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A novel Fe40Mn40Cr10Co10/SiC medium-entropy nanocomposite reinforced by the nanoparticles-woven architectural structures

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abstract

A novel Fe40Mn40Cr10Co10/SiC nanocomposite was designed and fabricated by adding SiC nanoparticles through mechanical alloying and SPS treatment. Compared with pure Fe40Mn40Cr10Co10 mediumentropy alloy (MEA), addition of 10 vol.% SiC nanoparticles increased the ultimate compressive strength from 1.571 to 2.513 GPa as well as the hardness from 320 to 805 HV. Meanwhile, defects such as visible porosities were considerably lowered. The improved properties are mainly attributed to (a) the formation of nanoparticles-woven architectural structures consisting of externally-added SiC nanoparticles between neighboring grains and (b) the in-situly formed M23C6 (M ¼ Fe, Cr, Co) nanocarbides forgrain refinement and precipitation strengthening in Fe40Mn40Cr10Co10 MEA, respectively. Combined with experimental investigation, solidification pathway of different potential phases was verified using thermodynamic calculation.

1. Introduction

The entropy-based solid-solution alloys, in particular for medium- and high-entropy alloys, have stimulated much research attraction because of their superior properties [1e4]. These superior properties include high hardness, wear-resistance, strength, stability, and fracture-resistance [3e7]. It has induced considerable excitement in the community of materials science and engineering.

In many aspects, the entropy-based alloys shape an entirely new field of materials design [5,6,8]. Typical medium-entropy alloys (MEAs) and high-entropy alloys (HEAs) usually possess single phase rather than intermetallic compound [6,9]. For instance, CrCoNi [3], Fe40Mn40Cr10Co10 MEAs [4] and FeCoCrNiMn HEA [10] have a face-centered cubic (FCC) crystal structure while AlCoCrFeNi HEA [11] presents a body-centered cubic (BCC) crystal structure. However, in the case like FeCoNi(AlSi)x, the single FCC phase has relatively low strength because of the only solution strengthening effect [12]. Mechanical properties of the MEAs or HEAs with such single phase may not be sufficient in the industrial application where strength is the key requirement. Crystal structures of FeCoNi(AlSi)x can be tuned by adding larger Al and smaller Si atoms, which leads to the impediment dislocation movement [12]. Normally, a duplex (FCC þ BCC) FeCoNi(AlSi)x possesses a good combination of strength and plasticity. This is not only due to the increasing lattice distortion [13], but also resulting from a duplex crystal structures (i.e. FCC þ BCC) [12]. Compared with BCC crystal structure in Ti0.5CrFeCoNiAlxCu1x, FCC crystal structure presents higher atomic packing efficiency [13]. FCC crystal structure facilitates plasticity while BCC crystal structure usually retains stronger lattice resistance against plastic deformation [13]. Slip along the {110} planes in BCC occurs more difficultly than that along the {111} planes in FCC. For dislocation movement, {111} planes exhibit larger interplanar spacing and smaller lattice friction than {110} planes [14].

Moreover, different manufacturing approaches may also yield different levels of mechanical properties. The yield strength (YS) of FeCoCrNi MEA prepared by drop casting and powder metallurgy is only 165 and 395 MPa, respectively [15,16]. Through generating dual-phase (FCC and hexagonal closed-packed (HCP)), excellent strength-ductility trade-off was achieved in the Fe80-xMnxCo10Cr10 (at.%) HEA [4]. The hardness of AlTiVNb HEA with a BCC single phase increased from 7.4 GPa at the as-processed state to 10.4 GPa at an annealing temperature of 700 C [17]. In Refs. 4, 15e17, FeCoCrNi and Fe80-xMnxCo10Cr10 were categorized as HEAs.

Strictly, they should be termed as MEAs according to the original definition [5,8]. Moreover, the addition of Al element enhances the mechanical properties of AlCrFeCoNi HEA [11]. Al actually promotes formation of BCC phase. In addition, thermodynamic stability of HEAs does not always depend on the high configurational entropy [18]. These HEAs or MEAs with only single phase, in particular for FCC crystal structure, are not enough for engineering applications [19]. Thus, the increasing demand for better HEAs’ properties has given rise to requirement of new approaches. Currently, strengthening of entropy-based MEAs and HEAs relies on grain refinement [20,21], precipitation [15,22], particle dispersion [23,24], strain/work hardening [15,25], and etc. Reduction in the grain sizes of CoCrFeMnNi HEA from 155 to 4.5 mm caused a dramatic increase in the YS from 170 to 360 MPa, respectively [20]. Similarly, Ganji et al. [21] investigated the mechanical properties of AlCoCrCuFeNi HEA with average grain size values between 112 and 1550 nm. The fine-grained AlCoCrCuFeNi HEA presented very high YS [21]. In order to realize precipitation hardening, He et al. [15] added minor Ti and Al to the FeCoCrNi MEAs. Coherent L12Ni3(Ti,Al)-type nano precipitates uniformly dispersed in the FCC FeCoCrNi MEA grain matrix. Then, after experiencing thermo-mechanical treatment, it resulted in an excellent combination of YS (645 MPa) and ductility (39% elongation) at room temperature [15]. Similarly, addition of 0e30 at.% Mo facilitated to develop s and m intermetallic compounds from the CoCrFeNi MEA [22]. Liu et al. [22] determined the tensile strength (TS) and elongation of CoCrFeNiMo0.3 HEA. TS and elongation of CoCrFeNiMo0.3 HEA were 1.2 GPa and ~19%, respectively [22].

Moreover, no serious embrittlement occurred in such an alloy. Using arc melting, Guo et al. [23] prepared Mo0.5NbHf0.5ZrTiC0.1 and Mo0.5NbHf0.5ZrTiC0.3 alloys. The two HEAs consist of one disordered BCC solid solution and some in-situly formed MC carbides. The compressive yield strength (CYS) (or fracture strain) of Mo0.5NbHf0.5ZrTiC0.1 and Mo0.5NbHf0.5ZrTiC0.3 were 1183 MPa (or 38.39%) and 1201 MPa (or 32.62%), respectively [23]. Compared with the Mo0.5NbHf0.5ZrTi matrix alloy with its initial YS/fracture strain (1176 MPa/24.61%), the addition of carbon generated marginal effect on the tensile properties. Similar reinforcing MC precipitates were observed in the FeCrNiCoAlxCuy HEAs [24]. Besides in-situly formed precipitates, nanoscale particles can also be externally added as a different reinforcing method to achieve particle dispersion strengthening. Rogal et al. [26,27] uniformly distributed the nanoscale SiC and Al2O3 particles in the CoCrFeMnNi HEA, respectively, yielding composites with improved properties. Additions of 5 wt.% SiC and Al2O3 nanoparticles to CoCrFeMnNi HEAs delivered a CYS (or elongation) up to 1480 and 1600 MPa (or 31 and 6.5%), respectively [26,27]. Clearly, the introduction of precipitates or particles into the matrix is effective in improving the strength and ductility of HEAs and MEAs.

In the present work, we report to design and manufacture a novel Fe40Mn40Co10Cr10-SiC nanocomposite containing a 3D nanoparticles-woven architectural structure. The compressive strength-ductility of Fe40Mn40Co10Cr10-SiC nanocomposite was improved largely, compared with its pure Fe80-xMnxCo10Cr10 counterpart [4]. Meanwhile, defects such as porosities were significantly decreased. Such a 3D nanoparticles-woven architectural structure can be constructed through: (a) generating nanoprecipitates in the single phase MEA matrix using powder metallurgy for the accurate control, (b) adding SiC nanoparticles into the Fe40Mn40Co10Cr10 MEA to form unique microstructures after sintering. A higher compressive strength-ductility in Fe40Mn40Co10Cr10-SiC was obtained than some other representative reported HEAs [26e30], MEAs [30,31] and bulk metallic glasses (BMGs) [32,33]. Then, the discussion section focuses on the microstructural characterization and mechanical properties in line with different strengthening mechanisms.

2. Experimental

2.1. Materials process

The average sizes of pre-alloyed Fe40Mn40Cr10Co10 MEA powder are 10e15 mm (supplied by Beijing Guanjinli New Material Co., Ltd.). Chemical compositions of Fe40Mn40Cr10Co10 MEA powder were similar to those reported elsewhere [4]. The SiC nanoparticles has a D50 value of 250 nm and a purity of 99.7%, which was made by Shandong Qingzhou Micropowder Co., Ltd. Its particle sizes are between 100 and 400 nm. Two groups of starting powders were prepared through mixing the Fe40Mn40Cr10Co10 MEA powder with 0 and 10 vol.% SiC nanoparticles, respectively. Then, these two groups of powders were mechanically alloyed using ball milling, as shown in Fig. 1. Ball milling was performed at 400 rpm for 3-hr wet milling under ambient condition, followed by another 3-hr dry milling before spark plasma sintering (SPS) treatment. After mechanical alloying, the milled two powders were then compressed in a graphite die mould (~40 mm in inner diameter) to experience SPS.

The cylindrical SPS samples have a diameter of ~40 mm and a length of 7 mm, respectively. SPS was operated at a pressure/temperature of 40 MPa/1100 C for a holding time of 15 min. The assintered Fe40Mn40Cr10Co10-SiC composite was machined into a cylindrical shape with 5 mm in diameter and 7 mm in thickness for hardness and compressive testing. Then, the Vickers hardness was measured by a microhardness instrument under a load of 5 kgf. Compressive properties of as-sintered Fe40Mn40Cr10Co10-SiC composites were tested using an Instron® 3369 universal testing machine at a cross-head speed of 1 mm min1. Each data reported was based on the average value of 5 tested samples.

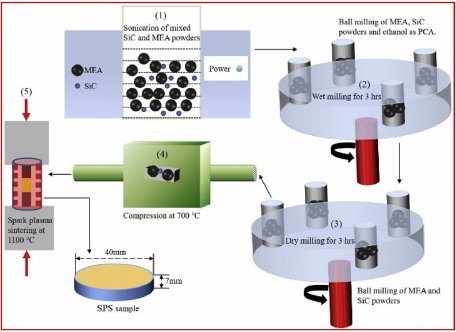


Fig. 1. Schematic diagram of essential experimental procedures, showing how to fabricate the Fe40Mn40Cr10Co10-10 vol.% SiC nanocomposites.

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2.2. Microstructural characterization

Phase constituents in the samples were identified using X-ray diffraction (XRD). XRD identification was operated at 40 kV in a Rigaku X-2000 diffractometer with Cu Ka radiation (lka ¼ 1.54 Å). The microstructures of as-sintered samples were examined using a FEI nano230 field emission scanning election microscope (FE-SEM) equipped with an energy dispersive X-ray spectrometer (EDS). To measure average grain sizes of matrix grains and to identify distribution of different phases (i.e. Fe40Mn40Cr10Co10 MEA, SiC and carbide), characterization of microstructures was conducted at microscale using EBSD in a different SEM (Hitachi S-3400 N). EBSD was equipped with an Oxford Instrument Aztec HKL® imaging system. Before EBSD examination, the EBSD samples were mechanically polished and baked for 6 hrs in a vacuum oven at 65 C, followed by surface cleaning using plasma. EBSD observation was performed at 20 kV. To distinguish the externally-added SiC nanoparticles and the in-situly formed M23C6 nanoprecipitates, microstructural characterization was further conducted using transmission electron microscopy (TEM; Tecnai G2 F20). Meanwhile, the corresponding selected area electron diffraction (SAD) patterns were accordingly studied. TEM samples were prepared based on the mechanical polishing and the precision ion polishing system (PIPS) at a voltage/an incident angle of 5 kV/1 ~ 3.

3. Results

3.1. Microstructural design and characterization

Fig. 2 shows the microstructures of Fe40Mn40Cr10Co10 alloys without and with 10 vol.% SiC nanoparticles. It can be seen that the significant grain refinement occurred in the as-sintered MEAs after adding SiC nanoparticles (Fig. 2(a) and (b)). The measurement showed that the average grain size of the pure MEA was 4.2 mm and that was 1.3 mm in the MEA with SiC nanoparticles (Fig. 2(c)). Meanwhile, severe porosities were observed in the microstructure of pure Fe40Mn40Cr10Co10 alloy (black areas in Fig. 2(a)), although it was hard to find porosities in the alloy with SiC nanoparticles (Fig. 2(b)). To identify phase constituents, XRD examination was carried out. XRD spectra of the Fe40Mn40Cr10Co10 MEAs with 0 and 10 vol.% SiC are indicated in Fig. 2(d). It is clear that the pure Fe40Mn40Cr10Co10 MEAs only exhibit the peaks of FCC phase, implying that there are no other phases except Fe40Mn40Cr10Co10. However, extra peaks (i.e. SiC and M23C6) were also identified in the Fe40Mn40Cr10Co10-10 vol.% SiC nanocomposites. It is surmised that SiC and M23C6 originated from external addition and in-situ formation, respectively. In terms of their microstructural formation, more details will be elucidated later. Tremendous SiC nanoparticles mainly distributed between neighboring grains, as shown by the 2D view of microstructures in Fig. 3. SiC nanoparticles agglomerated between their surrounding MEA grains. Due to EBSD resolution, one may felt that: the size of SiC nanoparticles is not significantly smaller than the MEA matrix grains. EBSD phase mapping in Fig. 3 only reflects the overall distribution of SiC particles inside MEA. Detailed microstructures from TEM examination will be elucidated in section 3.3. Then, SiC nanoparticles led to a strong pinning effect to restrict further grain growth during sintering, resulting in significant grain refinement. Therefore, the addition of SiC nanoparticles in the Fe40Mn40Cr10Co10 alloy not only caused grain refinement and reduced the defects in the materials, but also generated new phases in the materials. Such pinning effect has already been reported in steel [34] and magnesium alloys [35]. Ni promoted to develop M23C6 carbides in the medium C-Cr steel [34]. Numerous M23C6 carbides, distributing along the grain boundaries, lead to an effective grain refinement below 1050 C [34]. In Mg-Mn alloys, fine Mn particles precipitated at 300 C. These Mn particles are very resistant to grain coarsening (termed as particle pinning [35]).

3.2. Mechanical deformation behaviour

The compressive deformation behaviour of Fe40Mn40Cr10Co10 MEAs with and without SiC addition was investigated, and the stress-strain curves are shown in Fig. 4. It can be seen that the Fe40Mn40Cr10Co10 alloys exhibited very good ductility with substantial strain hardening. Addition of SiC into the MEA alloy enhanced strength and ductility, in particular for the strain hardening. The ultimate compressive strength (UCS) increased from 1.571 to 2.513 GPa, and the fracture strain increased from 28.5 to 37.2% in the alloys after adding 10 vol.% SiC nanoparticles. Moreover, the associated hardness was improved from 320 (0 vol.% SiC) to 805 HV (10 vol.% SiC). To compare improvement in the properties upon, the stress-strain curves for Fe40Mn40Cr10Co10-10 vol%SiC nanocomposite were interpreted combined with other work reported in different Refs. [26e33]. The compressive properties of Fe40Mn40Cr10Co10-10 vol.% SiC are better than some typical HEAs (i.e. CoCrFeMnNi [28], NbCrMo0.5Ta0.5TiZr4.5 [29], and V20Nb20rMo20Ta20W20 [30]), MEAs (i.e. CoCrFeNi [31], and Nb25Mo25Ta25W25 [30]), and the bulk metallic glasses (BMGs) (i.e. Al86Ni6Y4.5Co2La1.5 [32], and Zr55Cu30Ni5Al10 [33]). They are also comparable with the recently-developed HEA composites (i.e. CoCrFeMnNi-5wt.% Al2O3 [26], an CoCrFeMnNi-5wt.% SiC [27]).

3.3. 3D nanoparticles-woven architectural structure

In order to identify the distribution of new phases, the bright field (BF) TEM images of Fe40Mn40Cr10Co10-10 vol.% SiC are shown in Fig. 5. Two types of nanoparticles were found in the microstructure (Fig. 5 (a)). Further, the selected area diffraction patterns (SADPs) analysis confirmed that these two type of particles are SiC and M23C6 phases. Clearly, many SiC nanoparticles were exclusively found at the grain boundaries (see Fig. 5(b)). Sizes of SiC nanoparticles were between 150 and 400 nm. Similar phenomenon has already been reported in steel [34] and magnesium alloys [35]. The existence of SiC nanoparticles at grain boundaries would generate a strong pinning to prevent grain growth during sintering and result in significant grain refinement. M23C6 phase was mainly found inside the FCC matrix phase and rarely existed at the grain boundaries (Fig. 5(c)). During SPS process at 1100 C, C atoms reacted with other elements including Fe, Cr and Co to form M23C6 compounds. SEM and TEM observations confirmed that the sizes of M23C6 particles are at nanoscale, having an average particle size of 200 nm. The high resolution TEM image in Fig. 5(d) indicates one nanoparticle (SiC)-MEA-nanoprecipitate (M23C6) unit of the 3D architectural structure. Fig. 6 indicates the local interface between the MEA matrix and the M23C6 nanoprecipitate within the grain, which confirmed the clear and well-bonded interface between the reinforcement phase and the matrix. Based on the microstructural characterization, a representative 3D microstructure of the assintered Fe40Mn40Cr10Co10-SiC nanocomposites is constructed, as shown in Fig. 7. Fig. 7 demonstrates the principal constituents of assintered Fe40Mn40Cr10Co10-10 vol.% SiC nanocomposite. In terms of present experimental results, some local neighboring MEA grain boundaries may not be fully filled with SiC nanoparticles. However, Fig. 3 shows that most of the MEA grain boundaries were separated by SiC nanoparticles. Thus, the proposed model in Fig. 7 enables to rationalize the structural constituents of as-sintered Fe40Mn40Cr10Co10-10 vol.% SiC nanocomposite. Actually, the distribution of MEA and SiC nanoparticles can be modified through optimizing experimental process. Using an optimal process, the structural constituents will be exactly consistent with the model in Fig. 7.

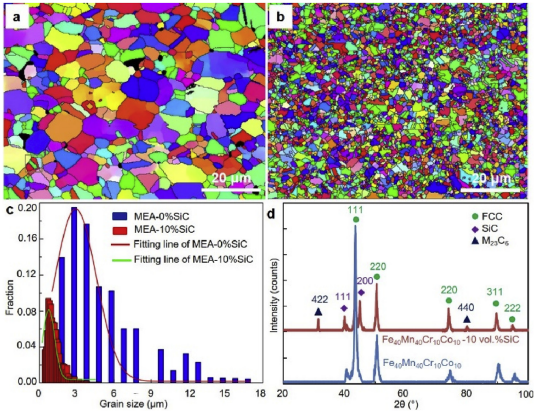


Fig. 2. EBSD orientation mapping images showing grain refinement in the microstructure of (a) Fe40Mn40Cr10Co10 MEA and (b) Fe40Mn40Cr10Co10-10 vol%SiC composite, (c) the distribution of grain sizes, and (d) XRD patterns of Fe40Mn40Cr10Co10 alloy and Fe40Mn40Cr40Co40-10 vol%SiC composite. Black areas in (a) indicate some large visible porosities.

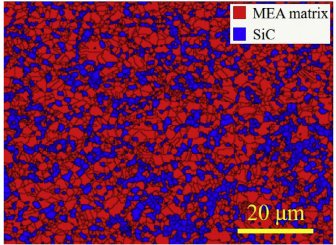


Fig. 3. Two-dimensional (2D) electron backscattered diffraction (EBSD) phase mapping image, showing distribution of SiC nanoparticles in the Fe40Mn40Cr10Co10 MEA matrix.

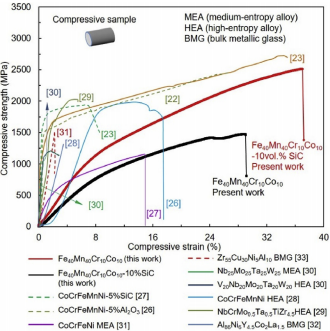


Fig. 4. Compressive stress-strain curves of the pure Fe40Mn40Cr10Co10 MEA alloy and Fe40Mn40Cr10Co10-10 vol.% SiC composite in association with the data collected from literature. HEA, MEA and BMG on this figure refer to the high-entropy alloy, the medium-entropy alloy and the bulk metallic glasses, respectively.

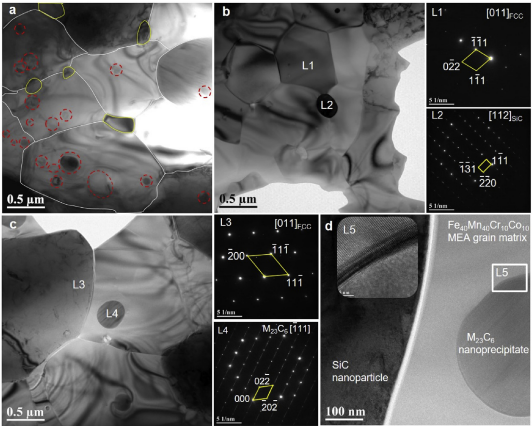


Fig. 5. Bright field TEM micrographs showing (a) the typical microstructure of Fe40Mn40Cr40Co40 -10 vol.% SiC composite, (b) the SiC nanoparticle at the grain boundary and their corresponding SADPs (L1 and L2), (c) the M23C6 nanoprecipitate in the FCC matrix and their corresponding SADPs (L3 and L4), and (d) HRTEM micrographs showing one nanoparticle (SiC)-MEA-nanoprecipitate (M23C6) unit of the 3D architectural structure. Grain boundaries, SiC nanoparticles, and M23C6 nanoprecipitates in (a) are highlighted using the solid white lines, the closed yellow circle, and the dashed red circles, respectively. The inset L5 in (d) indicates the local interface between the M23C6 and the FCC matrix. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

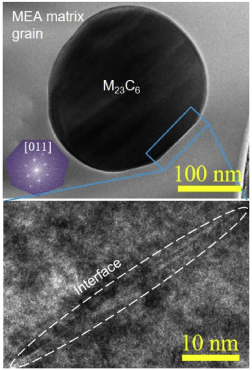


Fig. 6. Bright field TEM micrographs showing a local interface between the MEA matrix grain and the M23C6 nanoprecipitates. The dashed area below show the highresolution TEM image of local interface

4. Discussion

Thermodynamic calculation of equilibrium phase evolution during sintering were performed using CALPHAD method through a JMatPro® software to analyze solidification pathway. CALPHAD calculation showed that the potential phases (M23C6 and M7C3) can develop in the Fe40Mn40Cr10Co10-SiC composite between 750 and 1130 C (see Fig. 8(a) and (b)). But the M7C3 phase was not detected by XRD and TEM examination, which is attributed to the complete decomposition of M7C3 between 750 and 890 C. Similar experimental results have already been reported in the C-doped Fe40.4 Ni11.3Mn34.8Al7.5Cr6 HEAs [29] and Si-doped 20Cr32Ni1Nb alloy [30]. Daviau et al.’s work showed that SiC decomposes at ~ 1726 C under a pressure of 60 GPa or at ~ 2526 C under ambient pressure [36]. In the present experiment, SPS process was carried out at 1100 C under a pressure of 40 MPa for 15 min. Both temperature and pressure are much smaller than those reported by Daviau et al. [36]. Unfortunately, SPS process could involve carbon, which resulted from carbon contamination. Carbon contamination from the SPS graphite die mould cannot be fully avoided. Thus, the formation of carbides in our work may be attributed to the carbon contamination into the MEA during SPS. However, another possible mechanism of carbide formation was also proposed by Rogal et al. [22]. Rogal et al. believed that the presence of high carbon carbides was caused by the partial decomposition of SiC. It could facilitate formation of the Cr-enriched carbides [22], which is due to a very high affinity of Cr to C [37]. Thus, it raises an open question regarding the origin of carbide formation. The microstructural characterization above have clearly demonstrated that the synthesized Fe40Mn40Cr10Co10-10 vol.% SiC composite has following features: (a) the MEA matrix grains with small grain sizes; (b) insituly formed nanoprecipitates within the FCC matrix; (c) uniform distribution of secondary phase (SiC nanoparticles) at the grain boundaries; (d) clear and well-bonded interface between the reinforcement and the matrix grains without any undesirable reactions in between, and (e) lack of porosities in the fabricated composite materials. Several strengthening mechanisms rationalize the improvement of mechanical properties of the nanocomposite studied. The primary strengthening mechanisms Fig. 5. Bright field TEM micrographs showing (a) the typical microstructure of Fe40Mn40Cr40Co40 -10 vol.% SiC composite, (b) the SiC nanoparticle at the grain boundary and their corresponding SADPs (L1 and L2), (c) the M23C6 nanoprecipitate in the FCC matrix and their corresponding SADPs (L3 and L4), and (d) HRTEM micrographs showing one nanoparticle (SiC)-MEA-nanoprecipitate (M23C6) unit of the 3D architectural structure. Grain boundaries, SiC nanoparticles, and M23C6 nanoprecipitates in (a) are highlighted using the solid white lines, the closed yellow circle, and the dashed red circles, respectively. The inset L5 in (d) indicates the local interface between the M23C6 and the FCC matrix. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) include load transfer effect, grain refinement, Orowan strengthening, mismatch between the coefficient of thermal expansion and the elastic modulus, and the increased dislocation density [26,27,38]. Grain refinement is a well-known approach to improve the strength. The general role of strengthening follows the classic Hall-Patch relationship. Because the stress at the head of a pile-up increases linearly with the number of dislocations, the local stress concentrations at grain boundaries in the refined microstructure will be reduced and thus the crack nuclei will be less. Also because the stress at a crack tip is closely associated with the grain size. Grain refinement increases the fracture stress. Therefore, the fracture is inhibited when grain size is reduced, resulting in the improvement of strength. The particles located at grain boundaries can generate a strong drag force between two adjacent grains [33]. Grain boundary movement may be hampered during sintering. Therefore, the movement is stagnated when the drag force is balanced by the migration resistance of grain boundary. At this balance, the sizes of grain matrix and the external SiC nanoparticles satisfy Eq. (1) [33].

d ¼ 4r=3f (1)

where d, r, and f represent the grain size, the radius of external particles, and the volume fraction of external particles, respectively. Obviously, d values decrease when increasing f and decreasing r. SiC nanoparticles have a high melting temperature of 2700 C [39]. M7C3 nucleation starts from 1130 C; however, it will decompose between 750 and 890 C, as shown in Fig. 8(b). M23C6 (M ¼ Fe, Cr, Co) nucleates from 890 C, but presenting a stable weight fraction (20 wt.%) 750 C. According to the CALPHAD simulation in Fig. 8, M6C may develop below 710 C. Its maximum weight fraction is only 5 wt.%. In addition, other potential phases (i.e. ferrite, Laves phase, and M2(C,N)) can be ignored because they nucleate below 400 C. Cooling rate in the present work is relatively fast below 400 C. Thus, a hierarchical degree of thermal stability below 400 C after sintering was obtained, i.e. M7C3 M6C M23C6 SiC. During deformation, SiC nanoparticles act as a hard phase at grain boundaries, which impedes the movement of grain boundaries. Compared with large-sized particles, numerous SiC nanoparticles at the grain boundaries retard the grain boundary sliding for property improvement. M23C6 nanoprecipitates are uniformly located in the MEA FCC matrix, which contribute to the precipitation hardening either through the dislocation by-pass mechanism (Orowan-type) [40] and/or the particle shearing mechanism [41].

Slip trace within a single grain can move forward when dislocations bypass M23C6 nanoprecipitates. During SPS process, some C atoms in SiC dissolved into the FCC matrix of Fe40Mn40Cr10Co10 MEA. This increases the lattice distortion degree of the FCC matrix and induces strengthening in the designed composite material. Meanwhile, the large stress concentration usually occurs at the interfaces between the FCC matrix and the strengthening particles. The nanoparticles may block the dislocation movement [26]. A higher dislocation density results in a higher yield strength. Although the experimental evidence for multiple strengthening components in Fig. 7 have been set in the nanocomposite obtained by adding SiC into the Fe40Mn40Cr10Co10 MEAs, the quantitative relationship for individual strengthening mechanism remains a challenge due to the lack of accurate data for calculation. Moreover, SiC nanoparticles mainly located on the grain boundaries, which will surely affect the tensile deformation and fracture mechanisms. The present work mainly focused on the compressive response, fracture strength and hardness due to its specific application in cutting tools. Tensile behaviour and the associated fracture toughness will be investigated in the near future.

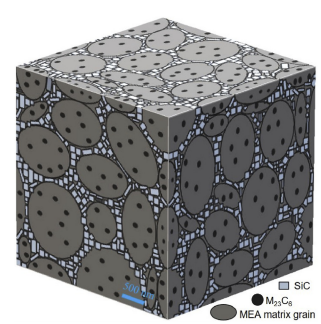


Fig. 7. Diagram showing the three-dimensional (3D) nanoparticles-woven architectural structure in the designed Fe40Mn40Cr10Co10-10 vol.% SiC nanocomposite, showing different major strengthening components.

contamination, resulting from the SPS graphite die mould. Formation of carbide phases (i.e. M7C3, M23C6 and M6C) in the Fe40Mn40Cr10Co10 MEA matrix may be attributed to the carbon contamination from graphite mould into MEA during SPS process. Additionally, the partial decomposition of SiC nanoparticles during SPS could also facilitate the formation of Cr-enriched carbides, resulting from a high affinity of Cr to C. Meanwhile, the neighboring Fe40Mn40Cr10Co10 MEA matrix grains were padded with some externally-added SiC nanoparticles. M7C3, M23C6 and M6C nucleated at 1130, 890 and 710 C, respectively. M7C3 is decomposed between 750 and 890 C. The maximum weight fraction of M6C is only 5 wt.%. Other potential phases, including ferrite, Laves phase and M2(C,N), are not observed due to fast cooling after 400 C. The principal microstructural constituents were characterized by a nanoparticles-woven architectural model, which promotes to maximize the reinforcement of particles in the nanocomposites.

Fracture strength and hardness of the nanocomposite have been improved by 59.96% (from 1.571 to 2.513 GPa) and 151.56% (from 320 to 805 HV), respectively, in comparison with its pure Fe40Mn40Cr10Co10 MEA counterpart. Moreover, the compressive properties of Fe40Mn40Cr10Co10-10 vol.% SiC are even better than some representative HEAs, MEAs, and BMGs. Due to the very high hardness and fracture strength, this sintered Fe40Mn40Cr10Co10- 10 vol.% SiC nanocomposite may have prospective application in wear-resistant parts and/or cutting tools. Moreover, this work provides new insights for developing the advanced powder-based materials with pursued properties for other applications, such as additively-manufactured industry.

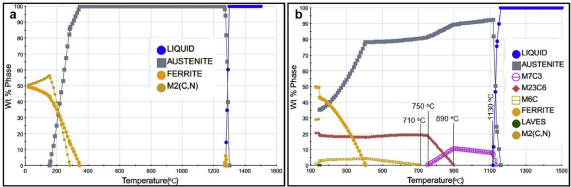


Fig. 8. Calculated formation of equilibrium phases in (a) Fe40Mn40Cr10Co10 and (b) Fe40Mn40Cr10Co10-10 vol.% SiC using CALPHAD method, revealing the possible solidification pathway during SPS treatment.

5. Conclusions

The Fe40Mn40Cr10Co10-10 vol.% SiC nanocomposite, with grain refinement and reduced porosity, has been successfully synthesized by a combination of mechanical alloying and spark plasma sintering (SPS) methods. SPS process could involve carbon Fig. 6. Bright field TEM micrographs showing a local interface between the MEA matrix grain and the M23C6 nanoprecipitates. The dashed area below show the highresolution TEM image of local interface.

References

[1] E.W. Huang, D. Yu, J.W. Yeh, L. Chi, K. An, A study of lattice elasticity from low entropy metals to medium and high entropy alloys, Scripta Mater. 101 (2015) 32-35.

[2] A. Gali, E.P. George, Tensile properties of high- and medium-entropy alloys, Intermetallics 39 (2013) 74-78.

[3] B. Gludovatz, A. Hohenwarter, K.V.S. Thurston, H. Bei, Z. Wu, E.P. George, R.O. Ritchie, Exceptional damage-tolerance of a medium-entropy alloy CrCoNi at cryogenic temperatures, Nat. Commun. 7 (2016) 10602.

[4] Z. Li, K.G. Pradeep, Y. Deng, D. Raabe, C.C. Tasan, Metastable high-entropy dual-phase alloys overcome the strength-ductility trade-off, Nature 534 (2016) 227-230.

[5] D.B. Miracle, O.N. Senkov, A critical review of high entropy alloys and related concepts, Acta Mater. 122 (2017) 448-511.

[6] Y. Zhang, T.T. Zuo, Z. Tang, M.C. Gao, K.A. Dahmen, P.K. Liaw, Z.P. Lu, Microstructures and properties of high-entropy alloys, Prog. Mater. Sci. 61 (2014) 1-93.

[7] B. Gludovatz, A. Hohenwarter, D. Catoor, E.H. Chang, E.P. George, R.O. Ritchie, A fracture-resistant high-entropy alloy for cryogenic applications, Science 345 (6201) (2014) 1153-1158.

[8] J.W. Yeh, Recent progress in high-entropy alloys, Ann. Chim. Sci. Mat. 31 (6) (2006) 633-648.

[9] J.W. Yeh, S.K. Chen, S.J. Lin, J.Y. Gan, T.S. Chin, T.T. Shun, C.H. Tsau, S.Y. Chang, Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes, Adv. Eng. Mater. 6 (5) (2004) 299-303.

[10] C. Zhu, Z.P. Lu, T.G. Nieh, Incipient plasticity and dislocation nucleation of FeCoCrNiMn high-entropy alloy, Acta Mater. 61 (2013) 2993e3001.

[11] Y.P. Wang, B.S. Li, M.X. Ren, C. Yang, H.Z. Fu, Microstructure and compressive properties of AlCrFeCoNi high entropy alloy, Mater. Sci. Eng. A 491 (2008) 154-158.

[12] Y. Zhang, T.T. Zuo, P.K. Liaw, Y.Q. Cheng, High-entropy alloys with high saturation magnetization and electrical resistivity, Sci. Rep. 3 (2013) 1455.

[13] F.J. Wang, Y. Zhang, G.L. Chen, Atomic packing efficiency and phase transition in a high entropy alloy, J. Alloys Compd. 478 (2009) 321-324.

[14] G.X. Hu, X. Cai, Y.H. Rong, Fundamentals of Materials Science, Shanghai Jiao Tong University Press, Shanghai, 2006.

[15] J.Y. He, H. Wang, H.L. Huang, X.D. Xu, M.W. Chen, Y. Wu, X.J. Liu, T.G. Nieh, K. An, A precipitation-hardened high-entropy alloy with outstanding tensile properties, Acta Mater. 102 (2016) 187-196.

[16] B. Liu, J. Wang, Y. Liu, S. Chen, C.T. Liu, Microstructure and mechanical properties of equimolar FeCoCrNi high entropy alloy prepared via powder extrusion, Intermetallics 75 (2016) 25-30.

[17] B. Schuh, B. Volker, V. Maier-Kiener, J. Todt, J. Li, A. Hohenwarter, Phase decomposition of a single-phase AlTiVNb high-entropy alloy after severe plastic deformation and annealing, Adv. Eng. Mater. 19 (4) (2017), 201600674.

[18] F. Otto, Y. Yang, H. Bei, E.P. George, Relative effects of enthalpy and entropy on the phase stability of equiatomic high-entropy alloys, Acta Mater. 61 (7) (2013) 2628-2638.

[19] C. Ng, S. Guo, J. Luan, S. Shi, C.T. Liu, Entropy-driven phase stability and slow diffusion kinetics in an Al0.5CoCrCuFeNi high entropy alloy, Intermetallics 31 (2012) 165-172.

[20] F. Otto, A. Dlouhý, Ch Somsen, H. Bei, G. Eggeler, E.P. George, The influences of temperature and microstructure on the tensile properties of a CoCrFeMnNi high-entropy alloy, Acta Mater. 61 (15) (2013) 5743-5755.

[21] R. SreeGanji, P. Sai Karthik, K. Bhanu Sankara Rao, K.V. Rajulapati, Strengthening mechanisms in equiatomic ultrafine grained AlCoCrCuFeNi highentropy alloy studied by micro- and nanoindentation methods, Acta Mater. 125 (2017) 58e68.

[22] W.H. Liu, Z.P. Lu, J.Y. He, J.H. Luan, Z.J. Wang, B. Liu, Y. Liu, M.W. Chen, C.T. Liu, Ductile CoCrFeNiMox, high entropy alloys strengthened by hard intermetallic phases, Acta Mater. 116 (2016) 332e342.

[23] N.N. Guo, L. Wang, L.S. Luo, X.Z. Li, R.R. Chen, Y.Q. Su, J.J. Guo, H.Z. Fu, Microstructure and mechanical properties of in-situ MC-carbide particulatesreinforced refractory high-entropy Mo0.5NbHf0.5ZrTi matrix alloy composite, Intermetallics 69 (2016) 74-77.

[24] Q.C. Fan, B.S. Li, Y. Zhang, The microstructure and properties of (FeCrNiCo) AlxCuy, high-entropy alloys and their TiC-reinforced composites, Mater. Sci. Eng. A 598 (2014) 244-250.

[25] F. Kabirian, A.S. Khan, T. Gnaupel-Herlod, Plastic deformation behavior of a thermo-mechanically processed AZ31 magnesium alloy under a wide range of temperature and strain rate, J. Alloys Compd. 673 (2016) 327-335.

[26] Ł. Rogal, D. Kalita, A. Tarasek, P. Bobrowski, F. Czerwinski, Effect of SiC nanoparticles on microstructure and mechanical properties of the CoCrFeMnNi high entropy alloy, J. Alloys Compd. 708 (2017) 344-352.

[27] Ł. Rogal, D. Kalita, L. Litynska-Dobrzynska, CoCrFeMnNi high entropy alloy matrix nanocomposite with addition of Al2O3, Intermetallics 86 (2017) 104-109.

[28] B. Wang, A. Fu, X. Huang, B. Liu, Y. Liu, Z. Li, X. Zan, Mechanical properties and microstructure of the CoCrFeMnNi high entropy alloy under high strain rate compression, J. Mater. Eng. Perform. 25 (2016) 2985-2992.

[29] O.N. Senkov, C.F. Woodward, Microstructure and properties of a refractory NbCrMo0.5Ta0.5TiZr alloy, Mater. Sci. Eng. A 529 (2011) 311-320.

[30] O.N. Senkov, G.B. Wilks, J.M. Scott, D.B. Miracle, Mechanical properties of Nb25Mo25Ta25W25 and V20Nb20Mo20Ta20W20 refractory high entropy alloys, Intermetallics 19 (2011) 698-706.

[31] J. Wang, T. Guo, J. Li, W. Jia, H. Kou, Microstructure and mechanical properties of non-equilibrium solidified CoCrFeNi high entropy alloy, Mater. Chem. Phys. 210 (2018) 192-196.

[32] X. Li, Additive manufacturing of advanced multi-component alloys: bulk metallic glasses and high entropy alloys, Adv. Eng. Mater. (2017), 1700874.

[33] D. Ouyang, N. Li, W. Xing, J. Zhang, L. Liu, 3D printing of crack-free high strength Zr-based bulk metallic glass composite by selective laser melting, Intermetallics 90 (2017) 128-134.

[34] Z. Dong, B. Jiang, Z. Mei, C. Zhang, L. Zhou, Y. Liu, Effect of carbide distribution on the grain refinement in the steel for large-size bearing ring, Steel Res. Int. 87 (6) (2016) 745-751.

[35] J.D. Robson, D.T. Henry, B. Davis, Particle effects on recrystallization in magnesium-manganese alloys: particle pinning, Mater. Sci. Eng. A 528 (12) (2011) 4239-4247.

[36] K. Daviau, K.K.M. Lee, Decomposition of silicon carbide at high pressures and temperatures, Phys. Rev. B 96 (2017), 174102.

[37] J.C. Hamaker, Tool Steels, ASM, Materials Park, OH, 1962.

[38] Z. Wang, I. Baker, W. Guo, J.D. Poplawsky, The effect of carbon on the microstructures, mechanical properties, and deformation mechanisms of thermo-mechanically treated Fe40.4 Ni11.3Mn34.8Al7.5Cr6, high entropy alloys, Acta Mater. 126 (2017) 346-360.

[39] N.D. Stepanov, N.Yu Yurchenko, M.A. Tikhonovsky, G.A. Salishchev, Effect of carbon content and annealing on structure and hardness of the CoCrFeNiMnbased high entropy alloys, J. Alloys Compd. 687 (2016) 59-71.

[40] J. Yan, Y. Gu, Y. Dang, X. Zhan, J. Lu, Y. Yuan, Z. Yang, H. Yin, Effect of carbon on the microstructure evolution and mechanical properties of low Si-containing centrifugal casting 20Cr32Ni1Nb alloy, Mater. Chem. Phys. 175 (2016) 107-117.

[41] N.A. Haroun, D.W. Budworth, Modifications to the Zener formula for limitation of grain size, J. Mater. Sci. 3 (1968) 326-328.