

Supplementary Material:

Dual-scale chemical ordering enables exceptional cryogenic mechanical properties of medium-entropy alloys

Tiwen Lu^{a†}, Binhao Sun^{a,b†}, Sheng Dai^c, Yue Li^b, Fan Ye^c, Jiacheng Niu^d, Alisson Kwiatkowski da Silva^b, Sihao Deng^e, Yu Xie^a, Ning Yao^a, Jianping Tan^a, Tianbing He^f, Dirk Ponge^b, Lunhua He^{e,g,h}, Xian-Cheng Zhang^{a*}, Dierk Raabe^{b*}, Shan-Tung Tu^a

^aKey Laboratory of Pressure Systems and Safety, Ministry of Education, East China University of Science and Technology, Shanghai 200237, China;

^bMax-Planck-Institut für Eisenforschung GmbH, Max-Planck-Straße 1, 40237 Düsseldorf, Germany;

^cKey Laboratory for Advanced Materials and Joint International Research Laboratory of Precision Chemistry and Molecular Engineering, Feringa Nobel Prize Scientist Joint Research Centre, East China University of Science;

^dGuangdong Key Laboratory for Advanced Metallic Materials Processing, South China University of Technology, Guangzhou, Guangdong, 510640, China;

^eSpallation Neutron Source Science Center, Dongguan 523803, China;

^fXiamen Hongfa Electroacoustic Co., Ltd, Xiamen 361021, China;

^gBeijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China.

^hSongshan Lake Materials Laboratory, Dongguan 523808, China.

[†]These authors contributed equally to this work.

*Corresponding author. E-mail: xczhang@ecust.edu.cn (X.-C. Z.); d.raabe@mpie.de (D. R.)

Supplementary Item 1. Calculation of dislocation density

The evolution of dislocation density in the presented alloys at different strains was calculated by the modified Williamson-Hall (MWH) method^[1] based on the neutron diffraction data. According to the MWH method, the full width at half maximum (FWHM), ΔK , of the diffraction peaks is a function of the average crystallite size (D) and the dislocation density (ρ) as follows^[2]:

$$\Delta K = \frac{0.9}{D} + \left(\frac{\pi A^2 b^2}{2}\right)^{\frac{1}{2}} \rho^{\frac{1}{2}} \left(K \bar{C}^{\frac{1}{2}}\right) + O(P^4 \bar{C}^{\frac{1}{2}}) \quad (S1)$$

where b and K represent the magnitude of the Burgers vector and the Bragg position, respectively, A is a constant depending on the effective outer cutoff radius of dislocations, O represents the high order terms which can be neglected for calculation. ΔK and K can be directly obtained from the neutron profiles.

$$\bar{C} = \bar{C}_{h00}(1 - qH^2) \quad (S2)$$

$$H^2 = \frac{h^2 k^2 + k^2 l^2 + h^2 l^2}{h^2 + k^2 + l^2} \quad (S3)$$

$$\bar{C}_{h00} = a_1 \left[1 - \exp\left(-\frac{A_i}{b_1}\right)\right] + c_1 A_i + d_1 \quad (S4)$$

$$q = a_2 \left[1 - \exp\left(-\frac{A_i}{b_2}\right)\right] + c_2 A_i + d_2 \quad (S5)$$

$$A_i = 2C_{44}/(C_{11} - C_{12}) \quad (S6)$$

where $\bar{C}_{h00}$, q , a_i , b_i , c_i and d_i are constants related to the anisotropic elastic constants (C_{11} , C_{12} and C_{44}) and dislocation characters^[3]. An extensive literature research on the elastic constants of FCC CoNi-based medium-entropy alloys shows that there is no significant difference in $\bar{C}_{h00}$ and q among these alloys^[4-7]. Therefore, C_{11} , C_{12} and C_{44} (296 GPa, 202 GPa and 176 GPa, respectively) taken from a CoCrNi MEA^[6] were used. q is a variable related to the fraction of screw and edge dislocations^[8], which can be determined experimentally by the linear regression of the $[(\Delta K_{tot}) - (0.9/D)]^2/K^2$ versus H^2 , hkl represents the crystal indices of FCC system. According to the anisotropic elastic constants and the determination of a_2 , b_2 , c_2 and d_2 ^[3], the theoretical value of q is 1.70 and 2.45 for edge dislocations and screw dislocations in CoNi-based medium-entropy alloys (also reflected in [Supplementary Fig. 11](#)), respectively.

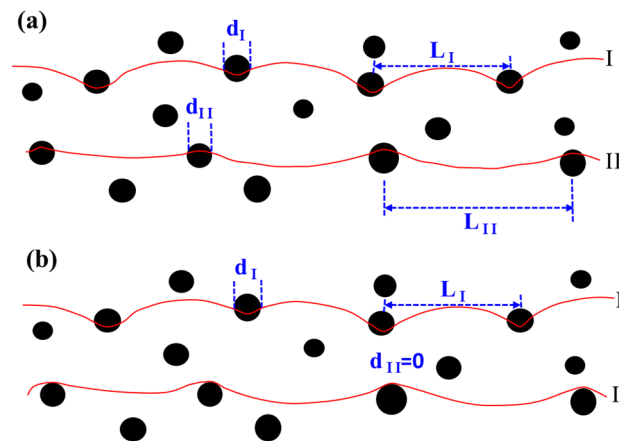
The value of ρ can be determined by the best linear fitting between ΔK and $KC^{1/2}$, and the slope is $(\pi A^2 b^2/2)^{1/2} \rho^{1/2}$, from which the overall dislocation density of the materials can be calculated. The fitting curves are shown in [Supplementary Fig. 10](#).

Supplementary Item 2. The contribution of chemical local ordering on the yield strength of the CoNiV-AlTi alloy

The enhancing effect of chemical local ordering (long-range order and short-range order) on the strength of a compositional complex material mainly lies in its order strengthening effect^[8]. This is associated with the dislocation shearing of ordering clusters which produces an antiphase boundary that has a high energy opposing the motion of the penetrating dislocations^[11, 12]. The relation between critical resolved shear stress (CRSS, τ_c) for dislocation gliding and the characteristics of chemical local ordering can be expressed as^[13]:

$$2\tau_c b = \gamma_{\text{APB}} \left(\frac{d_I}{L_I} - \frac{d_{II}}{L_{II}} \right) \quad (\text{S7})$$

where γ_{APB} is the antiphase boundary energy of the chemical local ordering domain (for LRO, the value is around the order of 10^{-1} J/m²^[9, 10]), d_i and L_i are the average length of one of the paired dislocation lying in ordering particles and the average spacing of the ordering particles along the dislocation, respectively, as schematically shown in the figure below, I denotes the first shearing dislocation which produces an antiphase boundary and II represents the second trailing dislocation that restores the ordering particle. The value of L also equals the mean free path of the dislocation.



Schematic diagram of ordered domains sheared by a pair of dislocations. In (a) d_{II} is finite, while in (b) $d_{II} = 0$.

This relation reveals that the strengthening effect caused by chemical local ordering is strongly influenced by both the γ_{APB} and L_i ; the former parameter describes the resistance of the ordering particle to dislocation shearing (i.e. how easy they can be sheared by a dislocation), and the latter parameter highlights the density and dispersion of the ordering particles (i.e. how dense they are distributed). A higher number density

78 and a more densely distributed ordering clusters reduce dislocation mean free path,
79 which can be calculated by^[14]

$$80 \quad L = \bar{d} \left(\sqrt{\frac{\pi}{4f}} - 1 \right) \quad (S8)$$

$$81 \quad \bar{d} = \sqrt{2/3} d \quad (S9)$$

82 $\bar{d}$ is the mean radius of a circular cross-section in a random plane crossing a spherical
83 precipitate, d is average diameter of the ordered domains, f is the volume fraction of the
84 ordered domains. The dislocation mean free path produced by SRO and LRO was
85 calculated to be 1.9 nm and 1.8 nm, respectively.

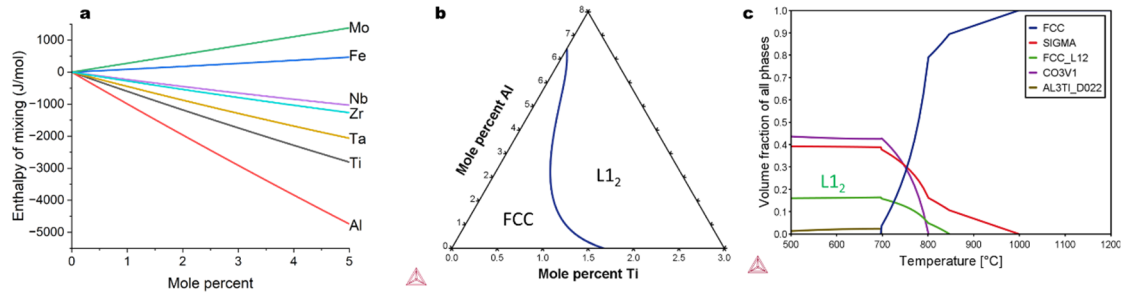


Figure S1. (a) Enthalpy of mixing of different elements in the FCC phase with CoNiV composition (equimolar) at 1000°C. (b) The promoting effect of Al and Ti addition on the formation of the L₁₂ ordered phase at 750°C assuming that the main elements have a same atomic concentration ($N(\text{Ni}) = N(\text{Co}) = N(\text{V})$). (c) Equilibrium volume fraction of different phases as a function of temperature for the $\text{V}_{32}\text{Co}_{32}\text{Ni}_{32}\text{Al}_2\text{Ti}_2$ (at.%) composition.

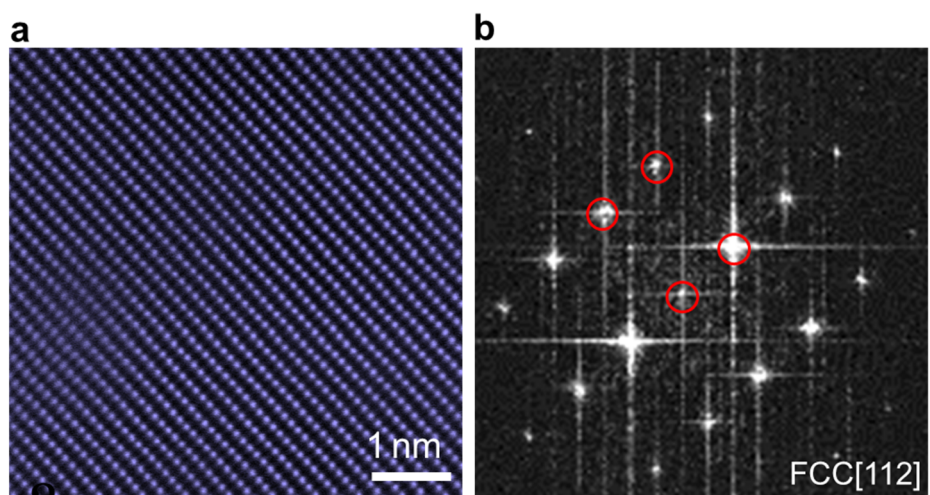


Figure S2. (a) Atomic-scale HAADF-STEM image along the [112] zone axis and (b) the corresponding FFT pattern of the CoNiV(SS) sample, showing the absence of ordering structures.

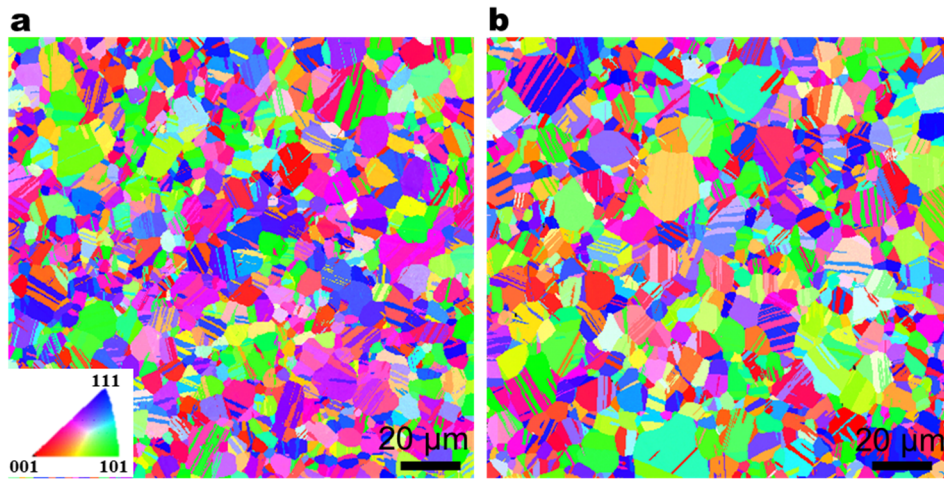


Figure S3. EBSD-inverse pole figures (IPF) of (a) the CoNiV(SS) and (b) the CoNiV(AT) samples with an average grain size of $\sim 10 \mu\text{m}$ (the average grain size of the CoNiV-AlTi sample is $11.2 \mu\text{m}$).

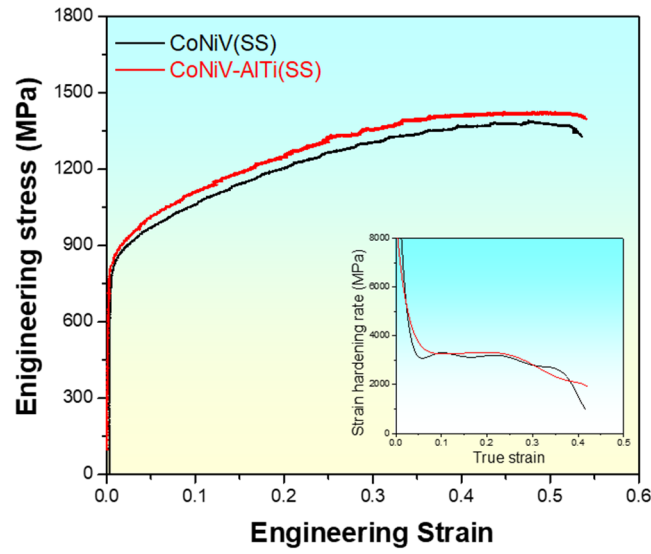


Figure S4. Engineering stress-strain curves and strain-hardening response of the ordering-free CoNiV(SS) and solid solution treated CoNiV-AlTi sample (without aging treatment and ordering) tested at the cryogenic temperature (87 K), suggesting only moderate influence of solute Al and Ti atoms on the cryogenic mechanical properties.

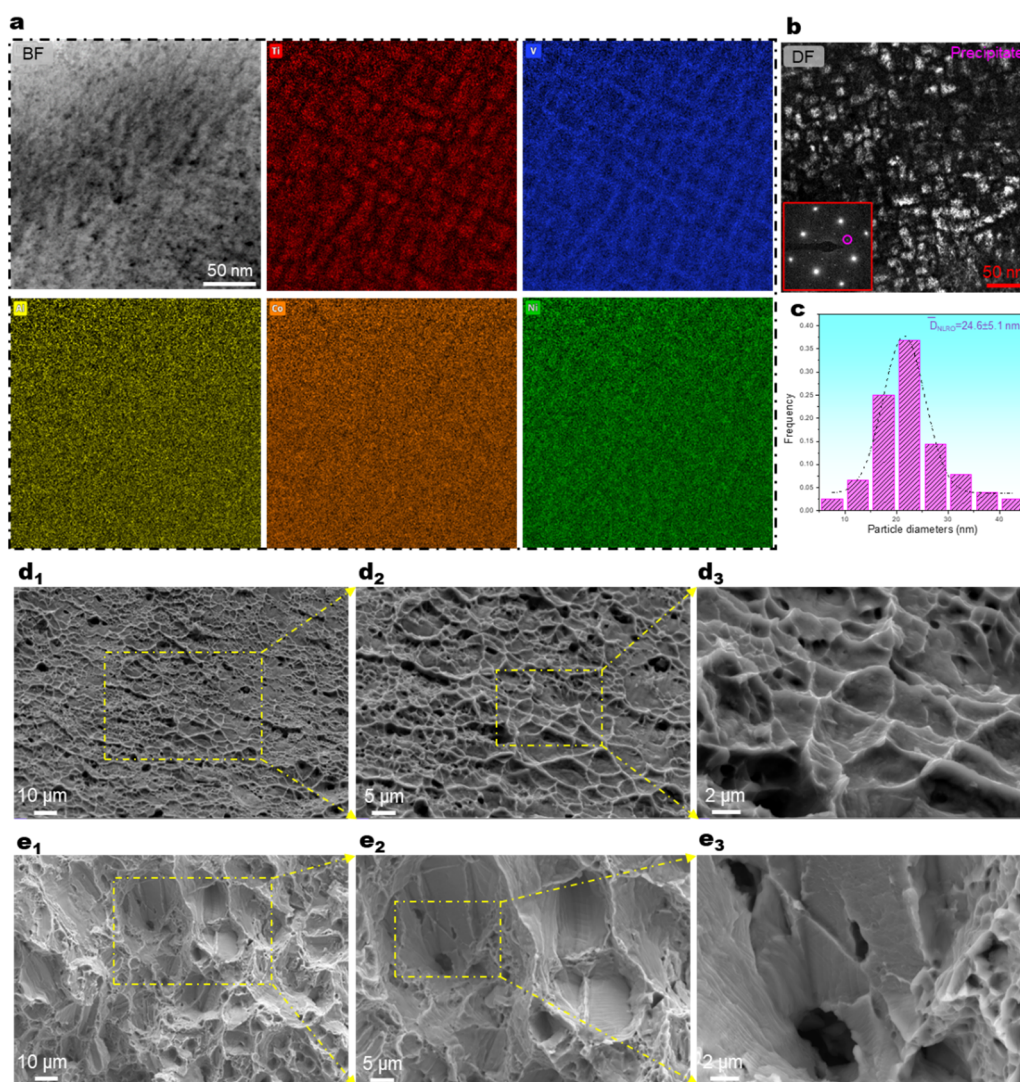


Figure S5. (a) TEM-BF image and the corresponding energy-dispersive X-ray spectroscopy (EDX) maps of the CoNiV-AlTi (24 h aged) sample, showing the Ti enrichment and V depletion in the L₁₂ precipitates. The typical modulated structure with interconnected patterns is observed, which is the feature of the spinodal decomposed microstructure. (b) Selected area diffraction pattern (SADP) and TEM-DF image of the same sample taken from the {011} superlattice spot, showing the morphology and size of L₁₂ precipitates. (c) The distribution of the size of L₁₂ precipitates, determined from the TEM-DF image. Fracture surface of (d₁₋₃) the CoNiV-AlTi sample and (e₁₋₃) the CoNiV-AlTi (24h aged) sample deformed at 87 K. The former sample is characterized by a dimple-typed ductile fracture, whereas the latter contains certain degree of embrittlement as shown from the brittle quasi-cleavage facets observed on the fracture surface.

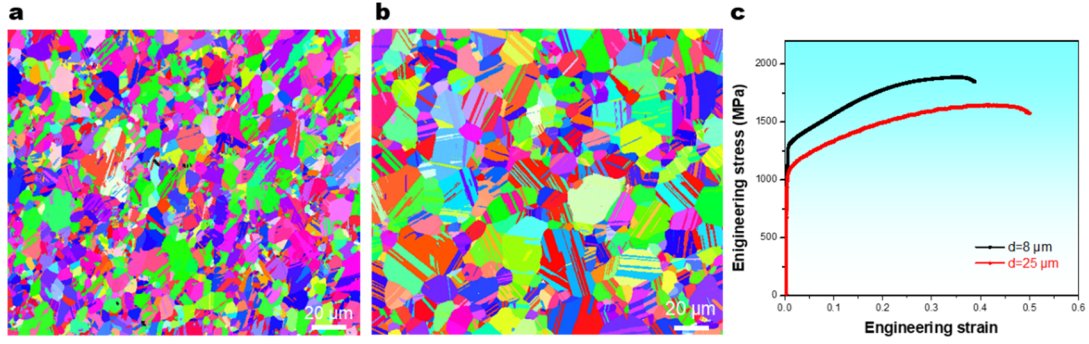


Figure S6. EBSD-IPF images of the CoNiV-AlTi sample with different grain sizes: (a) 8 μm and (b) 25 μm. (c) Engineering stress-strain curves of samples with different grain sizes tested at 87 K.

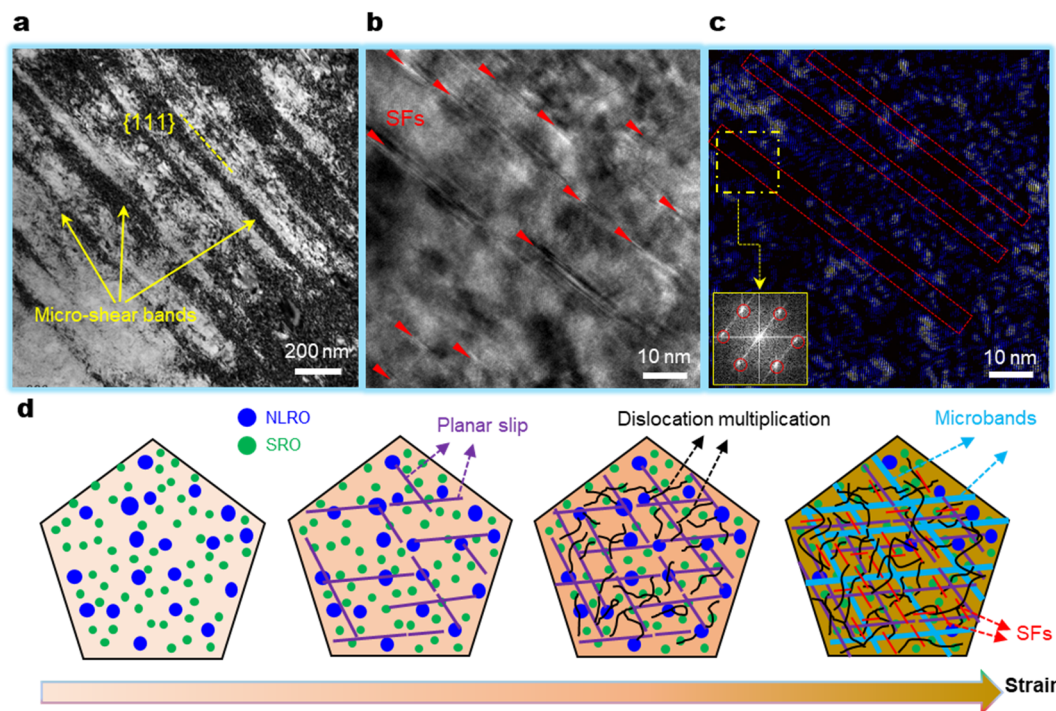


Figure S7. (a) TEM-BF micrographs of the CoNiV-AlTi alloy cryogenically deformed to 30% strain, showing a high density of micro-shear bands. (b) HRTEM image and (c) the corresponding IFFT image of a local region in (a), showing dense slip bands consisting of stacking faults within micro-shear bands and the destruction of NLRO by the slip bands. (d) Schematic diagram illustrating the plastic deformation mechanism in the CoNiV-AlTi alloy containing dual-scale chemical ordering.

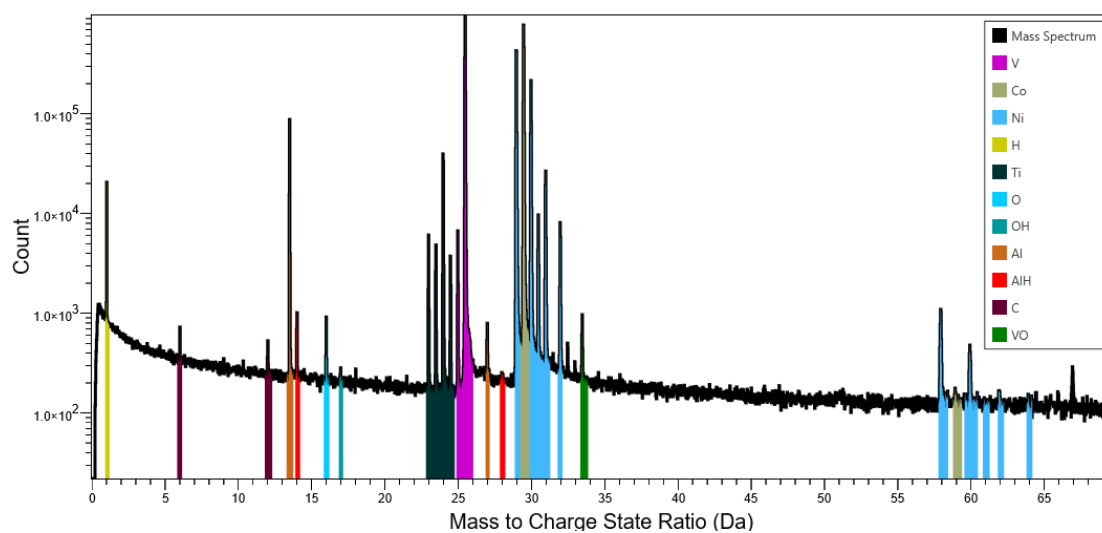


Figure S8. Typical APT time-of-flight mass spectrum with identified ions for the CoNiV-AlTi sample.

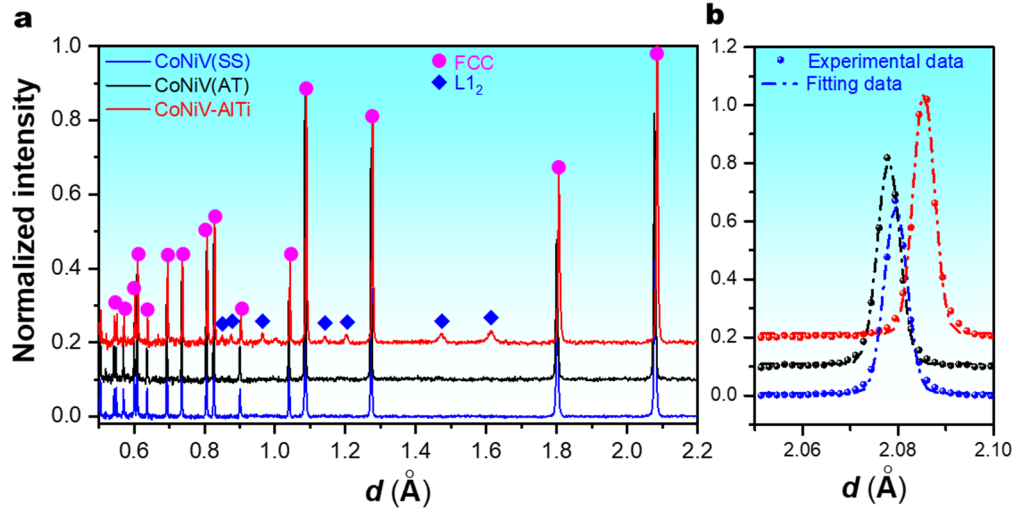


Figure S9. Neutron diffraction patterns of the CoNiV(SS), CoNiV(AT) and CoNiV-AlTi samples before deformation. The {111} peaks indicate that there is some difference in lattice parameters of the three samples (shown in the right image b).

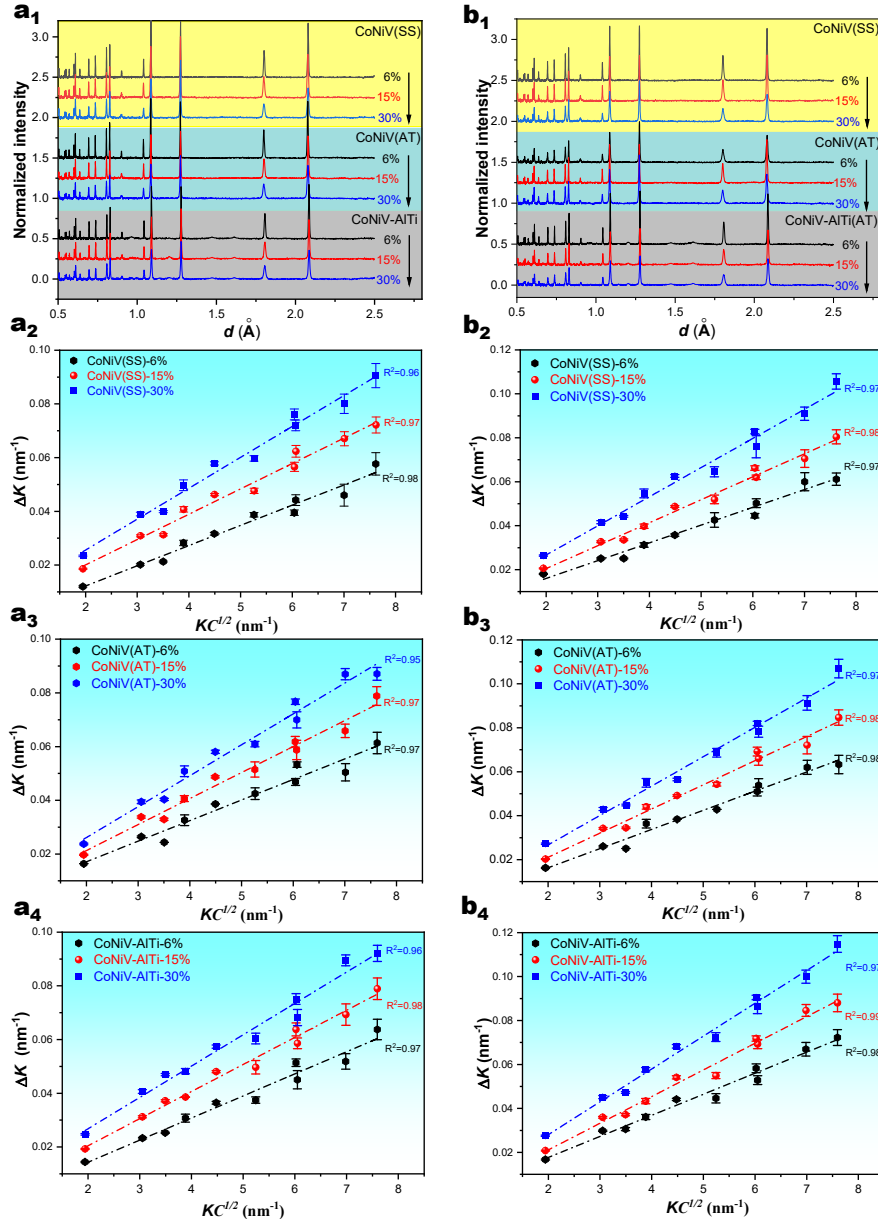


Figure S10. (a₁) Neutron diffraction profiles of the CoNiV(SS), CoNiV(AT) and CoNiV-AlTi samples deformed at different strains at 293 K. (a₂₋₄) The modified Williamson-Hall plots at the strain of 6%, 15% and 30% at 293 K, respectively. (b₁) Neutron diffraction profiles of the CoNiV(SS), CoNiV(AT) and CoNiV-AlTi samples deformed at different stages at 87 K. (b₂₋₄) The modified Williamson-Hall plots at the strain of 6%, 15% and 30% at 87 K, respectively.

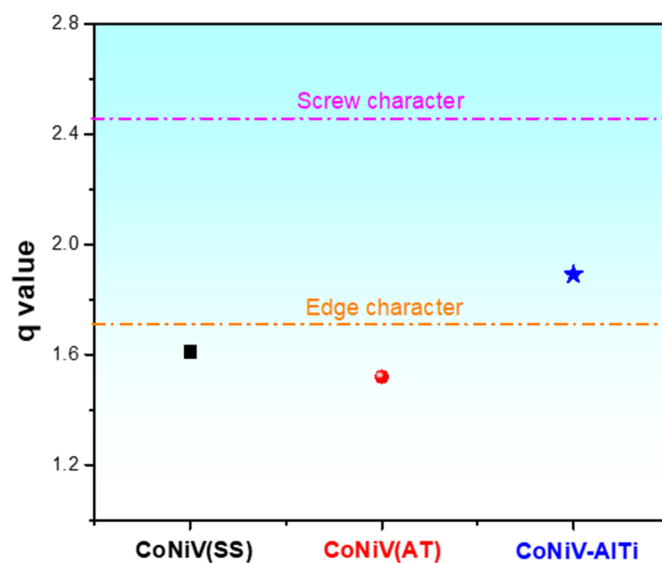


Figure S11. Dislocation characteristic parameters, q , of the CoNiV(SS), CoNiV(AT) and CoNiV-AlTi samples at 15% tensile strain at 87 K, which was calculated on the basis of the neutron diffraction data. The result indicates that the dominant dislocation type of the ordering-free CoNiV(SS) sample and the SRO-containing CoNiV(AT) sample is edge dislocation, while a higher fraction of screw dislocations are present in the CoNiV-AlTi sample at the strain of 15%.

Supplementary Table 1 Atomic radius, shear modulus, electronegativity and vacancy electron concentration (VEC) of the solute elements in the CoNiV alloy^[15, 16]

Element	Atomic radius (pm)	VEC	Crystal structure	Electronegativity	Shear Modulus (GPa)	Mixing enthalpy (kJ/mol)	
						Ni	V
Co	125	9	FCC (> 422 °C), Hexagonal (< 422 °C)	1.63	75	0	-14
Ni	124	10	FCC	1.91	76	-	-18
V	134	5	BCC	1.63	47	-	-

From a thermodynamic point of view, the driving force for forming SROs in CoNiV is originated from multiple aspects, including the fluctuation in the local strain, bonding state, electronic and magnetic interaction^[17]. The fluctuation of local strain energy in MEAs/HEAs becomes pronounced since they generally possess severe lattice distortion. The enlargement in the atomic size mismatch among solute elements would raise the variation of lattice distortion and consequently the strain energy. Therefore, the large atomic size mismatch between V and Co/Ni promotes the formation of SRO. The bonding energy, which can be simply reflected by the negative mixing enthalpy between different elements, is another important factor for the formation of SRO. The mixing enthalpy between V and Co with Ni is -14 KJ/mol and -18 KJ/mol, respectively, indicating a strong affinity between V and Co/Ni thus promoting the formation of SRO.

Supplementary Table 2 Details of the data presented in Fig. 2b.

Materials classification	Test temperature	Materials composition	Mechanical properties			
			$\sigma_{0.2}$	σ_{UTS}	TE	
FCC+SRO+NLRO (at.%)	87K	CoNiVAl ₂ Ti ₂	1172±18	1821±18	41.9±1.4	This work
FCC+SRO (at.%)	87K	CoNiV(AT)	931±19	1495±25	47.8±1.2	
FCC (at.%)	87K	CoNiV(SS)	794±26	1385±23	52.6±1.1	
FCC+Precipitates (at.%)	87K	CoNiVAl ₂ Ti ₂ (aged for 24h)	1206±32	1781±34	21.8±1.6	
Single-phase FCC MEA/HEAs (at.%)	77K	CoCrFeNi	590	1070	78	[18]
	77K	CoCrNi	860	1305	46.9	[19]
	77K	CoCrNi	520	1200	78	[20]
	77K	CoCrNi	657	1311	90	[21]
	77K	CoCrNiAl ₆ Ta ₂	786	1351	90	[22]
	77K	CoNiV	1217	1703	42.1	[23] N
	77K	CoNiV	960	1551	56.7	[23] N
	77K	CoNiV	895	1474	58.7	[23] N
	77K	CrFeCoNiPd	660	1010	69	[24]
	77K	CrFeCoNiPd	880	1220	52	[24]
	77K	CrMnFeCoNi	670	1270	72	[24]
	77K	CrMnFeCoNi	380	880	105	[24]
	77K	Cr ₂₆ Mn ₂₀ Fe ₂₀ Co ₂₀ Ni ₁₄	500	1100	62	[25]
	77K	Co ₄₀ Cr ₂₀ Ni ₃₀ Al ₅ Ti ₅	2022	2309	21.2	[26]
FCC+L1 ₂ (p) MEA/HEAs (at.%)	77K	Fe _{23.8} Co _{23.8} Ni _{23.8} Cr _{23.8} Ti _{4.8}	860	1580	46	[27] N
	77K	Co ₃₅ Ni ₃₅ Fe ₂₀ Al ₅ Ti ₅	930	1320	21	[28]
	77K	Co ₃₅ Ni ₃₅ Fe ₂₀ Al ₅ Ti ₅	1020	1460	26.4	[28]
	77K	Ni ₃₀ Co ₃₀ Fe ₁₃ Cr ₁₅ Al ₆ Ti ₆	1090	1700	51	[29] N
	77K	Co _{34.46} Cr _{32.12} Ni _{27.42} Al ₃ Ti ₃	730	1340	67	[30]
	77K	Co _{34.46} Cr _{32.12} Ni _{27.42} Al ₃ Ti ₃	980	1680	35.2	[30]
FCC+B2 MEA/HEAs (at.%)	77K	Al _{0.3} CoCrFeNi	1320	1600	17.5	[31]
	77K	Al _{0.3} CoCrFeNi	~1300	~1500	16.4	[31]
	77K	Al _{0.3} CoCrFeNi	~1300	~1500	18	[31]
	77K	Al _{0.5} CoCrFeMnNi	796	1329	30.5	[32]
	77K	AlCoCrFeNi _{2.0}	715	952	3.7	[33]
	77K	AlCoCrFeNi _{2.1}	690	1051	6.7	[33]
	77K	AlCoCrFeNi _{2.2}	705	1151	9.3	[33]
	77K	CoNiVAl ₅	1400	1900	38	[34]
	77K	CoNiVAl ₇	1350	1900	24	[34]
	77K	Al _{0.3} CoCrFeNi	730	1355	63	[35] N
TRIP HEA/MEAs (at.%)	77K	Fe ₆₀ Co ₁₅ Ni ₁₅ Cr ₁₀	600	1020	128	[36]
	77K	Fe ₆₀ Co ₁₅ Ni ₁₅ Cr ₁₀	660	1500	85	[36]
	77K	Fe ₆₀ Co ₁₅ Ni ₁₅ Cr ₁₀	600	1180	118	[36]
	77K	Fe ₄₉ Mn ₃₀ Co ₁₀ Cr ₁₀	398	1323	53	[37]
	77K	Fe ₄₉ Mn ₃₀ Co ₁₀ Cr ₁₀ N _{1.8}	1206	1620	11	[37]
	77K	Fe ₄₉ Mn ₃₀ Co ₁₀ Cr ₁	1078	1630	33.5	[37]
	77K	Fe ₆₅ Ni ₁₅ Co ₈ Mn ₈ Ti ₃ Si	1305	1800	45	[38]

	77K	Co _{17.5} Cr _{12.5} Fe ₅₅ Ni ₁₀ Mo ₄ C ₁	984	1762	54.7	[39]	
	77K	Co _{17.5} Cr _{12.5} Fe ₅₅ Ni ₁₀ Mo ₃ C ₂	1010	1978	53.3	[39]	
	77K	V ₁₀ Cr ₁₀ Co ₃₀ Fe ₄₀ Ni ₁₀	706	1256	64.4	[40]	
	77K	V ₁₀ Cr ₁₀ Co ₃₀ Fe ₄₅ Ni ₅	740	1358	71.2	[40]	
	77K	V ₁₀ Cr ₁₀ Co ₃₀ Fe ₅₀	520	1990	38.8	[40]	
	77K	(Fe ₄₀ Mn ₄₀ Co ₁₀ Cr ₁₀) _{96.7} C _{3.3}	551	1038	21	[41]	
	77K	(Fe ₄₀ Mn ₄₀ Co ₁₀ Cr ₁₀) _{96.7} C _{3.3} Ti	987	1477	51.5	[41]	
	77K	Fe ₅₀ Co ₂₅ Ni ₁₀ Al ₅ Ti ₅ Mo ₅	1305	2340	16	[42]	
	77K	Fe ₄₅ Cr ₁₀ Mn ₅ Co ₃₀ Si ₈ V ₂	457	1617	49	[43]	N
Iron base alloys (wt.%)	77K	19Mn-0.45C	680	1477	25.4	[44]	
	77K	22Mn-0.45C	646	1509	53.5	[44]	
	77K	19Mn-0.45C-2Al	759	1355	40.7	[44]	
	77K	22Mn-0.45C-2Al	811	1403	67.2	[44]	
	77K	20Mn-4Al-0.3C	698.6	1196.5	77.4	[45]	
	77K	27Mn-4Al-0.3C	729.8	1173.0	68.3	[46]	
	77K	18Cr-Ni-Mn-Si	401	1,417	13	[46]	
	77K	9Ni	980	1,201	24	[46]	
	77K	Fe-8.53Ni-0.002C	794	851	37.3	[47]	
	77K	Fe-8.53Ni-0.002C	700	1200	67	[47]	
	110K	Invar steel	600	870	50	[48]	
	77K	Fe-25Mn-4Cr-0.5C	800	1380	58	[49]	
	77K	Fe-25Cr-7Ni- 3Mo	1020	1280	45	[50]	
Other HEA alloys (at.%)	77K	TiZrHfNbTa	1547	1549	20.8	[51]	
	77K	FeCoCrNiMo _{0.2}	637	1212	71.2	[52]	
Al base alloys	77K	Al-Cu-Mn alloy	210	415	42	[53]	
	77K	1575C Al	260	470	16	[54]	
	77K	1575CAI	335	555	34	[54]	
	77K	AA2195	600	680	7	[55]	
	77K	AA2195	615	670	7	[55]	
	77K	AA5083	320	420	25	[48]	
Ni base alloys	100K	Haynes 282	700	1200	19	[56]	
	77K	GH3536	593	1198	76	[57]	
	77K	Alloy 625	550	1134	89.4	[58]	
	77K	Haynes 282	750	1350	15	[59]	
	77K	INCONEL 718	1327	1640	12.5	[59]	
Ti base alloys	77K	Ti-3Al-3Mo-3Zr alloy	1290	1310	10.5	[60]	
	77K	Ti-15Mo-2Al	1055	1536	22	[61]	
	77K	Ti-5Al-1V-1Sn-1Zr-0.8Mo	1252.3	1326.3	25	[62]	
	77K	Ti-6Al-4V	1600	1680	10.5	[63]	

160 N represents that no extensometer was used during the tests (the total elongation was overestimated).

161 $\sigma_{0.2}$: yield strength, σ_{UTS} : ultimate shear strength, TE: total elongation

References:

- [1] Ungár T., Révész Á., Borbély A. Dislocations and grain size in electrodeposited nanocrystalline Ni determined by the Modified Williamson–Hall and Warren–Averbach procedures. *J. Appl. Crystallogr.* 31(4), 554-558 (1998).
- [2] Liu L., Yu Q., Wang Z., et al. Making ultrastrong steel tough by grain-boundary delamination. *Science* 368(6497), 1347-1352 (2020).
- [3] Ungár T., Dragomir I., Révész Á., et al. The contrast factors of dislocations in cubic crystals: the dislocation model of strain anisotropy in practice. *J. Appl. Crystallogr.* 32(5):992-1002 (1999).
- [4] Tang L., Jiang F. Q., Wróbel J. S., et al. In situ neutron diffraction unravels deformation mechanisms of a strong and ductile FeCrNi medium entropy alloy. *J. Mater. Sci. Tech.* 116, 103-120 (2022).
- [5] Naeem M., He H., Harjo S., et al. Temperature-dependent hardening contributions in CrFeCoNi high-entropy alloy. *Acta Mater.* 221, 117371 (2021).
- [6] Qiu S., Zheng G. P., Jiao Z. B. Alloying effects on phase stability, mechanical properties, and deformation behavior of CoCrNi-based medium-entropy alloys at low temperatures. *Intermetallics* 140, 107399 (2022).
- [7] Wang Y., Liu B., Yan K., et al. Probing deformation mechanisms of a FeCoCrNi high-entropy alloy at 293 and 77 K using in situ neutron diffraction. *Acta Mater.* 154:79-89 (2018).
- [8] Ren J., Zhang Y., Zhao D., et al. Strong yet ductile nanolamellar high-entropy alloys by additive manufacturing. *Nature* 608(7921), 62-68 (2022).
- [9] Zhao Y. L., Yang T., Tong Y., et al. Heterogeneous precipitation behavior and stacking-fault-mediated deformation in a CoCrNi-based medium-entropy alloy. *Acta Mater.* 138, 72-82 (2017).
- [10] He J. Y., Wang H., Huang H. L., et al. A precipitation-hardened high-entropy alloy with outstanding tensile properties. *Acta Mater.* 102:187-196 (2016).
- [11] Ming K. S., Bi X. F., Wang J. Realizing strength-ductility combination of coarse-grained $\text{Al}_{0.2}\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.3}$ alloy via nano-sized, coherent precipitates. *Int. J. Plasticity* 100, 177-191 (2018).
- [12] Zhang R. P., Zhao S. T., Ophus C., et al. Direct imaging of short-range order and its impact on deformation in Ti-6Al. *Sc. Adv.* 5(12), x2799 (2019).
- [13] Ardell. A. J. Precipitation Hardening. *Metall. Trans. A* 16A, 1985-2131 (1985).
- [14] Yao N., Lu T. W., Feng K., et al. Ultrastrong and ductile additively manufactured precipitation-hardening medium-entropy alloy at ambient and cryogenic temperatures. *Acta Mater.* 236, 118142 (2022).
- [15] Jiang L., Yang H., Yee J. K., et al. Toughening of aluminum matrix nanocomposites via spatial arrays of boron carbide spherical nanoparticles. *Acta Mater.* 103, 128-140 (2016).
- [16] Salishchev G. A., Tikhonovsky M. A., Shaysultanov D. G., et al. Effect of Mn and V on structure and mechanical properties of high-entropy alloys based on CoCrFeNi system. *J. Alloy. Comp.* 591, 11-21 (2014).
- [17] Wu Y., Zhang F., Yuan X., et al. Short-range ordering and its effects on mechanical properties of high-entropy alloys. *J. Mater. Sci. Tech.* 62, 214-220 (2021).
- [18] Liu J. P., Guo X. X., Lin Q. Y., et al. Excellent ductility and serration feature of metastable CoCrFeNi high-entropy alloy at extremely low temperatures. *Sci. China. Mater.* 62(6), 853-

863 (2019).

[19] Han B. L., Zhang C. C., Feng K., et al. Additively manufactured high strength and ductility CrCoNi medium entropy alloy with hierarchical microstructure. *Mater. Sci. Eng. A* 820, 141545 (2021).

[20] Liu X. R., Feng H., Wang J., et al. Mechanical property comparisons between CrCoNi medium-entropy alloy and 316 stainless steels. *J. Mater. Sci. Tech.* 108, 256-269 (2022).

[21] Gludovatz B., Hohenwarter A., Thurston K. V., et al. Exceptional damage-tolerance of a medium-entropy alloy CrCoNi at cryogenic temperatures. *Nat. Com.* 7(1) (2016).

[22] Zhang D. D., Zhang J. Y., Kuang J., et al. Superior strength-ductility synergy and strain hardenability of Al/Ta co-doped NiCoCr twinned medium entropy alloy for cryogenic applications. *Acta Mater.* 220, 117288 (2021).

[23] Yang D. C., Jo Y. H., Ikeda Y., et al. Effects of cryogenic temperature on tensile and impact properties in a medium-entropy VCoNi alloy. *J. Mater. Sci. Tech.* 90, 159-167 (2021).

[24] Ding Q. Q., Zhang Y., Chen X. F., et al. Tuning element distribution, structure and properties by composition in high-entropy alloys. *Nature* 574(7777), 223-227 (2019).

[25] Ming K. S., Li B., Bai L. C., et al. Dynamically reversible shear transformations in a CrMnFeCoNi high-entropy alloy at cryogenic temperature. *Acta Mater.* 232, 117937 (2022).

[26] Li W. P., Chou T. H., Yang T., et al. Design of ultrastrong but ductile medium-entropy alloy with controlled precipitations and heterogeneous grain structures. *Appl. Mater. Today* 23, 101037 (2021).

[27] Tong Y., Chen D., Han B., et al. Outstanding tensile properties of a precipitation-strengthened FeCoNiCrTi_{0.2} high-entropy alloy at room and cryogenic temperatures. *Acta Mater.* 165, 228-240 (2019).

[28] Górecki K., Bała P., Bednarczyk W., et al. Cryogenic behaviour of the Al₅Ti₅Co₃₅Ni₃₅Fe₂₀ multi-principal component alloy. *Mater. Sci. Eng. A* 745, 346-352 (2019).

[29] Yang T., Zhao Y. L., Luan J. H., et al. Nanoparticles-strengthened high-entropy alloys for cryogenic applications showing an exceptional strength-ductility synergy. *Scripta Mater.* 164, 30-35 (2019).

[30] Zhang Z. H., Wang W., Qin S., et al. Dual heterogeneous structured medium-entropy alloys showing a superior strength-ductility synergy at cryogenic temperature. *J. Mater. Res. Tech.* 17, 3262-3276 (2022).

[31] Li D. Y., Li C. X., Feng T., et al. High-entropy Al_{0.3}CoCrFeNi alloy fibers with high tensile strength and ductility at ambient and cryogenic temperatures. *Acta Mater.* 123, 285-294 (2017).

[32] Park J. M., Moon J., Bae J. W., et al. Role of BCC phase on tensile behavior of dual-phase Al_{0.5}CoCrFeMnNi high-entropy alloy at cryogenic temperature. *Mater. Sci. Eng. A* 746, 443-447 (2019).

[33] Lu Y. P., Gao X. Z., Jiang L., et al. Directly cast bulk eutectic and near-eutectic high entropy alloys with balanced strength and ductility in a wide temperature range. *Acta Mater.* 124, 143-150 (2017).

[34] Nutor R. K., Cao Q. P., Wei R., et al. A dual-phase alloy with ultrahigh strength-ductility synergy over a wide temperature range. *Sci. Adv.* 7(34), i4404 (2021).

[35] Li Q., Zhang T. W., Qiao J. W., et al. Superior tensile properties of Al_{0.3}CoCrFeNi high entropy alloys with B2 precipitated phases at room and cryogenic temperatures. *Mater. Sci. Eng. A* 767, 138424 (2019).

- [36] Bae J. W., Seol J. B., Moon J., et al. Exceptional phase-transformation strengthening of ferrous medium-entropy alloys at cryogenic temperatures. *Acta Mater.* 161, 388-399 (2018).
- [37] He Z. F., Jia N., Wang H. W., et al. Synergy effect of multi-strengthening mechanisms in FeMnCoCrN HEA at cryogenic temperature. *J. Mater. Sci. Tech.* 86, 158-170 (2021).
- [38] Haftlang F., Asghari-Rad P., Moon J., et al. Simultaneous effects of deformation-induced plasticity and precipitation hardening in metastable non-equiatomic FeNiCoMnTiSi ferrous medium-entropy alloy at room and liquid nitrogen temperatures. *Scripta Mater.* 202:114013 (2021).
- [39] Kwon H., Moon J., Bae J. W., et al. Precipitation-driven metastability engineering of carbon-doped CoCrFeNiMo medium-entropy alloys at cryogenic temperature. *Scripta Mater.* 188, 140-145 (2020).
- [40] Kim D. G., Jo Y. H., Yang J., et al. Ultrastrong duplex high-entropy alloy with 2 GPa cryogenic strength enabled by an accelerated martensitic transformation. *Scripta Mater.* 171, 67-72 (2019).
- [41] Tang K., Wu Y. K., Wei R., et al. Achieving superior cryogenic tensile properties in a Ti-doped (Fe₄₀Mn₄₀Co₁₀Cr₁₀)_{96.7}C_{3.3} high-entropy alloy by recovering deformation twinning. *Mater. Sci. Eng. A* 808, 140927 (2021).
- [42] Kwon H., Sathiyamoorthi P., Karthik G. M., et al. 2.3 GPa cryogenic strength through thermal-induced and deformation-induced body-centered cubic martensite in a novel ferrous medium entropy alloy. *Scripta Mater.* 204, 114157 (2021).
- [43] Yang J., Jo Y. H., An W., et al. Effects of deformation-induced martensitic transformation on cryogenic fracture toughness for metastable Si₈V₂Fe₄₅Cr₁₀Mn₅Co₃₀ high-entropy alloy. *Acta Mater.* 225, 117568 (2022).
- [44] Sohn S. S., Hong S., Lee J., et al. Effects of Mn and Al contents on cryogenic-temperature tensile and Charpy impact properties in four austenitic high-Mn steels. *Acta Mater.* 100, 39-52 (2015).
- [45] Li C. S., Li K., Dong J. B., et al. Mechanical behaviour and microstructure of Fe-20/27Mn-4Al-0.3C low magnetic steel at room and cryogenic temperatures. *Mater. Sci. Eng. A* 809, 140998 (2021).
- [46] Anoop C. R., Singh R. K., Kumar R. R., et al. A Review on Steels for Cryogenic Applications. *Mater. Perform. Charact.* 10(2), 20200193 (2021).
- [47] Kwon K. H., Yi I. C., Ha Y., et al. Origin of intergranular fracture in martensitic 8Mn steel at cryogenic temperatures. *Scripta Mater.* 69(5), 420-423 (2013).
- [48] Park W S, Chun M S, Han M S, et al. Comparative study on mechanical behavior of low temperature application materials for ships and offshore structures: Part I—Experimental investigations. *Mater. Sci. Eng. A* 528(18), 5790-5803 (2011).
- [49] Luo Q., Wang H. H., Li G. Q., et al. On mechanical properties of novel high-Mn cryogenic steel in terms of SFE and microstructural evolution. *Mater. Sci. Eng. A* 753, 91-98 (2019).
- [50] Elkot M. N., Sun B., Zhou X., et al. Hydrogen-assisted decohesion associated with nanosized grain boundary κ -carbides in a high-Mn lightweight steel. *Acta Mater.* 241, 118392 (2022).
- [51] Wang S. B., Chen S. H., Jia Y. W., et al. FCC-L1₂ ordering transformation in equimolar FeCoNiV multi-principal element alloy. *Mater. Des.* 168, 107648 (2019).
- [52] Tang L., Yan K., Cai B., et al. Deformation mechanisms of FeCoCrNiMo_{0.2} high entropy alloy at 77 and 15 K. *Scripta Mater.* 178, 166-170 (2020).

- [53] Cheng W. J., Liu W., Fan X. B., et al. Cooperative enhancements in ductility and strain hardening of a solution-treated Al-Cu-Mn alloy at cryogenic temperature. *Mater. Sci. Eng. A* 790, 139707 (2020).
- [54] Zhemchuzhnikova D., Mogucheveva A., Kaibyshev R. Mechanical properties and fracture behavior of an Al-Mg-Sc-Zr alloy at ambient and subzero temperatures. *Mater. Sci. Eng. A* 565, 132-141 (2013).
- [55] Nayan N., Narayana Murty S. V., Jha A. K., et al. Mechanical properties of aluminium-copper-lithium alloy AA2195 at cryogenic temperatures. *Mater. Des.* 58, 445-450 (2014).
- [56] Jaladurgam N. R., Kabra S., Colliander M. H. Macro- and micro-mechanical behaviour of a γ' strengthened Ni-based superalloy at cryogenic temperatures. *Mater. Des.* 209, 109954 (2021).
- [57] Ding Q., Bei H., Wei X., et al. Nano-twin-induced exceptionally superior cryogenic mechanical properties of a Ni-based GH3536 (Hastelloy X) superalloy. *Mater. Today Nano*, 14:100110 (2021).
- [58] Nordström J., Siriki R., Calmunger M., et al. TWIP and Fracture Behavior in the Superalloy 625 at Room and Cryogenic Temperatures. *Procedia Structural Integrity* 23, 457-462 (2019).
- [59] Yoshinori O., Tetsumi Y., Hideshi S. High-Cycle Fatigue Properties at Cryogenic Temperatures in INCONEL 718 Nickel-based Superalloy. *Mater. Trans.* 45(2), 342-345 (2004).
- [60] Zang M. C., Niu H. Z., Yu J. S., et al. Cryogenic tensile properties and deformation behavior of a fine-grained near alpha titanium alloy with an equiaxed microstructure. *Mater. Sci. Eng. A* 840, 142952 (2022).
- [61] Zang M. C., Niu H. Z., Zhang H. R., et al. Cryogenic tensile properties and deformation behavior of a superhigh strength metastable beta titanium alloy Ti-15Mo-2Al. *Mater. Sci. Eng. A* 817, 141344 (2021).
- [62] Wang Q., Ren J. Q., Zhang B. B., et al. Simultaneously improved strength and elongation at cryogenic temperature in Ti-5Al-1V-1Sn-1Zr-0.8Mo alloy with a bimodal structure. *Mater. Sci. Eng. A* 824, 141792 (2021).
- [63] Zhao W., Su W., Li L., et al. Evolution of mechanical properties of Ti-6Al-4V alloy in the temperature range of 20 to -196 °C. *Met. Mater. Int.* 27(9), 3214-3224 (2021).