial understanding by making the assumption of independent atomic vibrations. However, the Debye model expands upon this understanding by

considering the collective and interdependent atomic behaviors. V. Pekarek found relation between thermal properties and elastic modulus:

$$c_p \cdot s = \frac{Ea}{1-4\cdot\sigma^2} \cdot \alpha \quad (1)$$

where c_p is specific heat at constant pressure per kilogram (J/(kg·K)); s is density (kg/m³); E_a is Young's modulus (GPa); α is linear coefficient of thermal expansion (1/K), and σ is Poisson's ratio [10].
Monte Carlo simulation was created by ten million alloy samples were under controlled conditions, aiming to achieve HEAs with specific Young's modulus values (70 GPa set as upper value). This approach has led to the discovery of dozens of promising alloys, and Table 1 presents information of these alloys. To maintain consistency with previous research in the literature, we limited the oxygen content to a maximum of 0.78 wt%. The primary elements used in these alloys are titanium, zirconium, tin, manganese, silicon, and niobium. These elements, as well as the other mentioned parameters, proved to be the most influential variables when it comes to predicting Young's modulus. The results obtained from this study, together with the proposed computational methods, can serve as valuable guidelines for future efforts in the design of multicomponent HEA.

Table 1 - Values of various parameters for modeled HEA.

Parameter:	**Unit:**	**Sample ID:**		
		2093590	**3829568**	**6719870**
Ti	**wt.%**	15.32	20.62	16.12
O	**wt.%**	0.26	0.21	0.31
Nb	**wt.%**	16.02	1.10	11.50
Zr	**wt.%**	11.72	11.10	6.73
Ta	**wt.%**	0.17	15.32	12.75
Sn	**wt.%**	11.72	11.97	11.11
Mn	**wt.%**	15.38	0.39	10.81
Si	**wt.%**	26.56	26.65	27.48
Mo	**wt.%**	2.55	10.46	3.06
Fe	**wt.%**	0.03	2.17	0.14
Bo-bond order	/	3.27	2.81	3.30
Md-d orbital energy level	/	2.40	1.98	2.40
Specific heat	**kgK**	408.13	312.50	399.36
Δr	/	-10.05	-6.12	-9.45
Predicted Young's modulus, exp	**GPa**	**66.28**	**66.34**	**66.66**

Equation 1 establishes a clear and direct relationship between the specific heat capacity and Young's modulus. This relationship is influenced by various additional factors, such as the density of the material and the coefficient of thermal expansion. As depicted in Figure 2, the specific heat values of the alloys shown in Table 1 exhibit a significant decrease, potentially falling below the established thresholds, when compared to the range observed in the extensive database of alloys being investigated. The characteristic necessitates additional investigation, potentially suggesting a new approach in the continuous efforts to improve the structural properties of high-entropy alloys.

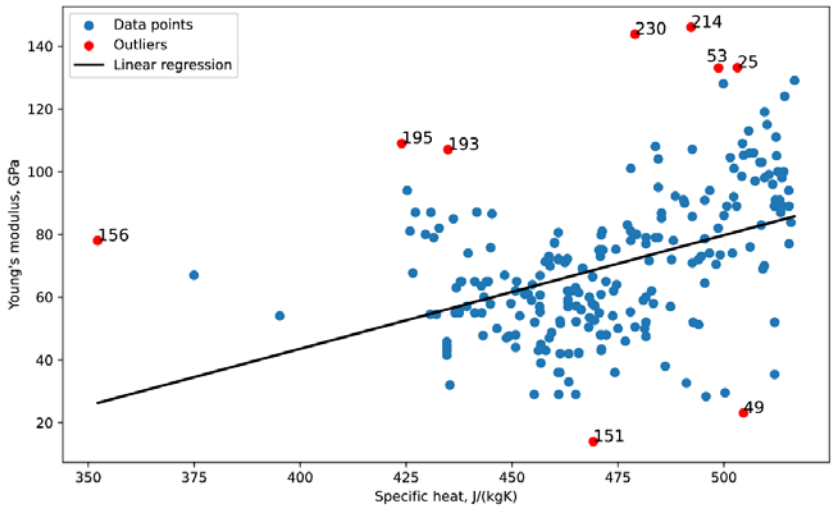

Figure 2- Relation between Young's modulus and specific heat within the Ti-alloys dataset

8. CONCLUSION

The present study presents an innovative method for predicting and analyzing the properties of high-entropy alloys (HEAs) through the use of Monte Carlo simulations. This approach is based on the observed strong correlation between the specific heat and Young's modulus, with particular attention given to HEAs that possess a modulus value of approximately 66 GPa. The integration of machine learning with simulations, physical models, and rigorous experimentation could provide a feasible approach to enhance composition design and microstructure control in high-entropy materials. This development holds the potential to redesign the predictive modeling and achievement of advanced high-entropy alloys.

ACKNOWLEDGEMENTS

This investigation was financed by the Ministry of Science, Technological Developments and Innovation of the Republic of Serbia (Contract number: 451-03-47/2023-01/200023; 451-03-47/2023-01/200135).

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