The Effect of Configurational Entropy of Mixing on the Design and Development of Novel Materials

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The configurational entropy of mixing ($\Delta S_{\text{mix}}$) has a profound influence on the stability of various phases in different materials at intermediate and high temperatures. Recently, it has been observed that $\Delta S_{\text{mix}}$ can be used as an important tool to design novel multicomponent materials with fascinating properties. $\Delta S_{\text{mix}}$ affects $\Delta G_{\text{mix}}$ and tends to stabilize the FCC/BCC/HCP multicomponent solid solutions over brittle phases including compounds. This opens up vistas to design novel solid solution-based materials with improved mechanical, functional properties. Accordingly, multicomponent and multiprinciple alloys were developed in 2004, and subsequently, novel ceramics and polymers have been designed. The present paper is intended to provide an insight into the role of $\Delta S_{\text{mix}}$ to design novel metallic, ceramic as well as polymeric materials.

Keywords: Entropy of Mixing; High Entropy Alloys; Ceramics; Polymer; Design

Introduction

The majority of the materials we use in our day-to-day life is in the alloyed form (Davis and Committee, 1990). Alloying, the greatest gift to humankind, is defined as chemically mixing two or more components (metals, ceramics or even polymers) to obtain an atomically mixed arrangement of atoms in the crystal lattice for improvement of properties; physical, chemical, functional, mechanical, etc. (Brandes and Brook, 1998). Therefore, the alloying has extensively been used for a long time (even during Indus Valley Civilization) to design and develop novel materials for various engineering applications (Cantor, 2014; Mohanty et al., 2015; Murty, Yeh and Ranganathan, 2014; Sharma, Yadav, Biswas and Basu, 2018; Tazuddin, Biswas and Gurao, 2016; Tazuddin, Gurao and Biswas, 2017; Yeh et al., 2004). The classical examples include steels, superalloys, brass, bronzes, mullite, silicates, etc. Alloys, in general, can be made in two basic forms, solid solutions and compounds. Solid solutions are like a liquid solution in the solid state consisting of various species atomically mixed to form a crystal. On the other hand, compounds are stoichiometric compounds with small solubility range.

As compared to the compounds, solid solutions with a simple crystal structure provide the right combination of mechanical and physical properties required to be useful in the application. Compounds, on the other hand, are strong but brittle and hence, mainly find functional applications. Therefore, solid solutions having a simple crystal structure, including Face Centre Cubic (FCC), Body Centre Cubic (BCC) are considered the best materials for structural applications. The widely utilized solid solutions consist of two or three components with one of the components as major components. These phases are stabilized by the interplay between enthalpy and entropy of mixing.

Configurational Entropy of Mixing ($\Delta S_{\text{mix}}$)

The entropy of mixing plays its vital role the free energy of mixing of a system. It is well known that free energy of mixing is given by $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$ at any temperature $T$; where $\Delta H_{\text{mix}}$ is the enthalpy of mixing. $\Delta H_{\text{mix}}$ depends primarily on bond energies of the elements. In general, for elements with a strong propensity to form strong bonds, $\Delta H_{\text{mix}}$ is considered to be negative. For elements with low
or zero solubility or unlikeness to form bonds, $\Delta H_{\text{mix}}$ is positive. However, $\Delta S_{\text{mix}}$ primarily depends on the arrangement of atoms in the crystalline lattice. For solid solutions, it is given by the Boltzmann hypothesis (Gaskell, 2008),

$$\Delta S_{\text{mix}} = -k(\ln X_A \ln X_A + \ln X_B \ln X_B)$$

where $k$ is Boltzmann constant = $R/N_A$ ($R$ = Universal gas constant, $N_A$ is Avogadro’s number) and $X_A$ and $X_B$ are mole fractions of $A$ and $B$ atomic species respectively.

Hence,

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - RT(X_A \ln X_A + X_B \ln X_B)$$

For the multicomponent system, i.e., $N \geq 5$,

$$\Delta S_{\text{mix}} = -R(X_A \ln X_A + X_B \ln X_B + \cdots X_E \ln X_E)$$

where, $X_A$, $X_B$, $X_C$, $X_D$, and $X_E$ have usual meaning, as defined earlier.

Hence, for equimolar systems $X_A = X_B = X_C = X_D = X_E$,

$$\Delta S_{\text{mix}} = -R(X_A \ln X_A + \cdots X_A \ln X_A)$$

$$= -R(5X_A \ln X_A) = R \ln 5$$

Hence, in general, $\Delta S_{\text{mix}} = R \ln N$ for any system having $N$ components in equimolar proportions. Thus, it is possible to estimate $\Delta S_{\text{mix}}$ as a function of $N$. Figure 1 shows such behavior. It is evident that $\Delta S_{\text{mix}}$ increases sharply for small values of $N$ and subsequently, it remains almost constant for $N = 13$ or more. This provides us avenues for stabilizing solid solution by increasing the number of components ($N$) even though $\Delta H_{\text{mix}}$ is strongly negative for elements having strong likeness to form bonds, as in case of compound formation. Therefore, it is possible to stabilize solid solution-based phases having a simple crystal structure, as compared to compounds by using a large number of elements (at least 5 or more). This has an important consequence and has recently been realized for use in the design of novel materials, which is discussed next. This also allows us to explore central part of the phase diagram, i.e., expand the compositional space by using a larger number of component and create an infinitely large number of alloy compositions, combining a large number of elements in the periodic table (Inset of Fig. 1A). By adopting a large number of components, a unique atomic structure can be created (Fig. 1B). In this figure, each coloured ball denotes one atomic species, and hence, the atomic environment can be varied locally as compared to that of the alloys consisting of two or three components such as steels, brass, bronzes, etc. Hence, this allows the tuning of materials property locally. The local variation of properties is effective in certain applications, especially in catalysis where the catalytic activity of any atomic species can be altered locally by changing the potential of the atom. In addition, a solid solution can be strengthened extensively by adopting such an atomic arrangement.
The solid solution hardening is primarily due to the atomic size difference, creating strain fields around the atom and causing motion of defects (dislocations, twins) difficult. For multi-component systems having atoms of different sizes, the barrier to the motion of the defect can be made to vary locally and hence, solid solution can extensively be strengthened (Mohanty et al., 2015; Tazuddin et al., 2017). Therefore, $\Delta S_{\text{mix}}$ allows us to divide the alloys into three categories. Figure 2 shows these three regions. The conventional alloys (steels, brass, bronze, super alloy), which are based on one or two principal elements are considered to be low entropy alloys. Since $\Delta S_{\text{mix}} \leq 0.693R (R\ln2)$. On the other hand, alloys with $N=5$, $\Delta S_{\text{mix}} \geq 1.61R$ and hence they are termed as high entropy alloys. The intermediate alloys having 2 to 4 principal elements are considered as medium entropy alloys. It is evident that the medium entropy alloys do not possess sufficient $\Delta S_{\text{mix}}$ to stabilize the solid solution phase, leading to the formation of complex and brittle intermetallic phases. From the application viewpoint, the suppression of the formation of intermetallic compounds is required in order to have sufficient ductility and toughness. Hence, high $\Delta S_{\text{mix}}$ significantly lower the free energy of the solid solution phase, leading to stabilization of these alloy phases.

Fig. 2: Alloy world as function of configurational entropy

The stabilization of solid solution-based phases over compounds makes the multicomponent alloys a reality in the potentials application. The solid solution-based phases with FCC/BCC structure can exhibit the best consideration of strength and ductility; much needed by the structural engineer to design various compounds for structures, machinery, automobile, etc. Achieving the right combination of strength, ductility and toughness are considered the holy-grail in materials science and engineering. The presence of a large number of elements can provide extensive hardening due to solid solutions; which can even be tuned by proper choice of elements and composition. Secondly, it opens up a large number of choices of possibility to achieve using an infinitely large combination of elements to explore the compositional space. Normally, the alloys are single, or two elemental bonds and other elements are added for the betterment of properties. Therefore, it allows the materials scientist to explore the vast composition space to design and develop different materials for various applications. The third aspect of the novel design concept involves.

Design of novel alloy (type, chemistry, specific properties) start using thermodynamics done primarily due to the fact the phase and microstructure play a significant role in the properties. The design is carried out by the estimation and comparing the free energy change as the formation of temperature and composition. This is normally carried out using a technique known as CALPHAD (calculation of phase diagram). This methodology has gained wider applicability due to sufficient computational power available recently. This is scientifically sound and more robust, and it can predict phase formation for the multi-component systems. However, such calculation for multicomponent ($n \geq 5$) systems requires an assumption to be made. CALPHAD predicts the phase based on extrapolation and minimization (Fig. 3A) (Kattner, 1997). At a given condition, the stability of phases is decided by Gibbs free energy minimization. For given conditions, the stability of phases is decided by minimizing total Gibbs free energy.

Figure 3B shows the results of one such five component alloy system (CoCuFeMnNi). The formation of different phases as a function of temperature is shown by plotting mole fraction of phases with respect to temperature. It is evident that a single phase solid solution having FCC (fcc#1) is stable in the large temperature domain (Tazuddin et al., 2017). Only at lower temperatures (<800K), some other solid solution phases (fcc#2 and bcc) can form. Therefore, CALPHAD allows us to design various alloy systems with a single phase FCC/BCC structures (Tazuddin et al., 2017).

Last 14 years, after the discovery in 2004 (Murty, Yeh and Ranganathan, 2014), have seen
extensive research on development of novel multicomponent alloys. It would be difficult to provide a detailed description of the volume of research carried out. However, some experimental results will be discussed to highlight the novel properties which can be achieved for high entropy materials. Avid reader can refer to the recent review (Sharma et al. 2017).

Moon et al. (Moon et al., 2018) have reported the microstructure and mechanical properties of high entropy alloy (Co$_{20}$Cr$_{26}$Fe$_{20}$Mn$_{20}$Ni$_{14}$) at a cryogenic temperature as well as room temperature and reported lower mechanical strength at a cryogenic temperature in cryo-High pressure torsion experiment. Chen et al. (Chen, Duval, Hung, Yeh and Shih, 2005) have reported the lower corrosion rate of HEAs (Cu$_{0.5}$NiAlCoCrFeSi) as compared to stainless steel (SS) 304 grade. Jiang et al. (Jiang, Han, Li and Cao, 2018) have reported hardness 590 HV of CoCrFeNiNb$_{1.0}$ coating on SS304, which is 2.8 times higher than the substrate (SS304). The well-known and widely studied cantor alloy (CoCrFeMnNi) having superior ductility (Cantor, Chang, Knight and Vincent, 2004). Nirmal et al. (Kumar, Tiwary and Biswas, 2018) have successfully prepared the nanocrystalline HEAs powder using cast ingot (Fe$_{0.2}$Cr$_{0.2}$Mn$_{0.2}$Ni$_{0.2}$Co$_{0.2}$, Cu$_{0.2}$Ag$_{0.2}$Au$_{0.2}$Pt$_{0.2}$Pd$_{0.2}$, Fe$_{0.2}$Cr$_{0.2}$Mn$_{0.2}$V$_{0.2}$Al$_{0.2}$).

It is quite commonly observed that the high entropy alloys get destabilized and phase separated under the influence of temperature. It is evident that high value of entropy of mixing ($\Delta S_{\text{mix}}$) will stabilize solid solutions at medium and high temperature as $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}$. At relatively lower temperature, $\Delta H_{\text{mix}}$ overrules the effect of $S_{\text{mix}}$, leading to destabilization of the solid solution phases (Cantor, 2014; Mohanty et al., 2015; Murty, Yeh and Ranganathan, 2014; Sharma, Yadav, Biswas and Basu, 2018; Tazuddin, Biswas and Gurao, 2016; Tazuddin, Gurao and Biswas, 2017; Yeh et al., 2004).

However, majority of experimental studies have shown the high stability of solid-solution within a broad range of temperature due to sluggish diffusion in these materials. Nevertheless, some recent studies show the instability at some intermediate temperatures due to minor addition of element with large atomic radius (He et al., 2017). This is expected to lead to nanoscale phase separation for reducing the lattice distortion (Xu et al. 2015). Basically, the destabilization of HEAs works on two thermodynamical phenomena such as super saturated solid solution and spinodal decomposition (Wei, He and Tasan, 2018). Similar aspects have been reported by authors’ group (S.Mohanty et al., 2014, 2016 and 2017). Based on these aspect, a section has been added.
Case of Multicomponent Ceramics

Recently, multicomponent entropy stabilized oxides and borides have been reported (Rost et al., 2015). In the case of the ceramics, the configurational entropy can be used to engineer novel materials by using multicomponent metallic species in the basic framework of oxygen or boron. The metallic cations are incorporated in the octahedral voids in a novel way to increase the entropy of mixing ($\Delta S_{mix}$) to obtain single phase entropy-stabilized oxides or borides. These works categorically indicate that entropy of mixing in particular, predominately dictate the energy landscape, stabilizing the solid solutions. It is evident that the effect of entropy seems to be lower as compared to metallic sublattice (Fig. 4A). The oxygen sublattice predominately order, baring same point defects. On the other hand, cationic sub lattice consisting of metallic elements provides the configurational entropy of mixing. As compared to single component oxides or borides, the multicomponent based lead to substantial increases in $\Delta S_{mix}$ providing stabilization of the solid solution borides or oxides. In the following part, the basic aspect of calculation of $\Delta S_{mix}$ for oxide is described. For metallic systems with random solutions consisting of two elements A-B, the materials interaction energy in given by $\Delta_{A-B} = \Delta_{A-A} + \Delta_{B-B}$ since there is an equal probability of bond formation. Thus, all lattice sites have an equal probability of occupation and entropy is considered to be maximized. This is an ideal situation in which all interaction energies, $\Delta_{A-B}$, $\Delta_{A-A}$, and $\Delta_{B-B}$ are equal. Any variation from the random mixture between A-B may be likely to have different values of interactions energies. $\Delta_{A-B}$, $\Delta_{A-A}$ and $\Delta_{B-B}$ and hence, such formalism may not work. This situation is different in case of oxides or borides in which the metallic ions sit on the cations sublattices (Fig. 4B). Here, anions, either oxygen or boron occupy at the intermediate space or hence, every cation lattices can be considered. The second nearest neighbour, the site-specific difference can also be evident. Therefore, the number of possible configurations can be maximized if each of the cationic site is considered identical as well as energetically similar. However, such consideration is not a perfect approximation as the second and higher interactions will definitely influence the possible configurations.

Nevertheless, this will increase $\Delta S_{mix}$ and hence, likely to stabilize the solid solution and lower the temperature at which entropy induced the formation of such a solid solution. It is to be noted here that, the effects of entropy on oxides system have already been investigated, i.e., cation occupancy in spinal (Navrotsky and Kleppa, 1967), order-disorder transformation is feldspar (Megaw, 1973). However, the technique of engineering $\Delta S_{mix}$ to stabilized multicomponent oxides in a single cation sublattice could only be achieved using the principles of high entropy alloys. Any such efforts of exploring the vast
compositional space for compound forming systems is definitely challenging, requiring both computational and experimental approaches.

Using a similar approach Gild et al. has reported the formation of entropy stabilized borides (Gild et al., 2016). These unique borides containing high melting metals [Ht, Ta, W, etc.] effectively improve the high-temperature capability of the existing materials utilized in space applications (Laura and Diletta, 2011). Conventionally TaB₂, HfB₂ are used for components in Space vehicles due to their unique properties including, high melting temperature low thermal conductivity low diffusivity and reactivity. These properties can further be improved by engineering novel mixed borides, carbides, oxides, etc. (Gild et al., 2016). In addition, Rost et al. have reported successful synthesis of multicomponent oxides (Rost et al., 2015). These oxides have been synthesized via solid state processing route, and have shown exceptional functional properties including improved CO oxidation (Chen et al., 2018). Design and successful synthesis of these multicomponent oxides and borides open up novel materials for various potential applications.

Case of Polymers

Polymers are another class of materials which find extensive usage in day-to-day life. Although there is no report of high entropy polymer till date, there has been a discussion on the existence of natural polymers stabilized by the entropy of mixing, akin to the metallic alloys or multicomponent ceramics. Many natural proteins are stabilized by using the strategy of maximizing the entropy of mixing. It involves allowing the change in entropy via folding/unfolding of a different chain of the proteins. Such a difference in the entropy between the folded and unfolded states can lead to improved thermodynamical stability of the proteins. This has intelligently been achieved by a substantial increase in the configurational entropy of the folded state. Figure 5 shows the model of a protein, known as hmAcP of horse muscle and a corresponding residue. The protein can contain various loop variants, altering the different states. It has been shown that the entropy of mixing is given by equation (6) (Dagan et al., 2013).

$$\Delta S_{mix} = cR\ln(n/n_{ref})$$  \hspace{1cm} (6)

Here, \(n\) refers to a number of residues in a particular loop whereas \(n_{ref}\) is known as the number of residues in the loop of any reference mutant, \(c\) is the correlation factor, connected to the persistence distance, \(R\) the universal gas constant. Therefore, by making \(n \gg n_{ref}\), it is possible to make \(\Delta S_{mix}\) extremely high and stabilize the protein structure. A similar approach can be extended to synthetic polymers, and soon high entropy polymer can be synthesized in the lab.

Conclusions

It has categorically been shown that the Configurational entropy of mixing (\(\Delta S_{mix}\)) has a significant effect on thermodynamical stability of various phases in metallic and ceramic systems. In fact, \(\Delta S_{mix}\) can be effectively used as a tool to design multicomponent alloys and ceramics with distinct and improved properties, which would allow them to be exploited technologically. In case of polymers, the entropy of mixing can be used to control folding/unfolding of a different chain of the polymers. The future will unfold many interesting cases of materials development.

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