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Recent Advances of Nanoindentation in High Entropy Alloys

Sushil Kumar[1] and Satpal Sharma[2]
[1]Research Scholar, Mechanical Engineering, School of Engineering,
Gautam Buddha University, Greater Noida, India.
[2]Faculty, Mechanical Engineering, School of Engineering,
Gautam Buddha University, Greater Noida, India.

(Corresponding author: Sushil Kumar)
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ABSTRACT: HEAs are equiatomic or non-equiatomic alloys which contained five or more metallic or non-metallic elements without any single base material and highly investigated in recent years to replace traditional alloys or composite materials which are currently being in use. The precise calculation of engineering properties of multicomponent alloys/ high entropy alloys on micro scale and nano scale proves nanoindentation an innovative and efficient tool. Nanoindentation technique is now broadly adopted for assessment of mechanical characterization of high entropy alloys for measurement hardness, Young's modulus, fracture toughness of the equiatomic and non-equiatomic complex concentrated/ multicomponent alloys/ high entropy alloys or high entropy nanostructured materials.

Keywords: Nanoindentation, High Entropy Alloys, Mechanical Properties, Design Strategies

I. INTRODUCTION

In the recent years, significant efforts have been made in mechanical characterization to evaluate the mechanical properties of the high entropy materials with high precision on small scale or nano scale. Although the idea of HEAs was reported before 2004, the research was accelerated after 2010 when Jien-Wei Yeh and Brian Cantor started investigating them [1-2]. The scientific development in technology now makes it possible to calculate mechanical properties precisely of homogeneous or heterogeneous engineering materials. Nano indentation or depth-sensing indentation is now becoming very popular technique for characterization of engineering materials and nanomaterials. Moreover, nanoindentation can be implemented to measure the fracture toughness of coatings which is difficult to compute by other conventional techniques [3].The indenter tip with very precise geometry is penetrating into the test specimen with a specific load and measurement of load and displacement with an increasing load up to a specific value. During the process, the load and displacement are recorded and analyzed to determine the indentation area. Nanoindentation normally does not require any sample preparation for testing of various types of materials ranging from hard metals to soft metals. Scanning probe microscopy (SPM) and atomic force microscope (AFM) have been used to study the properties of the nano-size materials. The measurement of nano indentation load and displacement curve generated by indenter is based on the technique invented by Oliver and Pharr [4].

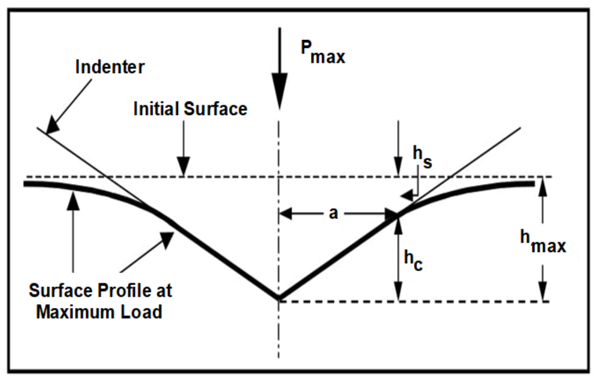

Fig. 1. Indentation geometry at maximum load for conical indenter.

The nanoindentation is very useful fastest technique of evaluation to establish a relation into crystalline structure and composition of high entropy alloys by knowing which phase holding high hardness and reduced modulus. The nanoindentation technique came into possession from conventional indentation tests but with the advancement of the technology, size of the tips was considerably reduced and the accuracy and resolution of depth were enhanced. In nanoindentation technique, the mechanical properties of the engineering materials are investigated by recording the load and displacement when indenter tip is driven into the test specimen [5]. The hardness and reduced modulus can be measured by examining the load-displacement curve. There are three things should be taken into consideration while performing the nanoindentation.

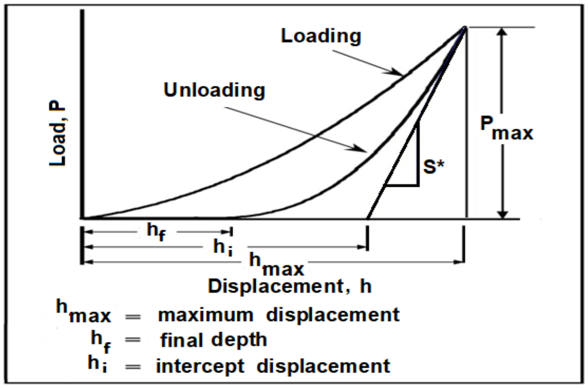

Fig. 2. Load displacement curve measured by indentation technique.

The first is to select the nanoindentation load, secondly, to analyze the effect of different phases of the test specimen during nanoindentation test. The last is that there should be minimum distance in between two indents to nullify work hardening.

II. MECHANICAL BEHAVIOR-HARDNESS AND YOUNG' S MODULUS

The nanoindentation technique calculates the hardness and Young's modulus employing indenter tip at low load at different temperatures with high accuracy and precision. The pronounced modulation in the amount of Young's modulus is as a result of evolution of additional metallic and intermetallic phases which contained larger modulus as compared to single-phase crystalline structure [3, 6]. Liu *et al* [7] examined and measured the mechanical properties of CoCrFeNi and AlCrFeNiTi high entropy alloy at room temperature and high temperature through nanoindentation equipped with laser heating system. The analysis of mechanical and microstructural properties of the high entropy alloys was observed by implementation of continuous stiffness method. Sun *et al* [8] evaluated the microstructural properties and phase formation of AlCoCrCuFeNi high entropy alloy with variable percentage of aluminium in HEA matrix by utilizing nanoindentation technique. It is observed that increase of addition of aluminium contents significantly improved the hardness of the BCC phase of the solid solution. Li and Bhushan [9] evaluated the substrates of thin films which greatly influenced at high loads and optimize the properties of thin films and coatings for discrete applications. Kiener *et al* [10] utilized nanoindentation to assess mechanical properties of the nanostructured high entropy alloys of different grain sizes. The investigation exhibited that grain sizes does not have control the Young's modulus but largely rely on existence or absence of intermetallic phases in the matrix of high entropy alloys. Tolstolutskaya *et al* [11] studied the ion irradiation effect on hardening of heat treated CrFeNiMn high-entropy alloys of different configurations and evaluated nanohardnes, secondary phases. The nanoindentation equipped with laser heating system is an efficient instrument for measuring the of high-temperature mechanical properties of heterogeneous engineering materials composed several phases for better interpretation and practical understanding of the compositional and microstructural changes in such materials at elevated temperatures and their responses to mechanical deformation. The nanoindentation technique is now widely considered fast and efficient approach to understand the chemical compositions, phase stability and configuration details of nanostructured HEAs [12]. The precise characterization and evaluation of reduced elastic modulus and nanohardness in each phase by nanoindentation imparts new insights to design new HEAs with optimum performance [13].

III. INCIPIENT PLASTICITY AND DISLOCATION NUCLEATION

The origin of instrumented nanoindentation has permitted the analysis of deformation behavior of crystalline structure, where the nucleation and motion of dislocations or defects can be ascertained [14-15]. Sun *et al* [16] implemented nanoindentation technique to characterize the deformation on the FCC and BCC phases of $AlCrCuFeNi_2$ high entropy alloys. It is observed that at high indentation loads, the dissipation of plastic energy increased. The outcome analysis demonstrate that elastic modulus is 93.1 GPa in the FCC phase which is higher compared to BCC phasewhile implementing a load range from 100 μN to 2000 μN on high entropy alloys. Fang *et al* [17] evaluated the deformation performance of $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ high entropy alloys with spherical indenter. The mechanical properties, shear strain, surface textures indentation force and radial distribution function were evaluated through nanoindentation technique of the high entropy bulk metallic glasses materials. Results revealed that atomic size difference provides better understanding of amorphous formation abilities and mechanical properties of high entropy bulk metallic glass materials. Jiao *et al* [18] evaluated the plastic deformations of high entropy alloy $Al_{0.5}CoCrFeNi$ at different strain rates by nanoindentation technique at room temperature. The results demonstrate that at different strain rates contact stiffness and elastic modulus does not change but hardness decreases due to increase in indentation depth and size of the indenter. The results demonstrated serrated behavior due to indentation rate and high localized plastic deformation observed during nanoindentation. Li *et al* [19] utilized spherical rigid indenter to study the both elastic and plastic deformations of indentation in FeCrCuAlNi high-entropy. The effects of shear strain, indentation force, radial distribution function, load displacement relationship, severe lattice distortion on the deformation processes were evaluated. Nanoindentation results show that addition of equal amount of element can significantly enhance the mechanical properties of high entropy alloy as compared to traditional alloy [20]. Low stacking fault energy and the dense atomic arrangement are responsible for improved mechanical and microstructural properties of the high entropy alloy [19]. Muthupandi *et al.,* [21] examined the nanoindentation behavior and microstructures of annealed AlCoCrFeNi high entropy alloy. Electron microscopy revealed different nanoindentation behaviors are due to the presence of multiple phases and pile-up and sink-in characteristics in the grain boundary and grain regions. The major dislocation activities observed under the pile up and minor dislocation activities were found to under the sink in or confined to indenter tip. The susceptibility to elastic and plastic deformation for every phase of the AlCoCrFeNi HEA was studied at different hardness-to-modulus ratio. The study susceptibility of plasticity can be proved a useful technique in finding the pile-up and sink-in characteristics of the other high entropy alloys. Pi *et al.,* [22] used continuous stiffness measurement mode of the nanoindentation to evaluate the $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ high entropy metallic glass. A good combination of excellent plasticity and homogeneity observed in glassy $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ high entropy alloys. The creep was observed at constant load at room temperature and mean values of nanohardness and modulus were found 7.45 GPa and 105.4 GPa, respectively.

The new mechanisms of dislocation and their propagation in new combinations of high entropy alloys and high entropy composites are yet to be known. Nanoindentation testing can enhance understanding in the deformation related mechanisms with their effects on mechanical properties of the high entropy alloys. The implementation of simulation techniques and their comparison with different experimental models may discover the outstanding mechanical properties of high entropy alloys.

IV. FRACTURE TOUGHNESS AND CREEP BEHAVIOR

It is challenging to precisely evaluate the fracture toughness, cracks propagation of brittle metals or alloys at a micro range. Repeated and accurately measurements of micro/nano properties makes nanoindentation a unique and efficient tool for nano fracture toughness for quality control and R&D of advanced materials. Ma *et al* [23] studied nanoindentation creep behaviors of a CoCrFeCuNi HEA deposited and annealed films synthesized by magnetron sputtering were investigated with a spherical tip. The calculation of strain rate sensitivity was obtained from steady-state creep and the creep deformation. Study revealed that internal crystalline structure and loading rate create a difference in the creep behavior. Wang *et al* [24] studied internal mechanism and behavior of the crossover in the initial creep stage during nanoindentation of CoFeNi high entropy alloy. The stress and holding time explained the different mechanism of the crossover before and after the crossover point. The analysis of attributes and conduct of the crossover point can be a useful technique to evaluate the creep rate in different engineering materials. Ma *et al.,* [25] investigated creep behavior of CoCrFeNiCu high entropy alloy films composed of FCC and BCC structures was investigated at room temperature by nanoindentation technique. The results showed that creep deformation of high entropy films can be improved by accelerating the loading rate. The activation volume, dislocation nucleation and strain rate sensitivity of nanostructured HEA films were evaluated. At different loads, the creep behavior of $Ti_{16.7}Zr_{16.7}Hf_{16.7}Cu_{16.7}Ni_{16.7}Be_{16.7}$ was evaluated by nanoindentation technique and outcomes were compared with different high entropy alloys. Study revealed that high entropy bulk metallic glass materials contain small strain rate leads to good creep resistance. Kelvin model was adopted to explain the creep curves, amorphous structure and complex configuration of high entropy bulk metallic glass [26]. Wang *et al.,* [27] measured notch fracture toughness of arc-melted TiZrNbTaMo high-entropy alloys at room temperature. The analysis showed that the increase of Mo concentration in HEAs results in an appreciable reduction in toughness. Gong *et al.,* [28] evaluated creep behavior of $Ti_{20}Zr_{20}Hf_{20}Be_{20}Cu_{20}Ni_{10}$ high entropy bulk metallic glasses at different loading rates by nanoindentation technique. Kelvin model was adopted to explain the experimental creep curves by the use of strain rate sensitivity, retardation spectra and creep compliance. Replacement of Cu with Ni, microstructure gets denser which improves the hardness and Young's modulus. After the study of related mechanism and the pronounced high entropy effect, experimental results demonstrated that addition of Ni effectively boost the creep resistance of high entropy alloy. The studies provide new insights into the understanding the observed creep characteristics in HEA, HEA films, distinct lattice structures, kinetics of plastic deformation in HEA at the nanoscale. Not much work has been reported on fracture and creep allied effects like oxidation, irradiation on the properties high entropy alloys which are yet to be explored.

V. SCRATCH TEST, COEFFICIENT OF FRICTION AND WEAR BEHAVIOR

Nanoindentation scratch tests were executed to know the adhesion of thin films and coatings under a ramping load and the point of failure to know the surface wear properties [29-30]. The nanoindentation and nanoscratch techniques calculates applied load and depth of indentation or scratch cycle to discover the coefficient of friction of films and coatings of an engineering material which is important to measures its tribological performance [31-32]. Varughese *et al* [33] effectively used nanoindentation in scratch testing by moving the test specimen relative to the indenter tip. The coefficient of friction was evaluated by measuring lateral force and normal force. The adhesion of the coatings is efficiently evaluated by nano scratch test by scratch by applying constant load or glide with respect to the sliding distance. Friction and wear behavior of TiZrHfNb high entropy alloy were investigated by nanoscratch technique under both ramping and constant load. The coefficient of friction (COF) reduced rapidly when the normal load increases in elastic regime. The applied load is proportional to the wear rate of the TiZrHfNb high entropy alloy and wears resistance scales linearly. TiZrHfNb high entropy alloy exhibit improved hardness/strength and wear resistance on ramping and constant load modes. Results demonstrated that TiZrHfNb high entropy alloy with low coefficient of friction and high wear resistance can be utilized for tribological applications [34]. Nanoindentation technique was implemented on the $Al_{0.5}CoCrCuFeNi$ high entropy alloy to analyze serration behavior and creep characteristics at two separate temperatures. The interaction of active dislocations and obstacles produced serrated flow at different temperatures. The creep was observed during the holding period and underneath the indenter due to pronounced dislocation activities [35].

The few reported studies and analysis of friction and wear behavior of HEA showed enhanced wear results and it will be interesting to investigate in the field of nanostructured high entropy alloys and high entropy nanocomposites at different loads and temperature ranges.

VI. CONCLUSIONS

Due to remarkable and excellent results, the conventional indentation methods are now completely replaced by nanoindentation in many areas in last few years. Recent developments in high entropy alloys, nanomaterials science and nanotechnology make nanoindentation an efficient tool. The nanoindentation technique provides the more useful information regarding properties of homogenous and heterogeneous materials and subjected to intensive research which recently extended to nanostructured materials. Recent advancement in testing tools and nanoindentation proves it as a novel technique for investigation of advanced high entropy alloys and high entropy nanomaterials.

FUTURE SCOPE

Nanoindentaion can be used as a screening tool to probe the phase decomposition and long term stability of the advanced high entropy alloys and high entropy based composites in short times. Nanoindentation can predict the long term behavior, grain boundary mechanisms and crystalline orientation of the newly developed high entropy alloys and high entropy nanocomposites therefore need to be further studied.

Conflict of Interest: The authors declare that there is no conflict of interest of any sort on this research.

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