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Nano-twin-induced exceptionally superior cryogenic mechanical properties of a Ni-based GH3536 (Hastelloy X) superalloy

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ABSTRACT

The GH3536 (Hastelloy X) superalloy is one of the most widely used Ni-based sheet alloys for gas turbine hot parts. To investigate its relationship among the processing, microstructure, and mechanical properties, GH3536 alloy was fabricated from pure constituent elements by arc melting and drop casting. The drop-cast ingots were homogenized, cold rolled, and recrystallized to obtain single-phase microstructure with average grain size of ~12 µm. Tensile tests were then performed at a wide temperature range between 77 K and 1,073 K. Surprisingly, although this alloy was developed for high temperature use, it has extraordinary cryogenic mechanical properties. Moreover, the yield strength, ultimate tensile strength, and elongation to fracture increased dramatically with decreasing temperature, exactly the same behavior as that of recently developed face-centered cubic medium/high-entropy alloys (M/HEAs). Transmission electron microscopy was used to study the deformation mechanisms of GH3536 alloy at 77 K and room temperature. Deformation-induced nano-twins were observed after interrupted/fracture tests at 77 K, but rarely in specimens tested at room temperature, where plasticity occurred exclusively by dislocation gliding. The similarity between this 70-year-old GH3536 (Hastelloy X) alloy and M/HEAs, which is recently considered as the revolution in alloy design, will be discussed from the viewpoint of the microstructure, entropy calculation, mechanical properties, and deformation mechanism.

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1. Introduction

The concept of medium/high-entropy alloys (M/HEAs) or multiprincipal element alloy has been considered to revolutionize the traditional alloy design principles using multiprincipal components with equal or near equal atomic ratios of the constituent elements [1,2]. This alloy design concept opens up an unusual compositional region located in the center of phase diagrams, different from the traditional alloy located in the corner of phase diagrams where one element dominates. Many promising properties have been reported in M/HEAs, such as high hardness, outstanding wear resistance, excellent high-temperature strength, good thermal stability, and unique physical properties [3–6]. These properties are presumably related to the four so-called 'core effects': high entropy, sluggish diffusion, severe lattice distortion, and cocktail effects [5]. The most attractive finding in the single/dual-phase M/HEAs is their exceptional mechanical properties, especially in cryogenic temperature [7–9]. Briefly, the yield strength (YS) of the face-centered cubic (FCC) single-phase M/HEAs shows a strong temperature dependence. Moreover, contrary to many traditional materials in which strength and ductility show a trade-off, a remarkable increase in strength accompanied by a simultaneous increase in ductility with decreasing deformation temperature from 293 K to 77 K was observed in M/HEAs. Those alloys also hold remarkable fracture toughness at 77 K, as high as 200 MPa m^{1/2} [7], which is comparable to the very best cryogenic steels (e.g., austenitic stainless steels and high-Ni steels).

From the viewpoint of the physical metallurgy, the exceptional mechanical properties must correlate with the microstructurerelated deformation mechanism. There are emerging studies which experimentally and theoretically explore the origin of the strength/ductility in M/HEAs. For example, the outstanding mechanical properties in cryogenic temperature accompany with the observation of deformation nano-twin for the CrCoNi [9,10],





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CrFeCoNi [11], MnCoNiCr₁₈ [12], CrMnFeCoNi [7,13], and CrFeCo-NiPd [14] FCC single-phase alloys. Thermal activation mechanisms and Labusch-type analysis are found to model the strengths very well for the family of CrMnFeCoNi HEA and its subsets of equiatomic solid-solution alloys [15–19]. It is well known that Labuschmodel considers two basic effects for traditional solid solution alloys, namely, atomic size match and modulus match [20–22], which is classic textbook theory. Despite the simplifications in Labusch model, design rules based on the above two mismatches have been successful in developing novel M/HEAs with even more improved mechanical properties.

The classic strengthening mechanism and nano-twinning observation in H/MEAs are reminiscent of the similarities of the M/HEAs to the traditional solid solution alloys, especially the widely used Ni-based solid solution superalloys, such as GH3536 alloy, or the counterpart Hastelloy X (HX) alloy in the United States. This alloy was born for the application of the gas turbine jet engine [23]. As early as in 1952, the alloy was developed for a replacement material for a failed combustor part in the JT-3 jet engine. Later, it was chosen for the JT-3 engine in Boeing 707 and JT-8D engine in Boeing 727 aircraft. Since then, 70 years passed, this alloy still remains one of the most widely used Ni-based sheet alloys for gas turbine hot parts. GH3536 or HX alloy is a Ni-based solid solution alloy with Cr, Fe, Mo, Co, and W additions [24]. Its high strength is provided mainly by solid solution strengthening of the Mo element. The concentrations of Cr and Fe are as high as 22 wt.%, that of Mo is about 9 wt.%, and the amount of Co and W is around 1 wt.% (as shown in Table 1). Here, we select this traditional alloy as a solid solution *model* allov because of recently renewed interests in the solution strengthening studies, particularly for the M/HEAs. Curiously, although this alloy is developed for high temperature use, we demonstrate here that it also provides exceptional mechanical behaviors at cryogenic temperature-something often acclaimed for M/HEAs. Moreover, from the microstructure, entropy calculation, mechanical properties over a wide range of testing temperature, and deformation mechanism, the 70-year-old GH3536 or HX alloy demonstrates many similar features as M/HEAs, which is considered a recent revolution in alloy design. Such a comparison naturally provides a platform for the structural materials community to reflect upon the degree of uniqueness and novelty in M/ HEAs.

2. Materials and methods

2.1. Material preparation

Tabla 1

GH3536 ingots with the nominal composition shown in Table 1 were prepared from the constituent elements Ni, Cr, Fe, Co, Mo, W, and so on (purity >99.9 wt.%) by arc melting in an Ar atmosphere in a water-chilled copper hearth. The alloy buttons were flipped and remelted more than five times to ensure thoroughly melting and mixing of all elements. The arc-melted alloys were then drop-cast into a water-chilled Cu mold with a dimension of $12.5 \times 12.5 \times 120 \text{ mm}^3$. The total weight loss after drop casting was less than 0.2%. Therefore, the as-cast alloy was assumed to have the designed composition, which was also confirmed later by energy

Nominal and m	easured (EDS quantification	n) compositions of th	ne GH3536 alloy.

Elements	Cr	Fe	Мо	Со	W	С	В	Ni
Nominal composition (wt. %)	22.0	18.0	9.0	1.5	0.6	0.1	0.008	Bal.
Nominal composition (at. %)	24.8	18.9	5.5	1.5	0.2	0.5	0.043	Bal.
Measured composition (wt. %)	22.0	18.0	9.8	1.6	0.7	-	-	Bal.

dispersive spectroscopy (EDS) quantification (Table 1). Because that EDS analysis of light elements with atomic number Z less than 11 is not reliable, boron (Z = 5) and carbon (Z = 6) have not been included in EDS quantification.

The drop-cast bars were homogenized at 1,473 K for 4 h, followed by quenching into a room temperature (RT) water bath. The homogenized materials were then cold rolled along longitudinal ingot direction to a total thickness reduction of ~76%. The cold rolled plate was then recrystallized at 1,373 K for 30 min to obtain fully recrystallized microstructure, and then quenched in water. The heat treatments were conducted in a vacuum/Ar protected tube furnace. Before heating, the tube was refilled by high-purity Ar after evacuation to a vacuum of <1 Pa. The evacuation and refilling processes were repeated three times to reduce the impact of oxidation on the sample.

2.2. Tensile testing

Dog-bone-shape specimens with gauge sections about $2.0 \times 1.3 \times 9.5 \text{ mm}^3$ were cut from the recrystallized plate by electrodischarge machining (EDM). The surfaces of the gauge section were carefully ground with 800 grit SiC paper to eliminate microcracks that may be introduced during EDM. Tensile tests were conducted at laboratory atmosphere on a screw-driven mechanical testing machine equipped with an induction heater. For elevated temperature tensile testing, a thermocouple was in direct contact with the sample gauge section to monitor testing temperature with +3 K of the set temperature. In addition, tensile specimens were heated to testing temperature by the induction heater and hold at least 15 min before applying load. For tests at 77 K, the specimen and grips were immersed in a liquid nitrogen bath for at least 15 min before loading. All the specimens were tested at a constant cross head displacement rate of 0.57 mm/min, which corresponds to an engineering strain rate of 10^{-3} s⁻¹. The length (marked by two Vickers hardness indentation impression in the gauge section) before and after fracture were measured to calculate the percentage elongation to fracture. The YS was calculated using the 0.2% offset method.

2.3. Microstructure characterization

After each fabrication process, samples with a thickness of 1–2 mm were cut, grind down with 800 grit SiC paper and then mechanical polished to observe their microstructures. The polished samples and fracture surfaces were observed in an FEI quanta 650 scanning electron microscope, equipped with a secondary electron detector, a backscattered electron detector and an Oxford EDS detector. X-ray diffraction (XRD) was performed to determine the crystal structure of the recrystallized GH3536 alloy.

Disks with a diameter of 2 mm for transmission electron microscopy (TEM) samples were punched from the gauge section of tensile deformed specimens, and then twin-jet electropolished in an alcoholic solution containing 5 vol.% perchloric acid at -30 °C. Scanning transmission electron microscopy (STEM) imaging were undertaken on a spherical aberration corrected (Cs-corrected) FEI 80-200 Titan G² TE microscope, operated at 200 kV, equipped with a high-angle annular dark field detector, an annular dark field (ADF) detector, and a bright-field detector.

3. Results

3.1. Microstructures

Fig. 1 shows representative microstructures, EDS mapping, and XRD of the GH3536 alloy in various conditions. The as-cast

specimen consists of large elongated dendrite grains extending from the edges to the center of the rectangular cross-section molds, in consistent with the heat flow directions during solidification (Fig. 1a). The EDS mapping, as shown in Fig. 1b, reveals that the dendrite is mainly caused by the segregation of the heavy refectory element Mo, which needs to be eliminated by following heat treatment. Fig. 1c shows typical homogenized microstructure of the GH3536 allov after annealing at 1.473 K for 4 h, indicating that homogenization has eliminated the dendrite segregation of Mo element. After cold rolling and annealing at 1,373 K for 30 min, the material is fully recrystallized and contains homogeneous equiaxed grain microstructure with large number of annealing twins (Fig. 1d). The average grain size without twin boundaries determined by a linear intercept method was found to be ~12 μ m. The EDS mapping shows all elements, namely, Ni, Co, Fe, Cr, Mo, and W, distributed homogeneously in the materials (Fig. 1e). In addition, XRD pattern (Fig. 1f) indicates that the GH3536 alloy is a FCC singlephase solid solution alloy, with lattice parameter of 3.608 Å. The single-phase feature remains during thermomechanically processing, which is used to control the microstructures.

3.2. Tensile properties

Fig. 2a shows the representative engineering stress vs. engineering plastic strain curves of the GH3536 alloy at five test temperatures from 77 K to 1,093 K, respectively. The plastic strain was obtained by subtracting the elastic strain at the 0.2% offset strain point on the curve from the total strain. Fig. 2b summarizes the 0.2% offset YS, ultimate tensile strengths (UTS), and elongations to fracture (EF). Values obtained from two different samples were presented to confirm the data reproducibility. Strong temperature dependence trend is observed for both strength and ductility. The highest values of YS, UTS, and EF are obtained at liquid nitrogen

temperature (77 K). An increase in temperature results in a monotonic decrease in both the YS and UTS. Similar case was also observed for the uniform elongation; however, a minimum in ductility occurs in the intermediate temperature range (around 673 K) for the GH3536 alloy. The temperature dependence mechanical behavior of the GH3536 alloy is exactly identical to single-phase FCC M/HEAs.

Fig. 3a–f are fracture surfaces of the GH3536 alloy after the samples tensile tested at 77 K and RT, respectively. As can be seen in the low-magnification fractograph in Fig. 3a, GH3536 alloy fractures almost without necking at 77 K. This is consistent with the high work hardening in the stress–strain curve in Fig. 2a, suggesting that the large elongation at cryogenic temperature is the result of the necking instability being postponed to higher strains. When fracture occurs finally, it is by dimpled rupture (ductile transgranular) as shown in the higher magnification fractograph (Fig. 3b and c). At RT, the fracture mode is similar dimple-like (Fig. 3e and f) but the fracture surface exhibits slight necking (Fig. 3d), which is in consistent with the reduction of the ductility at this temperature. The slightly lower ductility above RT is likely the result of an earlier onset of the necking instability.

3.3. TEM observation after tensile testing

TEM characterization has been conducted to study the deformation mechanisms of GH3536 alloy at different temperatures. Fig. 4 shows the defects in GH3536 alloy for the specimen fractured at RT with plastic strain of ~48%. Grains are filled with high density of dislocations and deformation twins are rarely observed (Fig. 4a). Thus, the continuous strain hardening of GH3536 alloy at RT (Fig. 2a) may be originated from dislocation interactions, which corresponds to the classic Taylor hardening. For better observation



Fig. 1. Micro/crystal structures of the GH3536 alloy in various processing stages. (a) Typical dendrite structures in as-cast conditions. (b) EDS mapping of the area marked by white dash rectangle in (a) showing that Mo segregations in the as-cast alloy. (c) Backscattered electron (BSE) image of the homogenized GH3536 alloy indicating that the dendritic segregations have been eliminated after annealing at 1,473 K/4 h. (d) Recrystallized microstructure with an average grain size of about 12 µm after annealing at 1,373 K/30 min. (e) EDS mapping of recrystallized alloy marked by white dash rectangle in (d) showing that the distribuation of all elements is microscopically uniform. (f) XRD pattern showing fully single-phase FCC in the recrystallized conditions.



Fig. 2. Tensile properties of the GH3536 alloy. (a) Engineering stress-strain curves of the recrystallized GH3536 alloy (grain size of ~12 μm) at various temperatures from 77 K to 1073 K. Temperature dependence of (b) 0.2% offset yield and ultimate tensile strengths; and (c) elongation to fracture.



Fig. 3. Secondary electron (SE) images showing fracture surfaces of GH3536 alloy after tensile testing at two different temperatures. (a–c) 77 K and (d–f) RT. The fracture surfaces are all ductile dimple-like. The rectangles in (a) and (d) outline the area of the fracture surfaces. Clearly, the reduction of area after fracture is larger at RT (d) than that at 77 K (a), even the elongation to fracture at 77 K is large, indicating significant necking at RT.

of dislocations, interrupted tensile experiment has been conducted. Fig. 4b shows the dislocation substructure in GH3536 alloy at early stage of plastic deformation (about 5%), indicating that plastic deformation of GH3536 alloy at RT mainly involved a/2<110>{111} full dislocations. High-resolution STEM image (Fig. 4c) reveals the atomic structure of a 60° full dislocation, consisting of two partial dislocations and a stacking fault between them. The average width of 60° dislocation cores is ~4.8 nm (about 20 dislocation cores have been captured and measured). The stacking fault energy γ_{sf} can be estimated as follows:

$$\gamma_{sf} = \frac{Gb_p^2}{8\pi d} \left(\frac{2-\nu}{1-\nu} \right) \left(1 - \frac{2\nu\cos 2\theta}{2-\nu} \right),\tag{3.1}$$

where θ is the angle between the dislocation line and the burgers vector of the full dislocation, b_p is the length of the Burgers vector of the partial dislocation, d is the width of dislocation core, ν and G are Poisson's ratio and shear modulus, respectively. The ν and G of GH3526 are 0.32 and 77.9 GPa, respectively [25], and d equals to 4.8 nm, thus, the stacking fault energy γ_{sf} of GH3536 alloy is calculated to be 41 mJ/m². For comparison, the γ_{sf} of pure Ni and some FCC M/HEAs are listed in Table 2, indicating the γ_{sf} of GH3536 is much lower than that of the pure Ni and falls in the comparable

range of M/HEAs, which is higher than that of CrCoNi, CrFeCoNi, and CrMnFeCoNi alloys, but lower than that of CrFeCoNiPd alloy.

Different from that at RT, besides dislocation glide, deformation twinning is one of the primary plastic deformation modes at 77 K. Large amounts of nano-twins were observed in the sample fractured at 77 K, as shown in Fig. 5a, which includes two twinning directions indicated by green arrows in the figure. Fig. 5b shows a high-resolution STEM image of the nano-twin bundle indicated by black dash rectangle in Fig. 5a, and the inset corresponds to the selected area diffraction pattern of the twin bundle. The thickness of the twins ranges from 3 nm to 6 nm in general. High density of twin boundaries, which could effectively hinder dislocations motion, divides the coarse grain into extremely small grains, which provides additional work-hardening, similar to Hall-Petch effects. Interestingly, the nano-twins in Fig. 5a is not straight (the green dash straight lines in Fig. 5a shown as references). Fig. 5c shows the high-resolution ADF-STEM image of these twisted twins, taken from the area marked by red dash rectangle in Fig. 5a. It is found that the distortion of nano-twins is resulted from small-angle grain boundaries (SAGB). The SAGBs are composed of high density of dislocations. For example, the dislocations, indicated by red " in Fig. 5c, result in two SAGBs, one of which is 11° and has been marked by the yellow lines. Fig. 5d is a fast Fourier transform



Fig. 4. STEM observation of deformation-induced substructures in GH3536 alloy at room temperature. (a) High density of dislocations in fractured GH3536 alloy. (b) Bright-field (BF)–STEM image showing dislocation structures of the alloy. (c) High-resolution high-angle annular dark field (HAADF)–STEM image taken along <110> direction, showing the atomic structure of a dislocation with Burgers vector a/2[110] in GH3536 alloy. Images (b) and (c) were captured in sample with plastic strain ~5%.

Table 2 Lattice parameter (*a*), stacking fault energy (γ_{sf}), shear modulus (*G*), and Poisson's ratio (ν) of GH3536 alloy and several typical FCC-structured M/HEAs.

Alloy	a (Å)	$\gamma_{sf} (mJ/m^2)$	G (GPa)	ν	References
GH3536	3.608	41	78 [25]	0.32 [25]	This work
CrCoNi	3.529	18	88	0.30	[26]
CrFeCoNi	3.565	27	85	0.28	[26]
CrMnFeCoNi	3.576	26.5	80	0.26	[26]
CrFeCoNiPd	3.670	66	89	0.28	[14]
Pure Ni	3.524	120-130	76	0.31	[27,28]

pattern of Fig. 5c, clearly indicating the existence of SAGBs. In addition, it should be noted that there is also high density of dislocations on twin boundaries, resulting in steps on twin boundaries, indicated by green arrows in Fig. 5c. These dislocations at 77 K are also full dislocations, with Burger vector a/2[110], as shown in the insert of Fig. 5c. Collectively, at cryogenic temperature, deformation nano-twins play an important role on mechanical behaviors of the GH3536 alloy, because twin boundaries can not only hinder the motion of dislocations, but also act as sites for dislocation accumulation, resulting in enhanced work hardening, postponed necking, and thus increased ductility.

4. Discussions

4.1. Entropy consideration

The concept of HEA is introduced by Yeh et al. [1] and Cantor et al. [2], independently. The mixing entropy for a N-component solid solution alloy can be calculated by the following equation:

$$\Delta S_{mix} = -R \sum_{i=1}^{n} c_i \ln(c_i)$$
(4.1)

where *R* is the gas constant, and c_i is the mole (atomic) fraction of the *i* constituent element. Note that the entropy in Eq. (4.1) is so called mixing entropy or configuration entropy, which is used for disordered solid solution alloy or bulk metallic glasses. If it is intermetallic phase, for example, fully ordered B2 NiAl, the mixing entropy is considered to be zero, rather than 0.69R. Based on the mixing entropy defined by Yeh. et al. [29], the alloy world can be divided into three categories, including low-entropy alloys ($\Delta S_{mix} \leq 0.69R$), medium-entropy alloys ($0.69R \leq \Delta S_{mix} \leq 1.61R$) and HEAs ($\Delta S_{mix} \geq 1.61R$). In addition, Yeh. et al. [29] call traditional alloys as low-entropy alloys. Based on Eq. (4.1), we calculate the

entropy of GH3536 alloy and several FCC-structured M/HEAs, and the result is shown in Table 3. Interestingly, entropy of GH3536 alloy is as high as 1.25R, much higher than the upper limit of lowentropy alloys (0.69R), even higher than typical equiatomic ternary alloy NiCoCr (1.10R) and non-equiatomic quaternary alloy Fe₅₀Mn₃₀Co₁₀Cr₁₀ (1.19R), only slightly lower than equiatomic quaternary alloy CrFeCONi (1.39R) and non-equiatomic quaternary alloy MnFeNiCr₁₈ (1.37R). Thus, GH3536, CrCoNi, Fe₅₀Mn₃₀Co₁₀Cr₁₀, CrFeCONi, and MnFeNiCr₁₈ alloys can be classified into mediumentropy alloys. Only two equiatomic quinary alloys listed in Table 3, CrMnFeCONi and CrFeCONiPd, is the '*real*' HEAs with their mixing entropy of 1.61R, if Yeh's definition is strictly being considered.

4.2. Manufacturing/microstructures consideration

Most FCC-structured M/HEAs are manufactured in the following order to control the microstructures of the alloys (especially the decent grain structures): melting and casting, homogenization, cold/hot rolling (thermomechanical processing), and annealing/ recrystallization [7,11,12,31]. Homogenization can eliminate the ascast dendrite segregation, and rolling can break the columnar coarse grains. After annealing, alloys with homogeneous equiaxed grains can be obtained. Grain sizes of these alloys are controlled by the recrystallization heat treatments, normally the higher the annealing temperature, the longer the annealing time, and the larger the grain size. Thus, from the point of physical metallurgy, the manufacturing processes of M/HEAs used to control the microstructures are essentially the same as that of GH3536 alloy, which again falls into the classic knowledge in metallurgy.

Thermal stability of the alloy is very important for potential structural applications at elevated temperatures. Luckily, the thermal stability of the GH3536 alloy was studied previously [32–34]. When the alloy was aged at a temperature range from 650 °C to 760 °C, σ phase, M₂₃C₆ and M₆C phases would precipitate, which might act as preferential initiation sites for crack during services [32–34]. Although M/HEAs are recrystallized as a single-phase FCC solid solution, their microstructure stability during long-time ageing is rarely studied and limited data of the quinary CrMnFe-CoNi alloy is reported [13]. Interestingly, the thermal stability of the CrMnFeCONi is very similar to that of the GH3536 alloy. The single FCC phase in CrMnFeCONi alloy decomposes into Cr-rich σ phase at 700 °C and different intermetallic phases (L₁₀-NiMn, B₂-FeCo, and a Cr-rich body-centered cubic phase) [13].

Thermodynamically, the phase stability of an alloy is governed by the changes in the Gibbs free energy (G), which includes both



Fig. 5. STEM observations of deformation-induced substructures in GH3536 alloy after fracture at 77 K. (a) BF-STEM image showing high density of nano-twins in a grain. (b) High-resolution HAADF–STEM image captured from the black square in (a) showing the atomic structure of the nano-twins and the corresponding diffraction pattern is shown in the inset. The twin and matrix are highlighted by yellow and purple colors, respectively. (c) ADF–STEM image obtained from the area marked by red dash rectangle in (a) shows atomic structure of the twisted nano-twins and boundaries among twins with different orientations. The small-angle grain boundary (SAGB) induced by high density of dislocations (indicated by red " \perp ") results in the twisted nano-twins. The insert of (c) is a zoom-in of the area marked by white dash rectangle, showing the core structure of a full dislocation, with Burgers vector of a/2[110]. (d) Fast Fourier transform (FFT) pattern of (c) clearly indicating three sets of twins with different orientations. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 3

Calculated entropy of GH3536 alloy and several typical FCC-structured M/HEAs.

Alloys	Mixing entropy	Notes
GH3536	1.25R	FCC single phase, this work
CrCoNi	1.10R	FCC single phase [30]
Fe50Mn30Co10Cr10	1.17R	HCP/FCC dual phases [31]
MnFeNiCr ₁₈	1.37R	FCC single phase [12]
CrFeCoNi	1.39R	FCC single phase [11]
CrMnFeCoNi	1.61R	FCC single phase [2]
CrFeCoNiPd	1.61R	FCC single phase [14]

enthalpy (*H*) and entropy (*S*) contributions at certain temperature of *T*, which is $\Delta G = \Delta H - T\Delta S$. When an alloy trends to form ordered intermetallic compounds, the enthalpies of formation can be less than zero, resulting in always negative Gibbs free energies. The appearance of intermetallic compounds is expected no matter the entropy values if thermodynamically equilibrium is reached after long term annealing, because the intermetallic phases are the stable phases. Clearly, for both GH3536 and CrMnFeCoNi alloys, the stability of FCC solid solution phases is competed with the formation of intermetallic phases, which has been reported in previous studies [13,35]. The effects of entropic stabilization on the solid solution state originally proposed in the M/HEA field [1,5,29] are very limited, even in the extensively investigated alloys, GH3536 and Cantor alloys. Therefore, the stability of M/HEAs should be carefully evaluated, especially if they are being considered for structural applications in certain vulnerable temperature ranges.

4.3. Mechanical properties consideration

As can be seen from Fig. 2, when temperature decreases from 293 K to 77 K, YS and UTS of GH3536 alloy increase by ~64% and ~50%, to 593 and 1198 MPa, respectively. Surprisingly, the elongation to fracture simultaneously increases by 60% to the fracture strain of 0.77, meaning that the GH3536 also shows the *unusual* strength-ductility trade-off behavior. The finding of simultaneously enhanced strength and ductility is considered as the most exciting discovery for the M/HEAs [7,31,36,37], because this makes them practically good candidates for structural applications at low temperatures, and moreover scientifically interesting materials for exploring the new alloy design theory [10,38–40].

For better comparison, YS, UTS, and elongation to fracture of GH3536 and typical FCC-structured M/HEAs, with similar average grain size, are summarized in Fig. 6, respectively. It is found that maximum values of YS (Fig. 6a), UTS (Fig. 6b), and elongation to

fracture (Fig. 6 c) are obtained at liquid nitrogen temperature (77 K). At lower temperatures (<293 K), as temperature decreases, the YS, UTS, and elongation to fracture of GH3536 alloy and all M/ HEAs are enhanced. The yield stress of GH3536 alloy is higher than that of CrMnFeCoNi alloy with even smaller grain size (4.4 µm), and also higher than that of the CrCoNi alloy, but slightly lower than that of the CrFeCoNiPd alloy. Meanwhile, the UTS of GH3536 alloy is higher than CrMnFeCoNi and CrFeCoNiPd allovs, and slightly lower than CrCoNi alloy. The elongation to fracture of GH3536, at lower temperatures, is also superior, which is comparable to the M/HEAs, such as CrMnFeCoNi and CrCoNi alloys. As can be seen from Fig. 6, the similarity of mechanical properties between GH3536 and M/ HEAs is not only limited to temperature lower than RT, but also hold true at high temperatures. As temperature increases from RT, YS and UTS of all alloys decrease, in which GH3536 alloy exhibits the strong strength and good ductility. Thus, mechanical properties of GH3536 alloy are similar to selected M/HEAs at lower temperatures, but is better than most M/HEAs, especially at higher temperatures. Most interestingly, the temperature dependence of mechanical properties for the GH3536 alloys shares the identical behaviors as FCC single-phase M/HEAs, which might be closely related to their deformation mechanisms.

Fig. 7a shows the true stress–strain curves of GH3536 alloy. Fig. 7b shows the corresponding strain hardening rates as a function of stresses at 77 K and 293 K, both of which have similar trends. The strain hardening rates of the samples first dropped rapidly. As stresses continuously increase, the decrease of the rates gradually slows down until reaching nearly constant hardening rates. And then the strain hardening rates decrease until rupture. It is noted that the strain hardening behaviors of GH3536 alloy at both 77 K and 293 K are also similar to that of M/HEAs [41,42].

Stress-strain curves in Figs. 2 and 7 clearly indicate that the tensile ductility is dictated by necking instability. The classic

Considère model gives the necking condition being the peak force in Fig. 2 (i.e., UTS location), or equivalently, $\frac{d\sigma}{d\epsilon} = \sigma$, as shown by the straight line in Fig. 7b. As necking is localized in the length direction of the magnitude of the diameter size, for long dog-bone samples, the strain localization in necking zone does not contribute noticeably to the total strain. That is, the necking condition and the final failure strain are about the same. However, this is not the case for the enhanced ductility at elevated temperature, e.g., 1,073 K curve in Fig. 2a.

At elevated temperature, such as 1,073 K for this alloy, the strain rate sensitivity, *m*, significantly contributes to total elongation and reduce the necking instability during tensile testing, as given by the Considère–Hart condition [43,44]:

$$\frac{1}{\sigma_t}\frac{d\sigma_t}{d\varepsilon_t} + m = 1 \tag{4.2}$$

where, the subscript 't' denotes elevated temperature, and *m* is strain rate sensitivity. For RT deformation, the *m* approaches to zero, which represents the straight line in Fig. 7b. At the other extreme, in high temperature, for some nanocrystalline materials with m = 1, superplasticity will occur. With the contribution of strain rate sensitivity of *m*, it experiences long process (e.g., diffuse necking) between the onset of necking (peak load) and the full development of necking (i.e., near failure) at 1,073 K, which is in consistence with the comparison between ~10% strain at peak load and ~60% failure strain in Fig. 2a. The mechanical behaviors of FCC structured alloys at high temperatures are well-documented, and plastic deformation at those temperatures primarily involved dislocation motion, diffusion, and grain boundary sliding and migration [45].



Fig. 6. Temperature dependence of mechanical properties. (a) The 0.2% offset yield stress; (b) UTS; and (c) the elongation to fracture for GH3536 alloy and typical medium/highentropy alloys (M/HEAs). M/HEAs data from: CrMnFeCoNi [49], MnFeNiCr₁₈ [12], CrFeCoNi [30], and CrCoNi [30].



Fig. 7. True stress–strain curve (a) and strain-hardening rate vs. true stress (b) of GH3536 alloy tensile deformed at 77 K and 293 K. The green line in (b) represents the onset of necking instability conditions, which is $\frac{d_{r_c}}{d_{r_c}} = \sigma_t$. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

4.4. Deformation mechanism consideration

Traditionally, the flow stress in the stress–strain curve has been modelled as the sum of the different strengthening contributions, which is closely related to the strengthening mechanism during plastic deformation. For a solid solution alloy, the strength of an alloy (σ_f) might be described as follows:

$$\sigma_f = \sigma_y + \Delta \sigma_{\text{strain-hardening}},\tag{4.3}$$

where σ_y is the YS, which represents the intrinsic solid solution effects by compositions and type of alloying elements, typically atomic/modulus mismatch effects. The $\Delta \sigma_{strain-hardening}$ term represents the microstructure/defects contributions dynamically as a function of strain, for a solid solution alloys excluding precipitationhardening. The following three effects are usually considered: Taylor hardening ($\Delta \sigma_{Taylor}$), dynamic Hall–Petch (dHP) due to twinning ($\Delta \sigma_{trip}$), and hardening due to transformationinduced plasticity (TRIP, $\Delta \sigma_{trip}$).

The Taylor hardening is observed in almost all solid solution alloys, which is associated with the dislocation interactions as the strain increases, which is as follows:

$$\Delta \sigma_{Taylor} = \alpha_1 G b \sqrt{\rho_{dis}} = \frac{\alpha_2 G b}{D_{dis}},\tag{4.4}$$

where α_1 and α_2 are constants, *G* is the shear modulus, *b* is the burgers vector, and ρ_{dis} is dislocation density which corresponds to the dislocation spacing D_{dis} .

The development of a twin substructure in an alloy results in a further decrease of the dislocation mean free path leading to so called dynamic twin-induced hardening, similar to the Hall—Petch effects in grain boundary hardening, thus, sometimes this is often denoted as dHP effect. Twin boundaries act as obstacles to dislocation motion and serve as efficient sites for dislocation accumulation, which has also observed in traditional twin steels [46,47]. The contribution of twinning to hardening can be described by the following equation:

$$\Delta \sigma_{twinning} = \frac{K_{dHP}}{\sqrt{D_{twin}}},\tag{4.5}$$

where K_{dHP} is a constant and D_{twin} is the average twin spacing. Collectively, take account of all three contributions of strain hardening, the flow stress or strength as function of strain, Eq. (4.3) might be rewritten as follows:

$$\Delta \sigma_f = \sigma_y + \alpha_1 G b \sqrt{\rho_{dis}} + \frac{K_{dHP}}{D_{twin}} + \Delta \sigma_{trip}.$$
(4.6)

The strain-hardening behavior of GH3536 has been calculated and their deformation mechanism is discussed based on Eq. (4.6) in combination with careful investigation of deformation substructures and defects.

TEM characterization reveals that plastic deformation of GH3536 allov at RT primarily involved a/2<110>{111} full dislocations (Fig. 4), which is reasonable, because of its relatively intermediate stacking fault energy (41 mJ/m²). At the initial stage of deformation, dislocations multiply and accumulate, resulting in the formation of dislocation walls along different {111} planes, thus effectively acting as obstacles for further movements of other dislocations (Fig. 4b). As the strain increases, dislocation density increases, interaction between dislocations would be more complex. As shown in Fig. 8a, hexagonal dislocation networks have been formed when strain reaches ~5% at RT. In addition, in the sample with strain (~5%), we have also observed cross-slipped dislocations, which is also observed in CrFeCoNiPd alloy at 293 K [14]. Some dislocations, indicated by red arrows (Fig. 8b), are wavy, which is typical symbol for dislocation cross-slip. Fig. 8c shows two dislocation bands (indicated by green arrows) cross slipped from the primary slip band (red arrows). Cross slip would effectively increase the dislocation density and decreases the dislocation spacing, thus eventually increase the chance for dislocation interactions. All types of dislocation interactions mentioned earlier result in the high density of dislocations in the fractured sample (Fig. 4a). From Eq. (4.4), strain hardening effect is proportional to the square root of the dislocation density or inversely proportional to the spacing of the dislocations, resulting in continuously strain hardening (Taylor hardening) in the alloy, the flow stress of the alloy is the sum of yield stress and dislocation interactions ($\Delta \sigma_{f-293 K} = \sigma_y +$ $\Delta \sigma_{Taylor}$).

At 77 K, plastic deformation of GH3536 alloy becomes more complicated as compared with that at RT. At the early stage of deformation (strain ~5%), not only full dislocations but also partial dislocations are activated, as shown in Fig. 9, in which partial dislocations are indicated by green arrows. As partial dislocations can be activated at 77 K, twin formation normally accompanies in the deformation processing. Moreover, the amounts of deformation nano-twins increase as the strain increasing, which continuously provide additional hardening. As mentioned previously, the size of deformation nano-twins is only 3-6 nm when strain is as high as 77%. Similar to grain boundaries, nano-twin boundaries can also provide obstacles to dislocation movement, and therefore, the



Fig. 8. ADF–STEM images showing cross-slipped dislocations in GH3536 alloy deformed at room temperature with ~5% plastic strain. (a) Dislocation network. (b) Wavy dislocations, which is a symbol for dislocation cross-slip. (c) Two dislocation arrays indicated by green arrows have cross slipped from the primary slip plane, which is indicated by red arrows. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

twinning-induced hardening is defined as dHP effects (Eq. (4.5)). Thus, the strain hardening of GH3536 alloy at 77 K consists of not only dislocation interactions but also deformation twinning contributions. In this case, the low temperature strength of the alloy can be expressed as $\Delta \sigma_{f-77 \text{ K}} = \sigma_y + \Delta \sigma_{Taylor} + \Delta \sigma_{twinning}$.

The temperature dependence of nano-twin activity might be attributed to the higher critical stress required for twinning formation than the dislocations in solid solution alloys, similar to FCC high-entropy cantor alloy CrCoFeMnNi [48]. Laplanche et al. [48] found that twinning occurred at a tensile stress of 720 \pm 30 MPa, roughly independent of temperature for the cantor alloy. At 77 K, twinning is activated at the early stage of deformation because of the relatively high strength of the cantor alloy at this temperature. However, at RT, because the strength is relatively lower as compared to 77 K, which may not achieve the stresses required for nano-twin, deformation mainly occurs by dislocation plasticity with little nano-twin formation [48]. We expect that the GH3536 alloy behaves in similar way. As deformation twins have not been



Fig. 9. Full dislocations and partial dislocations (indicated by green arrows) are activated at 77 K at strain of ~5%. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

observed in the fracture sample of GH3536 at RT, indicating that the critical stress for twinning in GH3536 alloy is higher than the UTS of the alloy (~798 MPa at RT), but the exact value cannot be accurately determined in current stage, which is subjected to future studies by either in situ tensile testing or careful interpreted experiments at 77 K.

Fig. 10 summarizes the deformation mechanisms of GH3536 at 77 K and 293 K. At RT, multiplication and motion of full dislocations is the dominant mechanism, and continuous strain hardening originates from dislocation interactions. At 77 K, plastic deformation is composed of complicated interactions among full dislocations, partial dislocations, and deformation twins. Again, the deformation mechanism of the traditional GH3536 is almost the same as that of the FCC M/HEAs, namely the contributions of dislocations and/or nano-twins, which is closely associated with the stacking fault energy of the alloy [7,10,40,42,49]. The deformation mechanism of GH3536 alloy is exactly the same as that of CrFe-CoNiPd and CrFeCoNiMn HEA alloys, because the stacking fault energy of the GH3536 is about 41 mJ/m², which lies in between of the CrFeCoNiPd (66 mJ/m²) [14] and CrFeCoNiMn (26.5 mJ/m²) alloys [26]. The stacking fault energy of CrCoNi is the lowest in Table 2, which eventually prompts the strain-induced transformation of FCC to hexagonal close-packed (HCP) phases in 77 K [42], resulting in additional deformation mechanism of transformation induced plasticity, similar to the TRIP-HEA of Fe₅₀Mn₃₀Cr₁₀Co₁₀ [31]. Similar TRIP or TWIP behavior has been seen in MP10N ($Co_{60}Cr_{20}Ni_{10}Mo_{10}$ wt.%) and MP35N $(Co_{35}Cr_{20}Ni_{35}Mo_{10} \text{ wt.}\%)$ [50]. When the Ni content is low so that the stacking fault energy is extremely low (e.g., MP10N), TRIP behavior (FCC \rightarrow HCP) dictates the deformation behavior. Increasing the Ni content leads to the transition from TRIP, TRIP/ TWIP, and to TWIP dominance (e.g., MP35N). Consequently, Nibased superalloys and the aforementioned Co-Cr-Ni-Mo alloys provide similar tunability/flexibility, if not more, to the M/HEAs in terms of the stacking fault energy and TRIP/TWIP behavior. The latter is very effective in ductility enhancement because both TRIP and TWIP may significantly increase the work hardening rate, albeit from different mechanisms.

5. Summary and conclusions

GH3536 alloy was fabricated from pure constituent elements by arc melting and drop casting. The drop-cast ingots were homogenized, cold rolled, and recrystallized to obtain single-phase



Fig. 10. The deformation mechanisms of GH3536 at 77 K and 293 K.

microstructure with grain sizes of ~12 μ m. Tensile tests were then performed at a wide temperature range between 77 K and 1073 K. To interpret the mechanical properties, microstructural analyses were performed by TEM after deformation. The following conclusions can be drawn:

- 1. Strong temperature dependence trend is observed for both strength and ductility. The highest values of YS, UTS, and EF are obtained at liquid nitrogen temperature (77 K). An increase in temperature results in a monotonic decrease in both the YS and UTS. Similar case was also observed for the uniform elongation; however, a minimum in ductility occurs in the intermediate temperature range (around 673 K) for the GH3536 alloy.
- 2. At 77 K and RT, the fracture mode is all dimple-like (ductile fracture). The large elongation at cryogenic temperature is the result of the necking instability being postponed to higher strains, while the fracture surface at RT and above exhibits slight necking. Although the ductility enhancement at cryogenic temperature can be rationalized by the delay of necking instability when the work hardening rate increases, the improved ductility at very high temperature (1073 K) arises from the delay in neck growth due to the strain rate sensitivity.
- 3. TEM characterization indicates that the motion of full dislocations is the dominant mechanism of plasticity at RT, continuous strain hardening originates from the dislocation interactions.
- 4. At 77 K, plastic deformation of GH3536 alloy becomes more complicated as compared with that at RT and the deformation nano-twins were observed after interrupted/fracture tests. The interactions of full dislocations, partial dislocations, and deformation twins provide additional strain hardening than that at RT.
- 5. From the viewpoint of the microstructure, entropy calculation, mechanical properties, and deformation mechanism, the traditional Ni-based superalloy behaves exactly in the similar manner to the recently developed FCC single-phase M/HEAs.

CRediT authorship contribution statement

Q. Ding: Conceptualization, Methodolgy, Formal analysis, Investigation, Writing - original draft, Writing - review & editing. **H. Bei:** Conceptualization, Methodology, Formal analysis, Investigation, Resources, Writing - original draft, Writing - review & editing. **X. Wei:** Resources, Writing - review & editing. **Y.F. Gao:** Formal analysis, Writing - review & editing. **Z. Zhang:** Conceptualization, Formal analysis, Resources, Writing - review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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