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BINARY AMORPHOUS ALLOYS OF REFRACTORY TRANSITION METALS AND GOOD ELECTRIC CONDUCTING METALS

NIKOLA RADIĆ and DAVOR GRACIN

Ruđer Bošković Institute, Department of Physics, Division of Materials Science and Electronics, Laboratory for Ionized Gases, Bijenička c. 54, P.O.B. 1016, Zagreb, Croatia

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The amorphous alloys of refractory transition metals (Nb, Mo, Ta, W) and good electric conducting metals (Al, Cu, Ag, Au) are studied. The expected glass forming ability and range of amorphous phase formation in such binary systems is examined and compared to the range of actually formed amorphous alloys so far. Data on thermal stability are reviewed. Finally, a set of promising binary combinations is selected for technological application.

1. *Introduction*

Conventional electronics cannot function properly at sustained elevated temperature for any significant period of time. The main cause of the device failure is the enhanced interdiffusion between metals used as interconnectors and semiconductors. Metals desirable for the VLSI packaging for their high conductivity, such as copper and aluminium, are also fast diffusers into SiO_2 and Si, which forbid their use in a direct contact with the substrates. In the case of aluminium, a large electromigration further aggravates the interdiffusion problem. A number of diffusion–barrier layers are inserted between metallic and semiconductor components as a remedy to the interdiffusion problem. However, at elevated temperature, they fail to function properly due to their polycrystalline structure, since the diffusion along the grain boundaries proceeds readily at high temperature. Since there is a considerable need for electronic devices which can function properly in hostile environment, such as high temperature (several hundred degrees Celsius) or corrosive atmosphere, efforts have been made to solve the interdiffusion problem. A promising concept was a complete elimination of grain boundaries in the barrier layer prepared as a continuous amorphous film. Such film ought to remain amorphous in the temperature range of interest. Further, it should have a good electric conductivity, adhesion and thermal–expansion coefficient matched to that of the substrate. The obvious candidates for the task are binary alloys of good electric conductors (Al, Cu, Ag and Au) and refractory transition metals (Nb, Mo, Ta and W) which are generally corrosion resistant, fairly good conductors and are expected to increase the temperature of crystallization of binary amorphous alloy. In what follows, we examine the glass forming ability (GFA) of binary alloys based on refractory transition metals (RTM) and good electric conducting metals (GEC), review the composition range of such alloys achieved so far, and, finally, examine their thermal stability.

2. *Glass forming ability of the RTM–GEC binary alloys*

To see which combinations of RTM–GEC metals can be prepared in the form of amorphous alloys by various preparation techniques, we first consider technical limitations imposed by the pure metals. As can be seen in Table 1, a liquidity range of all GEC metals lies below the melting points of tungsten and tantalum, while the liquidity range of molybdenum and niobium overlap with the liquidity range of copper and gold. Silver and aluminium boil before any of the RTM elements melts. Further, by reviewing the respective equilibrium phase diagrams [1], one finds that these facts correspond to the almost complete liquid immiscibility of silver with all considered RTM's, as well as complete liquid immiscibility of copper with tantalum and tungsten and gold with tungsten, respectively. The fact of liquid immiscibility of two components obviously prevents the preparation of the amorphous binary alloys by rapid solidification from the melt (RQ and LQ). Further, a technical limitation prevents the RQ techniques (melt spinning) which require melt containing crucibles at temperatures higher than 1800 °C [2]. Thus, for preparation of all considered RTM–GEC combinations one should apply mechanical alloying (MA), ion beam mixing (IBM) or codeposition technique.

To estimate the feasibility of preparation of a particular amorphous alloy, one can employ one or another of the empirical rules based on accumulation of the considerable set of data about the realized amorphous systems. The "qualitative" criteria are:

a) Hägg rule [3]: Early formulated (1931) for the metal–metalloid systems; it states that the amorphous alloys can be formed only if the ratio of constituent's atoms radii satisfies the inequality

$$0.59 < \frac{r_1}{r_2} < 0.88, \tag{1}$$

where lower limit comes from the geometric constraints in dense packing structures, while the upper limit is an empirical value derived from the early experiments on the RQ. Table 1 shows that none of the binary systems considered here satisfies this criterion.

TABLE 1.
*Physical parameters of refractory transition metals (*Nb, Mo, Ta ,W*) and good electric conducting metals (*Al, Cu, Ag, Au*). Sources: r_a, T_m, T_b, H_m and el. resistivity from CRC Handbook Chemistry and Physics; at. volume, Φ^* and n_{WS} from Ref. 8.*

Quantity	Al	Cu	Ag	Au	Nb	Mo	Ta	W
r_a (pm)	143.2	127.8	144.5	144.2	142.9	136.3	143.0	137.0
T_m (K)	933	1356	1235	1338	2741	2893	3269	3683
T_b (K)	2740	2903	2485	3353	5015	5073	5698	5933
H_m (kJ/mole)	10.7	13.0	11.9	12.1	25.1	27.8	29.3	33.5
el. res. ($10^8\Omega$m)	2.65	1.67	1.59	2.35	12.5	5.2	12.45	5.65
at. vol. (cm^3)	10.0	7.1	10.2	10.2	10.8	9.4	10.8	9.5
Φ^* (V)	4.2	4.45	4.35	5.15	4.05	4.65	4.05	4.80
n_{WS} (d.u.)	2.70	3.18	2.52	3.87	4.41	5.55	4.33	5.93

b) Liu's structural difference rule [4]: It was formulated after the accumulation of numerous data on amorphous phase formation by IBM technique in metal–metal systems which exhibit an intermetallic compound in phase diagram. It states that the amorphous alloy can be prepared by IBM, only if the crystal structures of involved metals are different. This condition is satisfied for all combinations of RTMs (all being b.c.c.) and GECs (all being f.c.c.) considered.

c) Liu has subsequently proposed [5] a phenomenological method of predicting GFA which takes into account finer details of the system equilibrium thermodynamics: Two parameters used to plot the system readiness to amorphize are MPAR (maximum possible amorphization range) defined as 100% minus the maximum solid solubility on both sides of phase diagram, and heat of formation/mixing of binary amorphous alloy at equiatomic composition (see Fig.1). Since, in our case, the range of mutual solid solubility of components is very restricted, except in the Au-Nb and Au-Ta systems, whether particular binary system will be readily glass forming (RGF) or possibly glass forming (PGF) depends entirely on the sign of the heat of mixing.

Among the "quantitative" predictions of GFA, we will briefly present the proposal of Liou and Chien [6] and currently dominant model of calculation of the GFA range and predictions of subsequent thermal stability based upon Miedema's semiempirical model of alloy formation thermodynamics and the effects of elastic contribution into the alloy/solid solution free energy [7-11].

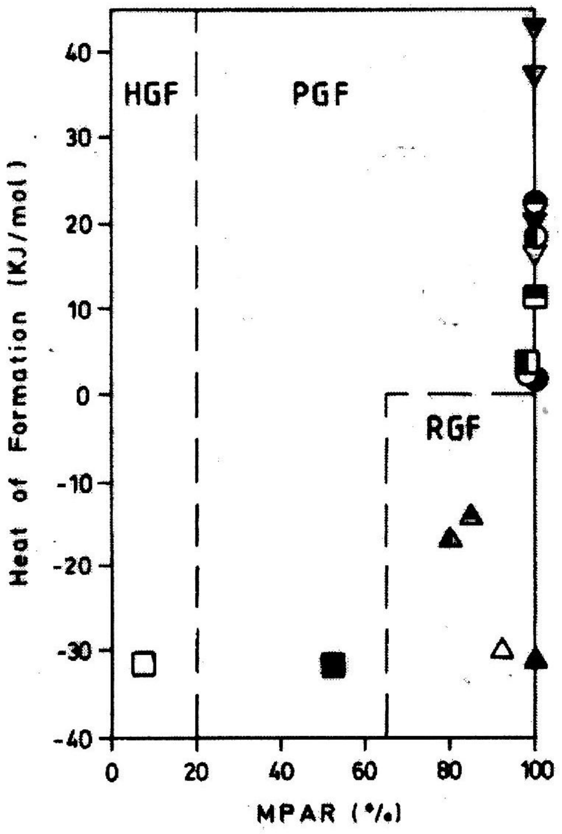

Fig. 1. Liu's map(5) of MPAR- Hf parameters for the prediction of GFA of the RTM-GEC systems. The abbreviations are explained in text. Graphic symbols for the GEC metals are as follows: △–Al; ○–Cu; ▽–Ag and □–Au. *Shading of symbols denotes combinations with:*□–Nb; □–Mo; □–Ta *and* □–W.

d) Through the study of numerous early ETM-LTM binary systems prepared by the same vapour–quenching method and under very consistent conditions, Liou and Chien found that the single important parameter governing the composition range of amorphous alloy formation is the ratio of the constituent atomic radii. For the A_xB_{1-x} alloy composition, they proposed the lower and upper limits of amorphous phase formation as

$$x_{min} \approx \frac{0.09V_B}{|V_A - V_B|}, \qquad (2a)$$

$$x_{max} \approx 1 - 0.07 \frac{V_A}{|V_A - V_B|}. \tag{2b}$$

Here, $V_{A,B}$ are the volumes of the constituent atoms, and the coefficients in formulas (2a,b) have been determined by comparison with the experimental results on a series of the Fe- based alloys. A simple consequence of their formulas would be a relaxed condition on size difference required for the formation of amorphous phase according to Hägg's rule. Namely, upper limit for the r_1/r_2 ratio would increase to 0.95. Thus, many of the previously ruled out binary combinations come within or close to the new condition. According to Liou and Chien, predictions concerning the GFA range in RTM-GEC systems are as follows: Only copper of GEC metals would form amorphous phase in any considerable range with all RTMs. In addition, silver and gold might form the amorphous alloys with molybdenum in a very narrow composition range of few atomic composition. All other combinations would yield no amorphous phase according to the Liou and Chien criterion.

e) "Eindhoven & Valladolid" (E& V) model [7-12]: Currently the most widely used theory in predicting GFA and GF range employ the comparison between the Gibbs free energy of the potential/possible amorphous phase and the competing crystalline phases. Two dominant terms, which determine the glass–forming range of binary system, are the heat of formation of binary alloy, derived in a semi–empirical way by Miedema and coworkers [7,8,12], and the elastic contribution to the enthalpy of solid solution due to the atomic size mismatch of the constituents [9-11].

Fig. 1 shows that only aluminium has strongly negative heat of mixing with all RTM's and, exhibiting only a limited solid state miscibility with them, enters into the class of readily glass forming binary alloys with them. Copper has a small positive heat of mixing with niobium and tantalum, as well as gold with molybdenum, and might be expected to form amorphous alloys. Although gold and niobium have a strongly negative heat of mixing due to their wide range of solid state miscibility, their amorphous alloys are not expected to form. All other combinations are not expected to form a stable amorphous alloys due to their high positive heat of mixing.

Further, the difference of the Gibbs free energy between amorphous and crystalline phase of pure elements involved should be taken into account. This is usually done in approximative way according to Turnbull's formula or, for the refractory metals [11], by the Thompson and Spaepen formula. In both cases of amorphous and solid solution, the entropy of mixing is assumed to correspond to ideal mixing. It is expected that the phase with lower Gibbs free energy is more stable at a given temperature. Further, the composition range, where the amorphous phase has lower Gibbs free energy, is considered a glass–forming range for the particular binary system.

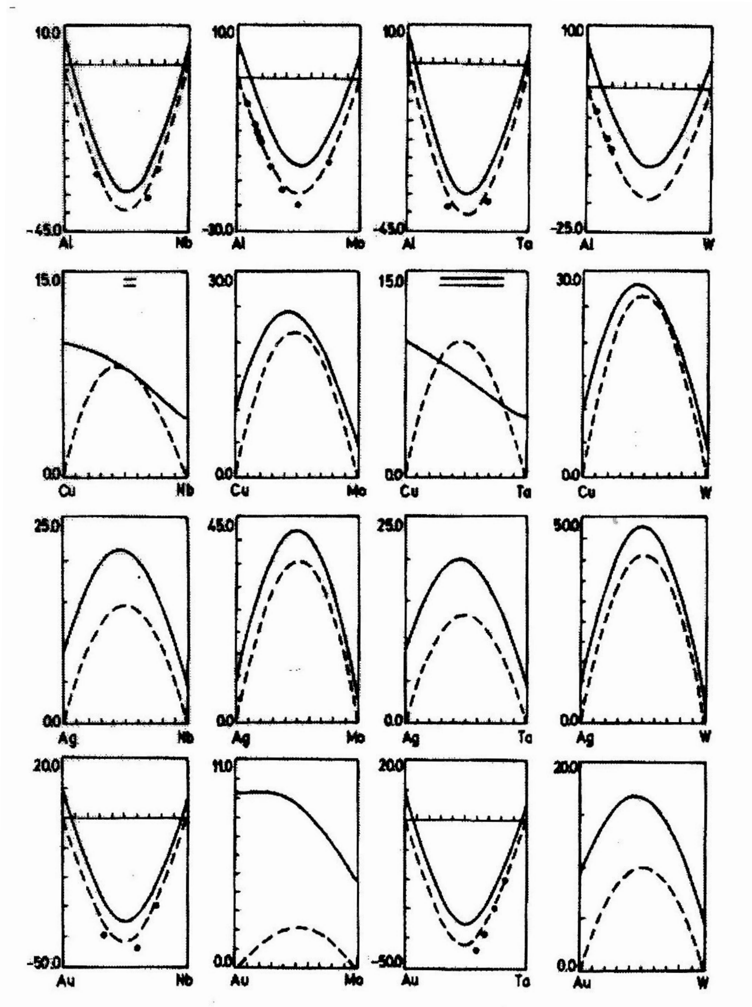

Fig. 2. Free energy diagrams of the RTM-GEC binary systems calculated according to E&V model at 300 K. *Solid line represents amorphous phase and dashed line represents a solid solution. Dots correspond to the free energy of intermetallic compounds. Two horizontal parallel lines in the upper part of the digram mark a tentative glass forming range.*

The model outlined above has been widely used to predict the GFA range in binary systems. Calculated free energy diagrams for the RTM–GEC binary systems are shown in Fig. 2. All calculations were performed according to the model presented in Refs. 7-12, with coefficient $\Gamma = 0$ in case of positive heat of formation, and $\Gamma = 4.5$ otherwise [12]. The values of other relevant parameters are given in Table 1. Several remarks are due:

1) Silver exhibits rather high positive excess Gibbs free energy with any of the

RTMs considered. It is concurrent with the fact of complete solid and liquid immiscibility of the respective binary systems. According to the model, this resistance to alloying is due to the comparatively low electron density at the Wigner-Seitz cell boundary in comparison to that of RTMs.

2) Aluminum exhibits large negative heat of mixing with all RTMs. Although the solid solubility is less than 20% in all cases, taken together from both sides of phase diagram, a whole series of intermetallic compounds are formed upon alloying in Al-RTM binary systems as a concequence of this chemical driving force. Therefore, all Al-RTM systems are readily glass formers, and the amorphous phase might be expected to appear in non-equilibrium processing.

3) Gold has a large negative heat of mixing with niobium and tantalum, a modest positive heat of mixing with molybdenum and considerable positive heat of mixing with tungsten. Concurrently, it forms several intermetallic compounds with both Nb and Ta, respectively. However, its almost complete mutual solid solubility with niobium might prevent the amorphous phase formation in Au-Nb system. Since the MPAR for the Au-Ta system is 52%, it belongs to the PGF according to Liu's classification. One might also expect the formation of amorphous phase in the Au-Mo system on the basis of its nonprohibitively high positive heat of mixing.

4) Copper exhibits considerable positive heat of mixing with Mo and W, while only modestly positive with Nb and Ta. Being almost completely immiscible with all four RTMs, their combinations belong to the class of possible glass formers according to Liu. However, due to the large difference in atomic volumes between Cu and RTMs (which increases elastic energy in solid solutions), the amorphous alloys of Cu-Nb and Cu-Ta are thermodynamically more stable than solid solutions in certain composition ranges, although exhibiting a positive overall excess free energy. However, no conclusions about precise GFA range in those systems based on the calculated phase diagrams, seem pertinent.

3. Experimentally achieved amorphous phase range in RTM–GEC systems

As to the experimentally achieved amorphous phase range in RTM- GEC systems one finds following:

1) Silver and gold: Silver exhibits a smallest positive heat of mixing with niobium among the RTMs, and that system belongs to PGF according to Liu. However, an attempt to produce this amorphous alloy by IBM has proved unsuccessful [13]. The authors also tried the Au-W system which exhibits even smaller heat of mixing, and obtained a metastable solid solution. However, according to the predictions of Liu's plot, the Au-Ta system belongs to the PGF class

with considerable negative heat of mixing and is expected to form amorphous alloys.

2) Aluminium: Although aluminium should not form amorphous phases with RTMs according to Hägg's rule, Loiu and Chien predicting method and *E&V* calculations, it actually does with all of them if the alloys are prepared by codeposition (cosputtering) [14,15] techniques. Furthermore, such GFA is in accordance with the predictions of both Liu's criteria, who produced $Al_{55}Nb_{45}$ amorphous alloy by the IBM, although IBM produced only solid solution in the $Al_{58}Ta_{42}$ system [13]. It should be noted, however, that attempts to produce bulk Al-RTMs amorphous alloys by MA technique proved futile so far (Al-Nb [16], Al-Mo [17]). The production of Al-RTMs amorphous alloys by cosputtering method is of technological importance, since those alloys exhibit a high corrosion resistance and can be used as a protective coatings in hostile atmosphere.

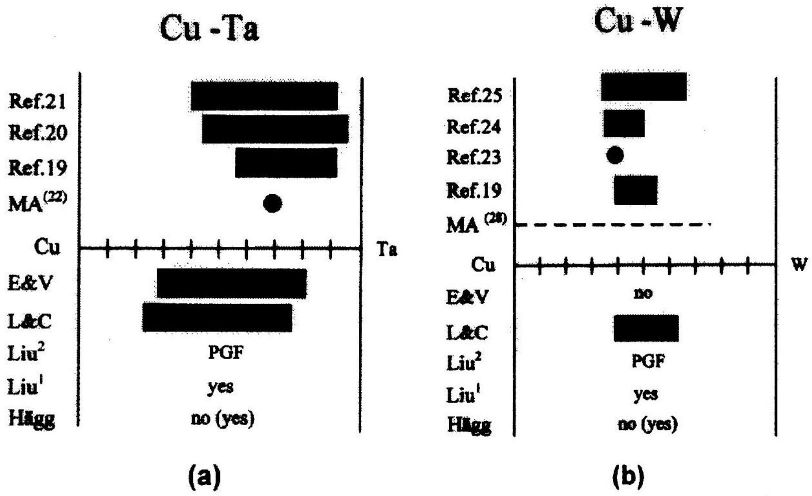

Fig. 3. A predicted (lower panel) and realized (upper panel) range of amorphous phase formation in Cu-Ta *system (a) and* Cu-W *system (b). The Hägg's criterion decisions given in parenthesis results from the relaxed conditions following from Liou and Chien proposal (6). The abbreviations are selfexplanatory.*

3) Copper: Copper alloys with tantalum and tungsten have been most extensively studied. No results on Cu-Mo have been reported, and an attempt to produce amorphous alloy in the Cu_5Nb_{95} and $Cu_{50}Nb_{50}$ systems by the MA proved unsuccessful [18], although the heat of mixing is rather close to zero and *E&V* type calculations predicts a narrow range of amorphous phase.

Elastic contribution seems to be decisive, as it is in other combinations containing copper. In the case of Cu-Ta and Cu-W, the most fruitfull technique has been codeposition of pure metals from independent evaporation or sputtering sources. As can be seen in Fig. 3a, a considerable range of Cu-Ta amorphous alloys have been prepared by this method [19-21], in addition to successful amorphization of $Cu_{70}Ta_{30}$ by the mechanical alloying [22]. According to all predictions, this system seems to be the most readily amorphized of all RTM–GEC combinations and deserves a particular attention.

The results on Cu-W system are presented in Fig. 3b. Again, amorphous phases have been produced exclusively by the codeposition technique [19,22-25] and in the range roughly predicted by the Liou and Chien method. However, no attempt to amorphize Cu-W mixtures by ion implantation [26], mechanical alloying [27,28] (although the authors of Ref. 28 found coexisting Cu-W amorphous phase up to the 75% of Cu), ion beam mixing [13,29,30] and laser quenching [29] has been successful. In some cases even coevaporation technique yielded only crystalline solid solutions [31]. A large positive heat of mixing and strong immiscibility of Cu and W are probably the causes which prevent formation of the amorphous phase alloy starting from the pure elements.

The general conclusion from this review of experimental results is the prominence of codeposition techniques for the production of amorphous alloys of RTM-GEC metals. So far, it is along the lines of possible application of such alloys. The next point to examine is the thermal stability of such films.

4. *Thermal stability of amorphous RTM–GEC alloys*

Data on crystallization of RTM-GEC amorphous alloys are scarce. It was reported that $Al_{64-54}Mo_{36-46}$ alloys, investigated as high temperature corrosion resistant coating up to 1000 °C, crystallize to from $AlMo_3$ and Al_8Mo_3 intermetallic compound in the course of heat treatment, but temperature of transformation was not revealed [15]. Liu et al. [4] found that the $Al_{55}Nb_{45}$ amorphous alloy produced by the IBM crystallize at 350-400 °C. From our own observations it seems that $Al_{65}W_{35}$ alloy remains amorphous at least up to 430 °C.

Most reported results concern copper alloys with Ta and W. In Ref. 19 a comparative study of amorphous Cu-Ta and Cu-W stability against ion irradiation and temperature rise have been reported. Alloys with approximately equal content of Cu and Ta crystallize at about 600 °C and the Ta-rich alloys crystallize at approximately 800 °C. On the contrary, $Cu_{45}W_{55}$ and $Cu_{60}W_{40}$ alloys transform into crystalline solid solution below 200 °C. We have observed crystallization already at 150 °C in $Cu_{50}W_{50}$ and $Cu_{66}W_{34}$ alloys [32], with initial separation of copper.

According to the Buschow kinetic model [33,34], the crystallization of amorphous alloys proceeds via vacancy-like or interstitial long–range diffusion of its constituents. Therefore, the temperature of crystallization should be related to the energy required to produce a hole/vacancy equal to the volume of smaller constituent atom, H_h. This energy can be calculated according to Miedema's model

[35], and the results from many data on crystallization temperature support relationship $T_c \approx 7.5H_h$. However, in many cases this proportionality does not hold, due to the unusually low temperature of amorphous alloy crystallization. It seems that such discrepancies arise with systems exhibiting a high positive heat of mixing which, therefore, readily polymorfically transform into metastable solid solutions. It should be noted, however, that the amorhous phase in $Cu_{50}W_{50}$ alloy is persistent up to 700 °C [32], and the properties of such mixed–phase systems are still to be investigated.

Following the thermal stability scrutiny, it seems that only a few combinations of RTM–GEC metals fulfill the promises expected from their individual properties.

5. Conclusion

After a thorough analysis of the expected and realized amorphous alloys in RTM–GEC binary systems, and considering their thermal stability, one might conclude that Cu-Ta system, aluminium based alloys and probably Cu-Nb, Au-Mo and Au-Ta systems bear some promises as the technological materials suitable for the applications in hostile environment. The other combinations seem to be only of academic interest at the moment.

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BINARNE AMORFNE SLITINE VISOKOTEMPERATURNIH PRIJELAZNIH METALA S METALIMA VISOKE ELEKTRIČNE VODLJIVOSTI

Razmatraju se amorfne binarne slitine visokotemperaturnih prijelaznih metala (Nb, Mo, Ta, W) s metalima visoke električne vodljivosti (Al, Cu, Ag, Au). Procijenjena je izglednost stvaranja amorfne faze i istražen raspon sastava u kojem se ona realizira. Načinjena je usporedba s rasponima sastava amorfnih slitina pripravljenim raznim postupcima. Prikupljeni su dostupni podaci o toplinskoj stabilnosti razmatranih amorfnih slitina. Konačno, izdvojen je skup binarnih kombinacija razmatranih metala s očekivanim osobinama koje su prikladne za primjenu u visokotemperaturnoj mikroelektronici i antikorozivnoj zaštiti.