Effect of Processing Route on the Phase Evolution of High Entropy Alloys: A Review

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Abstract: High entropy alloys (HEAs) are playing great role in material industry. The unique composition of HEAs results in a high degree of structural complexity, which can lead to enhanced mechanical, physical, and chemical properties. These alloys can be prepared with various processing routes. This article presents various processing techniques for CoCrCuFeNiSi (cobalt chromium copper iron nickel & silicon) based HEAs. The processing routes can be majorly categories into meting and casting (liquid state), powder metallurgy (solid state) and films (gaseous state). The specific technique used will depend on factors such as the desired alloy composition, the intended application, and the desired properties of the final product. The addition of Si can obviously improve the micro-hardness and wear resistance of traditional materials. This article discusses about the different processing routes suited for CoCrCuFeNiSi based HEAs.

Keywords: High entropy, multi-principal elements, processing routs, strengthening mechanism

1. Introduction

Now a days, “material engineering more torch on new class of high-entropy alloys (HEAs) to met the industrial requirement as it promise best phase structure and properties like superior corrosion, wear resistance, high thermal stability, fracture toughness, and excellent strength. HEA crystal structure contains five or more metallic elements in concentrations. The first generation HEAs allow stable solid solutions like (FCC) face-centered cubic, (BCC) body-centered cubic, and (HCP) hexagonal close-packed structures [4,5]. To met the desire configuration processing routs and synthesis techniques to be selected properly”.

There are a variety of processing methods available for manufacturing the alloy.

Recently, numerous researchers have endeavoured to develop various alloys. Nonetheless, there is a paucity of literature examining the various manufacturing techniques and issues associated with HEAs. As industrial rapid development in HEAs manufacturing with diversity filed cannot categories processing routes exactly Consequently, This article's principal goals are to summarise, with appropriate schematics and flowcharts, every approach that can be employed for HEAs, starting with alloy preparation.

2. Overview of HEAs

Figure 1: Historical development of engineering materials [1]
The wide range of HEA is promising since 10000 BC. The Akshyb map depicting the historical development of engineering material. It has been shown Metals, polymer and elastomers, composites, and ceramics and glasses.

Figure 1 depicts the evolution of engineering materials throughout human history. A new alloying concept emerged at the beginning of the twenty-first century, when alloying technology had matured and materials were capable of more advanced applications. J. W. Yeh [3] coined the term In liquid or solid solution phases, HEAs have a larger mixing entropy than typical alloying systems. Defined structural properties, broad ranges of composition, and a better likelihood of identifying simpler microstructures have allowed HEAs to gain increasing interest among academics. The other two alloying process developments are HEAs, metallic rubbers, and bulk metallic glasses [6].

Professor jien-weiyeh of Taiwan and Professor Barin Canter of the United Kingdom have been researching microcomponent alloy systems with equal and nearly equivalent molar/atomic ratios since 1995 and 1981, respectively. In 2004, Yeh and his team of researchers developed the first High Entropy Alloys (HEAs), so these novel alloys were dubbed "High Entropy Alloy" (HEAs). Experimentation led to the development of the multi-element alloy known as HEA.

When compared to other MEAs and conventional alloys, the CoCrNi alloy with a single face centered cubic phase exhibits excellent cryogenic and middle temperature range characteristics. [4]. The CoCrCuFeNiSi alloy, like other FCC structured MEA alloys, has a lower tensile strength and cannot meet the mechanical property requirements of engineering applications, resulting in a greater focus on HEAs with this composition and a new manufacturing process. [5,7].

3. Classification of Processing Routes

In this context, “Figure 2 illustrates recent advances in the fabrication of HEAs in terms of their composition, microstructure, and mechanical properties, including ultimate tensile strength (UTS), tensile elongation (ε), yield strength (YS), hardness (H), compressive strength (CS), compressive yield strength (CYS), and the amount of compression (C)”.

As various non-equiaxial compositions and manufacturing procedures were examined, the development of a HEA got increasingly challenging. Alshataif et al. [14] addressed practically all of the processing approaches used for HEA synthesis thus far. Solid state processing liquid state processing, thin film deposition, and additive manufacturing were all covered. The bulk of these methods of production are commercially available.

3.1 Solid Mixing Based HEAs

The mixing of elements powder and their composition are mostly done by mechanical alloying. Different alloy phases applied during synthesis of solid powder particle. Powder metallurgy is forming process that allow for high compositional accuracy, which provide excellent control on microstructure. There are various solid state processing approaches shown in figure 3.
The particle production has four primary techniques including atomization, solid-state reduction, electrolysis, and chemical synthesis. Powder atomization employed for solidification using a gas or liquid stream. Figure 4 represented powder atomization process.

Typically atomization device consists of two stages furnace chamber and molten melt liquid. In which in furnace chamber metallic powders are melted in a vacuum atmosphere and drag melt liquid through a nozzle through cooling chamber. There are various factors affected the particular size while driving the atomization such as coolant, flow rate, velocity, temperature, angle of impingement [32]. The gas atomization procedure produced spherical powder particles ranging in size from 3 to 40 m, with an average particle size of 20 m. This HEAs gives better tensile strength, ductility and nanocrystalline structures properties.

### 3.1.1 Ball Milling Method
Ball milling is machine that is commonly used to grind all types of metals and ceramics. The traditional ball milling technique, which typically consists of a slow spinning drum and grinding balls composed of hardened stainless steel, titania, or ceramics. Synthesize the nanostructured materials and HEA powders cannot be use through this ball milling. Figure 5 depicted (a) grinding jar and (b) high energy ball milling schematics.

### 3.1.2 Cold Pressing Process
By crushing powder particles together into a single piece with the help of pressing tools at room temperature said to be cold pressing process. The powder materials are to be loaded into the die between two punches for pressing the powder particle. This is generally known as uniaxial compaction. It is easy and cost effective process mostly used in mass production. The resultant Yuhi et.al employed this techniques on AlNiCrFeMo0.2CoCu composition compressed at 310 Pa achieved 91 % density. This cold pressing technique altered the phase structure and HEAs properties.

### 3.1.3 Sintering Process

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**Figure 3: HEA solid-state processing approaches [1,8]**

**Figure 4: Powder atomization process [1,8]**

**Figure 5: (a) Jar for Grinding (b) High Energy Ball Milling Schematic [1]**
The sintering procedure is a key thermochemical operation in the blast furnace iron making system. This procedure is adopted for the improvement of chemical and mechanical properties. Basically sintering is categories into solid-phase sintering and liquid phase sintering. The most prevalent consolidation processes for HEA powders are vacuum hot pressing sintering and spark plasma sintering. Figure 6 depicted the different sintering stages such as, (a) bonding points at particles linked to each other (b) Necks produced bonding points (c) holes between grain boundaries shrink, and (d) boundaries expand between particles [1]. Because of alterations in the microstructural phases, LPS is not encouraged in HEAs [15]. The sintering process is categorized into three stages: heating, holding, and cooling. The various results presented in Xu et al. [16] promises the sintering under protective environmental conditions can be adopted for manufacturing HEAs.

3.1.4 Hot Pressing Process
The hot pressing method is a simultaneous combination of the cold pressing and sintering processes. The key advantage of this technique is that it improves the density of the product while decreasing porosities. Utilise a hot process to combine HEA granules into a bulk form. Principal drawbacks of this HP method include the formation of intermetallic phases and the extended consolidation time as indicated in figure 7.

3.1.5 Spark Plasma Sintering
Engineering unique microstructures is crucial for attaining the goal, which can be accomplished through the use of a developing processing method. One such novel approach for producing the desired microstructure in HEAs and HEA-based composites is spark plasma sintering [17]. Since this method conserves energy and requires fewer stages than traditional sintering methods, it is frequently employed to densify powders quickly. Spark Plasma Sintering is also known pressure-assisted pulse energizing method, is a cutting-edge sintering process. Powders are penetrated (750-1500 A) and compressed (25-150 MPa) using a graphite punch. SPS, with the right sintering parameters, can create nanostructured, grain-limited, extremely dense products.
Figure 8: Schematic of park plasma sintering method

Figure 8 illustrate the schematic of park plasma sintering method. The majority of experts agree that spark plasma sintering is a promising approach for delivering HEAs that improve microhardness, compressive/tensile strength, tribology, thermal characteristics, and corrosion resistance for low and extreme temperatures [18].

3.2 Liquid State Processing Methods

In liquid state processing HEAs can be manufactured with melting and casting procedure include vacuum arc melting and mechanical stirring. HEAs like CoCrFeNiSi is cost effective. Figure 9 shows a diagram of LSP techniques for HEA synthesis. The evaporation of low melting materials is the main disadvantage of the LSP process, which can be handled heated furnaces. Another disadvantage of the HEA casting method is the formation of diverse microstructures due to the sluggish solidification rate. Several researchers have used LSP techniques for efficiently building HEAs [20-23].

3.2.1 Arc melting Process

Most of the researcher studies promising that Arc Melting (AM) is the widely adopted techniques for producing quality “CoCrFeNiSi based HEAs with physical, chemical, and mechanical properties [24,25,26]. The key advantages of the AM technique are the low energy consumption, time savings, and decreased amount of porosity; thus, scientists and investigators have focused on manufacturing HEAs using this AM approach. Figure 10 demonstrates the AM method in which alloy ingots or alloy powders were placed on metallic crucibles and melted by tungsten electric arc striking under inert gas (argon atmosphere)after vacuuming the chamber to avoid oxidation”.

3.2.2 Process of Vacuum Induction Melting

It’s the process of applying heat to materials that conduct electricity by inducing a magnetic field within them using electromagnetic waves. Eddy current is generated when the magnetic field penetrates the electrical current through the conducting material and is subsequently utilized to generate heat. Figure 11 depicted vacuum induction melting process. Vacuum induction melting process has the benefit over the arc melting process, which controlled temperature, speed and homogeneity, but scale down due to unfurnishing the product [27].

3.2.3 Directive Solidification

The HEAs microstructure can be enhance with this directive solidification, solidification and casting in confirm direction, which are immersed in alumina (Al2O3) and begin to melt due to the heating system that surrounds them. Transformation of solid to liquid has been depicted in figure 12.
3.2.4 Infiltration Process

The HEAs can be manufactured with liquid state processing based infiltration procedure. This approach has the advantage of allowing for the quick production of complex patterns made of HEAs with low porosity percentages. Heat the powder element with lowest melting point, then apply a capillary force as shown in figure 13.

Figure 13: Infiltration process Schematic diagram

4. Thin Film HEA

Figure 14 depicts thin-film deposition processes that could be proposed for generating refractory-based HEA coatings over the substrate in order to improve component surface qualities. “Magnetron sputtering deposition, pulsed laser deposition, and plasma spraying deposition” [28] are advanced thin-film technologies that allow for the coating of a thin layer ranging from nano to micro.
Additive Manufacturing Process (AMP)

HEAs are produced utilizing the Solid state process and liquid state route, with Additive manufacturing as the most common techniques regardless; producing HEAs with a homogenous structure via AM, improved particle structure, and single phase SS by MA followed by SPS is extremely difficult. Furthermore, standard procedures cannot be used to produce HEAs on a large scale. However, there may be a demand for HEAs in specialist applications that require a less sophisticated manufacturing approach, a high level of process control to achieve a specific internal structure, and a short fabrication time. Furthermore, current research suggests that these are possible using laser-based AMP

Many techniques, including fusion deposition modelling, stereolithography, 3D charting, and selective laser sintering, are utilised to build the components layer by layer in AMP.

5. Conclusion

When the concept of HEAs was first conceived, arc melting was the most prevalent method for their production due to its simplicity. “In recent years, however, interest in AM processes (SLM, EBM, and DED) has increased due to their potential to offer greater shape and property freedom by altering process parameters. However, there are problems that must be addressed. With the incremental resolution of these issues, additive manufacturing could become a robust and versatile method for the production of application-specific HEAs with desirable properties for certain compositions. The preponderance of AM HEAs are examined in their as-cast (post-AM) state. Regarding the characterization of HEAs, the majority of studies have focused on the microstructure as determined by SEM, the tensile behaviour, and the hardness. Using a transmission electron microscope to characterise the structure at a reduced length scale would aid in understanding the evolution of the structure under various loads. There have been recent efforts to make HEAs using AM methods. Several AM HEAs displayed enhanced mechanical characteristics. However, various challenges must be rectified before AM can be used for mass manufacture of HEAs.

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