

# Tuning the grain and domain sizes to achieve superior room-temperature tensile ductility in a B2-ordered refractory $\text{Al}_{15}\text{Nb}_{40}\text{Ti}_{40}\text{V}_5$ medium-entropy alloy

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## ABSTRACT

Herein, we showed that the grain size, rather than the domain size, controlled room-temperature properties of a B2-ordered refractory  $\text{Al}_{15}\text{Nb}_{40}\text{Ti}_{40}\text{V}_5$  medium-entropy alloy. Grain refinement to 20  $\mu\text{m}$  at any size of B2 domains resulted in elongation of  $\sim 50\%$ , which was superior to all the reported refractory high/medium-entropy alloys.

## 1. Introduction

Refractory high/medium-entropy alloys (RH/MEAs) are of great interest for the researchers worldwide due to their capacity to withstand extreme loads and oxidation at temperatures exceeding the operation limit of Ni-based superalloys [1–7]. However, most of RH/MEAs suffer from brittleness at ambient-to-medium temperatures under tension [8, 9] or even compression [2,10–13] that hinders their industrial-scale structural applications. Until 2014, only one inherently ductile RHEA, namely, an equiatomic HfNbTaTiZr alloy with a body-centred cubic (bcc) structure [14–16], was discovered. The HfNbTaTiZr alloy could be processed by a simple routine including cold rolling and subsequent annealing [17]. Applying such thermomechanical treatment, Juan et al. [18] refined the grain size of this alloy and simultaneously improved its strength and ductility. Although the grain boundary strengthening in the HfNbTaTiZr RHEA was less effective than that of face-centred cubic (fcc) H/MEAs and austenitic steels [19], it remained an attractive way to achieve advanced and, most importantly, balanced mechanical performance compared to the secondary phase hardening [20] leading to reduced ductility [21].

Since 2014, many ductile RH/MEAs have been reported [22–45], and, among them, Al-containing alloys attracted particular attention [23,29,35,37–40,44,45], as some of the latter demonstrated better mechanical properties compared to Al-free counterparts owing to a B2

(ordered bcc) structure that appeared in a form of B2 domains [37–39, 44,45]. Meantime, most of the data are still presented for either unprocessed, as-cast state, or for the processed state with a certain grain size, thus making the estimation of grain boundary strengthening unreliable. In the case of B2 domains, which size can range from  $<1$  nm to tens and hundreds of nanometers depending on the chemical composition [37–39,44,45], it is also unclear how this parameter affects the strength and ductility, especially considering scarce experimental data on intermetallic alloys that suggest that the lower size of ordered domains led to the higher strength [46–48]. Thus, it seems highly important to evaluate the effect of both grain and domain sizes on the mechanical properties of these Al-containing B2-ordered RH/MEAs more systematically.

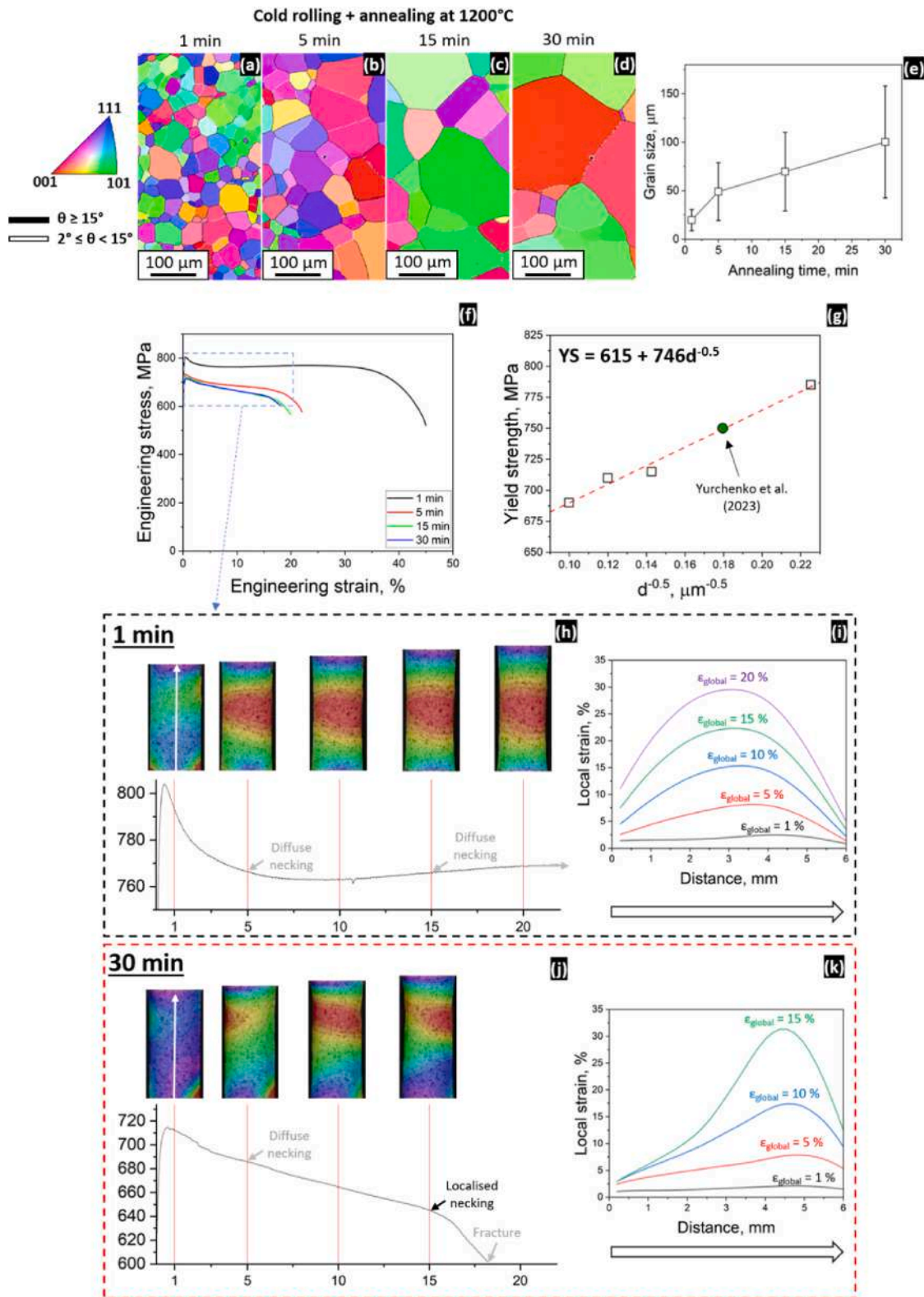
To address this issue, we comprehensively investigated the room-temperature tensile behaviour of recently introduced  $\text{Al}_{15}\text{Nb}_{40}\text{Ti}_{40}\text{V}_5$  (at.%) RMEA with a weakly B2-ordered structure [39], in which both grain and B2 domain sizes could be tailored separately by varying processing (annealing treatment) conditions.

## 2. Materials and methods

The alloy with a nominal composition of  $\text{Al}_{15}\text{Nb}_{40}\text{Ti}_{40}\text{V}_5$  was produced by vacuum arc melting of pure ( $>99.9$  wt%) metals; the actual composition of the alloy is presented in Table S1, Supplementary

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**Fig. 1.** Characterisation of the  $\text{Al}_{15}\text{Nb}_{40}\text{Ti}_{40}\text{V}_5$  alloy annealed at 1200 °C for 1–30 min: (a–d) – Inverse Pole Figure (IPF) maps, showing typical microstructures after annealing; (e) – dependence of grain size on annealing time; (f) – engineering stress–strain curves obtained during room-temperature tensile tests; (g) – dependence of yield strength on the inverse square root of grain size, including data from Ref. [39], with the resulted Hall-Petch relation obtained by linear fitting; (h) – enlarged part of the stress–strain curve of the small-grained specimen and DIC snapshots of gauge section, corresponded to certain values of the global strain,  $\epsilon_{\text{global}}$ ; (i) – local strain distribution in the small-grained specimen along the gauge length (denoted with white arrow in the first DIC snapshot (h)) at corresponding values of the  $\epsilon_{\text{global}}$ ; (j) – enlarged part of the stress–strain curve of the coarse-grained specimen supplied by DIC snapshots of gauge section, corresponded to certain values of the  $\epsilon_{\text{global}}$ ; (k) – local strain distribution in the coarse-grained specimen along the gauge length (denoted with white arrow in the first DIC snapshot (j)) at corresponding values of the  $\epsilon_{\text{global}}$ .

**Table 1**

Yield strength,  $YS$ , ultimate tensile strength,  $UTS$ , and elongation at fracture,  $EF$ , obtained during room-temperature tensile tests of the  $Al_{15}Nb_{40}Ti_{40}V_5$  alloy annealed at 1200 °C for 1–30 min.

Annealing at 1200 °C	$YS$ , MPa	$UTS$ , MPa	$EF$ , %
1 min	785 ± 15	805 ± 10	45.0 ± 1.8
5 min	715 ± 5	735 ± 5	22.0 ± 1.5
15 min	710 ± 5	720 ± 10	20.0 ± 0.8
30 min	690 ± 5	715 ± 10	18.2 ± 1.4

material. The as-cast ingot was subjected to a thermomechanical treatment including cold rolling to 80% of thickness and subsequent annealing in a Nabertherm furnace at 1200 °C for 1, 5, 15, and 30 min followed by water quenching. Some specimens annealed at 1200 °C for 1 min were further annealed at 800 °C for 5, 15, and 30 min followed by water quenching. Prior to annealing, the specimens were sealed in vacuumed ( $10^{-2}$  torr) tubes filled with titanium chips to prevent any oxidation.

Tensile tests of dog-bone specimens with the gauge dimensions of  $6 \times 3 \times 1 \text{ mm}^3$  were performed at room-temperature at a constant strain rate of  $10^{-3} \text{ s}^{-1}$  using an Instron 5882 machine. The digital image correlation (DIC) technique was employed to visualise the distribution of local strains produced during the tensile tests. The in-plane Lagrangian strains were measured using a commercial Vic-3D™ system (Correlated Solutions, Inc) [37,39].

Microstructural investigations were performed using electron backscatter diffraction (EBSD; FEI Quanta 600 FEG) and transmission electron microscopy (TEM; JEM JEOL-2100). The average grain or B2 domain sizes were estimated using the linear intercept method [49].

### 3. Results and discussion

#### 3.1. Effect of grain size

Fig. 1 collects data on the microstructure and corresponding mechanical properties of the  $Al_{15}Nb_{40}Ti_{40}V_5$  RMEA annealed at 1200 °C for 1–30 min. According to EBSD analysis, annealing led to the formation of fully recrystallised microstructures (Fig. 1(a–d)), which average grain sizes increased with the annealing time from  $\sim 20 \mu\text{m}$  after 1 min to  $\sim 100 \mu\text{m}$  after 30 min (Fig. 1(e)). TEM studies revealed close sizes of B2 domains ( $\sim 40 \text{ nm}$ ; Fig. S1, Supplementary material) and no secondary phase particles, while gas fusion analysis showed comparative levels of contamination (Table S2, Supplementary material) for each annealing time, thereby excluding other (than grain size) factors which could affect the mechanical properties.

Fig. 1(f) demonstrates engineering tensile stress-strain curves of the specimens with different grain sizes; Table 1 summarises yield strength,  $YS$ , ultimate strength,  $UTS$ , and elongation at fracture,  $EF$ , obtained during the tests. The small-grained specimen (referred to as 1 min in Fig. 1(f)) showed the highest  $YS$ ,  $UTS$ , and  $EF$ . The grain growth up to  $50 \mu\text{m}$  (5 min) led to a steep degradation of mechanical properties, especially ductility. The  $EF$  value of the  $50 \mu\text{m}$ -specimen was twice lower than that of the  $20 \mu\text{m}$ -specimen. Meantime, the further grain growth up to  $70$ – $100 \mu\text{m}$  (15–30 min) resulted in more gradual softening and ductility reduction (Fig. 1(f), Table 1).

The dependence between the  $YS$  and grain sizes, including our previous data [39], was found (Fig. 1(g)) to be properly described by a linear function and agreed with the well-known Hall-Petch relation [50]:

$$\sigma_{YS} = \sigma_0 + k_y d^{-1/2} \quad (1)$$

where  $\sigma_0$  is a friction stress,  $k_y$  is the Hall-Petch coefficient, and  $d$  is the grain size. We found that  $\sigma_0 = 615 \text{ MPa}$  and  $k_y = 746 \text{ MPa } \mu\text{m}^{-1/2}$ . The  $k_y$  value determined for the  $Al_{15}Nb_{40}Ti_{40}V_5$  RMEA was  $\sim 3$  times higher than that of the  $HfNbTaTiZr$  RHEA [18,19], indicating a more

pronounced grain boundary strengthening in the alloy studied. Still, this value was smaller compared to some other RH/MEAs [51–53].

The alteration of post-yielding behaviour with an increase in the grain size should also be noted. In all the specimens, we observed a short strain-hardening stage before attaining the  $UTS$  then followed by a pronounced softening stage (Fig. 1(f)). But, if, in the small-grained specimen, this softening reached an inflection point, after which slight strain hardening was recovered, in the specimens with the larger grain sizes, the softening stage was continuous, leading to a much faster failure.

To get a better perception of such distinct behaviours, we applied the DIC method during testing (Fig. 1(h–k)). Snapshots of the gauge sections taken at certain global strains,  $\epsilon_{\text{global}}$ , showed that the plastic deformation was non-uniform in the specimens both with the smallest ( $20 \mu\text{m}$ ; 1 min) and the largest ( $100 \mu\text{m}$ ; 30 min) grain sizes; however, the level of this localisation differed notably. Independently on the grain size, the plastic deformation up to  $\epsilon_{\text{global}} = 5\%$  was accompanied by the formation of diffuse necking, as seen from both DIC snapshots and the local strain distributions. Meantime, with the further increase in the  $\epsilon_{\text{global}}$  up to 15%, the local strain distribution indicated that the diffuse necking still preserved in the  $20 \mu\text{m}$ -specimen, yet, in the  $100 \mu\text{m}$ -specimen, it evolved into localised necking, judging from the sharpening of the local strain distribution (Fig. 1(h–k)).

Apparently, such a difference in the deformation behaviour could stem from the distinct microstructural response to straining. We have examined the near-fracture regions of the tensile specimens with various grain sizes (Fig. 2). EBSD analysis showed that the  $20 \mu\text{m}$ -specimen was deformed more homogeneously compared to the specimens with larger grain sizes. Similar to conventional alloys [54–56], Kernel Average Misorientation (KAM) maps (Fig. 2) revealed that the small-grained specimen contained high density of geometrically necessary dislocations (GNDs) within the grain interiors, while, in the coarse-grained specimens, GNDs accumulated near the grain boundaries mainly. The higher density of GNDs and their more homogeneous distribution in the small-grained specimen indicated better compatibility and coordination of plastic deformation without severe localisation at both micro- and macro-level (localised necking) [56]. Meanwhile, the coarse-grained specimens with GNDs located nearby the grain boundaries had lesser possibilities to accommodate strains that arose during the tensile load resulting in a faster formation of localised necking followed by a premature fracture [56].

#### 3.2. Effect of B2 domain size

For the small-grained state, which showed the best mechanical properties, we also evaluated the effect of B2 domain size. To manipulate the latter parameter, we additionally annealed the specimens at 800 °C for various times. Before annealing (this state is denoted as 0 min hereafter), the grain interiors consisted of profuse B2 domains (white entities) with a size of  $\sim 40 \text{ nm}$  separated by antiphase domain boundaries (APDBs; dark interlayers) (Fig. 3(a)). After annealing at 800 °C for 5, 15, and 30 min, B2 domains grew up to  $\sim 105$ , 210, and 430 nm, respectively (Fig. 3(b–e)). The existing data suggest that the coarsening of B2 domains could occur without the alternating degree of order [57]. Besides, no secondary phases, grain growth (Fig. S2, Supplementary material), or changes in the contamination level (Table S3, Supplementary material) were detected, thus omitting other (than B2 domain size) factors that could impact the mechanical performance.

Unlike the grain size, the variations in the B2 domain sizes had almost no effect on the mechanical properties (Fig. 3(f), Table 2). At all the B2 domain sizes, we found very close values of  $YS$ ,  $UTS$ , and  $EF$ ; however, small deviations of  $EF$  should be noted. We did not find any correlation between the  $YS$  and B2 domain sizes (Fig. 3(g)). No significant difference in the post-yielding behaviour was also revealed. Similar to the specimens with the smallest B2 domains (Fig. 3(h)), the stress-strain curves of the specimens with the largest B2 domains contained

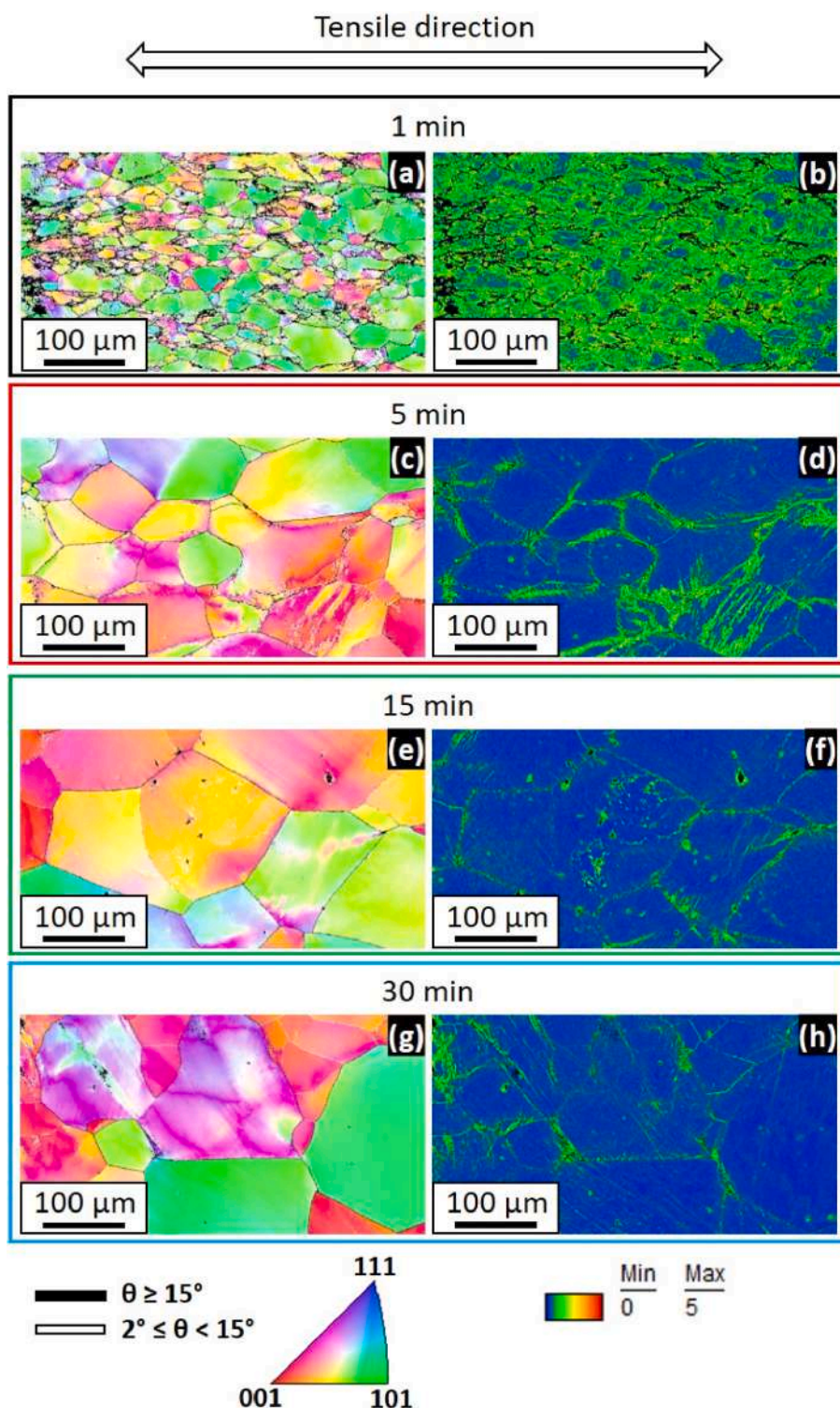
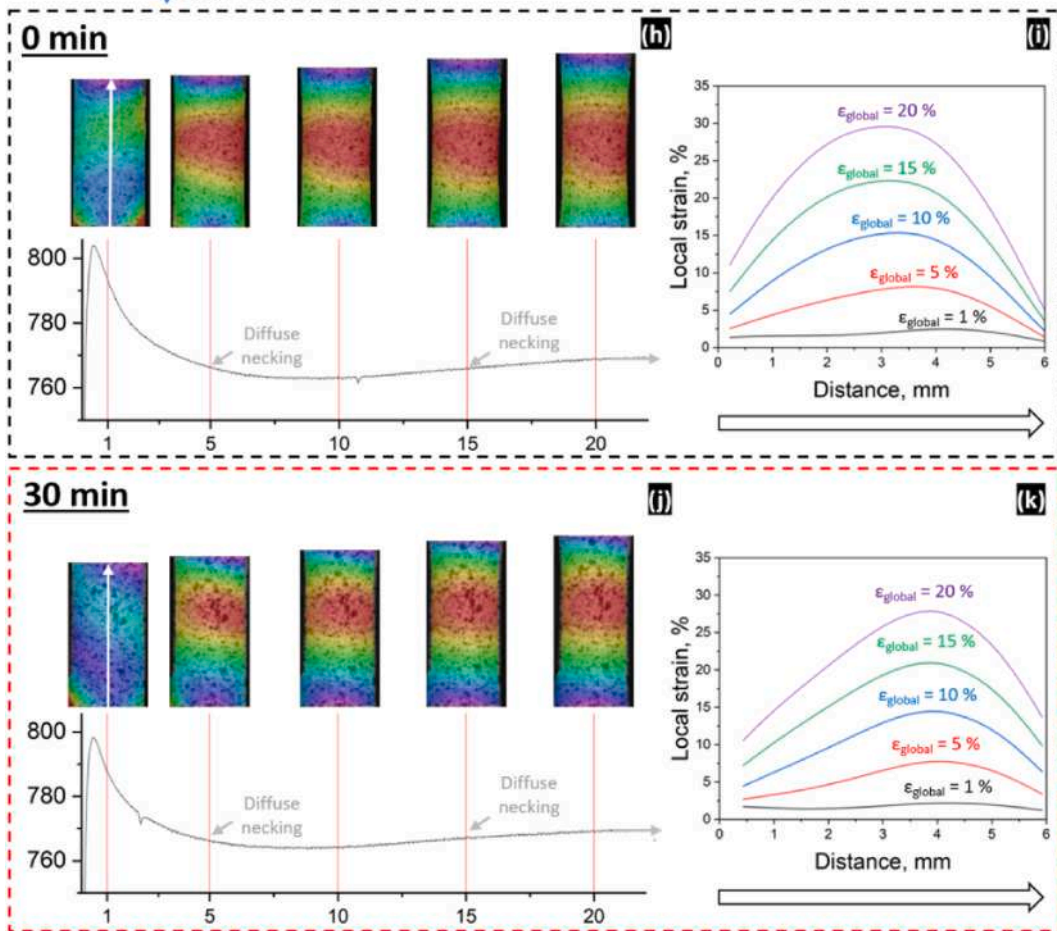
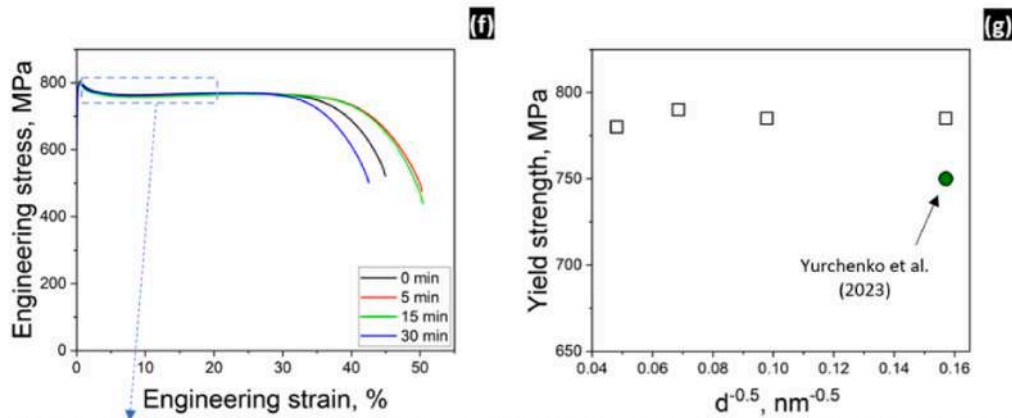
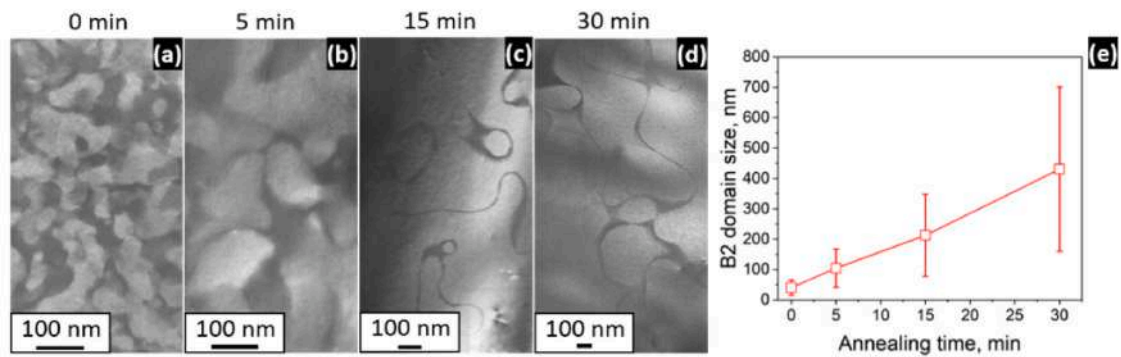


Fig. 2. Characterisation of the near-fracture regions of tensile specimens of the  $Al_{15}Nb_{40}Ti_{40}V_5$  alloy annealed at 1200 °C for 1 (a, b), 5 (c, d), 15 (e, f), and 30 (g, h) min: (a, c, e, g) – IPF maps; (b, d, f, h) – KAM maps.

a short strain hardening stage followed by an exponential-like decay of the flow stress with the formation of the diffuse necking, and then reaching the inflection point at the  $\epsilon_{global} = 10\%$ , after which minor strengthening stage reappeared (Fig. 3(j)). According to the local strain distribution, the diffuse necking persisted in the specimens with the large B2 domains even after achieving the  $\epsilon_{global} = 15\%$  (Fig. 3(i, k)), a critical value for the localised necking in the coarse-grained specimens.

Scarce experimental data reported that the size of ordered domains, which was controlled by isothermal annealing, could affect mechanical properties in such a fashion that their coarsening led to a lower strength [46–48]. Contrarily, we found that the B2 domain size, at a constant degree of order, had no notable influence on the strength-ductility synergy and deformation behaviour. The detailed TEM studies showed almost no difference in the spatial distribution of dislocations in the

Cold rolling + annealing at 1200°C, 1 min + annealing at 800°C



(caption on next page)

**Fig. 3.** Characterisation of the  $\text{Al}_{15}\text{Nb}_{40}\text{Ti}_{40}\text{V}_5$  alloy after annealing at 1200 °C for 1 min and additional annealing at 800 °C for 0–30 min: (a–d) – dark-field TEM images taken at {100} superlattice spots in a  $\langle 001/011 \rangle$  zone axis, showing a typical fine structure within the grain interiors, consisted of the B2 domains (white entities) and APDBs (dark interlayers); (e) – dependence of the B2 domain size on annealing time; (f) – engineering stress–strain curves obtained during room-temperature tensile tests; (g) – dependence of yield strength on the inverse square root of the B2 domain size, including data from Ref. [39]; (h) – enlarged part of the stress–strain curve of the specimen with the smallest B2 domains supplied by DIC snapshots of gauge section, corresponded to certain values of the  $\varepsilon_{\text{global}}$ ; (i) – local strain distribution in the specimen with the smallest B2 domains along the gauge length (denoted with white arrow in the first DIC snapshot (h)) at the corresponding values of the  $\varepsilon_{\text{global}}$ ; (j) – enlarged part of the stress–strain curve of the specimen with the largest B2 domains supplied by DIC snapshots of gauge section, corresponded to certain values of the  $\varepsilon_{\text{global}}$ ; (k) – local strain distribution in the specimen with the largest B2 domains along the gauge length (denoted with white arrow in the first DIC snapshot (j)) at corresponding values of the  $\varepsilon_{\text{global}}$ .

**Table 2**

Yield strength, *YS*, ultimate tensile strength, *UTS*, and elongation at fracture, *EF*, obtained during room-temperature tensile tests of the  $\text{Al}_{15}\text{Nb}_{40}\text{Ti}_{40}\text{V}_5$  alloy after annealing at 1200 °C for 1 min and additional annealing at 800 °C for 0–30 min.

Annealing at 1200 °C, 1 min + annealing at 800 °C	YS, MPa	UTS, MPa	EF, %
0 min	785 ± 15	805 ± 10	45.0 ± 1.8
5 min	785 ± 5	800 ± 5	50.3 ± 3.2
15 min	790 ± 10	800 ± 5	50.4 ± 4.6
30 min	780 ± 15	800 ± 10	42.5 ± 2.9

specimens with small and large B2 domains (Fig. 4). Independently on the B2 domain sizes, the dislocation motion was confined within intersected dislocation bands, and no pinning of dislocations by B2 domains was found, compared to intermediate temperature [39].

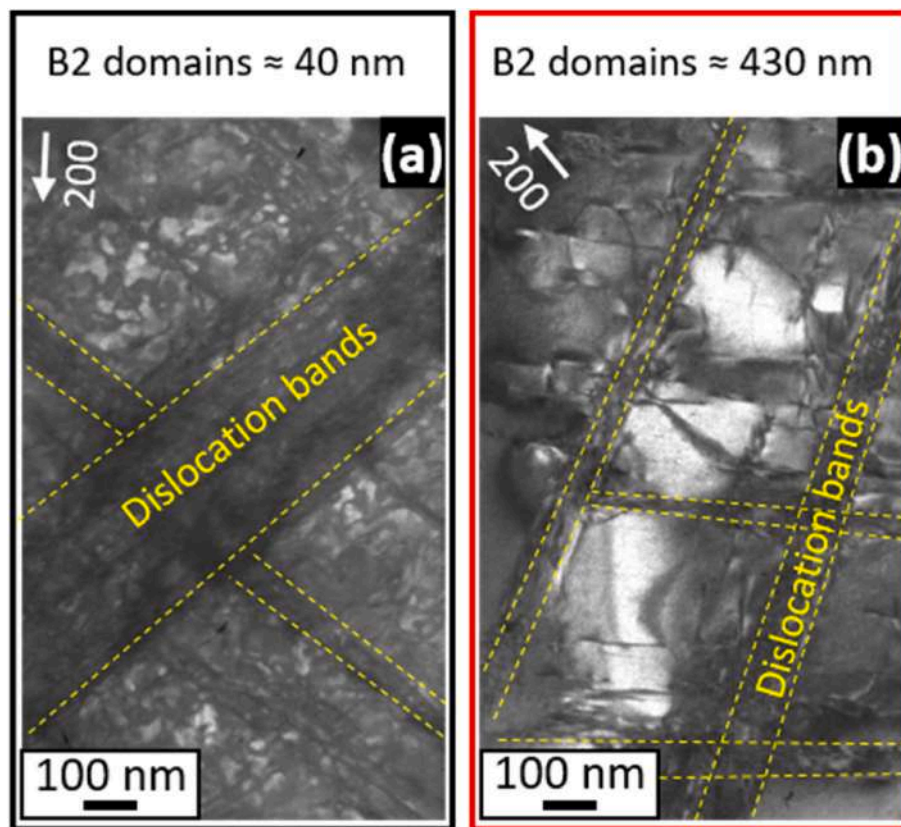
The degree of interaction of dislocations with the B2 domains should depend on the antiphase boundary (APB) energy [58]. Several studies showed that, in ternary B2-ordered Nb-rich alloys [59,60], the APB

energy was rather low thus allowing relatively easy glide of dislocations albeit within narrow bands. In the case of the  $\text{Al}_{15}\text{Nb}_{40}\text{Ti}_{40}\text{V}_5$  alloy, the results obtained also suggest the modest APB energy (however, the estimation of the exact APB energy value requires an additional in-depth study) that could reasonably explain an insensitivity of the mechanical properties to the variations in the B2 domain sizes in terms of the weak interactions of dislocations with these entities [61].

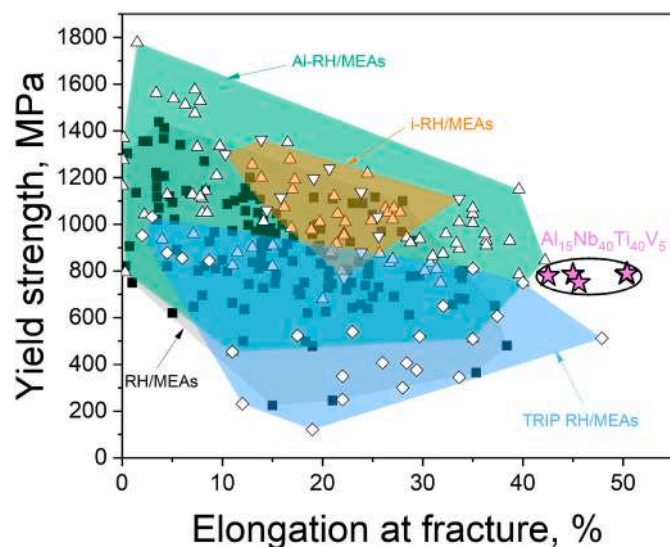
### 3.3. Comparison of mechanical properties

Grain refinement of the  $\text{Al}_{15}\text{Nb}_{40}\text{Ti}_{40}\text{V}_5$  alloy to  $\sim 20 \mu\text{m}$  at any size of B2 domains resulted in the best properties, namely  $YS \approx 780\text{--}790$  MPa and  $EF \approx 50\%$ . We compared these values with other RH/MEAs. For that, we collected dataset of room-temperature tensile properties for different RH/MEAs both in the as-cast and processed states (see Table S4, Supplementary material; the dataset contains more than 140 entities), and grouped them as follows: (i) RH/MEAs comprised of mostly refractory metals (RH/MEAs in Fig. 5), (ii) Al-containing RH/MEAs (Al-RH/MEAs), (iii) RH/MEAs manifested transformation-induced plasticity (TRIP) effect (TRIP RH/MEAs), and (iv) interstitial-containing RH/MEAs (i-RH/MEAs).

Within the dataset, a typical strength-ductility dilemma could be



**Fig. 4.** Dark-field TEM images of typical dislocation structures of the  $\text{Al}_{15}\text{Nb}_{40}\text{Ti}_{40}\text{V}_5$  alloy with the smallest (a) and largest (b) B2 domain sizes. Dashed yellow lines denote the dislocation bands. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



**Fig. 5.** Comparison of the tensile yield strength and elongation at fracture values of the small-grained  $\text{Al}_{15}\text{Nb}_{40}\text{Ti}_{40}\text{V}_5$  alloy with different groups of RH/MEAs available in literature, including RH/MEAs, Al-RH/MEAs, i-RH/MEAs, and TRIP RH/MEAs. Data used for comparison are summarised in Table S4, Supplementary material.

revealed: the YS decreased with an increase in the EF. The highest YS values were observed in Al-RH/MEAs, while TRIP RH/MEAs demonstrated the lowest strength, and, in-between, RH/MEAs and i-RH/MEAs were positioned. In turn, none of the previously reported RH/MEAs could achieve the 50 %-elongation. The former most ductile ( $EF \approx 48\%$ )  $\text{Ti}_{50}\text{Zr}_{30}\text{Hf}_{10}\text{Nb}_{10}$  TRIP RMEA had the YS = 512 MPa [62]. The  $\text{Al}_{15}\text{Nb}_{40}\text{Ti}_{40}\text{V}_5$  alloy appeared to be even more ductile and  $\sim 35\%$  -stronger. The superior combination of mechanical properties in the small-grained  $\text{Al}_{15}\text{Nb}_{40}\text{Ti}_{40}\text{V}_5$  alloy confirms the efficiency of grain refinement as an alternative way to conquer strength-ductility trade-off in RH/MEAs [18,19,24,37].

#### 4. Conclusions

For the first time, the effect of grain and domain sizes on the room-temperature tensile behaviour of B2-ordered RH/MEAs was systematically studied. For a model B2-ordered  $\text{Al}_{15}\text{Nb}_{40}\text{Ti}_{40}\text{V}_5$  RMEA, we showed that the mechanical properties were highly dependent on the grain size and insensitive to the B2 domain sizes. Grain boundary strengthening in this alloy was found to be  $\sim 3$  times more efficient than in a well-known bcc  $\text{HfNbTaTiZr}$  RHEA. Independently on the B2 domain size, the smallest grains of  $\sim 20 \mu\text{m}$  ensured the most stable plastic flow without the premature formation of the localised necking, thereby achieving the elongation of  $\sim 50\%$ , which was superior to all the RH/MEAs reported to date.

#### Originality statement

I write on behalf of myself and all co-authors to confirm that the results reported in the manuscript are original and neither the entire work, nor any of its parts have been previously published. The authors confirm that the article has not been submitted to peer review, nor has been accepted for publishing in another journal. The author(s) confirms that the research in their work is original, and that all the data given in the article are real and authentic. If necessary, the article can be recalled, and errors corrected.

#### CRediT authorship contribution statement

**N. Yurchenko:** Conceptualization, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition. **E. Panina:** Methodology, Investigation. **A. Tojibaev:** Methodology, Investigation. **V. Novikov:** Methodology, Investigation. **G. Salishchev:** Validation, Formal analysis, Data curation, Writing – review & editing, Supervision. **S. Zhrebtsov:** Writing – review & editing, Supervision. **N. Stepanov:** 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.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.msea.2023.145073>.

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