Design of new coatings using magnetron sputtering – numerical estimations

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A new trend is set on coatings obtained via magnetron sputtering. Thus obtained alloys show remarkable mechanical, physical and chemical properties. These materials can be designed by adjusting the magnetron configuration. Using thermodynamic calculations an optimal magnetron setup can be designed and the structure and composition of the new material may be inferred.

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1. Introduction

Recent years showed an increase in study of bulk metallic glasses, BMGs, [1] new metallic materials with an amorphous structure. Also, less studied, but with promising perspective, high entropies alloys, HEAs, equiatomic or near-equiatomic multicomponent alloys usually in a single solid solution form show similar properties [2].

Conventional alloys usually contain one principal element as the matrix and a limited number of other elements incorporated for property/processing enhancement. The HEAs are alloys composed of at least five principal elements in near- or equimolar ratios [3].

For our studies we intend to use Cu, Si, Ti, Y, Yr and C to obtain new alloys. Several critical questions arise: which magnetron setup to use, which chemical composition would these materials have, and, given a composition with known constituents, can we estimate the structure – amorphous, solid solution?

2. Experimental details

2.1 Basic considerations

Magnetron sputtering is preferred to obtain coatings using ions of an inert gas, usually Ar. To obtain a specific chemical composition, to design the coating, and to estimate several characteristics of the new obtained materials basic theories are used.

Sputtering is defined as surface atom removal by energetic ions, which is quantified by the sputtering yield, the mean number of atoms removed per incident particle.

Thus, for sputtering yield estimation various models are available: Sigmund, Bhodansky, Yamamura and Wilhelm [4, 5, 6, 7], the later three are base on the Sigmund model.

The sputtering yield was calculated using the Bhodansky and Yamamura models, considering targets from elements of interest, i.e.: Cu, Si, Ti, Y and Zr. The projectiles are Ar ions accelerated at 100eV.

The sputtering yield is strongly influenced by incident particle properties: energy, mass, angle of incidence and target properties: mass, surface binding energy, crystal orientation.

The results are shown in Table 1, which clearly shows the greatest value for the sputtering yield at Cu while Si, Ti, Y and Zr values show small variations.

Table 1. Sputtering yields at projectile energy of 100eV.

Element	Cu	Si	Ti	Y	Zr
Sputtering yield via Yamamura model	0.448	0.049	0.075	0.112	0.089
Sputtering yield via Bhodnasky model	0.482	0.052	0.0436	0.056	0.066

For sputtering to initiate the ion energy needs to outcome the bond energy. When an ion hits the target it can either bounce back, reflect, absorb on the surface or reflect by grazing collision sequence.

The threshold energy, the minimum energy required for sputtering, depends in a large extent on the mass of the target and ions. For practical reasons, the threshold energy is defined as the energy bellow which no observable sputtering occurs.

Several formulas are proposed for the sputtering threshold energy: Bradley [8], Wehner [9] Bhodansky [5], Yamamura [6], Mantiecks [12]. Since the Yamamura and Bhodansky models were used to find the sputtering yield, the according relations are used to estimate the sputtering threshold energy; the results are shown in Table 2.

Table 2. Sputtering threshold energy.

Element	Cu	Si	Ti	Y	Zr
Sputtering threshold energy via Yamamura [eV]	16.303	47.026	32.045	13.792	19.663
Sputtering threshold energy via Bhodnasky [eV]	23.189	42.646	36.088	28.481	35.936

A low threshold is to be observed for Cu, Y and Zr, while Si and Ti show larger values. If we consider a solid target of C, sputter energy thresholds of 95eV and 133eV are estimated with Yamamura and Bhodansky relations, which indicate that at 100eV no or very low sputtering may occur, thus no solid C target can be used.

Now with the sputtering yield determined and considering a target surface of 100mm^2 we can estimate the chemical composition of the coating at values indicated in Table 3.

Table 3. Chemical composition of the coating.

Model	Cu[%]	Si[%]	Ti[%]	Y[%]	Zr[%]	Total
Yamamura	57.95602	6.338939	9.702458	14.489	11.51358	100
Bhodanski	68.89651	7.432819	6.232133	8.004574	9.433962	100

This chemical composition is expected if we consider 100eV energy and a 0 degree incidence of the Ar ions on the target. We expect a higher amount of Cu, Y and Zr and a lower content of Si and Ti.

The angle of incidence is crucial; the angular sputtering yield formula is adapted by a parameter dependent of it. This parameter involves curve fit parameters correlated with experimental data from numerous experiments, unfortunately not available for our materials.

These investigations are required for the experimental setup of the magnetron. It is mentioned that several parameters, due to lack of information in literature in our case, are estimated using curve fitting and the presence of C is ignored.

2.2 Experimental materials

The coating is obtained by reactive magnetron sputtering with five cathodes, Cu, Si, Ti, Y and Zr of minimum purity of 99.95%. The pressure of CH_4+Ar in the deposition chamber was $5x10^{-1}$Pa, the distance between cathodes 170mm and the deposition temperature 300 degrees Celsius. The substrate, C45 steel, was cleansed prior deposition with Ar ions for 300second. The total deposition time was 3600seconds.

3. Results and discussion

The chemical composition of the coating is shown in table 4 and the variation in thickness is shown in Fig. 1.

Table 4. Chemical composition of the coating.

Element [% weight]	Mean	Standard deviation	Median
Ar	0.059923	0.04427	0.046786
C	1.029107	0.257597	1.085714
Cu	25.33625	0.974297	25.39536
O	0.070255	0.034884	0.071429
Si	2.848699	0.530856	2.711071
Ti	2.364056	0.385392	2.343929
Y	11.59469	0.734026	11.57107
Zr	56.65014	1.537973	56.82

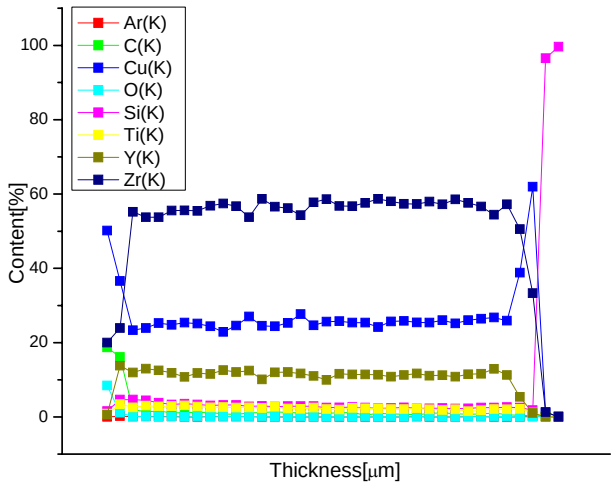

Fig. 1. Thickness variation of the chemical composition.

As predicted by previous calculations higher contents of Zr, Cu and Y are to be observed. The change in chemical composition is a result of the incidence angle of the energy ions and the presence of C.

To characterize and compare the experimental coatings three parameters are used. According to [13] the atomic size difference δ, the mixing enthalpy ΔH and the mixing entropy ΔS can be defined by equations (1-3):

$$\delta = 100 \cdot \sqrt{\sum_{i=1}^{n} c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2} \tag{1}$$

Where c_i, r_i are the atomic percentage and atomic radius of the element „i" and $\bar{r} = \sum_{i=1}^{n} c_i r_i$.

$$\Delta H = \sum_{i=1, i\neq j}^{n} \Omega_{ij} c_i c_j \tag{2}$$

where $\Omega_{ij} = 4\Delta_{mix}^{AB}$ and Δ_{mix}^{AB} represents the mixing enthalpy of binary alloys of elements "A" and "B".

To determine the mixing enthalpy of binary alloys the Miedema model was used. This is a semi empirical model based on the macroscopic perspective of the atom, where atoms are in fixed positions within the metal or alloy. For our calculations we used an adapted Miedema model byZhang [14, 15]. It must be emphasized that the Miedema model is restrictive when used for alloys with a transitional metal or elements like C, N, Si.

In most investigations these combinations are usually disregarded, thus we performed calculations by eliminating gradually these elements to evaluate their contribution to the final result.

$$\Delta S = -R \sum_{i=1}^{n} c_i \ln c_i \tag{3}$$

Where R is the gas constant.

Guo [16] includes two more additional parameters called the electro negativity difference Δχ, the valence electron concentration VEC, defined by equations (4, 5).

$$\chi = \sqrt{\sum_{i=1}^{n} c_i (\chi_i - \bar{\chi})^2} \tag{4}$$

where χ_i is the Pauling electro negativity and

$$\bar{\chi} = \sum_{i=1}^{n} c_i \chi_i$$

$$VEC = \sum_{i=1}^{n} c_i (VEC)_i \tag{5}$$

where $(VEC)_i$ represents the valence electron concentration of element "i".

Using the chemical composition obtained from the analysis the parameters for the experimental coating are computed. The final results obtained, by excluding gradually elements that are incompatible with the Miedema model, are indicated in Table 5.

Table 5. Computed parameters for the experimental coating.

Coating	VEC	Δχ	δ	ΔH[kJ/mol]	ΔS[J/(K mol)]
(CuSiTiYZr)C	5.693	0.324	14.988	-30.093	10.345
CuSiTiYZr	5.929	0.386	17.573	-34.306	11.734
CuTiYZr	5.409	0.352	18.997	-12.303	8.784

When C is excluded a higher value of VEC is to be expected. If we exclude also Si, then the VEC falls to the lowest value. The difference between highest and lowest value is 0.52.

For Δχ similar observations are applicable, the highest value is to be observed by excluding C and the lowest when excluding both C and Si.

For δ, by excluding C and Si the highest value is yielded, while when included the lowest value is attained.

VEC, $\Delta\chi$ and δ are not affected by errors from the Miedema model, since the mixing enthalpy is not an influence factor. They are estimated this way solely for comparison.

The mixing enthalpy is highly affected by the absence of C and Si in computations, the lowest value is thus attained. The difference between (CuSiTiYZr)C and CuSiTiYZr enthalpies is due to Cu-C and C-Cu high positive values as estimated by the Miedema model.

If we compare our results with several HEAs found in literature [15-40] we can compare our experimental coating.

GUO observed that a solid solution is obtained if:

$$-22 \le \Delta H \le 7kJ/mol$$
$$0 \le \Delta S \le 8.5$$
and
$$11 \le \Delta S \le 19.5J/(K*mol)$$

δ is a critical parameter, its value being a condition to the formation of solid solutions or BMGs if:

$$\delta \ge 9$$
$$-49 \le \Delta H \le -5.5kJ/mol$$
and
$$7 \le \Delta S \le 16J/(K*mol)$$

while a high mixing entropy is favorable to formation of BMGs.

We plotted the boundaries observed by Guo and included our coating and several examples found in literature in Fig. 2.

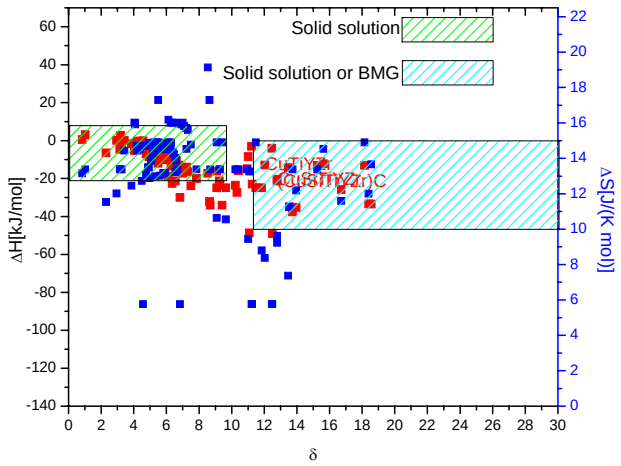

Fig. 2. Comparative plot with solid solution on BMGs formation boundaries.

Observing the placement of our experimental coating on the plot in Fig. 2 we can conclude that our alloy has an amorphous structure and it is comparable with other alloys studied. The amorphous structure was confirmed in investigations by XRD, SAED and HRTEM.

4. Conclusions

The configuration of the magnetron setup is crucial for the coating. Although multiple trials are required to elaborate a numerical model, the results obtained and implemented in the numerical design eliminate further waste of resources. Even basic knowledge of the configuration can offer valuable information for the setup.

A theoretical investigation is useful and can show, in a large extent, what to expect and how to improve the coating.

Even the basic theoretical investigations requires a large amount of information, most of which cannot be found in literature. Several parameters can be estimated by semi empirical models and some can only be obtained by repetitive experiments.

We predicted a high concentration of Cu, Y and Zr, which was confirmed by chemical analysis of the coating. Further trials should offer information regarding the incidence angle which would make chemical composition estimation more accurate.

When using transitional metals or elements like C, Si, N, incompatible with Miedema model for estimation of enthalpy, eliminating their contribution is not always safe, significant variation can be introduced, especially if the certain element is in considerable concentration.

Our experimental coating was placed within limits of a BMG, supposition confirmed by later investigations by XRD, SAED and HRTEM.

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