

High-temperature stability of Co-based amorphous/nanocomposite alloys in terms of oxidation and secondary crystallization behavior

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Abstract

This study examined the high-temperature stability of Co-based amorphous ribbons, with a focus on oxidation and secondary crystallization behavior. Five Co-based amorphous alloys with the composition $\text{Co}_{75.4}\text{Fe}_{2.3}\text{Mn}_{2.3}\text{Nb}_4\text{X}_2\text{B}_{14}$, where $\text{X} = \text{Si, Cr, Al, B, or Nb}$, were evaluated. The primary oxidation products observed were Co_3O_4 and an internal oxidation zone comprising CoO and FCC-Co. The addition of Si, Cr, and Al was found to enhance corrosion resistance significantly. Furthermore, adding Si, Cr, Al, and Nb increases the transformation temperature and the activation energy for boride formation. Among these elements, Si exhibits the most pronounced improvement in oxidation resistance.

1. Introduction

Co-based soft magnetic amorphous/nanocomposite alloys are highly valued for their exceptional soft magnetic properties, strong mechanical performance, and near-zero saturation magnetostriction. These attributes make them ideal for applications such as sensors [1,2], transformers [3], inductors [4,5] and other magnetic device technologies [6]. Compared to conventional crystalline soft magnetic materials, Co-based amorphous and nanocrystalline alloys exhibit significantly lower eddy current losses. This advantage results from their high electrical resistivity, a direct result of their non-crystalline atomic structure, which lacks long-range order [7]. Furthermore, the thin nature of the ribbon decreases the eddy current loss of the nanocomposite/amorphous alloys [8,9]. The absence of grain boundaries in the amorphous phase also prevents short-circuit diffusion pathways, conferring these materials with superior corrosion resistance relative to their crystalline counterparts [10]. Additionally, the Curie temperature of the amorphous phase is higher than that of Fe-based amorphous/nanocomposite alloys, providing a higher temperature limit for magnetic applications [11].

Despite these promising attributes, several challenges arise when Co-based amorphous and nanocrystalline ribbons are used in high-temperature environments. At an operational temperature

below the secondary crystallization temperature (T_{x2}), the detrimental boride could still form after a period of annealing [12], degrading soft magnetic properties [13]. Moreover, air oxidation, a significant degradation mechanism for alloys at elevated temperatures, is relatively unexplored in the literature for Co-based amorphous/nanocomposite alloys. A comprehensive understanding of how these alloys respond to high-temperature and oxidative environments is crucial for advancing practical use in demanding conditions. The scarcity of systematic studies on their corrosion resistance and microstructural evolution under high-temperature oxidation highlights a critical gap in materials science research. Therefore, investigating the secondary crystallization and oxidation behavior of Co-based nanocomposite alloys is essential for developing advanced materials with enhanced durability and performance.

This study investigates high-temperature stability of Co-based amorphous/nanocomposite alloys by examining their oxidation and crystallization behaviors. Five compositions were selected: $\text{Co}_{75.4}\text{Fe}_{2.3}\text{Mn}_{2.3}\text{Nb}_4\text{Si}_2\text{B}_{14}$, $\text{Co}_{75.4}\text{Fe}_{2.3}\text{Mn}_{2.3}\text{Nb}_4\text{Cr}_2\text{B}_{14}$, $\text{Co}_{75.4}\text{Fe}_{2.3}\text{Mn}_{2.3}\text{Nb}_4\text{Al}_2\text{B}_{14}$, $\text{Co}_{75.4}\text{Fe}_{2.3}\text{Mn}_{2.3}\text{Nb}_4\text{B}_{16}$, $\text{Co}_{75.4}\text{Fe}_{2.3}\text{Mn}_{2.3}\text{Nb}_6\text{B}_{14}$. The alloy elements Cr, Al, and Si were specifically chosen for their potential to improve corrosion resistance by forming continuous protective layers [14]. Furthermore, the addition of Si could significantly increase the transformation temperature of detrimental boride in Fe-based nanocomposite alloys [15]. Fe and Mn were incorporated as a variation of published compositions to explore their impact on alloy properties. Strong ferromagnetic exchange interaction of Fe with Co may contribute to high-temperature stability of magnetic properties in both amorphous and crystalline phases [13]. Minor Mn addition is also found to increase the magnetic moment of Co-based amorphous alloy [16]. B and Nb were introduced to improve the glass-forming ability (GFA) and suppress grain growth during primary crystallization [17,18]. Herein, we conducted oxidation annealing on these ribbons at 500°C in the air environment for up to 21 days. We characterized the microstructures after oxidation annealing using scanning electron microscopy (SEM), X-ray diffraction (XRD), and transmission electron microscopy (TEM) to explore microstructural evolution. Furthermore, the crystallization kinetics were investigated using differential scanning calorimetry (DSC).

2. Experimental methods

Five amorphous ribbons with compositions $\text{Co}_{75.4}\text{Fe}_{2.3}\text{Mn}_{2.3}\text{Nb}_4\text{X}_2\text{B}_{14}$, where X=Si, Cr, Al, B, Nb were synthesized. For simplicity, these alloys are referred to as #Si, #Cr, #Al, #B, and #Nb, respectively, throughout this paper. High-purity elemental materials were accurately weighed

according to the desired alloy compositions and alloyed in an arc furnace under an inert atmosphere to prevent oxidation. Resulting ingots were remelted at least three times to ensure chemical homogeneity. Ingots were then melted and rapidly quenched by ejecting through a narrow nozzle onto a rapidly spinning, water-cooled copper wheel, achieving cooling rates on the order of 10^6 K/s necessary to form fully amorphous ribbons [19]. This casting method, known as spin casting or melt spinning, is described in detail in previous publications [13]. XRD analysis was performed on the as-spun samples to confirm their amorphous nature, indicated by broad diffraction humps and the absence of sharp crystalline peaks.

The crystallization behavior of synthesized amorphous ribbons was investigated using DSC with a PerkinElmer STA 6000 instrument. In each test, approximately 20 mg of sample was placed in an alumina crucible and heated from room temperature to 750 °C at a constant heating rate of 20K/min under a nitrogen atmosphere to prevent oxidation. The exothermic peaks observed in the DSC thermograms correspond to crystallization events, allowing the determination of the crystallization characteristics.

Oxidation annealing was performed in a preheated box furnace at 500 °C in an ambient air environment of 7, 14, and 21 days. Ribbons were suspended using 316L stainless steel wire through a 3 mm hole at the top of each ribbon to ensure uniform exposure to the oxidizing atmosphere on all sides. Samples were weighed before and after oxidation annealing using an analytical balance with a precision of 0.1 mg to determine weight gain due to oxide formation. The weight of each sample is around 60mg.

XRD analyses were conducted on the samples after exposure using a Malvern Panalytical Empyrean diffractometer equipped with Co K α radiation ($\lambda = 1.78897$ Å). Diffraction patterns were collected over a 2θ range of 20° to 100°, with a step size of 0.02° and a counting time of 1 s per step. Quantitative phase analysis was performed using Rietveld refinement implemented in the HighScore Plus software. The thickness of oxide scales formed on ribbons was measured from cross-sectional SEM images using ImageJ, an image processing program developed by the National Institutes of Health (NIH) [20].

SEM observations, including secondary electron and backscattered electron imaging, along with associated EDS scans, were performed using a ZEISS 500 VP equipped with Oxford EDS detectors. An acceleration voltage of 20 kV and a 30 μ m aperture size were selected. For cross-sectional investigation, the samples were mounted using epoxy resin and cured for approximately 6 hours at room temperature. Once the resin was cured, the samples were polished using SiC

sandpapers with progressively finer grits up to 1200 grit, followed by diamond polishing to a 0.02 μm surface finish.

For detailed microstructural analysis of the oxidation and crystallization behaviors, cross-sectional transmission electron microscopy (TEM) samples were prepared using a focused ion beam (FIB) on a Thermo-Fisher Scientific Scios Dual-Beam system. TEM analyses were conducted using a JEOL JEM-2100F and a Thermo-Fisher Scientific Titan Themis G2 200 TEM, both equipped with EDS detectors for elemental analysis. The Gibbs free energies of formation for relevant oxides were calculated using Thermo-Calc software with the metal oxide solutions database (TCOX12) [21].

3. Results

XRD patterns were collected for all Co-based amorphous alloys after oxidation to investigate the phase evolution during oxidation. No significant differences related to phase identity were noted in the XRD patterns of the 14 and 21-day oxidized samples, so only the 7-day oxidized samples are shown in Figure 1a. The XRD patterns of Co-based amorphous/nanocomposite alloys with other oxidation durations and associated detailed phase indexing are available in supplementary materials. Diffraction peaks corresponding to FCC-Co and Co-based 23:6 type boride phase were indexed. Consistent with previous studies [13], the highly faulted, close-packed crystals appear as a primary crystallization product in these materials, while the Co-based 23:6 type borides are associated with secondary crystallization. Although not resolved based on the XRD patterns, HCP-Co is another typical primary crystallization product in this class of alloys. Data presented below attributes primary crystalline peaks measured by XRD is labeled as FCC-Co as a result. The broad nature of these primary crystallization products resulted from its nano-size.

In this work, Co-based 23:6 type boride was referred to as M_{23}B_6 , where M represents mainly the transition metallic element Co in this alloy and a trace of other alloy elements. All oxidized samples exhibited diffraction peaks corresponding to Co_3O_4 , indicating the formation of cobalt oxide upon oxidation. In addition, peaks corresponding to CoO were observed in all samples except for #Si. Minor traces of Nb_2O_5 and Fe_3O_4 were also detected; however, due to their weak diffraction signals, these phases were not included in the quantitative XRD analyses presented in the following sections.

Figure 1b presents the 2θ values of XRD patterns in the range of 63° to 71° , showing that the diffraction pattern of the M_{23}B_6 boride in the #Nb sample exhibits a smaller 2θ value compared to the other Co-based amorphous/nanocomposite alloys. This indicates that the lattice constant of

$M_{23}B_6$ boride in #Nb is larger than others which may be attributed to the occupation of Nb in the 8c site of $M_{23}B_6$ boride. According to the work summarized by Ohodnicki et al. [22], the 8c site of $M_{23}B_6$ boride has a large volume and is preferentially occupied by large atoms such as Nb. Since the atomic radius of Nb is greater than that of Co, Nb occupation of the 8c site leads to lattice expansion. If all 8c sites are fully occupied by Nb, the resulting stoichiometry would be $Co_{21}Nb_2B_6$. DFT calculations from the Materials Project [23] confirm that $Co_{21}Nb_2B_6$ has a lattice constant of 10.46 Å, larger than pure 23:6 cobalt boride, $Co_{23}B_6$ (10.37 Å). Therefore, since the #Nb sample contains 2 at.% more Nb than other alloys, more Nb occupies the 8c site, resulting in a larger lattice parameter in the $M_{23}B_6$ boride.

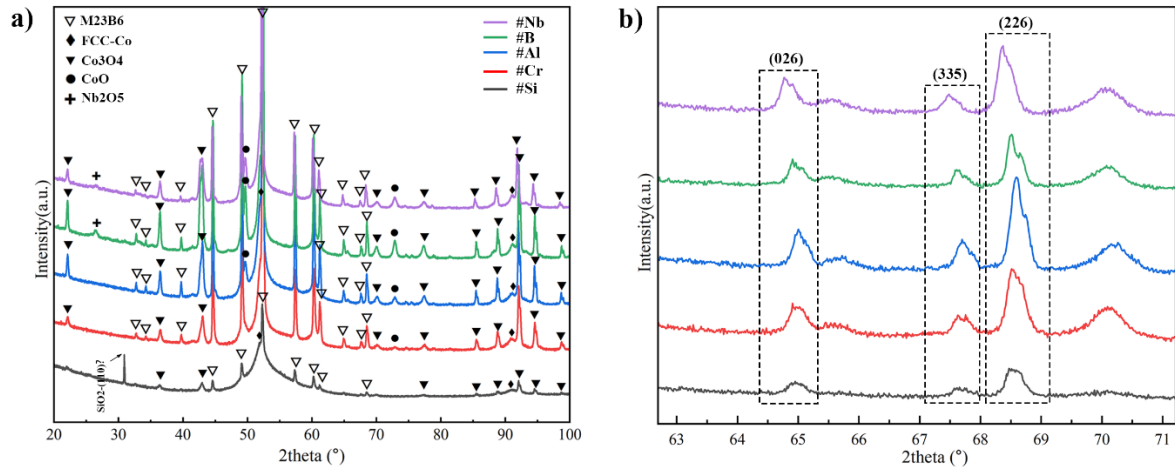


Figure 1: a) XRD patterns of 7-day oxidized Co-based amorphous/nanocomposite alloys; b) Zoom-in XRD patterns showing diffraction pattern of $M_{23}B_6$ boride in #Nb exhibit smaller 2 theta value of each crystalline plane meaning a larger lattice parameter of $M_{23}B_6$ in #Nb which presumably is associated with Nb incorporation within the $M_{23}B_6$ structure.

3.2 Non-isothermal DSC tests and activation energy

Figure 2a shows the non-isothermal DSC curves of Co-based amorphous/nanocomposite alloys obtained at a heating rate of 20K/min. The full table containing crystallization temperatures at the heating rates from 5K/min to 70K/min for all samples used in this project can be found in the supplementary material. The heat flux profile of these amorphous ribbons comprises two exothermic transformations during non-isothermal DSC [25]. Considering the crystallization temperature sequence, the process occurring at the lower temperature is referred to as primary crystallization, while the process occurring at the higher temperature is referred to as secondary crystallization. As the temperature increases further, the residual matrix crystallizes, corresponding

to the secondary crystallization peaks in the DSC traces. Different alloy compositions show a minor effect on the primary crystallization temperature but a relatively significant impact on the secondary crystallization temperature. Using the #B sample as a starting point, replacing B with Si, Cr, Al, and Nb significantly increased the secondary crystallization temperature, with the effect being $T_{x2Si} > T_{x2Nb} > T_{x2Al} > T_{x2Cr}$.

The activation energy represents the nature of the crystallization and is a crucial parameter for the thermal stability [26] and its magnitude presents the energy barrier of nucleation and growth of crystalline phases [19]. In this study, the Kissinger method was used to calculate the activation energy of these Co-based amorphous alloys' primary and secondary crystallization. The Kissinger method could be written as:

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E(x)}{RT_p} + C \quad \text{Eqn. 1}$$

Where β represents the heating rate, T_p indicates the peak temperature of crystallization at the specified heating rate, E denotes the activation energy of crystallization, and C is a constant. The activation energy could be calculated by finding the slope of $\ln\left(\frac{\beta}{T_p^2}\right)$ as a function of $-1/T_p$. For this purpose, additional non-isothermal DSC tests were performed at the heating rate of 5K/min, 10K/min, 20K/min, 40K/min, and 70K/min. The $\ln\left(\frac{\beta}{T_p^2}\right)$ as a function of $-1/T_p$ for primary crystallization and secondary crystallization of these Co-based amorphous alloys were presented in Figure 2b and Figure 2c respectively. The estimated activation energies of primary crystallization and secondary crystallization of these Co-based amorphous alloys are listed in Figure 2d. The #Si and #Nb samples exhibit the highest and second-highest activation energies, indicating higher energy barriers for secondary crystallization. In addition, #B exhibits the lowest energy barrier. Replacing part of B with Cr or Al could increase activation energy, but it is not as efficient as using Si and Nb.

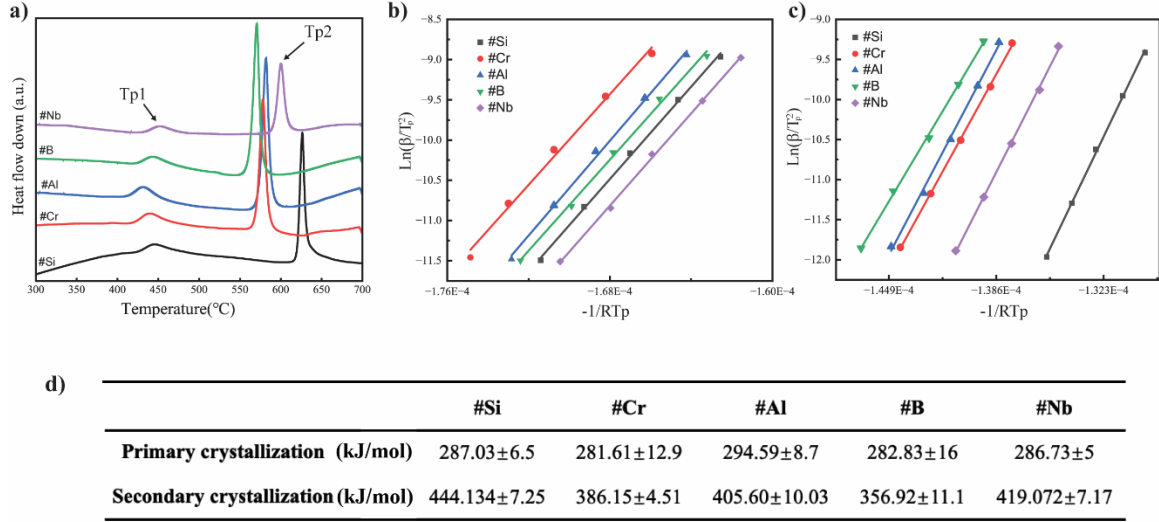


Figure 2: a) Non-isothermal DSC curves of Co-based amorphous alloys obtained at the heating rate of 20K/min; $\ln\left(\frac{\beta}{T_p^2}\right)$ as a function of $-1/T_p$ for b) primary and c) secondary crystallization showing the strong dependence of secondary crystallization temperature on alloy chemistry with a relatively weak dependence of primary crystallization; d) a table of measured activation energies, E_a , in kJ/mol

3.3 Oxidation kinetics

Figure 3 shows the mass gain data of oxidized Co-based amorphous/nanocomposite alloys under investigation. The #Si sample exhibits the lowest mass gain, indicating the highest oxidation resistance among the five compositions. The #Cr sample shows the second lowest mass gain, and the #Al sample shows the third lowest. #Nb and #B samples exhibit the fourth and fifth lowest mass gain, respectively, indicating lower oxidation resistance.

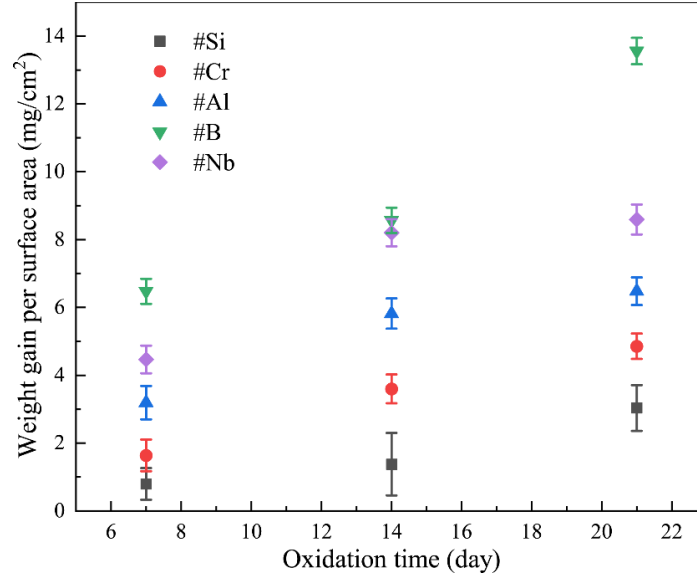


Figure 3: Mass gain data of oxidized Co-based amorphous/nanocomposite alloys

Figure 5 shows the SEM surficial SEM images of Co-based amorphous ribbons after oxidation tests at 500C. After 7 days of oxidation, the #Si sample (Figure 4a) exhibited only minor surface oxidation, with no notable morphological changes observed after 14 days (Figure 4b) and 21 days (Figure 4c). In contrast, the #Cr sample developed micro-sized oxide nodules on its surface after 7 days (Figure 4d), but the surface morphology remained largely unchanged after 14 days (Figure 4e) and 21 days (Figure 4f) of oxidation. The #Al sample also exhibited oxide nodule formation after 7 days (Figure 4g), although the nodules were slightly larger than those on the #Cr sample. Moreover, both the size and density of the oxide nodules on the #Al surface increased progressively with longer oxidation durations (Figure 4h, i). In the cases of the #Nb and #B samples (Figure 4j-o), extensive oxide nodule formation was already evident after 7 days, followed by rapid growth that eventually produced a continuous oxide layer fully covering the sample surfaces.

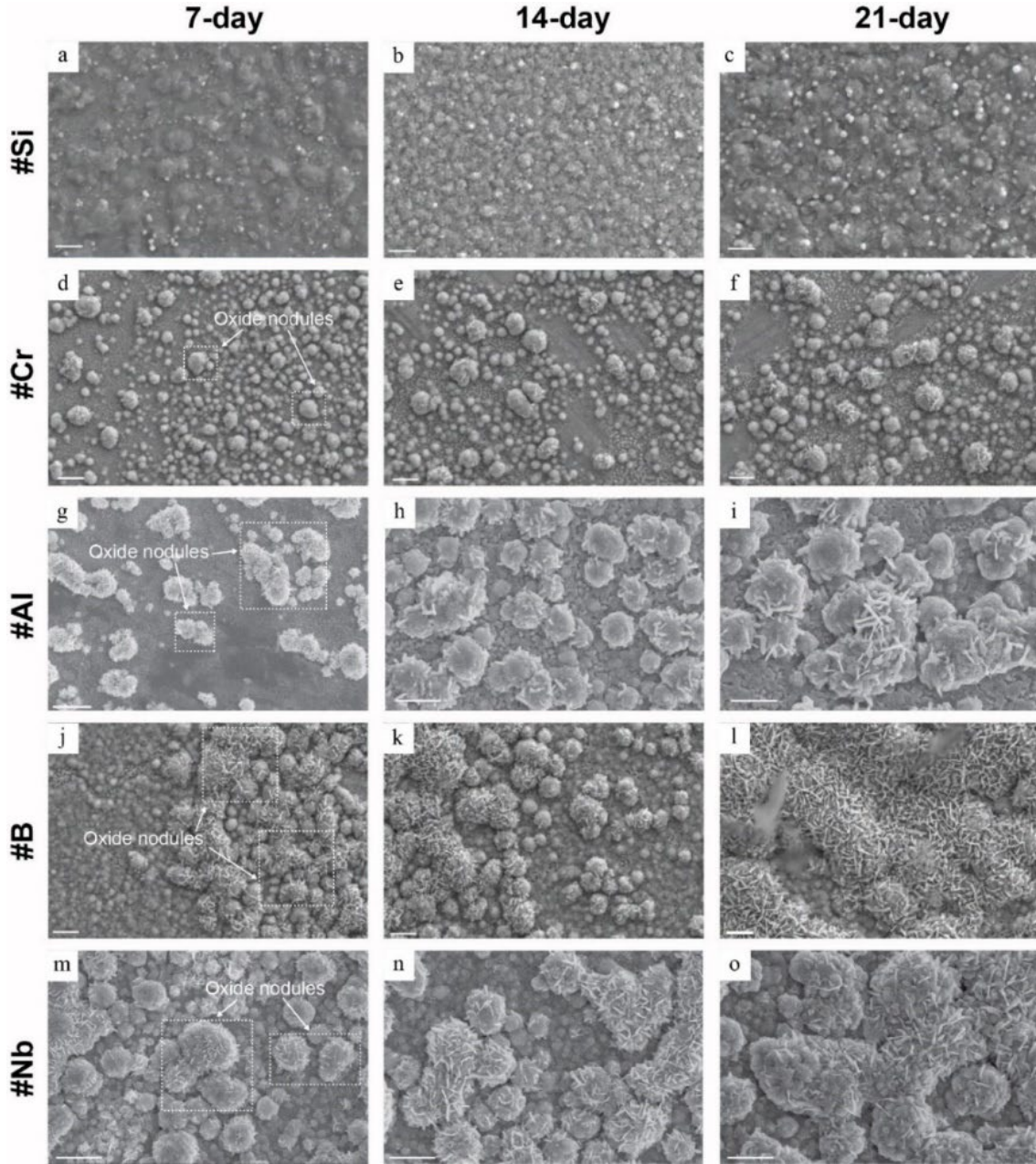


Figure 4: Surficial SEM images of oxidized Co-based amorphous/nanocomposite alloys (scale bar is 5 μm)

3.6 Cross-sectional morphology

Figure 5a-c shows the SEM images of #Si after oxidation at 500°C for 7, 14, and 21 days, respectively. Numerous voids were observed in the oxide scales. These voids isolated the oxide scales near the surface, resulting in a sandwich structure of oxide scales. Figure 5d-f represents the SEM images of the alloy matrix of the #Si samples after 7-day, 14-day, and 21-day oxidation treatment, respectively. Small amounts of SEM-detectable crystalline grains were observed after 7

days of oxidation, as indicated by arrows in Figure 5d, with an increase in phase fraction and particle size after 14 days and 21 days of oxidation as shown in Figure 5e, and Figure 5f respectively. The quantitative particle sizes were provided below the SEM images. After 21 days of oxidation, particle size and phase fraction (see) did not increase further, implying that a kinetic metastable microstructure may be achieved. These large crystalline grains are homogeneously distributed within the bulk of the alloy matrix, but there is a region near the alloy/scale interface that is free of these larger crystalline grains, as shown in Figure 5b-c. These observations are discussed in more detail in subsequent sections.

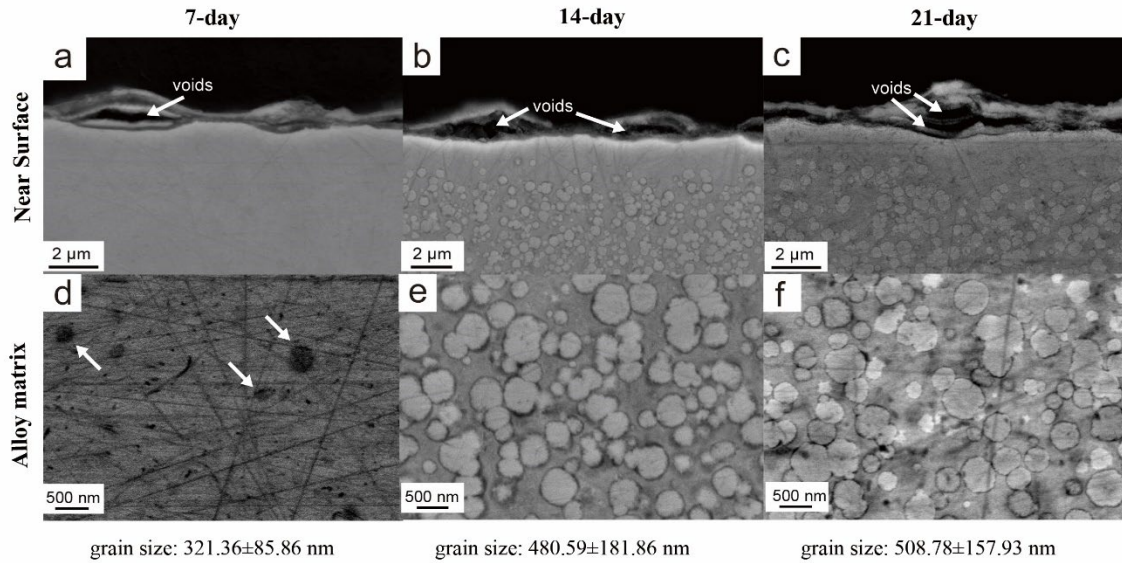


Figure 5: Cross-sectional SEM images (a-c) near the surface and (d-f) at the center of the alloy matrix of #Si after 7-day, 14-day, and 21-day oxidations, respectively

Figure 6 shows the cross-sectional STEM-HAADF image and associated EDS maps of 7-day oxidized #Si samples. The EDS maps indicate that the chemical composition of the oxide scales formed in the #Si sample is predominantly Co-rich oxide with traces of other elements. These minor composition differences were detected through EDS point analysis. The segregation of Fe and Mn in the outermost layer of the oxide was observed from the EDS point analysis at point 1. The thickness of this Fe- and Mn-rich oxide layer is about 30 nm. Beneath this layer, there is another thick oxide layer of approximately 200 nm. EDS analysis at point 2 shows that this oxide layer contains mainly Co and a small trace of Fe. Beneath this layer, the microstructure becomes complex, containing Co-rich oxides, voids, and a Co-rich phase. EDS point analysis at point 3 indicates this Co-rich phase contains very low oxygen content, likely due to surrounding oxides, and high Co

content, similar to the alloy matrix. Additionally, the image contrast of this Co-rich phase under STEM is similar to the alloy matrix. Thus, the crystal structure of this white Co-rich phase is likely the same as the alloy matrix as observed in the XRD patterns in Figure 1. The region where point 3 is located contains both oxide and alloy matrix. Thus, this region could be identified as an internal oxidation zone (IOZ).

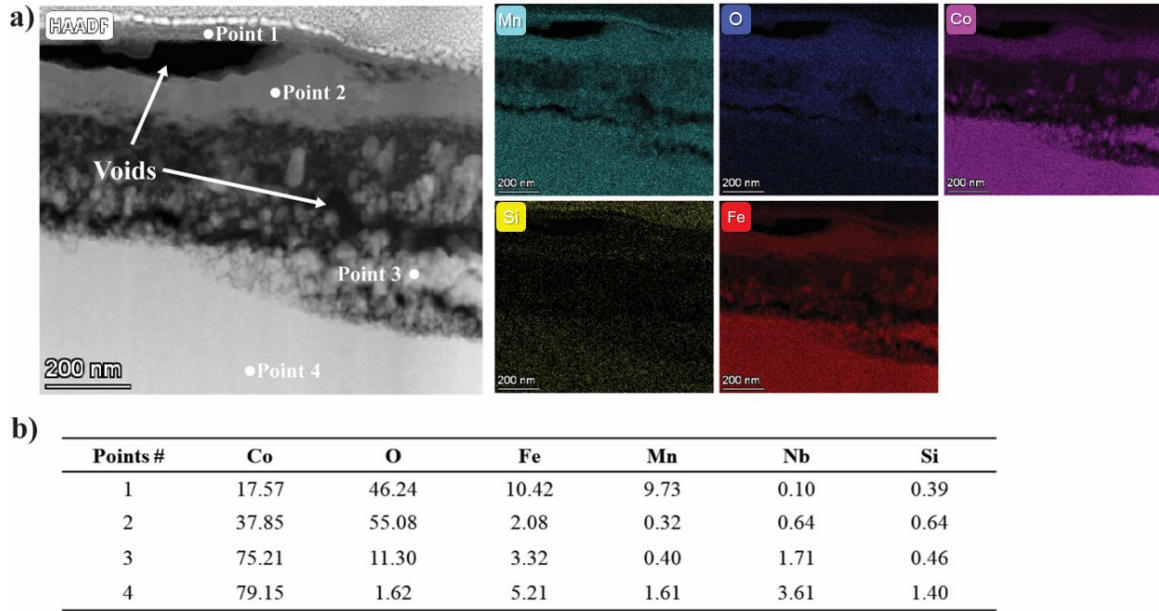


Figure 6: a) STEM-HAADF image of 7-day oxidized #Si sample and associated EDS maps; b) EDS point analysis (in at. %) at selected points in a)

Another FIB sample was prepared in the middle of the 7-day oxidized sample to study microstructural evolution in the alloy matrix. Large crystalline grains were observed in this region, as shown in the STEM-HAADF image in Figure 7a. The SAED image of the large crystalline grain is shown in Figure 7c, revealing its $M_{23}B_6$ boride nature. Figure 7b reveals that the microstructure of the alloy matrix after oxidation annealing consists of large 23:6 crystalline grains surrounded by nano-size primary crystalline grains.

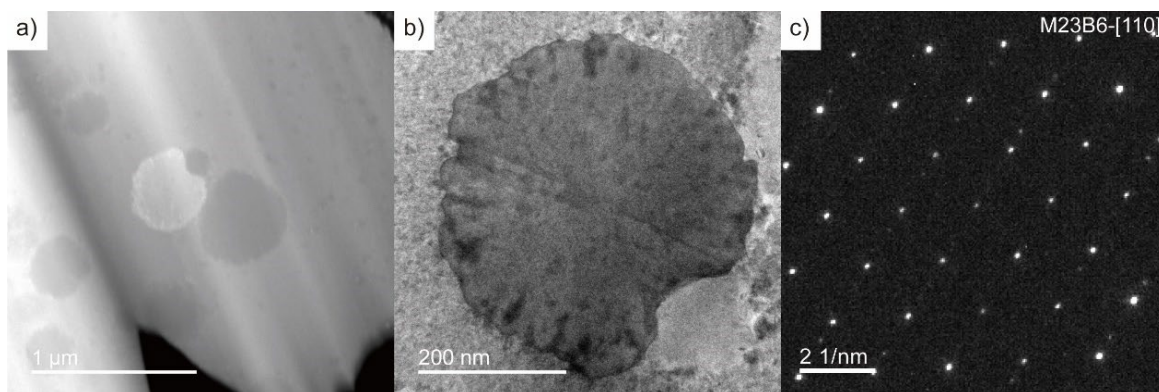


Figure 7: a) STEM-HAADF image of the middle part of the 7-day oxidized #Si sample; b) bright-field TEM image; and c) SAED image of the large crystalline grain identifying it clearly as a M23B6-type phase

Figure 8 shows the SEM image of the FIB area and STEM-HAADF image of the FIB sample of 7-day oxidized #Cr samples. This FIB sample contains two oxide nodules, the internal oxidation zone, and part of the alloy matrix. Figure 8a shows the FFT of one of the oxide grains in the marked area a, confirming the Co_3O_4 nature of the oxide nodule. Figure 8b presents the FFT image of a large crystalline grain in the alloy matrix in marked area b, indexed as M_{23}B_6 borides. Figure 8c presents the SAED of the internal oxidation zone. The continuous diffraction rings of FCC-Co and CoO oxide were indexed. Besides the relatively white region of the IOZ, a dark region is also observed. The SAED of this dark region is shown in the supplementary materials. The obvious continuous diffraction patterns could be identified as FCC-Co as well, with a trace of other diffraction patterns that may correspond to oxidation products such as CoO, Nb_2O_5 , etc. The EDS map shows that this dark region of IOZ contains higher oxygen.

Additionally, the dispersed diffraction patterns likely corresponding to Nb_2O_5 and Cr_2O_3 were observed in the SAED patterns. Figure 9 shows the STEM-HAADF image and associated EDS maps of nodule 1 marked in Figure 8, confirming that the oxide nodule is enriched in Co, verifying the Co_3O_4 nature of the oxide nodule. A thin layer of Fe, Mn-rich oxide was observed between the oxide nodule and IOZ. Based on the XRD patterns, this oxide is most likely $(\text{Fe}, \text{Mn})_3\text{O}_4$ oxide. Other alloy elements in #Cr, such as Cr and Nb, were only detected in the IOZ and alloy matrix and were not observed in the external oxide nodule. Furthermore, the core part of this nodule is hollow.

Figure 10 shows STEM and an associated EDS map of nodule 2 marked in Figure 8. Unlike nodule 1, the core of nodule 2 consists of a phase enriched in Co, the HRTEM and associated

diffraction pattern of the core are presented in Figure 10i and Figure 10ii, respectively, confirming that the core part is FCC-Co with a high density of stacking faults.

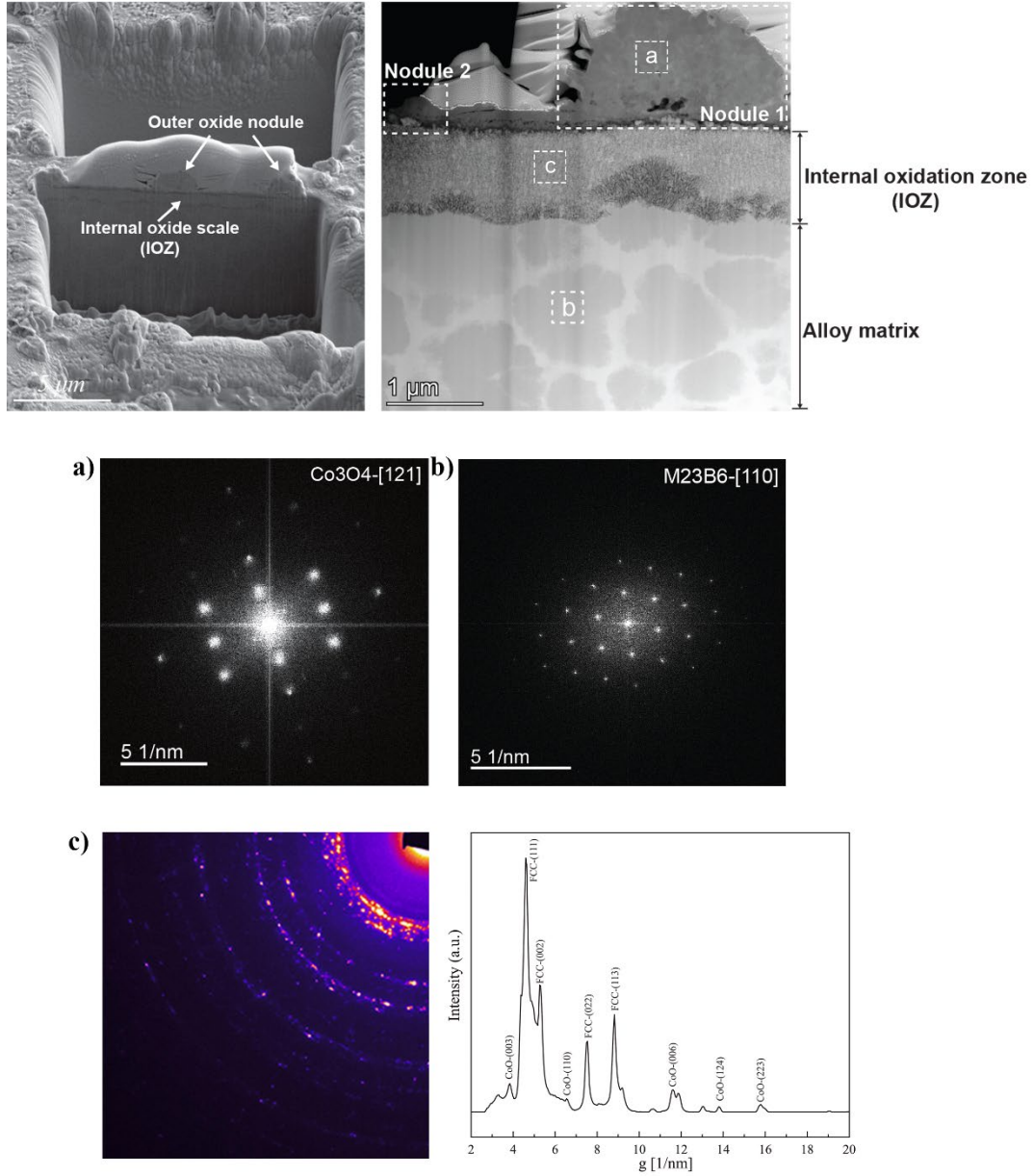


Figure 8: SEM image of FIB area and STEM-HAADF image of the 7-day #Cr FIB sample; the FFT of one grain of oxide in area a confirming its Co₃O₄ nature; the FFT of grain in area b confirming its Co-based M₂₃B₆ nature and the SAED of area c showing that the IOZ consists of FCC-Co and oxides

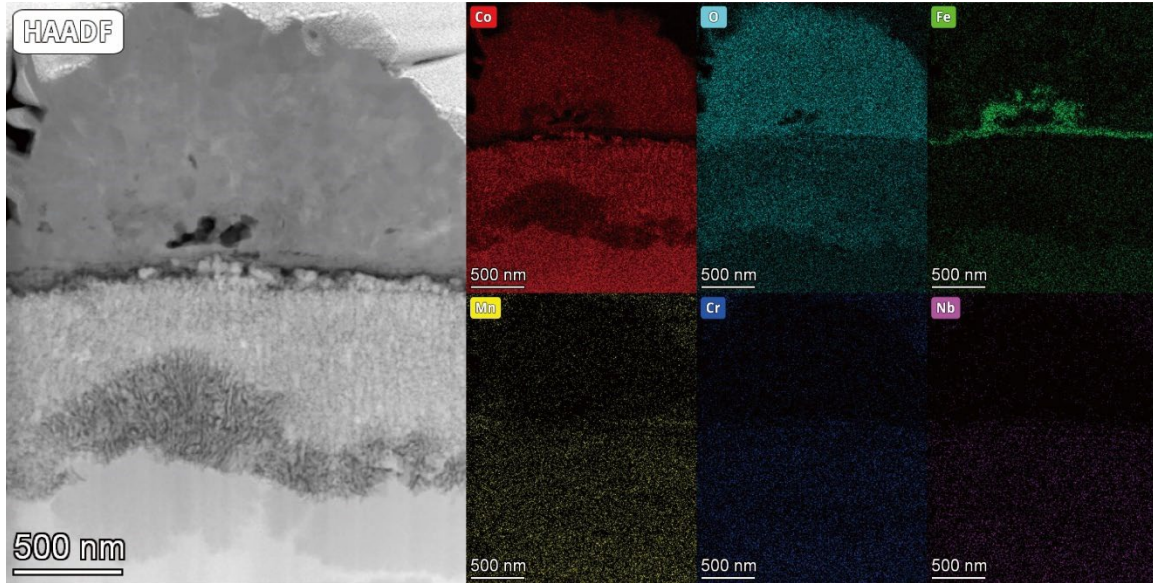


Figure 9: STEM-HAADF image of nodule 1 marked in Figure 8, and associated EDS maps

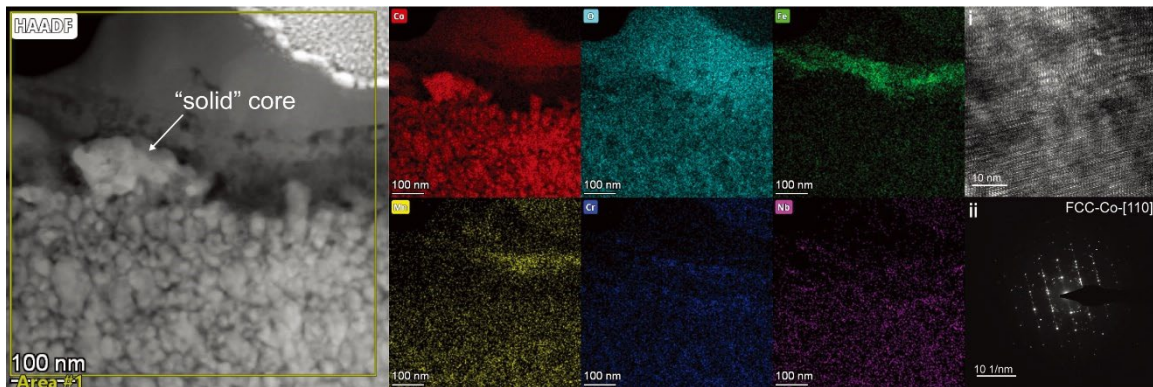


Figure 10: STEM-HAADF image of nodule 2 marked in Figure 8, and associated EDS maps

In contrast to the robust corrosion resistance exhibited by Co-based amorphous/nanocomposite alloys with Si addition, other Co-based amorphous/nanocomposite alloys develop measurable oxidation scales after corrosion testing at 500°C. Figure 11a shows the cross-sectional SEM image of the 7-day oxidized #Cr sample, and the associated EDS line scan from oxide nodule to alloy matrix. In these backscattered SEM images, the FCC-Co core of the oxide nodule exhibits a white contrast due to its distinct crystal structure and chemical composition compared to the surrounding oxides [27]. Its Co-rich nature can also be detected by SEM-EDS. These features are important for confirming the structure of oxide scales in other Co-based

amorphous alloys discussed in the following sections. Figure 12a-c shows the SEM image of the alloy matrix of 7-day, 14-day, 21-day oxidized #Cr samples respectively. The alloy matrix exhibits a microstructure with large crystalline $M_{23}B_6$ phases surrounded by intergranular primary crystalline phases. Figure 12m shows the grain size of oxidized samples, showing that the grain size of these large crystalline grains did not vary significantly from 7 days to 21 days of oxidation. Additionally, XRD quantitative analysis () shows the phase fraction of the $M_{23}B_6$ boride did not vary with oxidation time, suggesting that a kinetically metastable microstructure is established before 7 days of oxidation annealing. The EDS line scans reveal the enrichment of Nb and Cr in the internal oxidation zone of #Cr after oxidation. The enrichment of Nb may be due to Nb_2O_5 , as observed in both XRD patterns and SAED and the enrichment of Cr may be due to Cr_2O_3 , as observed under SAED. The thickness of the internal oxidation zone increased slightly: 1072 ± 88 nm after 7 days of oxidation, 1365 ± 97 nm after 14 days of oxidation, and 1549 ± 152 nm after 21 days of oxidation.

Figure 11d shows the cross-sectional SEM image and associated EDS line scan of #Al after 7 days of oxidation at 500°C . The microstructure is similar to that of oxidized #Cr, featuring a double-layer structure outer oxide nodule containing a Co-rich core and an internal oxidation zone. The EDS line scan reveals that the outer oxide nodule is mainly enriched in Co, similar to the oxide nodule on the surface of oxidized #Cr, suggesting a Co_3O_4 nature of the oxide nodule in #Al. The EDS line scan also indicates that the core part of the oxide nodule is enriched in Co, and this Co-rich core exhibits a similar image contrast to those in #Cr. This suggests that the core part of the oxide nodule here is also FCC-Co. Furthermore, Fe enrichment was observed in the oxide between the oxide nodule shell and the FCC-Co core. In addition, the enrichment of Al was observed in the internal oxidation zone, suggesting the formation of Al-rich oxide in IOZ.

Figure 11e and Figure 11f shows the cross-sectional SEM image and associated EDS line scans of #Al after 14 days and 21 days of oxidation, respectively. The morphology and chemical composition of the oxide scale did not change significantly with increasing oxidation time. Similar to the oxidized #Cr sample, significant internal oxidation and the formation of external oxide nodules were observed. However, the thickness of the internal oxidation zone increased: 1445 ± 266 nm after 7 days, 2026 ± 307 nm after 14 days, and 2192 ± 299 nm after 21 days of oxidation, implying an inward diffusion of oxygen with increasing oxidation time. Figure 12d-f shows the microstructure of the alloy matrix of #Al after oxidation, which exhibits a large crystalline grain surrounded by intergranular phases. The grain size was measured and posted on the side of SEM images, showing that the $M_{23}B_6$ grains grew slightly from 7 days of annealing to 14 days of

annealing and did not further grow during the annealing up to 21 days. Considering the similar behavior of #Al and #Cr, a similar conclusion is derived here: the large crystalline grain is $M_{23}B_6$ borides and the intergranular phase is mainly the primary crystallization product. The enrichment of Al and Nb in IOZ may correspond to the formation of Al_2O_3 and Nb_2O_5 .

Figure 11g-i Figure 12g-i present SEM images of the oxide scale and alloy matrix of oxidized #B samples, respectively. The grain size of crystalline grains was measured and posted on the side of the SEM images. The structure of the alloy matrix and oxide scale of #B is similar to that of #Cr and #Al discussed above, but the oxidation kinetics differ. Compared to the relatively slow growth rate in #Cr and #Al, the oxide nodule on the surface of #B grows significantly with increasing oxidation time. Additionally, #B exhibits a much faster inward development of the internal oxidation zone. Nb enrichment was observed in IOZ. Figure 11j-l Figure 12j-l presents SEM images of the oxide scale and alloy matrix of oxidized #Nb samples, respectively. The microstructure of the oxide scale and alloy matrix of oxidized #Nb is similar to that of #Cr, #Al, and #B. Replacing a portion of B with Nb decreased the oxidation kinetics, as reflected in the thickness of the internal oxidation zone. The thicknesses of the internal oxidation zones are 1736 ± 97 nm, 2718 ± 99 nm, and 3294 ± 110 nm, respectively. A slight decrease in B content, accompanied by its substitution with Nb, leads to an increase in the grain size of the $M_{23}B_6$ phase.

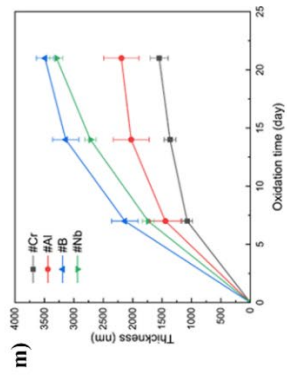
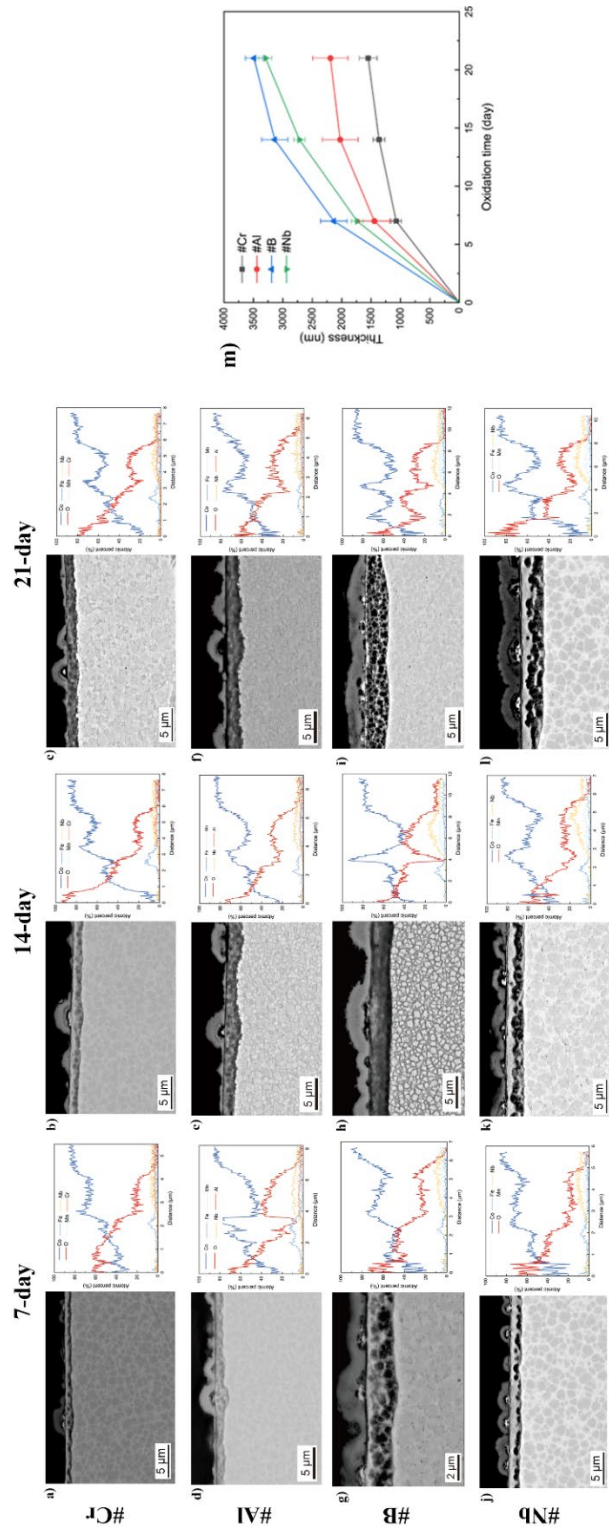


Figure 11: SEM images and associated EDS line scan of oxidized a-c) #Cr, d-f) #Al, g-i) #B, and j-l) #Nb Co-based amorphous/nanocomposite alloys; m) measurement of thickness of internal oxidation zone (IOZ)

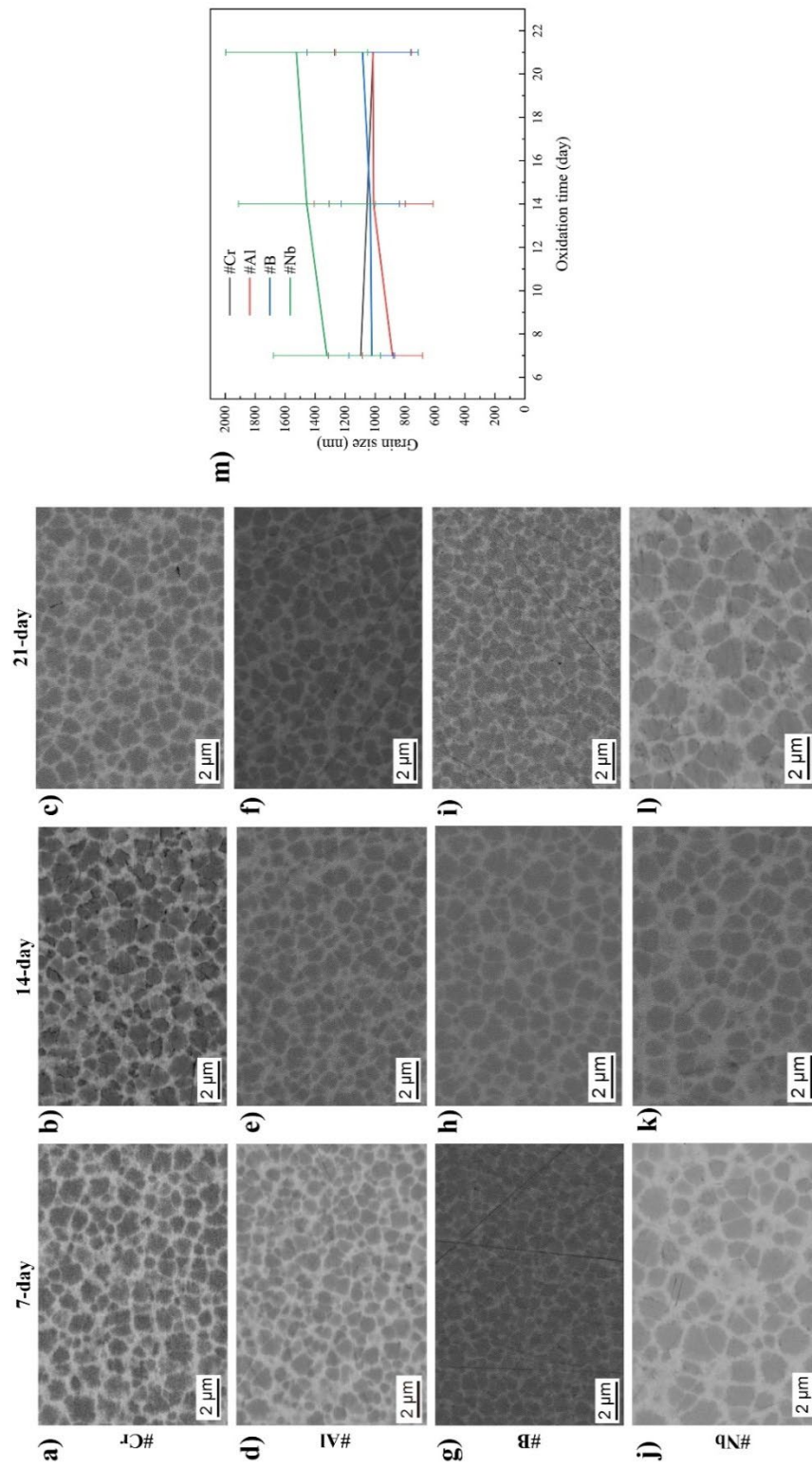


Figure 12: SEM images of the alloy matrix in oxidized samples: a–c) #Cr, d–f) #Al, g–i) #B, and j–l) #Nb; m) Grain size distribution of $M_{23}B_6$ crystalline grains

4. Discussion

Figure 13 shows the phase fractions of Co-based amorphous/nanocomposite alloys after oxidation annealing. The bar chart highlights the trends in crystallization and oxidation products over time, while the table presents the corresponding numerical data. Quantitative phase analysis was obtained by XRD Rietveld refinement from the XRD patterns shown in Figure 1. Considering the multiphase nature and the effect of the residual amorphous phase after oxidation annealing, an R-weighted pattern of less than 10 is accepted in XRD Rietveld refinements. Furthermore, the possible existence of residual amorphous phase after long-term oxidation tests was not included in the quantitative analysis using XRD Rietveld refinement [24].

Although secondary crystallization was induced in all compositions after 7-day oxidation annealing, the #Si exhibits the lowest phase fraction of $M_{23}B_6$ boride among five samples. After 14 days of oxidation annealing, the phase fraction of $M_{23}B_6$ boride in oxidized #Si samples increases and then decreases slightly after 21 days of oxidation, which could be attributed to the consumption from the oxidation. However, it should be noted that this observation is based on XRD measurements from the top surface, and the phase distribution in the bulk may differ. The ratio of phase fractions of FCC-Co and $M_{23}B_6$ borides is around 2:1 after 14 days of oxidation and did not change significantly from 14 days to 21 days of oxidation. In oxidized #Cr, #Al, #B, and #Nb, the ratio of phase fractions of FCC-Co and $M_{23}B_6$ did not change with the oxidation time, with a value of 1:1 for #Cr, #Al, and #Nb and 1:2 for #B. Among five compositions, the oxidized #Si exhibits the lowest phase fraction of $M_{23}B_6$, implying suppression of secondary crystallization by Si addition.

CoO phase was not measured by XRD in #Si samples. In #Cr and #Al samples, at the same oxidation times, the phase fraction of CoO is much less than in #B and #Nb samples, with #Cr showing lower than in #Al. Between oxidized #B and #Nb samples, the phase fraction of CoO in #Nb is less than in #B. These results suggest the addition of Cr, Si, and Al suppress CoO formation.

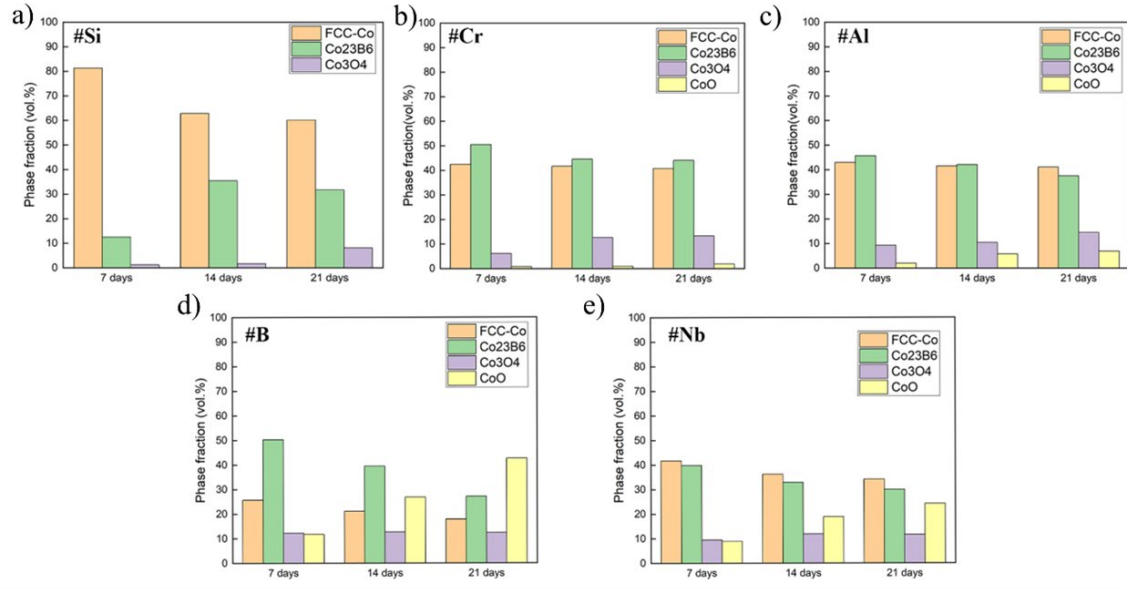


Figure 13: Phase fraction (in vol%) of oxidized a) #Si, b) #Cr, c) #Al, d) #B, and e) #Nb amorphous/nanocomposite alloys, determined by XRD Retrieved Refinement; f) a table of quantitative results is posted at the end

According to the non-isothermal DSC and associated activation energy measurements, we observed that replacing B with Si, Cr, Al, and Nb significantly affects the transformation temperature and activation energy for secondary crystallization, as shown in Figure 2. Si increases the secondary crystallization temperature the most, followed by Nb. The secondary crystallization temperatures of #Cr and #Al are similar and lower than that of #Nb. The different effects on

secondary crystallization temperature among #Si, #Cr, and #Al may be attributed to their different mixing enthalpy with Co and B. The mixing enthalpy of potential atomic pairs are presented in Table 1.

	Mixing enthalpy (kJ/mol)
Co-Si	-38
Co-Nb	-25
Co-B	-24
Co-Al	-19
Co-Cr	-4

Table 1: Mixing enthalpy for atomic pairs, data from ref [28]

The mixing enthalpy of Co-Si is more negative than that of Co-B, indicating that Co-Si clusters are more energetically favorable than Co-B clusters in the residual amorphous phase. Similarly, the Nb-B cluster is more energetically favorable than the Co-B cluster in the residual amorphous phase. In both cases, it is hypothesized that the reduced availability of B around Co in the amorphous phase due to the stronger bonding of alternative elements effectively increases the effective diffusion length required for $M_{23}B_6$ formation. Furthermore, the addition of Nb may delay the nucleation of the $M_{23}B_6$ phase by reducing the effective diffusion coefficient due to the larger atomic size of Nb compared to other alloying elements [29], thus resulting in a higher transformation temperature of $M_{23}B_6$. Co-Al and Co-Cr clusters are less energetically favorable than Co-B clusters; therefore, their impact on the secondary crystallization temperature is primarily attributed to decreased activity of B caused by dilution.

Secondary crystallization occurred in all five compositions during the isothermal oxidation annealing at 500°C. Except for #Si, the grain size and volume fraction (see and Figure 12) of $M_{23}B_6$ phase did not vary significantly with increasing oxidation time, implying achievement of their kinetically stable microstructure within 7 days of annealing. This indicates that #Si has the longest time-lag to the particular volume fraction of secondary crystallization at 500°C among these Co-based amorphous/nanocomposite alloys, consistent with the highest secondary crystallization temperature and activation energy for secondary crystallization, resulting in a more delayed TTT diagram [30,31]. In addition, the Si addition significantly decreased the volume fraction of detrimental $M_{23}B_6$ boride, as seen in the XRD phase quantitative analysis results, as shown in .

#Si, #Cr, and #Al samples exhibit significantly better oxidation resistance than #Nb and #B samples, which may be attributed to the formation of protective oxides within the IOZ. Figure 11m shows the thickness of IOZ of oxidized #Cr, #Al, #Nb, and #B as a function of oxidation time at 500°C. The growth rate of IOZ decreases with increasing oxidation time, suggesting a parabolic growth pattern, implying the development of IOZ is diffusion-controlled. According to the work done by Scott et al. [32], the diffusion-controlled development of IOZ could be expressed as:

$$\xi = 2\gamma(D_0 t)^{1/2}$$

Where ξ is the thickness of IOZ, D_0 is the diffusion coefficient of oxygen in the alloy matrix, t is time and γ is a dimensionless factor. Given the minor alloy composition difference between these alloys, we assume that γ is the same for all five Co-based amorphous alloys. The negligible thickness of IOZ in #Si and the thin nature of IOZ in #Cr and #Al suggest that these protective elements may reduce the inward diffusion of oxygen.

The reduced inward diffusion due to the addition of protective elements may result from blocking internal oxidation through the formation of a protective layer in the IOZ. Figure 14a shows the formation energy of oxides of alloy elements as a function of temperature. The oxides considered in the thermodynamic analysis are those with an equilibrium interface with pure metals. The formation energies of these oxides reflect the oxidation affinity of the corresponding elements, as more negative formation energies indicate a higher driving force for oxide formation under a given oxygen partial pressure. [33]. The potential protective oxide, Cr_2O_3 , Al_2O_3 , and SiO_2 exhibit more negative formation energy than Co_3O_4 , indicating their formation is more energy-favorable. In the oxidized #Cr and #Al samples, EDS signals of Cr and Al were observed in the IOZ, as shown in Figures 12 and 13, respectively, suggesting the formation of these oxides at the IOZ. Since the IOZ of the oxidized #Si sample has a nanoscale thickness, elemental analysis using EDS is challenging. The formation of these protective oxides at the IOZ may suppress the outward diffusion of oxygen and the inward development of the IOZ, leading to a significantly lower phase fraction of oxides compared to the oxidized #Nb and #B samples. Furthermore, the formation energy of NbO is also lower than Co_3O_4 , and the oxidation resistance of #Nb, in terms of weight gain or oxide thickness, is superior to that of #B, suggesting that Nb addition also contributes to the oxidation resistance.

As shown in SEM observations (Figure 4), all oxidized samples except #Si have large oxide nodules. TEM analysis (Figure 7) confirmed that these oxide nodules contain an FCC-Co core with a high density of stacking faults or a hollow core. The locally accelerated oxidation around this

FCC-Co core suggests that the outward diffusion of Co may be accelerated through this high-defect-density core. The hollow core observed in some oxide nodules may result from the Kirkendall effect, but requires more detailed investigation. However, the current experimental results show that adding Si can mitigate the formation of these nodules.

In our previous work [13], by using XPS, boron content was detected in the external oxide of Co-based amorphous/nanocomposite alloy oxidized at 500°C for 7 days, although no diffraction patterns were observed in the SAED or XRD analyses. As explained in the literature [34], this suggests that B_2O_3 exists in an amorphous form. In the current study, an amorphous oxide most likely corresponding to boron oxide was observed, with the associated TEM image shown in Figure 14b. As depicted in the figure, this amorphous oxide is present in the void area, likely due to the volatilization of boron oxide. The low melting point of B_2O_3 (450°C [35]) can result in volatilization at 500°C, leading to the formation of voids in the oxide scale, thus only a minority of residual amorphous oxide is detectable in the void area.

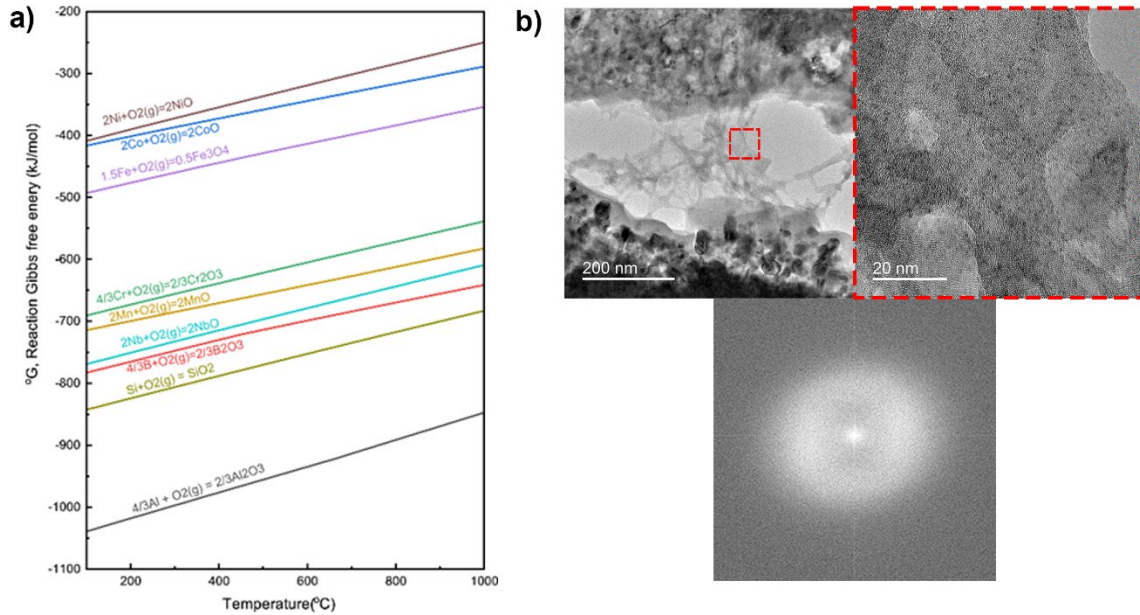


Figure 14: a) Formation energies of oxides of the alloying elements investigated in this study, calculated using Thermo-Calc; and b) TEM images and associated FFT of amorphous oxide observed in oxidized #Si sample

5. Conclusion

In this study, the high-temperature stability of Co-based amorphous ribbons in terms of oxidation and secondary crystallization resistance was investigated. Five Co-based amorphous

alloys with compositions of $\text{Co}_{75.4}\text{Fe}_{2.3}\text{Mn}_{2.3}\text{Si}_2\text{Nb}_4\text{B}_{14}$, $\text{Co}_{75.4}\text{Fe}_{2.3}\text{Mn}_{2.3}\text{Cr}_2\text{Nb}_4\text{B}_{14}$, $\text{Co}_{75.4}\text{Fe}_{2.3}\text{Mn}_{2.3}\text{Al}_2\text{Nb}_4\text{B}_{14}$, $\text{Co}_{75.4}\text{Fe}_{2.3}\text{Mn}_{2.3}\text{Nb}_6\text{B}_{14}$, and $\text{Co}_{75.4}\text{Fe}_{2.3}\text{Mn}_{2.3}\text{Nb}_4\text{B}_{16}$ were studied. The main findings can be summarized as follows:

- The oxidation product of Co-based amorphous alloys includes outward growth of Co_3O_4 and inward growth of an internal oxidation zone consisting of CoO and primary crystallization product, FCC-Co.
- The secondary crystallization product, 23:6 type boride, not only consumes the residual amorphous phase but also the primary crystallization product. This ultimately results in a microstructure with large crystalline 23:6 type borides surrounded by intergranular primary crystalline phases. The ratio of primary crystallization products and secondary crystallization products depends on the alloy compositions.
- Replacing B with Si, Cr, Al, and Nb can increase the activation energy and transformation temperature of secondary crystallization products and improve oxidation resistance as defined by measured mass gain and the thickness of IOZ.
- The addition of Si and Nb has the strongest impact on improving the transformation temperature and activation energy of secondary crystallization.
- The Co_3O_4 oxide nodule with hollow or FCC-Co core was formed during oxidation annealing. The addition of Si in the material could mitigate its formation.
- Voids in the oxide scale may result from the volatilization of boron oxide.

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