



Chromium-based BCC-superalloys reinforced by B2-CoAl intermetallic precipitates

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ABSTRACT

Chromium (Cr)-based body-centred cubic (BCC)-superalloys strengthened by ordered B2 intermetallic precipitates are promising for structural service at 700–1000 °C, where conventional Ni-based superalloys approach their temperature limits. However, their design space is restricted by the low solubility of B2-forming solutes such as Ni + Al in A2-Cr, which limits the attainable B2 fraction and compositional flexibility. Here, CoAl is introduced as an alternative B2 phase, and precipitation, coarsening, and strengthening in Cr-Co-Al alloys are systematically investigated. Vacuum arc-melted alloys were homogenised at 1450 °C, water quenched, and aged at 1000 °C for up to 240 h. Microstructural analysis reveals strong composition dependence of B2 precipitation. After homogenisation, Cr-5Co-5Al and Cr-10Co remain single-phase A2-Cr, whereas higher-alloyed compositions develop A2 + B2 microstructures. B2-CoAl precipitates remain spherical and reach a maximum area fraction of 34% in Cr-15Co-15Al after 240 h. The A2/B2 lattice misfit is small (−0.3% to −0.6%), indicating favourable coherency for high-temperature performance. Cr-10Co-10Al shows a substantially lower B2 coarsening rate than the reported Cr-10Ni-10Al analogue, indicating improved precipitate stability. All ternary alloys show peak hardness in the homogenised condition: Cr-20Co-10Al reaches 842 HV at room temperature and retains 489 HV at 1000 °C, while B2-free Cr-10Co remains ~510 HV because of strong Co solid-solution strengthening. Ageing softening is attributed to the combined effects of B2 coarsening and Co/Al partitioning, which reduce precipitation and matrix solid-solution strengthening, respectively. These results identify B2-CoAl precipitation as a promising strategy for Cr-based BCC-superalloys.

1. Introduction

The global transition toward sustainable energy systems has intensified the demand for advanced high-temperature structural materials capable of operating beyond the limits of conventional nickel-based superalloys [1]. This demand is especially relevant for concentrated solar power (CSP) systems, advanced nuclear reactors, and high-temperature industrial heat recovery, where improved thermal

efficiency requires materials that can sustain long-term exposure at or above 1000 °C while retaining mechanical integrity and environmental resistance. In this context, refractory metals and their alloys have attracted considerable attention because of their high melting points and excellent thermal stability [2–8].

Among the refractory elements, chromium (Cr) is a particularly attractive base element for next-generation high-temperature alloys. Compared with Ni, Cr has a substantially higher melting point (1907 °C

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vs. 1455 °C), lower density (7.14 vs. 8.91 g·cm⁻³) [9], and lower raw-material cost, while also offering good oxidation/corrosion resistance [10]. Recent studies have shown that Cr-based alloys can achieve promising combinations of strength, oxidation resistance, and high-temperature creep capability [5,11–13]. However, the broader application of Cr-based structural alloys has long been constrained by three major issues: (1) a relatively high ductile-to-brittle transition temperature (DBTT), (2) insufficient creep resistance, and (3) inadequate oxidation and nitridation resistance at temperatures above 1000 °C [10,14–18].

Considerable progress has been made through alloying. Mo additions can provide significant solid-solution strengthening and improve nitridation resistance [19], while Si additions can promote both intermetallic strengthening and the formation of protective SiO₂-based scales [11,18,20]. In particular, Cr-Mo-Si alloys with an A2 + A15 microstructure have shown excellent oxidation resistance and high compressive strength [5,21]. However, these alloys generally suffer from limited fracture toughness, which has been attributed largely to the coarse and brittle A15 phase [22]. This limitation motivates the search for alternative strengthening strategies capable of improving high-temperature strength without introducing excessively brittle second phases.

One promising approach is to introduce coherent ordered B2 precipitates into a disordered BCC A2 matrix [23], following a CALPHAD-guided (Calculations of Phase Diagram) design concept analogous to the γ - γ' architecture of Ni-based superalloys. This A2 + B2 microstructural template has led to the development of BCC-superalloys in Cr-, Fe-, Ti-, and other refractory-metal-based systems [12,24–33]. Ordered B2 precipitates are generally expected to improve strength and high-temperature creep resistance relative to single-phase A2 alloys [34–38].

In Cr-based systems, NiAl has been the most extensively studied B2-forming intermetallic because of its low lattice misfit with A2-Cr, which favours coherent interfaces and excellent precipitate stability [12,25,39–41]. Despite these advantages, the Cr-NiAl system has an important limitation: the solubility of NiAl in A2-Cr on the Cr-rich side is low, with the Ni + Al solubility limit being only about 14 at% [12,42–44]. As a result, the attainable B2 volume fraction is restricted, which constrains the precipitation-strengthening potential and limits the freedom to tune matrix and precipitate fractions through heat treatment. Even when additional alloying elements such as Fe are introduced to expand the A2 phase field, the available compositional window remains relatively narrow [12]. Therefore, identifying an alternative B2-forming intermetallic with higher solubility in A2-Cr is an important step toward expanding the design space of Cr-based BCC-superalloys.

In this regard, CoAl is particularly attractive. Like NiAl, CoAl has an ordered B2 structure and has been shown to provide precipitation

strengthening in BCC matrices [45]. More importantly, as shown in Fig. 1(a), the Co + Al solubility limit (~43 at% at 1460 °C) in A2-Cr is substantially higher than that of Ni + Al (~14 at% at 1390 °C) [12,42,43], suggesting that Cr-Co-Al alloys may enable significantly larger B2 fractions than Cr-Ni-Al alloys. Co is also attractive from the perspective of the matrix design. Previous studies have shown that Co additions can reduce the ductile-to-brittle transition temperature of Cr-based alloys and improve room-temperature ductility [16,46,47]. Binary Cr-Co alloys also exhibit relatively high hardness, indicating that Co can provide substantial solid-solution strengthening to the A2-Cr matrix [47]. Taken together, these features suggest that the Cr-Co-Al system offers a broader alloy-design window than Cr-NiAl by combining enhanced B2-forming capability with the potential ductilising and matrix-strengthening effects of Co.

However, the Cr-Co-Al system remains far less explored than Cr-NiAl, and several key questions remain unresolved. First, the composition dependence of B2-CoAl precipitation and coarsening in A2-Cr has not been systematically established. Second, although B2 precipitation is generally expected to strengthen A2 matrices [45,48], recent studies on A2 + B2 alloys have reported pronounced ageing softening associated with precipitate coarsening [12,49], with similar behaviour also observed in steels [50], and refractory high-entropy alloy (RHEA) [51]. This observation indicates that the mechanical response cannot be interpreted solely in terms of the presence of B2 precipitates. Instead, ageing changes both the precipitate population and the matrix composition: precipitate coarsening reduces the efficiency of precipitation strengthening, while B2 formation removes strengthening solutes from the A2 matrix and thereby reduces solid-solution strengthening. In Cr-Co-Al alloys, this issue is particularly important because Co may contribute both to B2-CoAl formation and to solid-solution strengthening of the matrix.

Therefore, the present work investigates a series of Cr-Co-Al alloys designed to produce a Cr-rich A2 matrix strengthened by B2-CoAl precipitates. By systematically comparing alloy compositions and ageing conditions, this study aims to: (i) establish the composition dependence of B2 precipitation and coarsening in the Cr-Co-Al system; (ii) determine the morphology and lattice misfit of B2-CoAl precipitates in the A2-Cr matrix; and (iii) elucidate the coupled roles of Co and Al in controlling precipitation strengthening, solid-solution strengthening, and ageing softening. This work presents a microstructural and hardness-based assessment of the A2 + B2 design concept and the potential of the Cr-Co-Al system as a BCC-superalloy candidate for high-temperature applications.

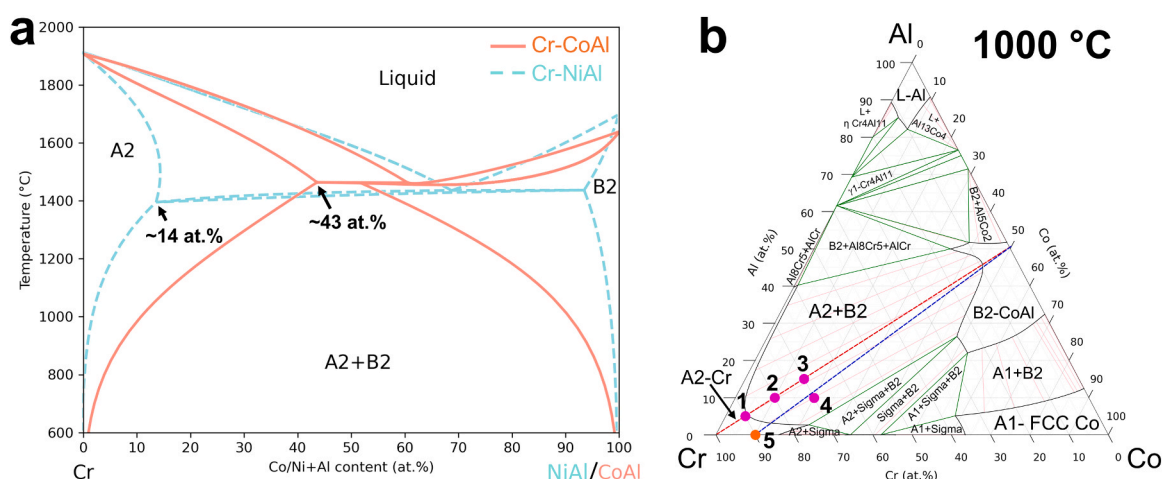


Fig. 1. (a) Vertical section of the pseudo-binary Cr-CoAl system; (b) isothermal section of the Cr-Co-Al ternary phase diagram at 1000 °C.

2. Experimental

The alloy design was guided by CALPHAD calculations using the TCHEA-6 database in the ThermoCalc software. The compositions of the Cr-Co-Al alloys were selected on the basis of the phase diagrams shown in Fig. 1, and are summarised in Table 1. The Co content was limited to 20 at% in order to suppress the possible formation of the Co-Cr sigma phase at around 1000 °C [52]. The alloys were prepared by arc melting high-purity Cr (99.95%), Co (99.98%), and Al (99.99%) metals under an Ar atmosphere. To ensure chemical homogeneity, each ingot was remelted at least five times, with flipping between successive melting steps. The as-cast ingots were sectioned into ~3 mm-thick slices by electrical-discharge machining, wrapped in Mo foil, and sealed in evacuated quartz tubes backfilled with Ar. The samples were inserted into a preheated furnace and homogenised (hereafter denoted as Hom) at 1450 °C for 20 h, followed by water quenching to obtain the Hom condition. Subsequently, the Hom samples were re-sealed in quartz tubes and aged at 1000 °C for 4, 20, 100, and 240 h, followed by water quenching. According to the phase diagram in Fig. 1(b), B2-CoAl precipitates are expected to form at 1000 °C.

The samples were sectioned, mounted, and mechanically ground using SiC papers of 320, 600, 1200, and 2000 grit, followed by polishing with 3 µm and 1 µm Al₂O₃ suspensions. Final polishing was carried out using a colloidal silica suspension (~40 nm) for 5 min. Microstructural characterisation was conducted using a field-emission scanning electron microscope (SEM; Apreo 2S LoVac, Thermo Fisher Scientific) operated at an accelerating voltage of 10 kV. The chemical compositions of the Hom samples were measured by SEM energy-dispersive X-ray spectroscopy (EDS, Table 1). High-magnification SEM images (65,000×) were acquired for quantitative analysis. For images with complex contrast, previously developed deep-learning-based segmentation method was employed [53]. The precipitate radius measured from 2D SEM images corresponds to the radius on a planar section. To obtain the true three-dimensional (3D) precipitate radius, a stereological correction factor of 0.82 was applied [12,54]. Hom and aged samples were manually crushed into powder using a 304 austenitic stainless-steel mortar and pestle. Synchrotron X-ray diffraction (SXRD) patterns were collected at the BL14B1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF) using a wavelength of $\lambda = 0.6887$ Å. Transmission electron microscopy (TEM) was performed using an FEI Talos F200XG2 microscope (Thermo Fisher Scientific), and TEM specimens were prepared using a focused ion beam (FIB) lift-out technique on an FEI Scios DualBeam system. Vickers hardness was measured at both room temperature (RT) and 1000 °C using a 500 g load and a dwell time of 10 s. For RT measurements, at least ten indentations were performed within grain interiors for each sample. For high-temperature measurements at 1000 °C, at least three indentations were carried out under an Ar atmosphere. The samples used for hardness testing were the same as those used for SEM characterisation.

3. Results and discussions

3.1. Microstructures

The nominal and EDS-measured compositions of the Cr-Co-Al alloys

Table 1
Nominal and EDS-measured compositions of the Hom alloys (in at%).

No.	Nominal alloy	EDS result		
		Cr	Co	Al
1	Cr-5Co-5Al	88.2	5.7	6.1
2	Cr-10Co-10Al	77.9	10.7	11.4
3	Cr-15Co-15Al	67.9	16.1	16.0
4	Cr-20Co-10Al	68.2	20.8	11.0
5	Cr-10Co	89.5	10.5	–

investigated in this study are summarised in Table 1. The measured chemical compositions agree well with the nominal values. Minor deviations are attributed mainly to Cr evaporation during melting, but the overall compositions remain close to the alloy design.

The evolution of CoAl-B2 precipitates of the alloys aged at 1000 °C is illustrated by high-magnification SEM images (65,000×) in Fig. 2. After homogenisation followed by water quenching, the Hom Cr-5Co-5Al alloy exhibits a clean A2 matrix without detectable B2 precipitates, as further confirmed by TEM (Fig. 6). In the Hom Cr-10Co-10Al alloy, individual precipitates are not resolved by SEM at this magnification, although weak B2 reflections are detected by SXRD (Fig. 5). In the Hom Cr-15Co-15Al and Cr-20Co-10Al alloys, weak nanoscale contrast of B2 precipitates can be observed in the SEM images, indicating that B2 precipitation cannot be completely suppressed even by rapid water quenching after homogenization at 1450 °C. For Cr-20Co-10Al, the B2 precipitates are further presented by the TEM observations in Fig. 7.

Notably, in the binary sample of Cr-10Co both Hom and aged conditions remain free of B2 precipitates, consistent with the Co-Cr binary phase diagram [52]. Furthermore, no other secondary phases, such as sigma phase, are detected in any alloys. For the Cr-5Co-5Al, Cr-10Co-10Al, Cr-15Co-15Al, and Cr-20Co-10Al alloys, the size of B2 precipitates increases significantly with prolonged ageing at 1000 °C. The precipitates retain a predominantly spherical morphology even after long-term ageing, which can likely be attributed to the small lattice misfit between the B2-CoAl precipitates and the A2-Cr matrix [40].

A quantitative analysis of the B2 precipitates, including radius distribution, mean radius, coarsening kinetics, number density, and area fraction, was carried out using a deep learning-based approach [53], with results presented in Fig. 3 and Fig. 4.

The B2 precipitate radius distributions and corresponding average radii of the Cr-5Co-5Al, Cr-10Co-10Al, Cr-15Co-15Al, and Cr-20Co-10Al alloys are presented in Fig. 3(a-d) respectively. For each ageing condition, the precipitate size distributions are approximately symmetric and relatively narrow, suggesting a fairly uniform coarsening behaviour within each alloy. The average B2 radius in each alloy increases with ageing time (Fig. 3), indicating continuous precipitate growth during ageing at 1000 °C. The coarsening kinetics were plotted in Fig. 4(a), where linear fitting indicates that the evolution of the average radius with time follows:

$$\bar{r}^3 - \bar{r}_0^3 = Kt \quad (1)$$

where $\bar{r}$ and $\bar{r}_0$ (nm) are the average radii of B2 precipitates in the aged and Hom conditions, respectively; K (nm³/h) is the coarsening rate constant, t (h) is the ageing duration.

This linear relation shows that the coarsening of B2 precipitates in the present Cr-Co-Al alloys followed the classical Lifshitz-Slyozov-Wagner (LSW) diffusion-controlled process, also known as Ostwald ripening [54,68,69]. Accordingly, the coarsening rate constants of these Cr-Co-Al alloys were calculated using Equation (1), with the uncertainties estimated by error propagation, as shown in Fig. 4(a).

The coarsening rate constants obtained in the present study are compared with literature data (Fig. 4(b)). The comparison includes precipitate coarsening rate in the present Cr-CoAl (B2) and other alloy systems, including Ni-based alloys [55–60], Co-based alloys [61–64], Fe-based alloys [26,65–67], RHEAs [27], and Cr-NiAl alloys [12,49]. The Cr-CoAl alloys show relatively lower coarsening rate than the γ - γ' (FCC + L1₂) structured Ni- [55–60], Co- [61–64], Fe-based alloys [26, 65–67], at 1000 °C. Notably, the RHEAs [27], i.e., Ta₂₇Mo₂₇Ti₂₇-Cr₈Al₁₀Zr₁ and Ta_{27.3}Mo_{27.3}Ti_{27.3}Cr₈Al₁₀ alloys showed coarsening rate of 48 and 158 nm³/h at 1000 °C, respectively, which are both lower than the present Cr-Co-Al system. The slow coarsening behaviour of B2 in A2 RHEAs can be explained by the sluggish diffusion effect commonly observed in HEAs [70].

In addition, reported values for similar A2 + B2 Cr-based Cr-NiAl alloys at the same temperature have $K = 222$ nm³/h for Cr-5Ni-5Al

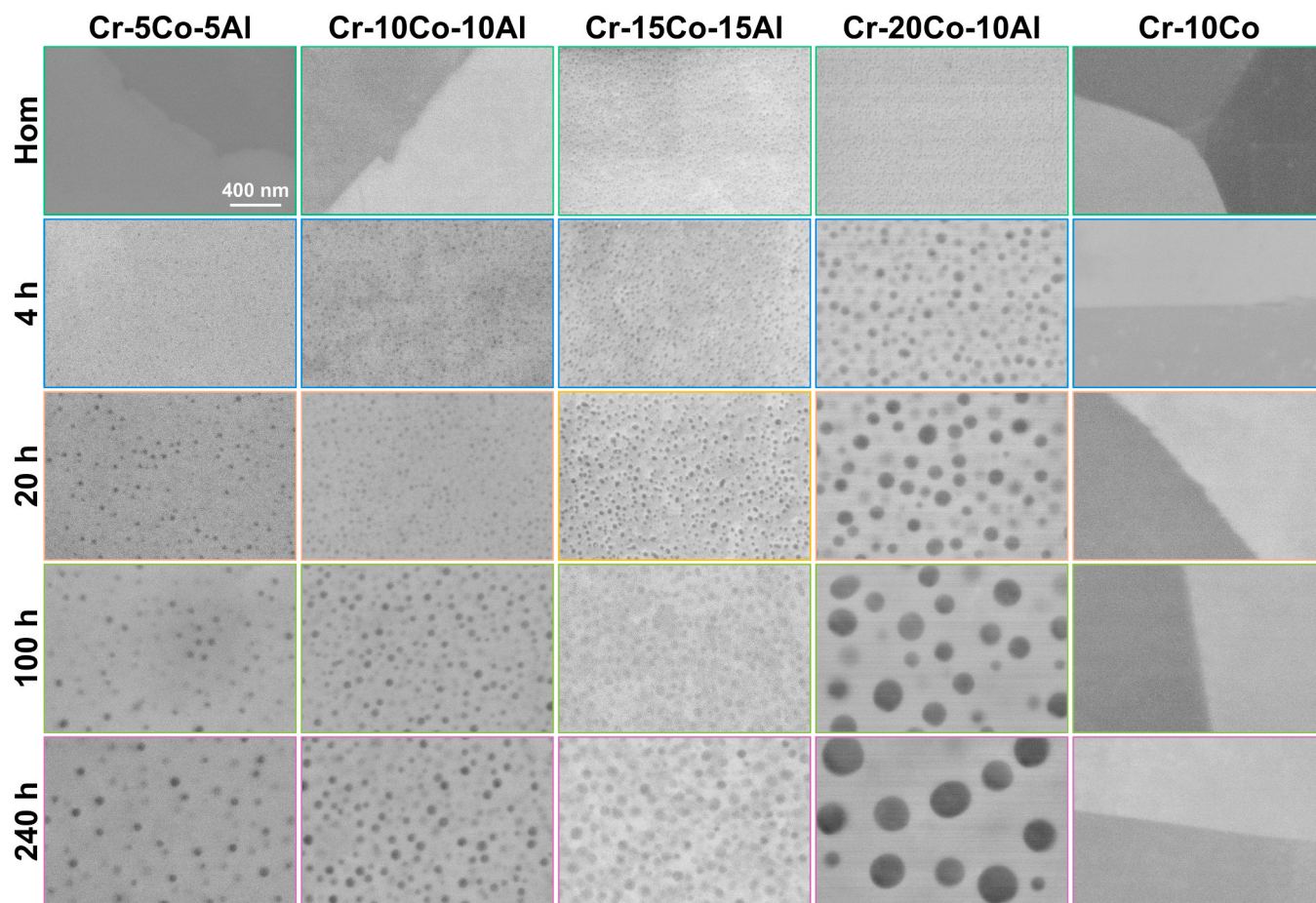


Fig. 2. SEM micrographs of Hom and 1000 °C-aged Cr-Co-Al samples visually showing precipitate nucleation and coarsening.

[12], and $K = 7980 \text{ nm}^3/\text{h}$ for Cr-10Ni-10Al [49]. In the present work, Cr-5Co-5Al and Cr-10Co-10Al exhibit $K = 258.9 \pm 38.8 \text{ nm}^3/\text{h}$ and $200.6 \pm 10.1 \text{ nm}^3/\text{h}$, respectively. Thus, Cr-5Co-5Al shows a low coarsening rate comparable to that of Cr-5Ni-5Al, whereas Cr-10Co-10Al shows a much lower coarsening rate than Cr-10Ni-10Al. Therefore, the B2-CoAl precipitates can achieve coarsening resistance comparable to or better than B2-NiAl precipitates in the A2-Cr matrix under comparable conditions.

In addition, Cr-15Co-15Al still has a low K value of $386.2 \pm 65.7 \text{ nm}^3/\text{h}$, however, the Cr-20Co-10Al exhibits a much higher coarsening rate constant of $9580.3 \pm 797.9 \text{ nm}^3/\text{h}$, significantly exceeding those of the other three alloys at 1000 °C. This result indicates that increasing the Co content from 10 to 20 at% greatly accelerates precipitate coarsening in the Cr-Co-Al system. According to the LSW framework [54,68,69], the coarsening rate is controlled by inter-diffusion/solute mobility, matrix solubility, supersaturation and interfacial energy. Increasing Co from 10 to 20 at% at fixed Al increases the amount of Co retained in the A2 matrix after B2 formation. The resulting Co-rich matrix can promote faster solute redistribution during ageing. At the same time, the lower relative Al content may reduce the density of stable B2 nuclei and favour the growth of existing B2 domains. This is consistent with the sharp decrease in number density and the much higher coarsening rate constant observed for Cr-20Co-10Al. Therefore, although additional Co improves matrix solid-solution strengthening, excessive Co at fixed Al is detrimental to precipitate stability.

The number density of B2 precipitates, expressed as the number of precipitates per unit area, is shown in Fig. 4(c). In all alloys, the number density decreases with ageing time, which is another characteristic feature of diffusion-controlled precipitate coarsening, as larger precipitates grow at the expense of smaller ones. This trend is consistent

with the LSW framework. The precipitate volume fraction was estimated from the measured area fraction based on stereological principles (Delesse's theorem [71]), assuming a random distribution of approximately equiaxed precipitates.

The area fractions are shown in Fig. 4(d), these alloys exhibit a gradual increase in area fraction with ageing time from 0 to 240 h. In general, the B2 area fraction successively increases in Cr-5Co-5Al, Cr-10Co-10Al, and Cr-15Co-15Al alloys, with peak fractions of 7%, 16%, and 34% at 240 h, respectively. However, Cr-20Co-10Al alloy has an intermediate fraction between Cr-10Co-10Al and Cr-15Co-15Al alloys, and reached a peak value of 21% at 240 h. Its area fraction is higher than Cr-10Co-10Al because of 10 at% extra Co, whereas lower than Cr-15Co-15Al due to less Al content. These values are higher than those reported for Cr-5Ni-5Al (~5.9%) and Cr-10Ni-10Al (~6.0%) aged at 1000 °C [12], indicating a higher attainable B2 precipitate fraction and thus a greater precipitation-strengthening potential in the present Cr-Co-Al alloys. Furthermore, compared to Cr-10Co-10Al, an increased B2 volume fraction for Cr-20Co-10Al, could contribute to faster coarsening: at comparable precipitate sizes, a higher volume fraction reduces inter-particle spacing and strengthens diffusional interactions, facilitating solute transfer from smaller to larger precipitates during Ostwald ripening [72].

Therefore, although the reduced number density with ageing time, the volume fraction of B2 precipitates still increased. This again highlighted the diffusion process of B2 precipitates during ageing at 1000 °C.

Lattice misfit strongly influences precipitate morphology, coarsening kinetics, strengthening mechanisms, and overall microstructural evolution [40]. Therefore, the lattice misfit between the A2 matrix and the B2 precipitates is an important parameter governing the precipitation behaviour and mechanical response. To evaluate the A2/B2 lattice

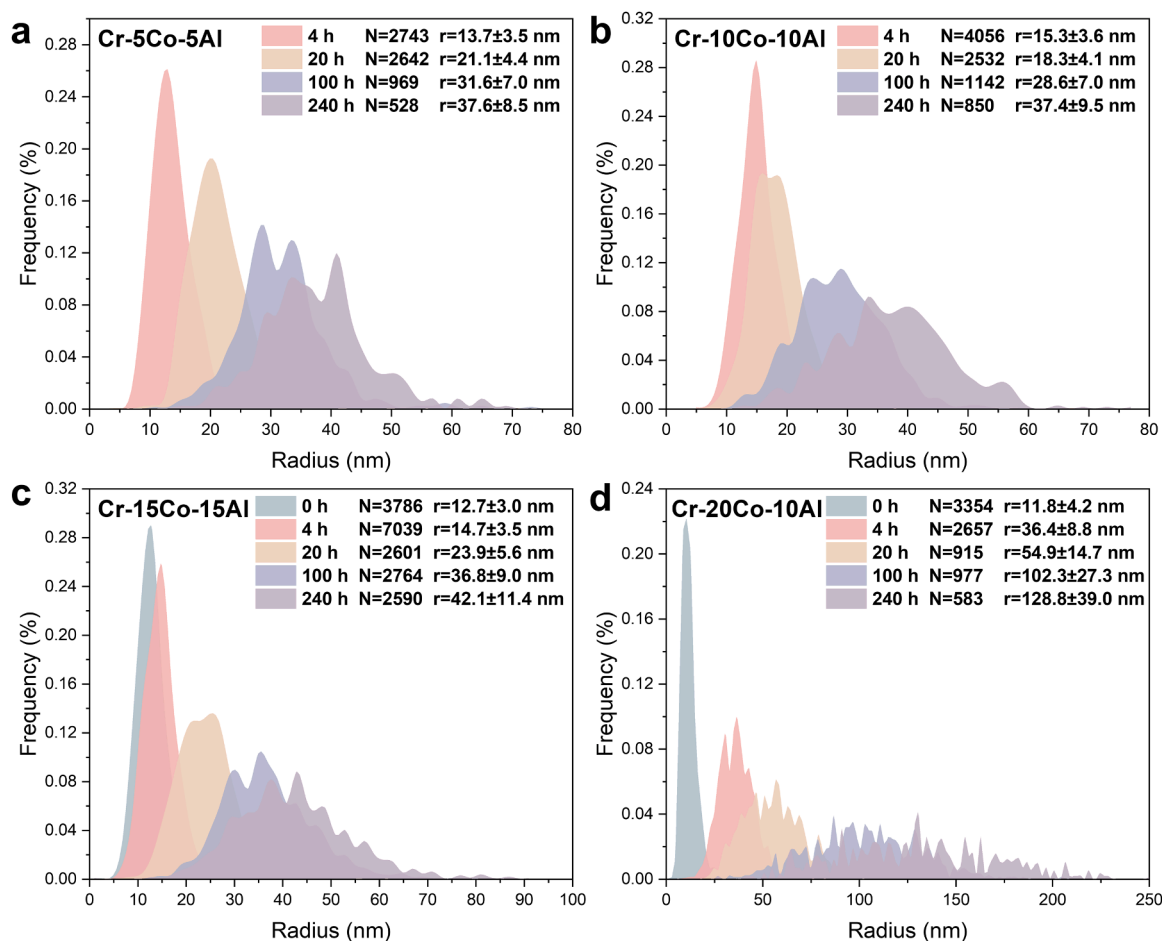


Fig. 3. Statistical analysis of the B2 precipitates. Radius distribution and average radii in (a) Cr-5Co-5Al, (b) Cr-10Co-10Al, (c) Cr-15Co-15Al, and (d) Cr-20Co-10Al alloys.

misfit, SXRD was conducted on selected samples, i.e., Hom and 240 h-aged samples of Cr-10Co-10Al and Cr-20Co-10Al alloys. As shown in Fig. 5, the SXRD patterns display the major reflections of both the A2 phase and the B2 precipitates. In addition, several unexpected peaks that could not be indexed to either A2 or B2 were detected. These peaks were identified as originating from FCC 304 austenitic stainless steel contamination introduced during powder preparation when it was used as mortar and pestle. It is worth noting that B2 precipitates were not detected by SEM in Hom Cr-10Co-10Al alloy (see Fig. 2), whereas SXRD confirmed the presence of the B2 phase. Several other weak reflections in Fig. 5 remain unindexed because they do not correspond to A2, B2, or FCC 304 steel, and were therefore ignored in the present analysis.

The lattice parameters of the A2 and B2 phases were determined from the SXRD data using an extrapolation method [48]. In the Cr-10Co-10Al alloy, both the A2 and B2 lattice parameters decrease after 240 h of ageing, whereas those of the Cr-20Co-10Al alloy remain nearly unchanged. The lattice misfit (δ) between A2 and B2 was then calculated using the following equation as adopted in previous studies on similar A2 + B2 Cr alloys [12,40]:

$$\delta = \frac{2(a_{B2} - a_{A2})}{a_{B2} + a_{A2}} \quad (2)$$

where a_{B2} and a_{A2} are the lattice parameters of the B2 precipitate and A2 matrix, respectively. The results were summarised in Table 2.

The lattice misfits between A2 and B2 are relatively small, ranging from approximately -0.3% to -0.6% , implying that A2/B2 interfaces are likely to be coherent or semi-coherent. This interpretation is consistent with the spherical morphology of the B2 precipitates

observed in the SEM images (Fig. 2), since low lattice misfit generally favours spherical precipitate morphologies [40]. A small lattice misfit may also facilitate the formation and stabilisation of fine B2 precipitates with high number density [48].

The SXRD result for the Hom Cr-10Co-10Al alloy shows that, although the B2 precipitates are invisible in SEM, they can still be detected by techniques with higher phase sensitivity such as SXRD. To verify whether B2 precipitates formed in the Hom Cr-5Co-5Al alloy, TEM was carried out. Fig. 6(a) shows a bright-field (BF) TEM image with the corresponding selected-area electron diffraction (SAED) pattern in the inset. The BF image shows only bending contours, and the SAED pattern contains reflections solely from the A2 phase. The high-resolution TEM (HRTEM) image in Fig. 6(a) shows only A2 BCC lattice fringes, and no B2 lattice can be reliably identified, despite local image noise caused by uneven foil thickness. The corresponding fast Fourier transform (FFT) image shown in the inset also indicates a single A2 phase, consistent with the SAED result. Therefore, the TEM results confirm that the Hom Cr-5Co-5Al alloy consists of a single A2 phase.

To further elucidate the morphology, orientation relationship, and chemical partitioning between the B2 precipitates and the A2 matrix, TEM and STEM analyses were conducted on the Hom and 240h-aged Cr-20Co-10Al alloy, with the results shown in Fig. 7. The inset in Fig. 7(a) shows a SAED pattern containing reflections from both A2 and B2, which were indexed accordingly. Dark-field (DF) images were obtained using the B2 reflection indicated by the yellow circle. A high number density of B2 precipitates is observed in the Hom sample. However, the enlarged DF image in Fig. 7(b) suggests that these B2 precipitates are present as clustered nanoscale domains rather than as well-defined

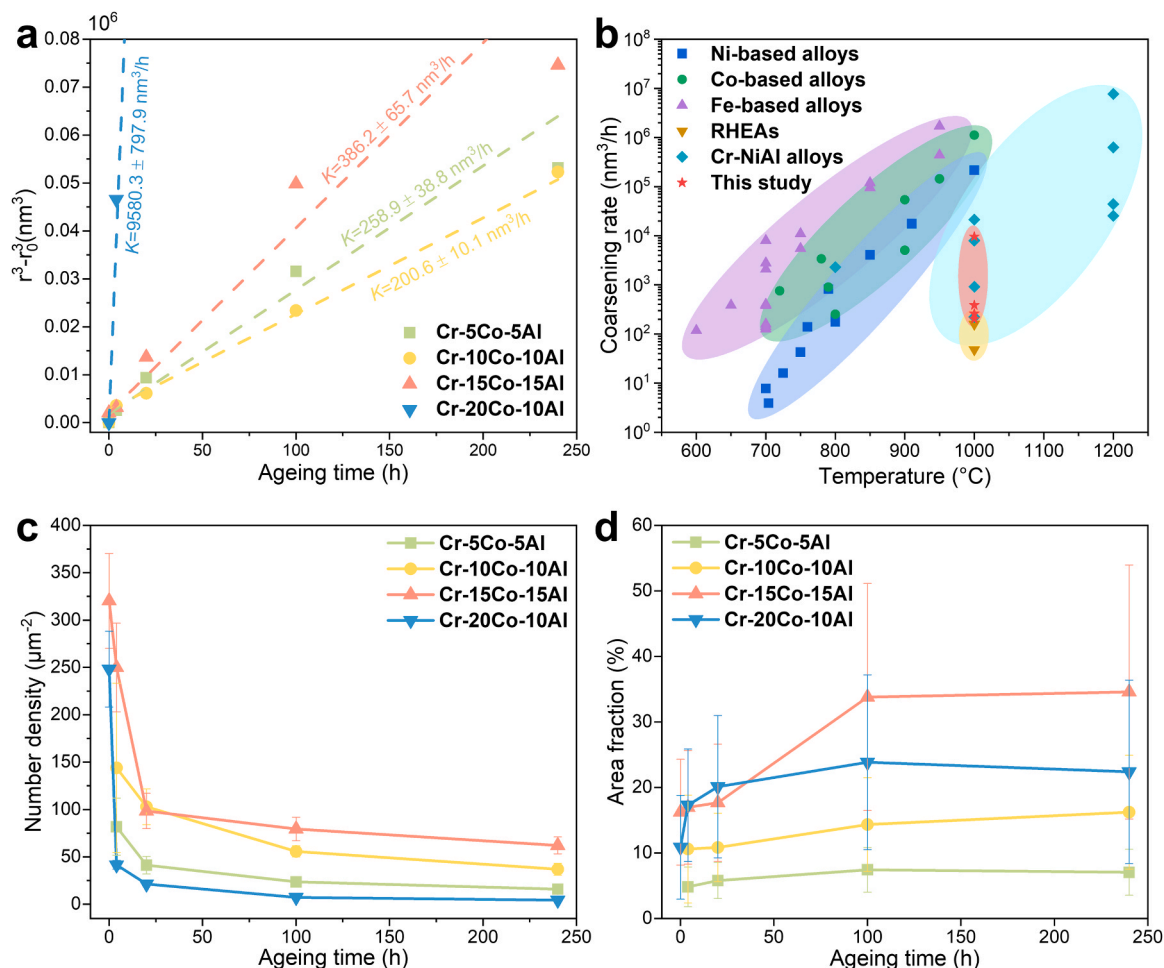


Fig. 4. (a) Coarsening kinetics, plotted as $r^3 - r_0^3$ versus ageing time, used to determine the coarsening rate constant. (b) comparison of precipitate coarsening rate in Ni-based alloys [55–60], Co-based alloys [61–64], Fe-based alloys [26,65–67], refractory high-entropy alloys (RHEAs) [27], Cr-NiAl [12,49] and the present Cr-CoAl alloys; (c) number density and (d) area fraction of B2-CoAl precipitates as a function of ageing time.

isolated spherical particles. The EDS elemental maps of Cr, Co, and Al in Fig. 7(c) reveal partitioning between Co- and Al-enriched B2 regions and the Cr-enriched A2 matrix. In the 240h-aged Cr-20Co-10Al sample, both A2 and B2 phases are also identified in the SAED pattern shown in the inset of Fig. 7(d). The DF image in Fig. 7(d) displays numerous spherical B2 precipitates, and the enlarged image in Fig. 7(e) provides a clearer view of an individual B2 particle. The EDS maps in Fig. 7(f) clearly distinguish the B2 precipitates from the surrounding A2 matrix. Point EDS analyses of Cr-20Co-10Al 240h-aged sample were performed in the A2 matrix (measured as Cr_{82.72}Co_{14.59}Al_{2.69}), and at the centres of B2 precipitates, the average B2 composition was determined as Cr = 10.78 ± 0.61 at%, Co = 55.52 ± 0.91 at%, and Al = 33.70 ± 0.90 at%.

In addition, the HRTEM image of the Hom sample in Fig. 7(g) reveals nanoscale B2 precipitates embedded in the A2 matrix, and the corresponding FFT images separately show the diffraction features of the B2 and A2 phases. In contrast, in the 240h-aged sample (Fig. 7(h)), a large B2 precipitate was observed in the A2 matrix, and the two phases can still be distinguished in the corresponding FFT images (Fig. 7(h1,h2)).

These TEM results demonstrate that B2 precipitates are already present in the Hom Cr-20Co-10Al alloy. In the Hom condition, the B2 phase tends to appear as dense clusters of nanoscale ordered domains within the A2 matrix. After prolonged ageing, these clusters evolve into coarse, well-defined spherical B2 precipitates.

3.2. Vickers hardness

The Vickers hardness of the Hom and aged samples was measured at RT, and the statistical results are presented in Fig. 8(a). Evidently, all Cr-Co-Al ternary alloys, i.e., Cr-5Co-5Al, Cr-10Co-10Al, Cr-15Co-15Al, and Cr-20Co-10Al, exhibit their highest hardness in the Hom condition. With increasing ageing time at 1000 °C, the hardness decreases continuously.

For the Cr-5Co-5Al alloy, a clean A2 matrix was observed in the Hom sample (Fig. 6). This condition exhibits higher hardness than the aged samples containing B2 precipitates, implying that solid-solution strengthening plays an important role alongside B2 precipitation strengthening. Besides, it is also likely that the peak ageing condition of Cr-5Co-5Al is between Hom and 4 h at 1000 °C. Over this range, coarsening and solute depletion reduce the net hardness. In contrast, the binary Cr-10Co alloy exhibits nearly constant high hardness of ~510HV (compared to ~150HV for pure Cr [12]) over the entire ageing period at 1000 °C, consistent with the strong solid-solution strengthening effect of Co reported elsewhere [47]. As shown in the SEM results (Fig. 2), no B2 precipitates form in this binary alloy. Since Cr-10Co remains a single-phase A2 solid solution during ageing, no significant microstructural evolution occurs, and the hardness therefore remains essentially unchanged.

To evaluate the role of B2 precipitates in high-temperature strengthening, the hardness of Cr-20Co-10Al in the Hom and 240h-aged conditions, together with that of the Hom Cr-10Co alloy, was measured at 1000 °C. The Hom Cr-10Co alloy was selected as the B2-

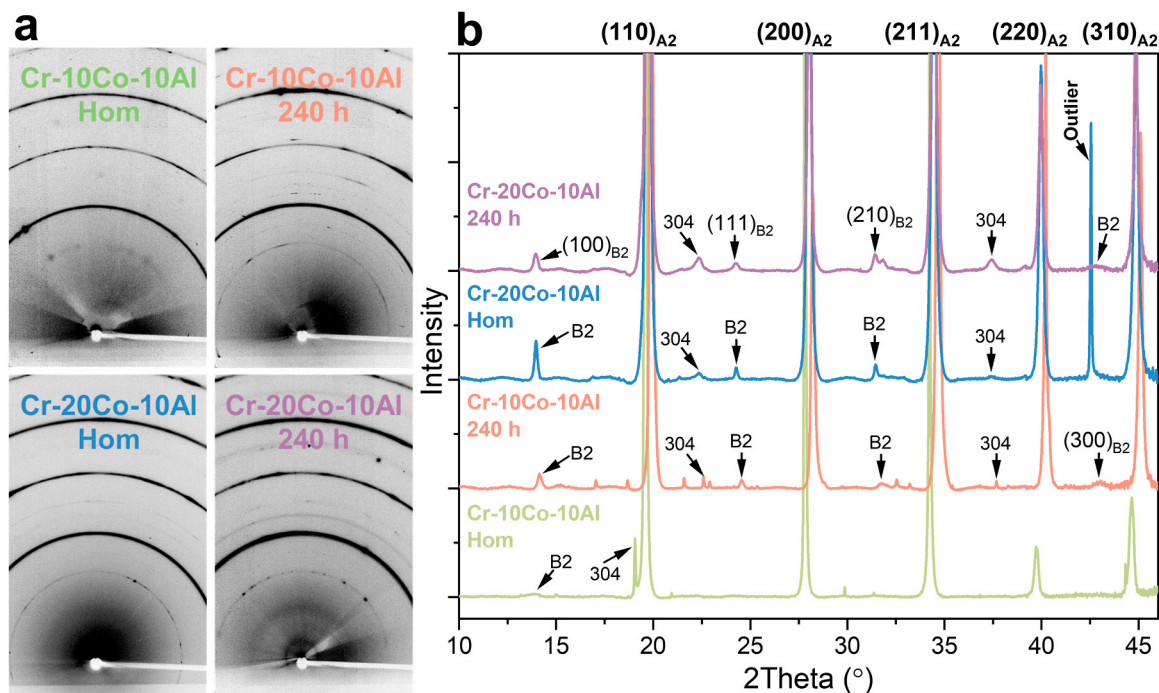


Fig. 5. Synchrotron X-ray diffraction (SXRD) results of selected samples. i.e., Hom and 240 h-aged samples of Cr-10Co-10Al and Cr-20Co-10Al alloys. (a) two-dimensional SXRD patterns and (b) integrated profiles. Note: 304 denotes FCC 304 austenitic stainless steel.

Table 2

Lattice parameters and lattice misfit determined by SXRD.

Sample	a_{B2} (Å)	a_{A2} (Å)	δ (%)
Cr-10Co-10Al, Hom	2.8541	2.8711	-0.5939
Cr-10Co-10Al, 240 h	2.8304	2.8477	-0.6094
Cr-20Co-10Al, Hom	2.8536	2.8632	-0.3359
Cr-20Co-10Al, 240 h	2.8538	2.8687	-0.5208

free, single-phase A2 reference for high-temperature hardness testing. The 240h-aged Cr-10Co condition was not additionally measured at 1000 °C because Cr-10Co remains a single-phase A2 solid solution after ageing at 1000 °C, consistent with the SEM observations and the Co-Cr binary phase diagram. As shown in Fig. 8(b), the Hom Cr-20Co-10Al alloy still exhibits significantly higher hardness than the 240h-aged condition. The RT-to-1000 °C hardness ratios are 1.72 and 2.69 for

the Hom and 240h-aged Cr-20Co-10Al samples, respectively, indicating that the 240h-aged sample undergoes more pronounced softening upon heating from RT to 1000 °C than the Hom sample. The Hom Cr-10Co alloy also shows substantially lower hardness at 1000 °C than at RT, with an RT-to-1000 °C hardness ratio of 3.31, indicating severe high-temperature softening in the absence of B2 strengthening. This behaviour is consistent with the general rationale of the BCC-superalloy concept, since precipitate strengthening is more effective than matrix solid-solution strengthening for retaining strength at elevated temperature. Overall, the Cr-Co-Al alloys exhibit the highest Vickers hardness in the Hom condition at both RT and 1000 °C, highlighting the important role of fine B2 precipitates and solid solution in strengthening these alloys.

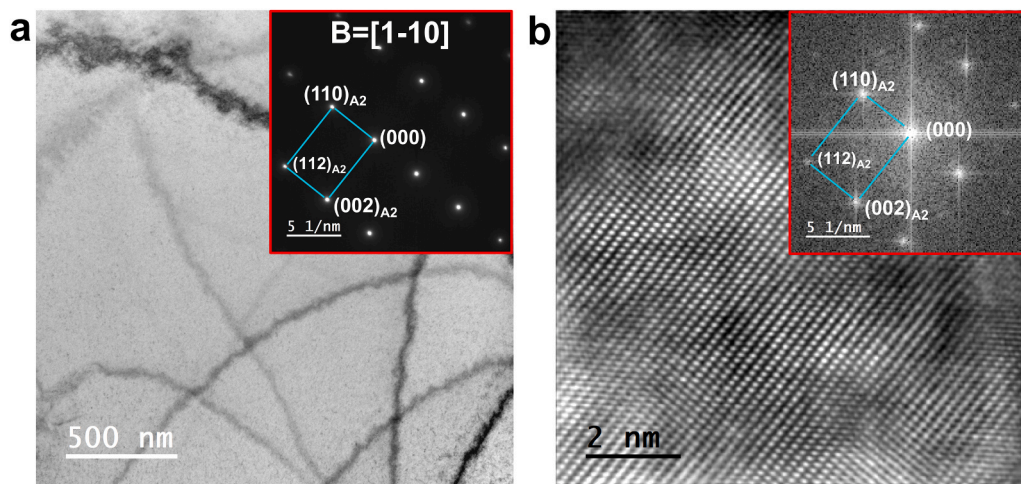


Fig. 6. Transmission electron microscopy (TEM) images of the Hom Cr-5Co-5Al alloy. (a) bright-field (BF) image and corresponding selected area electron diffraction (SAED) pattern, (b) high-resolution TEM (HRTEM) image and fast Fourier transform (FFT).

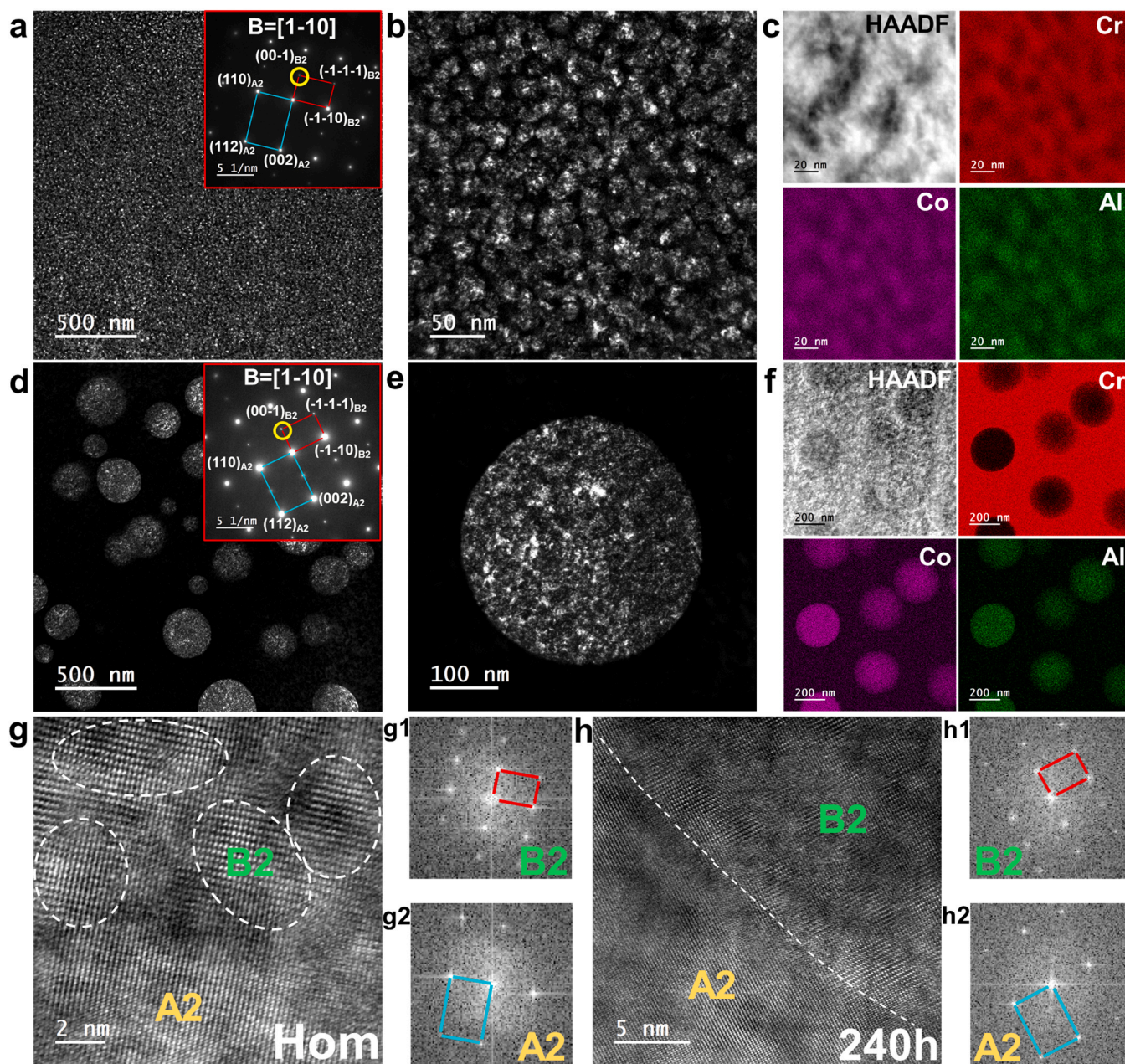


Fig. 7. TEM results of Cr-20Co-10Al alloy, (a-c,g) Hom and (d-f,h) 240h-aged conditions. (a,b,d,e) Dark-field (DF) images, (c,f) EDS maps, (g,h) HRTEM images and (g1,g2,h1,h2) corresponding FFT images.

3.3. Origin of ageing softening

Although B2 is generally regarded as a strengthening phase in BCC alloys [48,73], the hardness of an A2 + B2 alloy is determined by the combined contributions of precipitate strengthening and matrix solid-solution strengthening. On the one hand, the solid-solution strengthening contribution can be represented as the sum of the contributions from individual solute elements [50], which means solute leaning can result in loss of matrix solid-solution strengthening. On the other hand, the precipitation strengthening effect depends strongly on precipitate size, number density, and spacing. It is well established that precipitation strengthening reaches a maximum within a characteristic precipitate-size range and decreases once the precipitates coarsen beyond this optimum. In other words, there exists a peak-aged condition at which the strengthening effect of precipitates is maximised. For instance, in a refractory high-entropy alloy, the hardness first increases

to a peak value and then decreases upon further ageing as a result of B2 coarsening [51].

In the present study, Fig. 3 and Fig. 4 show that the B2 phase coarsens during ageing, as evidenced by the increasing precipitate radius, and its volume fraction continues to increase. This indicates that ageing is accompanied by ongoing precipitate growth together with continued partitioning of Co and Al from the A2 matrix into the B2 phase, leading to progressive solute depletion of the A2 matrix. Therefore, the hardness evolution in the present Cr-Co-Al alloys cannot be interpreted simply in terms of B2 precipitation alone. Rather, the observed ageing softening should be understood as the combined result of two concurrent processes: (i) reduction in the strengthening efficiency of B2 precipitates as they coarsen during ageing; and (ii) weakening of matrix solid-solution strengthening due to the progressive partitioning of Co and Al from the A2 matrix into the B2 phase.

Particularly, for Cr-5Co-5Al, the B2-free Hom condition has higher

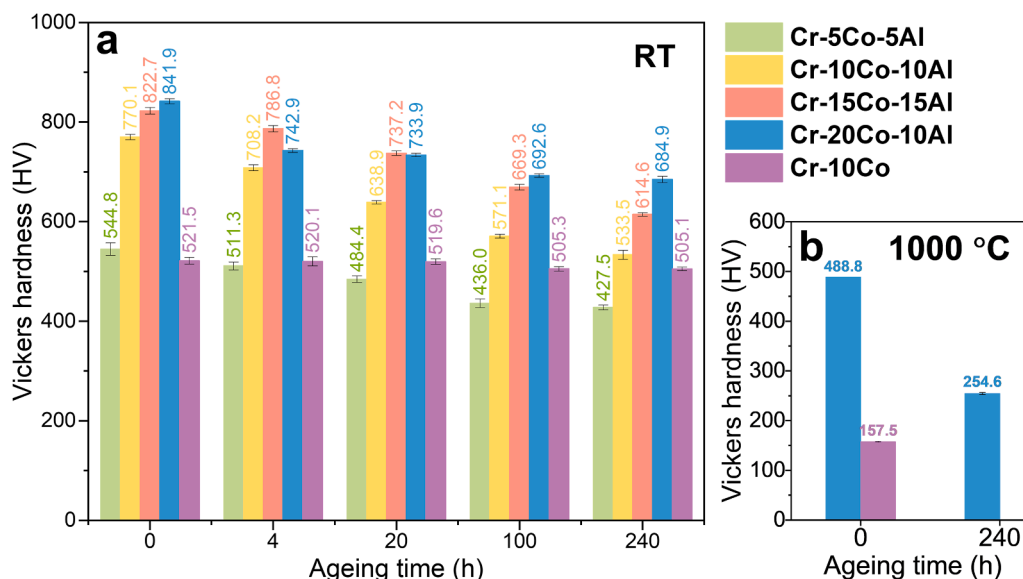


Fig. 8. Vickers hardness of (a) all Hom and aged samples at room temperature and (b) Hom and aged Cr-20Co-10Al and Hom Cr-10Co alloys at 1000 °C.

hardness than the 4h-aged, it seems that the solid-solution strengthening plays a role over the B2 precipitation. In addition, the optimum B2 size could lie between the B2-free Hom condition and the 4h-aged condition with an average B2 radius of 13.7 nm, and beyond this range, coarsening and solute depletion reduce the net hardness. Similar phenomena have also been reported in previously studied B2-strengthened A2-Cr alloys [12,49].

The present results therefore suggest that precipitation strengthening and solid-solution strengthening made coupled contributions to the ageing response, consistent with similar interplay previously reported in Ni-based alloys [74]. However, the hardness data only provided an initial measure of strengthening and high-temperature softening resistance. The effect of B2 on ductility, DBTT, fracture toughness and creep resistance must be assessed in future work before realistic component-level application can be established.

3.4. Implications for the design of A2 + B2 Cr-based superalloys

The composition-dependent comparisons in the present work clarify the distinct yet coupled roles of Co and Al in the Cr-Co-Al system. The comparison between Cr-10Co and Cr-10Co-10Al shows that Al addition enables B2-CoAl precipitation and introduces a substantial precipitation-strengthening contribution, whereas the comparison between Cr-10Co-10Al and Cr-20Co-10Al shows that an additional 10 at% Co markedly enhances matrix solid-solution strengthening but also significantly accelerates B2 coarsening. Furthermore, the systematic comparison Cr-5Co-5Al, Cr-10Co-10Al, and Cr-15Co-15Al indicates that increasing equiatomic Co and Al additions progressively enhances the tendency for B2 precipitation and raises the overall strengthening level.

Compared with Cr-NiAl alloys [12,42,49], the Cr-Co-Al system offers a broader and more flexible design window because of the higher solubility limit of CoAl in A2-Cr. This provides greater freedom to balance precipitate fraction, precipitate stability, and matrix solid-solution strengthening, and therefore makes Cr-Co-Al a promising platform for the development of Cr-based BCC-superalloys. At the same time, the alloy design must be carefully optimised in order to maximise the beneficial synergy between solid-solution strengthening and B2-CoAl precipitation strengthening while minimising the loss of precipitate stability associated with excessive Co addition.

4. Conclusions

This work demonstrates that the Cr-Co-Al system enables the design of an A2 + B2 microstructure in Cr-based BCC-superalloys for high-temperature applications. Through a systematic comparison of alloy compositions and ageing conditions, the formation, stability, coarsening behaviour, and strengthening effect of B2-CoAl precipitates in an A2-Cr matrix were clarified. The main conclusions are as follows:

- (1) B2-CoAl precipitation in the Cr-Co-Al system is strongly composition-dependent. The Hom Cr-5Co-5Al alloy remained single-phase A2, whereas B2 was already present or detectable in the higher-alloyed compositions; by contrast, Cr-10Co remained B2-free.
- (2) The B2 precipitates retained an approximately spherical morphology during ageing at 1000 °C, consistent with the small A2/B2 lattice misfit measured by SXRD. Their coarsening behaviour was strongly composition-dependent, with relatively slow coarsening in Cr-5Co-5Al, Cr-10Co-10Al, and Cr-15Co-15Al, but much faster coarsening in Cr-20Co-10Al.
- (3) All Cr-Co-Al ternary alloys showed their highest Vickers hardness in the Hom condition, followed by continuous softening during ageing. The B2-free Cr-10Co alloy showed nearly unchanged hardness, indicating that the softening in the ternary alloys is mainly associated with B2 coarsening and solute depletion of the A2 matrix.
- (4) Overall, compared with Cr-NiAl, the Cr-Co-Al system therefore offers a broader and more flexible alloy-design window for Cr-based BCC-superalloys, provided that precipitate fraction, precipitate stability, and matrix solid-solution strengthening are balanced appropriately.

CRediT authorship contribution statement

Xianbing Zhang: Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Thomas Blackburn:** Writing – review & editing, Validation, Methodology, Investigation. **Cheng Ding:** Methodology, Investigation. **Jie Wang:** Validation, Methodology. **Mengmeng Wang:** Validation, Methodology. **Minghao Ma:** Visualization, Validation, Methodology. **Luobin Yu:** Validation, Data curation. **Shengnan Yang:** Validation, Methodology. **Zeyu Xia:** Validation, Data curation. **Sibo Cheng:** Validation, Data curation, Methodology,

Investigation. **Binbin He:** Writing – review & editing, Supervision, Funding acquisition. **Alexander J. Knowles:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Kan Ma:** Writing – review & editing, Validation, Supervision, Project administration, Funding acquisition, Conceptualization.

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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