

Review

The Grain Boundary Wetting Phenomena in the Ti-Containing High-Entropy Alloys: A Review

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Abstract: In this review, the phenomenon of grain boundary (GB) wetting by melt is analyzed for multicomponent alloys without principal components (also called high-entropy alloys or HEAs) containing titanium. GB wetting can be complete or partial. In the former case, the liquid phase forms the continuous layers between solid grains and completely separates them. In the latter case of partial GB wetting, the melt forms the chain of droplets in GBs, with certain non-zero contact angles. The GB wetting phenomenon can be observed in HEAs produced by all solidification-based technologies. GB leads to the appearance of novel GB tie lines T_{wmin} and T_{wmax} in the multicomponent HEA phase diagrams. The so-called grain-boundary engineering of HEAs permits the use of GB wetting to improve the HEAs' properties or, alternatively, its exclusion if the GB layers of a second phase are detrimental.

Keywords: titanium alloys; high-entropy alloys; grain boundary wetting; phase transitions; phase diagrams

1. Introduction

According to the generally accepted definition, high-entropy alloys (HEAs) are materials that contain at least five different components, among which the main component cannot be selected [1–4]. Therefore, they are also called alloys without principal components or multiprincipal component alloys. High-entropy alloys have become extremely popular among researchers in recent years. There are literally thousands of articles devoted to them. For this reason, this review will be limited to two aspects. First, this review will consider alloys that contain titanium as principal or secondary component. Secondly, we will restrict ourselves to the phenomena associated with grain boundaries. Moreover, among the grain-boundary phenomena, emphasis will be placed on the phenomena associated with wetting-phase transformations.

High-entropy alloys containing titanium can be conventionally divided into two groups. The first group includes alloys containing zirconium and hafnium, together with titanium [5–7]. Ti, Zr and Hf are in the same group in the Mendeleev periodic table of

elements. Just like titanium, they have a body-centered crystal lattice at high temperatures (bcc, β -Ti, β -Zr, β -Hf), and at low temperatures, they possess a hexagonal close-packed lattice (hcp, α -Ti, α -Zr, α -Hf). Moreover, at high pressure, all three metals transform into the high-pressure ω -phase with a more complex hexagonal lattice [8,9]. In some Ti-alloys, the metastable ω -phase appears even after certain heat treatment, without application of high pressure [10–12]. In HEAs containing titanium, zirconium and hafnium, other elements with a bcc lattice are most frequently present (for example, vanadium, molybdenum, tungsten, etc.). Therefore, such HEAs will also have a body-centered cubic lattice. The second group is composed of alloys in which titanium plays a somewhat subordinate role [13–16]. In particular, these are the alloys with a face-centered cubic lattice (fcc) [17–21].

Generally speaking, from the very beginning of the studies of HEAs, it was noticed that in a certain range of compositions and temperatures, high-entropy alloys contain only one phase, namely a solid solution where all five or more components form a random solid solution [1–4]. Recently, the interest of researchers has shifted from such simple HEAs consisting of only one phase of a multicomponent solid solution to the alloys with certain elements of heterogeneity. These include the spatially inhomogeneous distribution of the components, the second-phase precipitates in a multicomponent solid solution, various grain-boundary layers, etc. For such studies, a special term, “metastability engineering”, has been coined [22,23]. In many cases, the formation of such heterogeneous structures instead of a homogeneous multicomponent solid solution can be discussed in terms of phase transitions at grain boundaries (GBs). Such phase transformations include the wetting of grain boundaries with a melt or a second solid phase, as well as the formation of various thin grain-boundary layers of the second phase at the boundaries [24–27]. These phenomena depend non-trivially on the composition, temperature and pressure in a multicomponent system. This review is devoted to these grain-boundary processes in HEAs containing titanium.

2. Grain Boundary Wetting by the Liquid Phase

In the majority of cases, multicomponent alloys are synthesized by crystallization from the melt (arc or induction melting in vacuum or argon [5–7,13–18,28–43], plasma spark sintering [19], electric current assisted sintering [20,21], laser or plasma cladding deposition of coatings [44–55], additive manufacturing by the laser-powder bed fusion [56,57] or laser-metal deposition [58], self-propagating high-temperature synthesis (SHS) [59], and by brazing within the brazing joints [60,61]). Figure 1 shows a schematic phase diagram for the simplest case when there are only two components in the system. Cooling routes are shown by dashed lines 1 to 5 in Figure 1 for alloys with different compositions. Upon cooling, after crossing the liquidus line, the alloy first enters the two-phase region, where the melt, L , is in equilibrium with the solid solution, S . The melt solidifies completely when the temperature drops below the solidus line. We will use this schematic phase diagram in further explanations of GB phenomena. In the case of HEA, the situation is much more complicated. For example, six-component alloys are described by a phase diagram in six dimensions. In this case, between the single-phase melt, L , and the completely solidified material, S , there can be not one two-phase region, $S + L$, but many regions in which more than one solid and more than one liquid phase can coexist. If a polycrystalline sample is in the two-phase region, $S + L$, of the phase diagram, then it contains GBs in the solid phase and interphase boundaries between the solid phase and the melt. A triple junction of two interphase boundaries and one GB is formed in the locations where the GB is in contact with the melt (see Figure 1, schemes between Routes 1 and 2).

If the energy of the GB σ_{GB} is less than the energy of the two solid/liquid interphase boundaries, $2\sigma_{SL}$, contacting this GB at the triple junction, then the contact angle, θ , at this triple junction is non-zero (see Figure 1). This situation with $\theta > 0$ is called incomplete (or partial) wetting of the GB by the melt. If the energy of the grain boundary is higher than the energy of the two solid/liquid interphase boundaries, $\sigma_{GB} > 2\sigma_{SL}$, then the contact angle will be equal to zero. In this case, the GB must be replaced by a sufficiently thick

layer of the liquid phase. This situation is called complete wetting of the GB by the melt. In a number of systems, the angle between the GB and the melt decreases with increasing temperature [62–65]. Moreover, after reaching a certain temperature, T_w , the contact angle can become zero. In other words, incomplete wetting is replaced by complete wetting of the boundary. This temperature, T_w , is called the GB wetting phase-transition temperature. The wetting phase transition, like any other phase transformation, can be of either the first or the second order [66–68]. In the case of a first-order phase transition, the first derivative of the contact angle, with respect to temperature, exhibits a discontinuity at the temperature T_w [62,66,67]. It drops abruptly from a certain finite value to zero [62,66,67]. In the case of a second-order (continuous) phase transition, the first derivative of the contact angle with respect to temperature continuously decreases with increasing temperature and becomes equal to zero at the transformation temperature, T_w [66,67]. The energy of GBs depends on their misorientation angle, χ , and inclination angle, ψ [69]. It exhibits sharp cusps at certain χ and ψ values [70]. The energy spectrum of GBs can be very wide. Obviously, the higher the GB energy, the smaller the contact angle, θ , at its triple junction with the melt [71]. Thus, at a fixed temperature, a wide range of contact angles is observed in a two-phase polycrystal. As the temperature rises, these contact angles, θ , also decrease at different rates. This leads to the wide scatter of the GB wetting phase-transition temperatures for the GBs with different energies.

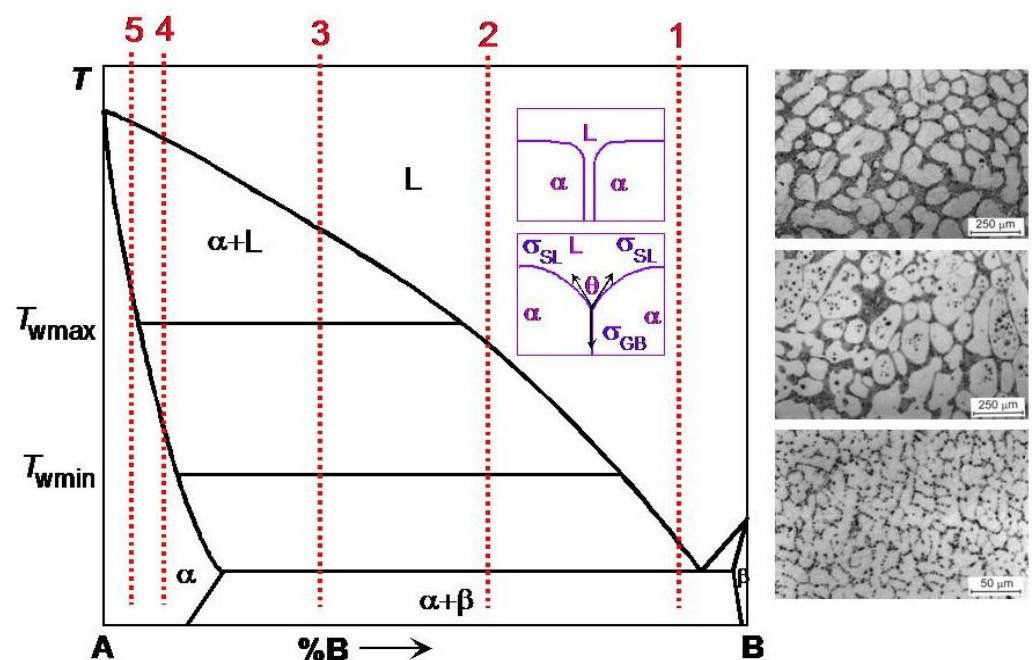


Figure 1. Schematic binary phase diagram for the explanation of GB wetting phenomena. Bold solid lines show the bulk-phase transformation. Thin solid lines show the tie lines of the GB wetting by the melt at T_{wmin} and T_{wmax} . Vertical red dotted lines 1 to 5 show different solidification routes. Schematics between Routes 1 and 2 show the cases of complete (top) and partial (bottom) GB wetting. Micrographs on the right-hand side of the diagram are for the Al-Mg samples annealed above T_{wmax} (top micrograph, all GBs are completely wetted), between T_{wmin} and T_{wmax} (middle micrograph, some GBs are completely wetted and other GBs are partially wetted) and below T_{wmin} (bottom micrograph, no completely wetted GBs).

The typical microstructures of such two-phase polycrystals are shown in Figure 1 for the binary Al–Mg alloys. Two tie lines for the transition from partial to complete wetting appear in the phase diagram. The first line at T_{wmin} corresponds to the GBs with the highest energy, σ_{GB} . Below this temperature, there are no completely wetted GBs in a polycrystal. It exhibits only partially wetted GBs with a nonzero contact angle, θ . Above the minimum wetting phase-transition temperature, T_{wmin} , the completely wetted GBs

appear in the polycrystal. With a further increase in temperature, the fraction of such completely wetted boundaries in the sample increases until it reaches unity at T_{wmax} . This temperature, T_{wmax} , is indicated on the phase diagram by another horizontal tie line. Above this line, all grain boundaries are completely wetted (see diagram), and each grain is fully embedded in the melt without touching the other solid grains since the formation of “dry” GBs is thermodynamically unfavorable. Thus, in this region of the phase diagram, all solid crystallites are separated from each other by interlayers of the liquid phase. Consequently, in the phase diagram in the S + L two-phase region, where the solid and liquid phases are in equilibrium, the new tie lines appear. They are associated with GB wetting phase transformations. These lines are absent in traditional phase diagrams, which do not take into account the presence of grain boundaries in the sample. Accordingly, the microstructure of the polycrystal after solidification will be different for different solidification routes (see dotted lines 1 to 5). It will depend on the path along which the sample crosses the two-phase region during solidification. Such principally different situations for solidification are schematically shown in Figure 1 by vertical dotted lines 1 to 5.

The first dotted line, 1, on the right-hand side of Figure 1 does not intersect the grain boundary lines, T_{wmin} and T_{wmax} , in the phase diagram. When the melt is cooled, Route 1 crosses only the lines of bulk liquidus and the line of eutectic transformation. When such a sample solidifies, grain boundaries inside are formed immediately since they are not separated from each other by the liquid phase. The last pockets of the melt (the richest in the second component) are pushed into the triple junctions between the boundaries upon cooling and solidify there. This is the classical dendrite structure. Thus, after the solidification of such a melt, we can observe a relatively small difference in concentration between the centers of grains and the border regions, while the highest concentration of the second component is observed at the triple junctions of the GBs. As a result, the relatively homogeneous solid solution crystallizes, in which the enriched areas are well-visible. This scheme also works for multicomponent high-entropy alloys. Classical samples of single-phase high-entropy alloys, most likely, are just formed according to the scheme corresponding to the rightmost dotted line, 1. A typical sample of such a microstructure is shown in Figure 2 from Ref. [5]. When the melt is cooled, the second dashed line (Route 2) on the right-hand side of Figure 1 intersects not only the lines of the bulk liquidus and eutectic transformation but also the GB line at T_{wmin} . This means that the solid grains are separated from each other by liquid layers between the bulk liquidus and the grain-boundary tie line. Below the T_{wmin} tie line, these GB interlayers, enriched with the second component, solidify. Thus, enriched interlayers remain in the solid sample along these first GBs. Upon further cooling, the melt solidifies without the formation of grain-boundary-enriched interlayers. As dashed line 2 moves from right to left to Route 3, the sample will contain more and more GBs enriched with the second component after solidification. If the vertical dashed line (Route 3) also intersects the upper grain boundary tie line, T_{wmax} , then at the first stages of solidification, a continuous network of enriched interlayers is formed in the polycrystal between the solid grains (see the respective micrograph). It is subsequently clearly visible on the microstructure of the solidified alloy. At high concentrations of the second component, such a network has characteristic discontinuities (see, for example, the microstructure shown in Figure 3). The fourth vertical dashed line (Route 4) crosses only the bulk liquidus and tie line at T_{wmax} , and then the bulk solidus. In this case, thick enriched layers are visible at many GBs in the solidified sample. If the alloy does not cross the GB lines during cooling (the fifth dotted line, Route 5), then the melt interlayers rich in the second component have no chance of redistributing in the solid state at all. They remain in the solidified sample in the form of a continuous network surrounding the grains poor in the second component (see, for example, the microstructure in Figure 4).

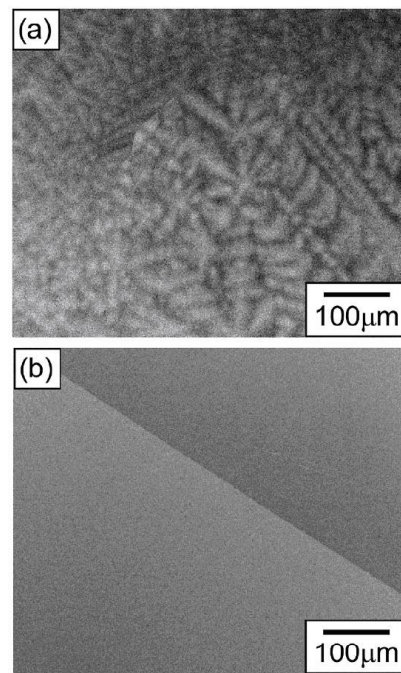


Figure 2. SEM micrographs of equiatomic HfNbTaTiZr polycrystal after arc melting, followed by homogenization treatment at 1773 K for 5 h; (a) as cast, (b) homogenized. Reprinted with permission from Ref. [5]. Copyright 2021 Elsevier.

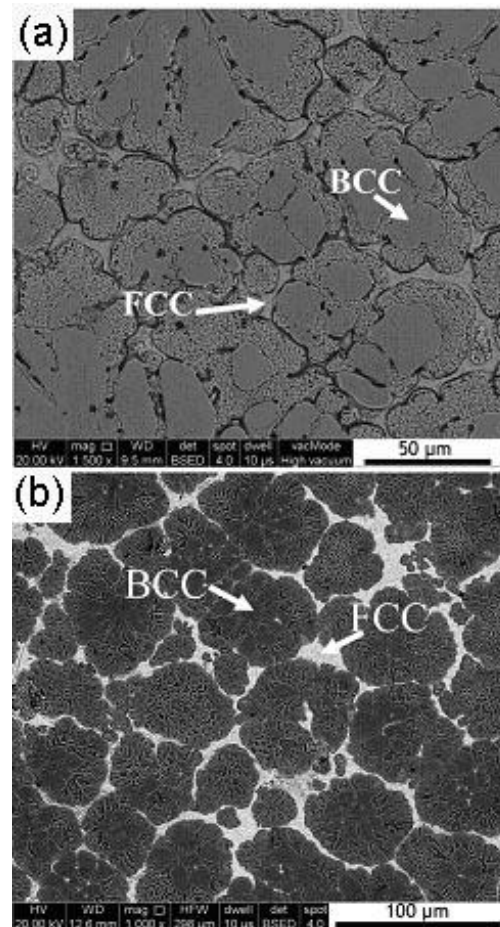


Figure 3. SEM micrographs of as-cast HEAs AlCoCuFeNiC (a) and AlCoCuFeNiCrTi (b). Reprinted with permission from Ref. [37]. Copyright 2017 Elsevier.

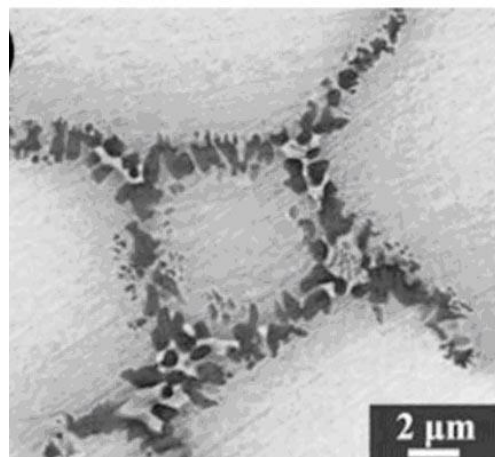


Figure 4. SEM BSE micrograph of the as-cast $\text{Ti}_3\text{V}_2\text{NbNi}_{0.5}$ alloy. The matrix grains are surrounded by the eutectic bcc+ C15 mixture. Reprinted with permission from Ref. [13]. Copyright 2021 Elsevier.

The scheme in Figure 1 is drawn for the simple binary systems. The real HEAs *per definitio* contain at least five components. This means that the respective HEAs' phase diagrams need five, six or more dimensions to be drawn. Moreover, according to the thermodynamic rule of phases, the multiphase areas containing different amounts of several solid and liquid phases should exist in the equilibrium phase diagrams for HEAs. This simple fact makes the description of GB wetting phenomena in HEAs much more complicated in comparison to binary systems. This review is a first attempt to discuss GB wetting in HEAs, to give the respective examples and draw the attention of readers to the open questions. We also hope to shed some light on possible causes of the formation of inhomogeneities in (traditionally homogeneous) HEAs.

3. GB Wetting in HEAs Obtained by the Arc or Induction Melting

The scheme shown in Figure 1 describes the most important scenarios of solidification in the presence of GB wetting phase transitions. However, in reality, the positions of $T_{w\max}$ and $T_{w\min}$ tie lines in relation to the melting temperature, T_m , and eutectic temperature, T_e , can be different. Let us consider some examples of HEA solidification. First, we discuss the crystallization from the melt during arc or induction melting in vacuum or argon [5–7,13–18,22–37]. If the two-phase S + L area of the phase diagram does not contain any tie lines, $T_{w\max}$ or $T_{w\min}$, of the GB wetting transition, then the one-phase solid solution polycrystal with typical dendritic structure forms after solidification of the melt. This is the case of the equiatomic HfNbTaTiZr high-entropy alloy with bcc structure prepared by plasma arc melting (Figure 2a) [5]. After homogenization at 1473 K, this dendritic structure disappears and the bcc solid solution becomes homogenous (Figure 2b).

Quite a different microstructure forms if the HEA solidifies following Route 3 or 4. In Figure 3, the SEM images of as-cast AlCoCuFeNiC (Figure 3a) and AlCoCuFeNiCrTi (Figure 3b) HEAs prepared by arc melting are shown [37]. The primary grains of the bcc phase were surrounded by the melt solidified as fcc phase. The majority of GBs were completely wetted by the melt. We describe the GB in a micrograph as completely wetted in the case when the melted layer is continuous from one GB triple junction (TJ) to another. If the melt layer between two TJs is broken and the portions of dry GB remain in between, we describe the GB as partially (incompletely) wetted. In this case, one can measure the non-zero contact angles in the contact points between the liquid phase and GB. However, some partially wetted GBs are also visible in micrographs in Figure 3. A similar microstructure was observed in the as-cast $\text{Al}_{0.5}\text{CoCuNiTi}$ alloy prepared by arc melting [14]. In the as-cast state, the $\text{Al}_{0.5}\text{CoCuNiTi}$ alloy is composed of the fcc matrix grains separated by the 1–4 μm thick layers of the bcc phase. It is also well visible from the micrographs in Ref. [14]

that not all GBs were completely wetted by the liquid phase. Some of the GBs remained incompletely wetted with a non-zero contact angle.

The change in HEA composition can modify the position of GB wetting T_{wmax} and T_{wmin} tie lines and, therefore, also the solidification route. Thus, in Ref. [28], two equiatomic AlCrCuFeTi and AlCrCuFeV HEAs were prepared by arc melting in a titanium-getter argon atmosphere. After solidification, the HEA consist of a bcc matrix with pronounced GB layers from other phase(s) (Figure 4 in [28]). These GB phases formed after solidification of the last (intergranular) fractions of the melt. They are Cu-rich and are fcc in AlCrCuFeV alloy and bcc-2, with $L1_2$ Heussler and hexagonal Laves phases in the AlCrCuFeTi alloy. It is visible in Figure 4 in [28] that in the V-containing HEA, the fraction of completely wetted GBs is much higher (though even not 100%) than in the Ti-containing HEA (where it is 10–20%). This means that AlCrCuFeTi HEA solidified following Route 2 and AlCrCuFeV alloy solidified following Route 3 or 4 (see scheme in Figure 1).

A good example of complete GB wetting can be seen in the $Ti_3V_2NbNi_{0.5}$ alloy produced by the vacuum arc melting with multiple remelting passes (Figure 4) [13]. XRD, TEM and SAED data show that the matrix grains have disordered bcc structure, while the GB precipitates have cubic $MgCu_2$ -type (C15) structure (so-called Laves phase). Here, the bcc solid crystallites were completely surrounded by the melt. Further, the last fractions of the melt eutectically decomposed into a bcc+ C15 mixture of solid phases.

Another example of concentration dependence of solidification route in the presence of GB wetting tie lines can be found in the Ti-free CoCrFeNi-Ta_x HEAs with different concentration of Ta ($x = 0.1, 0.25, 0.75, 1$) [29]. HEAs were prepared by arc melting under argon atmosphere. The first two HEAs are hypoeutectic, and last two are hypereutectic (see phase diagram in Figure 5). In first two HEAs, the matrix has fcc structure, and GB layers contain the Laves phase formed after solidification. Figure 6a,b demonstrate that CoCrFeNi-Ta_{0.1} HEA solidifies according to Route 2 (few completely wetted GBs), and the CoCrFeNi-Ta_{0.25} HEA solidifies following Route 4 (nearly all GBs are wetted). In hypereutectic CoCrFeNi-Ta_{0.75} and CoCrFeNi-Ta_{1.00} HEAs, the situation is more complicated, but the GB wetting phenomena are, nevertheless, obvious (Figure 6c,d).

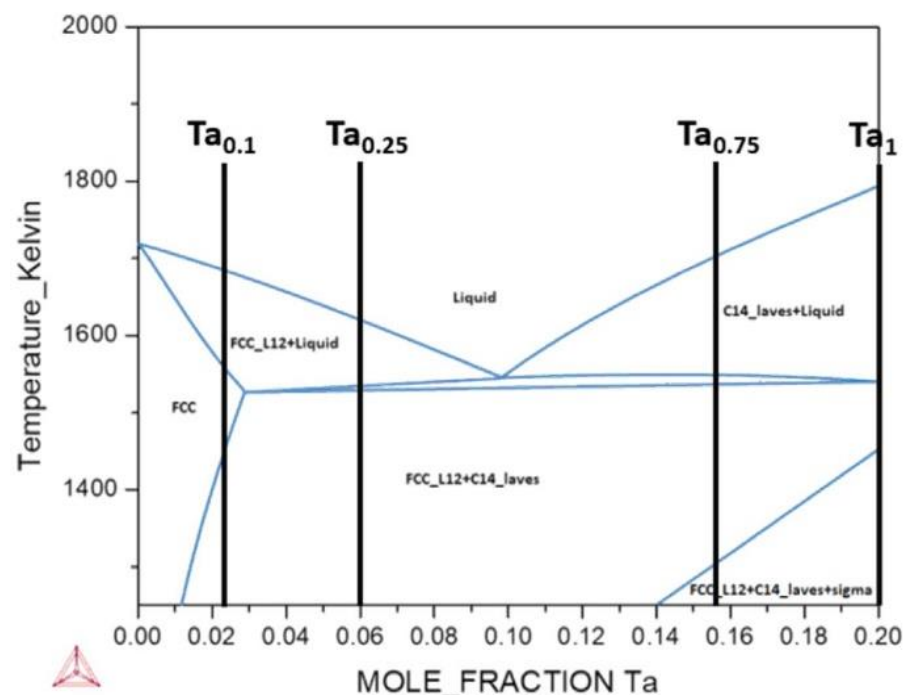


Figure 5. Pseudo-binary phase diagram of CoCrFeNi-Ta. Reprinted with permission from Ref. [29]. Copyright 2021 Elsevier.

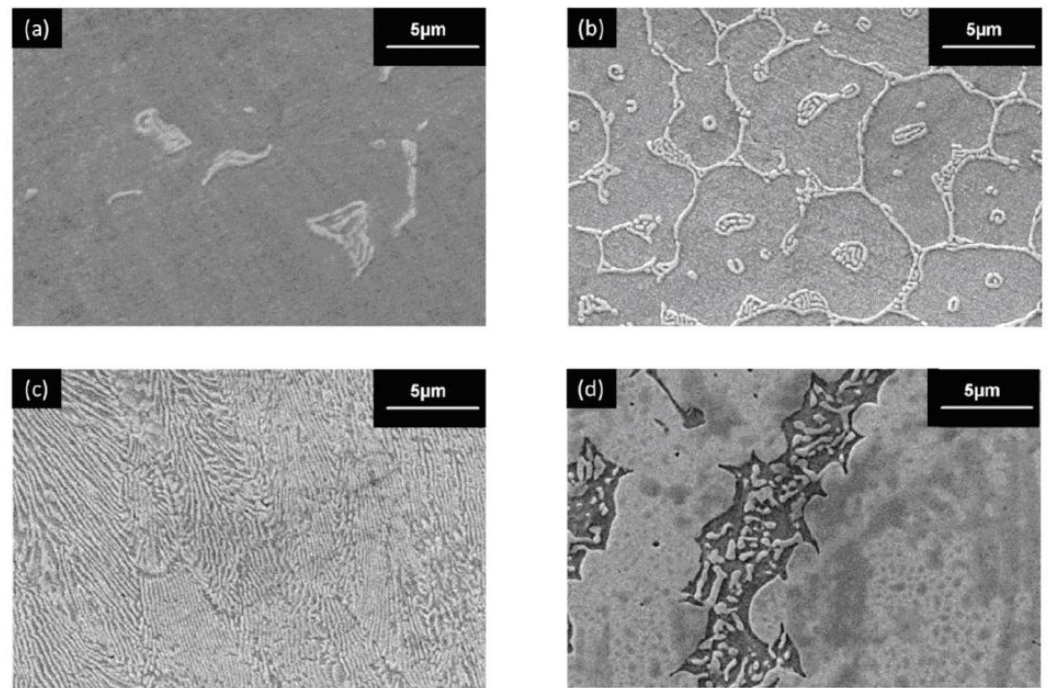


Figure 6. SEM micrographs of CoCrFeNi-Ta_x HEA. (a) $x = 0.1$, (b) $x = 0.25$, (c) $x = 0.75$, (d) $x = 1$. Reprinted with permission from Ref. [29]. Copyright 2021 Elsevier.

4. GB Wetting in HEAs Obtained by Electric-Current-Assisted Sintering

In HEAs produced by methods other than arc melting, one can also observe the indications of GB wetting transitions. In Ref. [20], CoCrFeNi, CoCrFeNi Ti_{0.5}Al_{0.5} and CoCrFeNiAl_{0.5} high-entropy alloys were produced using electric-current-assisted sintering (ECAS). After the production of HEAs, they were laser remelted (LR). The CoCrFeNi alloy contained only one fcc phase and was completely uniform after LR (Figure 7a). Its solidification corresponds, therefore, to Route 1 (Figure 1). In the CoCrFeNiAl_{0.5} and CoCrFeNi Ti_{0.5}Al_{0.5} HEAs, however, the GBs of the bcc grains were completely wetted by the melt (Route 1 or 2). After solidification, the GB layers contained the second bcc phase rich in Cr (Figure 7b,c). This result also demonstrates that slight modification of the composition one can strongly change the morphology of phases by shifting the position of GB wetting tie lines, T_{wmax} and T_{wmin} , or (alternatively) the position of the solidification route when the temperatures, T_{wmax} and T_{wmin} , are fixed.

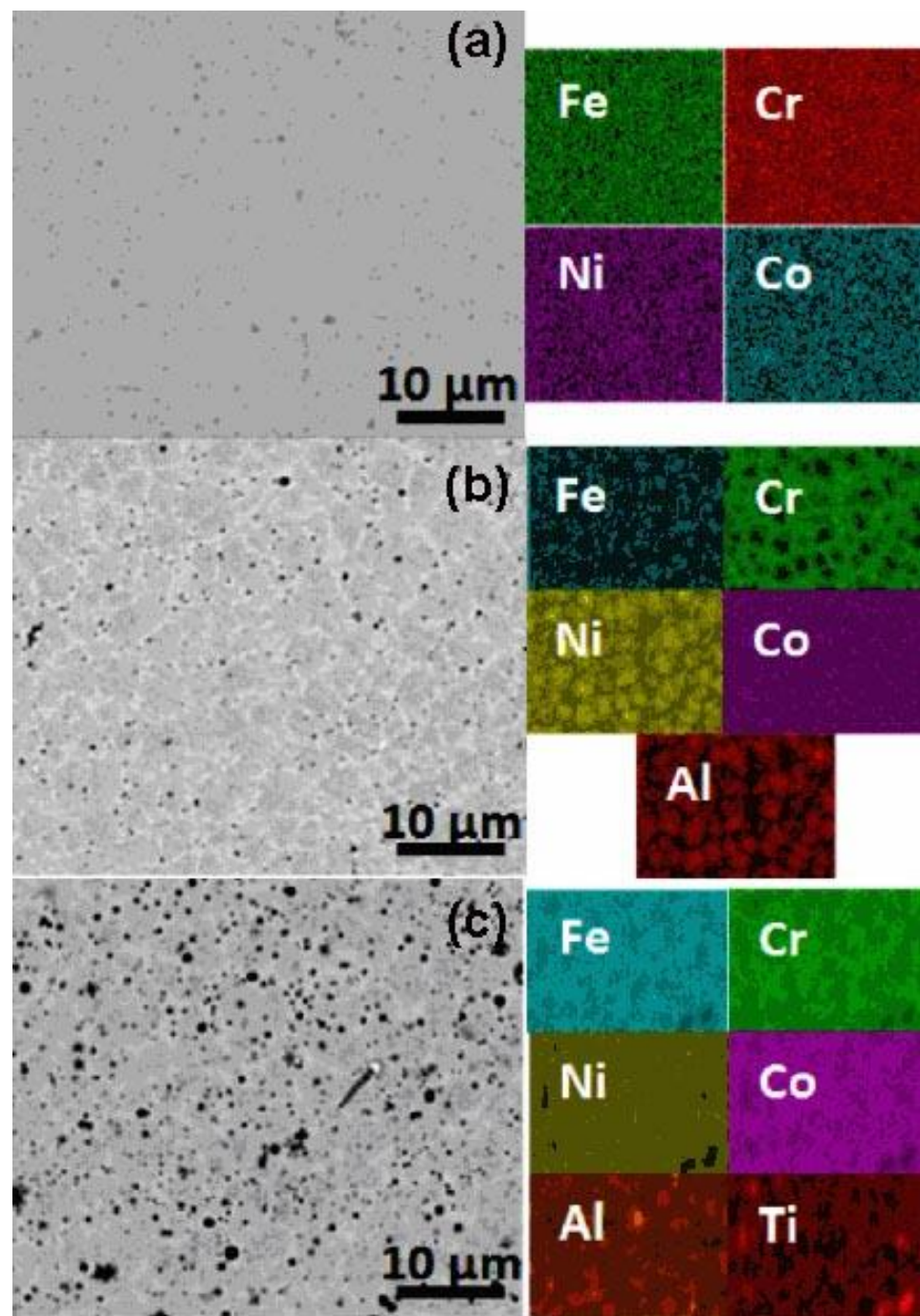


Figure 7. SEM-EDX-mapping analysis of sintered and laser-remelted HEAs: (a) CoCrFeNi, (b) CoCrFeNiAl_{0.5}, (c) CoCrFeNiTi_{0.5}Al_{0.5}. Reprinted with permission from Ref. [20]. Copyright 2021 Elsevier.

5. GB Wetting in HEAs Obtained by Laser Cladding and Additive Manufacturing

In Ref. [45], MgMoNbFeTi₂Y_x ($x = 0, 0.4\%, 0.8\%, 1.2\%$) HEA coatings were synthesized by laser cladding. After crystallization, they contain the matrix grains of the bcc-phase rich in Mo and Ni surrounded by the layers of Mg, Ti-rich phase (Figure 8). Almost all bcc grains are separated from each other by the Mg, Ti-rich 200–300 nm thick layers. Only a few GBs were partially wetted by the melt. This corresponds to solidification Routes 5 or 4 (Figure 1).

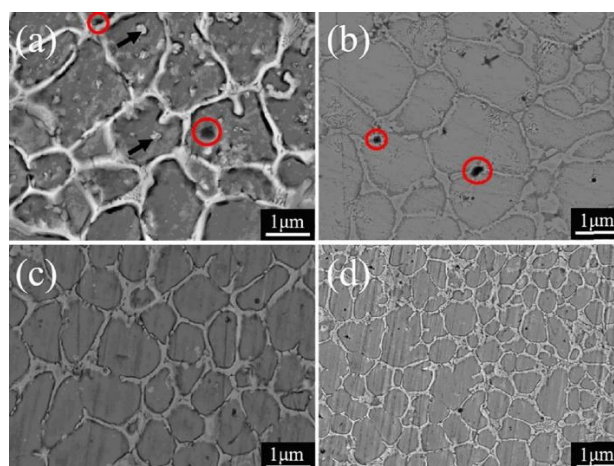


Figure 8. SEM micrographs of MgMoNbFeTi₂Y_x HEA coatings (a) $x = 0$, (b) $x = 0.4\%$, (c) $x = 0.8\%$, (d) $x = 1.2\%$ deposited by laser cladding. Reprinted with permission from Ref. [45]. Copyright 2021 Elsevier.

In Ref. [46], Al_xMo_{0.5}NbFeTiMn ($x = 1, 1.5, 2$) HEA coatings were synthesized by laser cladding. Their microstructure consists of an Mo,Ni-rich bcc-phase (matrix grains) surrounded by the layers of Mg,Ti-rich phase (Figure 9), similar to the alloys studied in Ref. [45]. It is interesting that the amount of former liquid phase (crystallized then as Mg,Ti-rich phase) increases with increasing concentration of aluminum (Figure 9a–c). It is important to underline that in Figure 9a,b some GBs are visible that are incompletely wetted by the melt (with non-zero contact angle). In Figure 9c, however, all GBs are completely wetted, and thick layers of the Mg,Ti-rich phase separate all grains of the Mo,Ni-rich bcc-phase from one another. The reason for that could be the so-called apparently complete GB wetting [72]. In case of apparently complete GB wetting, also GBs with a low but non-zero contact angle can also become completely replaced by the melt just because the wedges of the liquid phase from neighboring GB triple junctions meet each other and thus separate the solid grains.

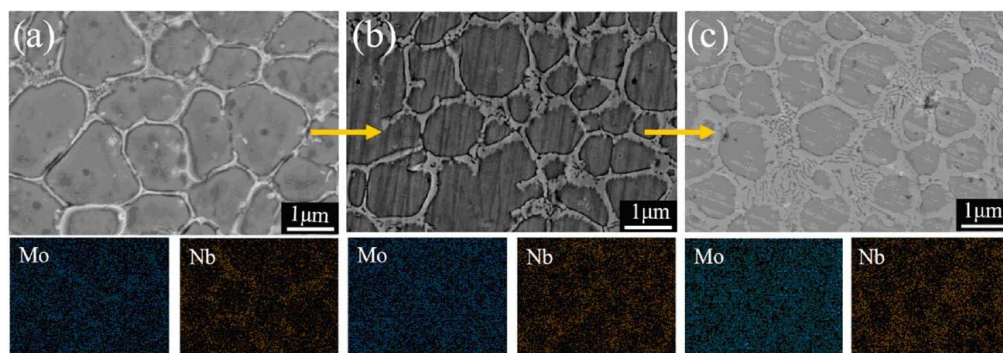


Figure 9. SEM micrographs of Al_xMo_{0.5}NbFeTiMn HEAs deposited by laser cladding. (a) $x = 1$, (b) $x = 1.5$, (c) $x = 2$. The corresponding EDS maps for Nb and Mo are given in the bottom part. Reprinted with permission from Ref. [46]. Copyright 2020 Elsevier.

In Ref. [58], AlCoCrFeNiTi_{0.5} HEA was prepared by the additive manufacturing method, namely laser metal deposition (LMD). The resulting microstructure consists of Al-, Ni-, Ti- and Co-rich grains (with fully ordered bcc structure B2), which are completely surrounded during solidification by the melt (see Figure 10). The melt later crystallized in the Cr- and Fe-rich solid phase with disordered bcc structure A2. It has been observed that changing the LMD regimes one can switch from a structure with equiaxial B2 grains

surrounded by thick A2 layers (Figure 10) to a conventional dendrite structure similar to that shown in Figure 2a.

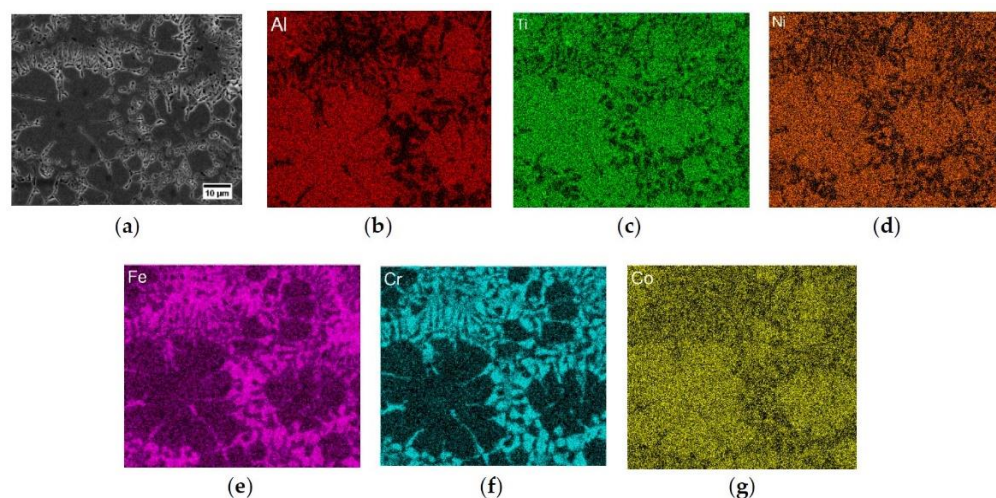


Figure 10. (a) Secondary electron image and the corresponding elemental maps of (b) Al, (c) Ti, (d) Ni, (e) Fe, (f) Cr and (g) Co of the AlCoCrFeNiTi_{0.5} HEA. Reprinted with permission from Ref. [58]. Copyright 2020 MDPI.

In this review, we presented several examples of complete and partial GB wetting in solidified HEAs. These examples do not exhaust the cases of GB wetting in HEAs. They are just typical cases from recent publications. Indeed, similar microstructures can be frequently seen in publications devoted to HEAs.

As we can see, modern HEAs frequently contain more than just one random solid solution phase. Moreover, the morphology of minor phase(s), especially their distribution between the grains of major phases, can be governed by the GB wetting phenomena. These phenomena are well studied for the binary metallic alloys [73–78], and the respective knowledge can be successfully applied to multicomponent HEAs. In particular, in the two-phase S + L area(s) of a multicomponent phase diagram, the additional tie lines of the GB wetting phase transition can appear (at minimum T_{wmin} and maximum T_{wmax} temperatures). As a result, the minor melt phase (which later crystallizes) can form rather thick (at least few μm) layers separating the grains of major phases. The influence of such layers on HEA properties can be both favorable or detrimental. Knowledge of GB wetting transformations in HEAs can be used for tailoring their properties, as well as for the further development of these advanced materials.

6. Conclusions

The thick (at least few μm) grain-boundary layers of the second phase(s) can appear in HEAs during crystallization of the melt in all synthesis technologies (such as arc or induction melting, plasma-spark or electric-current-assisted sintering, deposition of coatings by laser or plasma cladding, additive manufacturing, self-heating synthesis or even in brazing applications). These thick GB layers are liquid during cooling in the S+L area of the HEA phase diagram and then crystallize as a second solid phase or decompose in eutectic or peritectic reactions. The formation of such thick GB layers is due to the phenomenon of complete or partial GB wetting. Thus, the equilibrium liquid layers between solid grains appear if the GB energy is higher than the energy of two solid-liquid interfaces. The presence of GB layers of a second phase(s) can have either a positive or a negative effect on the properties of HEAs. In any case, one can use the GB wetting phenomena to tailor the microstructure and properties of HEAs. For such so-called grain-boundary engineering of HEAs, knowledge of the position of GB wetting tie lines in the S + L areas of HEA phase diagrams is required.

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