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NANOINDENTATION IN HIGH ENTROPY ALLOYS– A REVIEW

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Abstract
This The focused research on high entropy alloys due their unique configurational design and phase formation makes nanoindentation a efficient tool and innovative method for precise calculation of the mechanical properties of high entropy alloys on micro scale andnano scale. The nanoindentation technique is now widely implemented to evaluatethe mechanical characterization, inter molecular interaction, Young's modulus, fracture toughness and hardness of the heterogeneous and homogeneous materials. The indenter size effects on elastic and plastic deformations of HEAs and high entropy composite materials from nano to micro sizes can be explored with nanoindentation.

Keywords: *Nanoindentation; High Entropy Alloys; Mechanical Properties; Design Strategy.*

1. Introduction and Overview of Nanoindentation

In the recent years, significant efforts have been made to analyse the mechanical properties of the engineering material with high precision on small 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 advancement in technology made it possible to manufacture and achieve the high accuracy in mechanical properties of the 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 used 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 analysed 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) has 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].

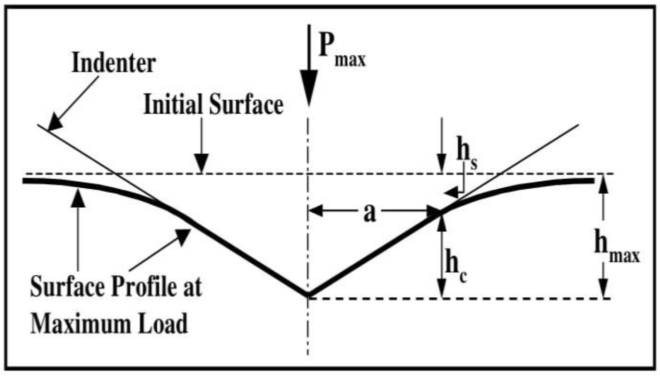

Fig. 1: Indentation geometry at maximum load for conical indenter [4].

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 advancement of the technology, size of tips was considerably reduced, and the accuracy and resolution of depth were enhanced. The elastic and plastic deformation produced when indenter is pressed into the specimen during the measurement and analysis of mechanical properties [5]. The hardness and reduced modulus can be measured by examining the load-displacement curve.

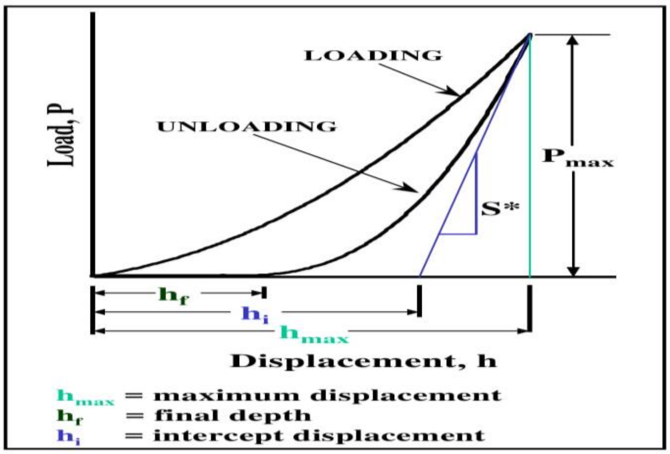

Figure 2: load displacement curve measured by indentation technique [5]

There is three things should be taken into consideration while performing the nanoindentation. The first is to select the upper limit of indentation load, secondly, to analyse 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.

2. Mechanical Behaviour - Hardness and Young's Modulus

The nanoindentation technique uses small indenter tip and low loads to measure the hardness as well Young’s modulus. To calculate the stiffness of engineering material to derive a relationship between strain and stress, Young modulus is measured by nano indentation technique. The observed changes in values of the Young’s modulus are due to formation or presence of the additional metallic and intermetallic phases which consist of higher modulus than the single-phase crystalline structure. The sum of the elastic depth and plastic depth considered as elastic flexure during the testing and direct assessment of the specimen properties specimen made [3,6]. Verena et al implemented nanoindentation technique to evaluate mechanical properties of the nanocrystalline high-entropy alloys and compared with coarser grained materials. The study revealed that grain size does not affect the Young’s modulus but depend upon presence or absence of secondary phases [7]. Thin films contain and grain boundaries irregularities which require variety of hardness tests to discover the utmost rigidity of the coating of tool materials [8-9]. X. Li evaluates the substrates of thin films which greatly influenced at high loads and optimize the properties of thin films and coatings for discrete applications [10]. G. D. Tolstolutskaya et al used nanoindentation technique to analyse the ion irradiation effect on hardening of three different compositionally CrFeNiMn high-entropy alloys. Different types of nanoindentation particulars processing techniques were implemented to evaluate exact values of nanohardness in this high entropy alloys. Nanoindentation hardness of the samples which were heat treated at 850°C show the tendency to increasing on irradiation dose. The inclusions of the secondary phases lead to increasing rate of such scatter in high entropy alloys [11]. Junpeng Liu et al [12] studied and calculated the mechanical properties of CoCrFeNi and AlCrFeNiTi high entropy alloy at room temperature and high temperature by nanoindentation technique which equipped with laser heating system. The continuous stiffness method was implemented for evaluation ofthemechanical properties along with microstructure of the high entropy alloys. Yanan Sun et al [13] examined the microstructural properties and phase formation of AlxCoCrCuFeNi high entropy alloy by varying the percentage of aluminium in matrix by utilizing nanoindentation technique. It was observed that increase of addition of aluminium significantly enhanced the hardness of the BCC phase as compared to FCC phase of the solid solution.

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. Thenanoindentation technique is considered fast and efficient approach to understand the chemical compositions, phase stability and configuration detail of nanostructured HEAs. The precise characterization and evaluation of elastic modulus and hardness in each phase by nanoindentation imparts new insights to design new HEAs with optimum performance.

3. Incipient Plasticity and Dislocation Nucleation

OnThe origin of instrumented nanoindentation has permitted the analysis of deformation behaviour of crystalline structure, where the nucleation and motion of dislocations or defects can be ascertained [14-15]. Yuan Sun et al [16] implemented nanoindentation technique to characterize the deformation on the FCC and BCC phases of AlCrCuFeNi2 high entropy alloys. It is observed that at high indentation loads, the dissipation of plastic energy increased. The outcome analysis demonstrate that elastic modulus in the FCC phase is higher compared to BCC phase while implementing a load range from 100 µN to 2000 µN on high entropy alloys. Qihong Fang [17] evaluated the deformation performance of Cu29Zr32Ti15Al5Ni19 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. Z. M. 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 behaviour due to indentation rate and high localized plastic deformation observed during nanoindentation. Jia Li [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. Low stacking fault energy and the dense atomic arrangement are responsible for improved mechanical and microstructural properties of the high entropy alloy. GokulMuthupandi et al [20] examined the nanoindentation behaviour and microstructures of annealed AlCoCrFeNi high entropy alloy. Electron microscopy revealed different nanoindentation behaviours 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 AlCoCrFeNiHEA 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. Jin Hong Pi et al [21] used continuous stiffness measurement mode of the nanoindentation to evaluate the $Cu_{29}Zr_{32}Ti_{15}Al_{5}Ni_{19}$ high entropy metallic glass. A good combination of excellent plasticity and homogeneity observed in glassy $Cu_{29}Zr_{32}Ti_{15}Al_{5}Ni_{19}$ high entropy alloys. The creep was observed at constant load at room temperature and mean values of nano-hardness 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.

4.Fracture Toughness and Creep Behaviour

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.Y. Ma et al [22] studied nanoindentation creep behaviours 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 behaviour. Zhijun Wang et al [23] 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. Y. Ma et al [24] investigated creep behaviour 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 nanocrystalline HEA films were evaluated. At various loads, the creep behaviour $Ti_{16.7}Zr_{16.7}Hf_{16.7}Cu_{16.7}Ni_{16.7}Be_{16.7}$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 [25]. Shao-Ping Wang et al [26] 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. Pan Gong et al [27] 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.

5.Scratch Test, Coefficient of Friction and Wear Behaviour

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 [28-29]. 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 [30-31].S. Varughese et al [32] effectively used nanoindentation in scratch testing by moving the test specimen relative to the indenter tip. The coefficient of friction 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 behaviour 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 [33] Nanoindentation technique was implemented on the $Al_{0.5}CoCrCuFeNi$ high entropy alloy to analyse serration behaviour 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 [34]. The few reported studies and analysis of friction and wear behaviour of HEA showed enhanced wear results and it will be interesting to investigate in the field of nanostructured high entropy alloys and high entropy nano composites at different loads and temperature ranges.

6.Conclusion

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

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