THE SOLUBILITY OF THE ALKALI AURIDES CSAU, RBAU AND KAU IN THE CORRESPONDING MOLTEN BROMIDES.

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SUMMARY

The solubility of the alkali aurides MAu (M= K, Rb and Cs) in the corresponding alkali bromides has been determined by difference thermal analysis along the MAu/MBr section of the ternary M/Au/MBr phase diagrams. In the Cs system complete miscibility in the liquid and in the solid state is obtained whereas for the Rb system complete miscibility is only observed in the liquid state. In the K system, which changes from ionic to almost metallic charge transport with increasing KAu content, a miscibility gap appears even in the liquid state.

INTRODUCTION

It has been well recognized since the work of Sommer (refs. 1,2) that the binary intermetallic compounds CsAu and RbAu are nonmetallic. Their high degree of ionicity has been most convincingly demonstrated by the experimental verification of an almost entirely ionic charge transport in molten CsAu (ref. 3). Thus the Au^- anion is the only transition metal anion so far, which has been obtained in a pure binary compound.

The purpose of this work is to investigate the solubility of the alkali aurides CsAu, RbAu and KAu in a chemically inert polar matrix such as the corresponding alkali bromides. The latter were chosen, because the nearest neighbour distances in CsAu and RbAu, both crystallizing in the CsCl structure, are very similar to those of CsBr and RbBr respectively (refs. 4,5). Thus at least some solubility of the compound without decomposition may be anticipated, which allows studies of further properties of the Au^- ion. However the mixing behaviour of these systems may strongly be influenced by the electronic structure of the alkali aurides, where the energy gap between the valence and the conduction band apparently decreases with decreasing cation radius in contrast to the alkali halides (ref. 6) and vanishes almost for KAu (refs. 7,8).

EXPERIMENTAL

The solubility of the alkali aurides in the molten alkali bromides was determined by difference thermal analysis. The samples have been prepared by direct mixing of accurately weighed amounts of the pure components M (= K, Rb and Cs), Au and MBr in the measuring cells. Since the stoichiometric ratio of M:Au=1:1 had to be carefully observed even at low MAu contents, fairly large samples (~ 3 cm^3) were needed. The alkali metals (purity better than 99.9%, Ventron, Karlsruhe) and gold (99.99%, Degussa, Pforzheim) were used without further purification, the alkali bromides (99.5%, Merck, Darmstadt) were dried under a

vacuum of 10^{-3}mbar at 200–300°C before use. All handling of the samples was performed in the high purity argon atmosphere of a glove box.

Due to the specific properties of the MAu/MBr systems, the DTA–apparatus had to meet the following requirements: The useful temperature range had to extend at least up to the melting point of gold for the detection of any undissolved gold. The sample cells must be closed tightly to avoid any loss of alkali metal by evaporation. In view of the large samples an efficient stirring had to be provided to enable fast equilibration within the sample. The DTA–apparatus used in this work was a somewhat simpler version of the apparatus described by Grob et al. (ref. 9) with two NiCr/Ni thermocouples in the axis of the samples to determine the temperature difference between sample and reference cell instead of the thermopiles. The thermocouple inside the sample cell was used at the same time to determine the sample temperature. Stirring was provided by slowly rotating the furnace together with the sample cells about a horizontal axis inside a vacuum container kept at a constant He pressure of about 50mbar.
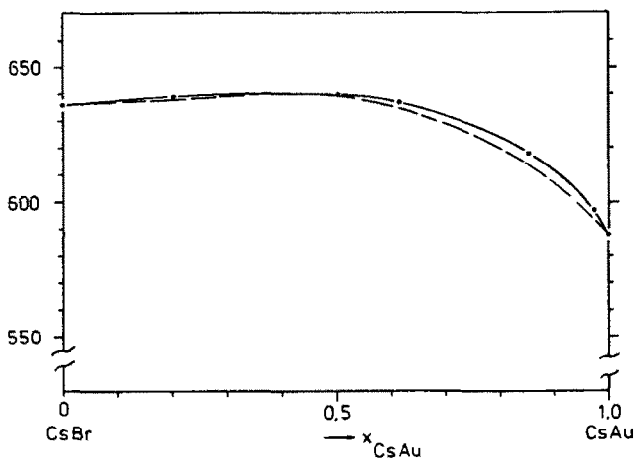

Fig. 1. Phase diagram of the pseudobinary CsBr/CsAu system

RESULTS

Fig. 1–3 show the thermal effects observed on heating or cooling the samples. Due to stirring no supercooling was observed: the onset temperature of the peaks of the cooling curves coincided within experimental reproducibility of ±1°C with the end points of the corresponding peaks of the heating curves and vice versa. For the CsAu/CsBr system the liquidus line is shown in fig. 1 according to the pseudobinary nature of this system. Since the RbAu and KAu compounds form peritectically according to ref. 10, fig. 2 and 3 show the respective MAu/MBr section of the ternary M/Au/MBr systems together with the corresponding three limiting binary systems M/Au, M/MBr and MBr/Au, the former two taken from literature (refs. 10,11). Due to the mutual insolubility of Au and MBr in the liquid

and solid phases, the last reduces to the eutectic line at the melting point of MBr and the monotectic line at the melting temperature of gold. The compositions of the Rb/Au/RbBr and K/Au/KBr mixtures in the following text are always given according to the ternary nature of these systems as $x_{MBr} = 1 - x_M - x_{Au}$ with $x_M = x_{Au}$.
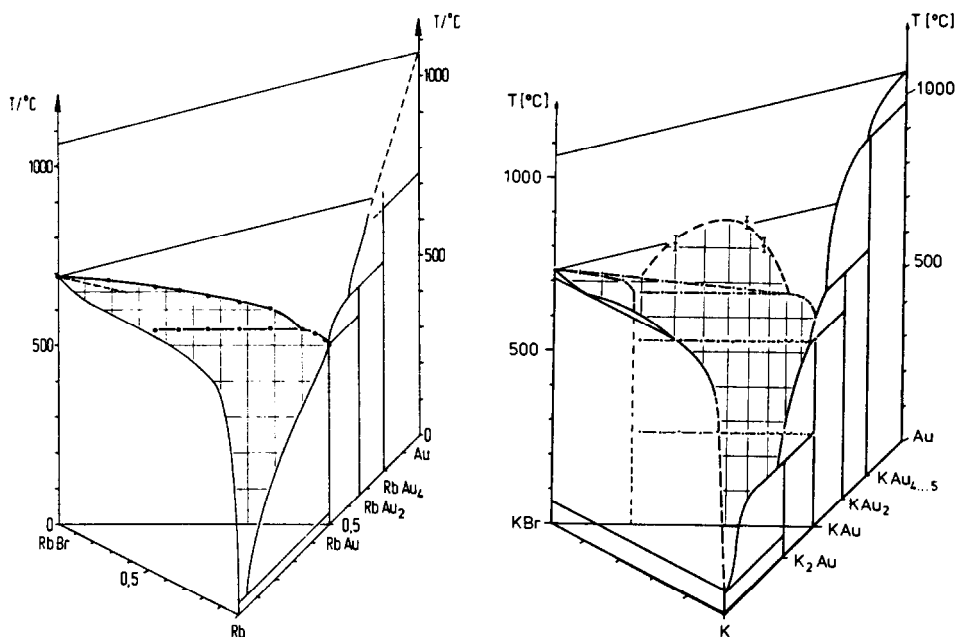

Fig. 2 and 3: MBr/MAu section of the ternary M/Au/MBr phase diagrams
for M=Rb and K

DISCUSSION

System CsAu/CsBr

Only one thermal effect has been observed for all compositions. The onset temperatures of these peaks as well as their end points depend on composition. Accordingly CsAu and CsBr are completely miscible in the liquid and in the solid state. This miscibility has been verified in the meantime by X—ray diffraction (ref. 12). Whereas the liquidus line was obtained directly from the thermograms, part of the solidus line had to be estimated on the basis of general thermodynamic requirements.

Section RbAu/RbBr of the system Rb/Au/RbBr

Heating and cooling curves for $0.21 \leq x_{RbBr} \leq 0.64$ show two thermal effects. The lower

temperature peak appearing only for x_{RbBr} $\leq$0.64 occurs at 542±2⁰C independently of composition. The higher temperature peak shifts with increasing RbBr content towards the melting point of RbBr, thus belonging undoubtedly to the solid–liquid phase transition. The existence of only one thermal effect at x_{RbBr} >0.7 together with the fact, that onset temperatures and end points of this peak in heating and cooling curves all approach continuously the corresponding values of the melting peak of pure RbBr with increasing RbBr content, indicate some limited solid solubility of RbAu in crystalline RbBr.

For x_{RbBr} $\leq$0.1 again only one peak is observed which approaches the "melting peak" of RbAu with further decreasing RbBr content. The latter consists of two well identifiable but noticeably overlapping signals, the lower one with an onset temperature of 498±2⁰C and the higher one at 504±2⁰C, corresponding to the peritectic decomposition of RbAu and to the liquidus temperature at the equiatomic composition (ref. 10). These two events coalesce already at x_{RbBr}=0.05, leaving only one peak up to x_{RbBr} $\leq$0.1. The most probable explanation of this behaviour is the assumption of some solid solubility of RbBr in the RbAu phase causing some increase of the solidus temperature in analogy to the CsAu/CsBr system. With this assumption the composition independent thermal event at 542⁰C would correspond to a peritectic reaction between the RbAu phase saturated with RbBr, the RbBr phase saturated with RbAu and the coexisting melt. Thus the RbAu/RbBr section seems to be almost a true pseudobinary except at the very RbAu rich end, where – as already mentioned – the RbAu phase decomposes peritectically in the Rb/Au system.

Section KBr/KAu of the system K/Au/KBr

For x_{KBr} $\geq$0.74 only one peak is obtained on heating and cooling, which continuously approaches the melting peak of pure KBr with increasing KBr content. As in the case of the Rb system this effect belongs to the melting process of a KBr/KAu solid solution. The solid solubility range may extend – according to the observed thermal effects – to 0.74>x_{KBr}>0.66. For x_{KBr} $\leq$0.66 three thermal effects have been observed, of which the lower two appear independently of composition at 268±2⁰C and 530±2⁰C respectively. These two belong to equilibria between 4 condensed phases in addition to the vapour phase always present in the sample containers. Comparison with the phase diagram of the K/Au system (ref. 10) suggests at 268⁰C an equilibrium between the melt and the crystalline phases KBr saturated with KAu, K_2Au and KAu saturated with KBr and at 530⁰C an equilibrium between KBr, KAu, KAu_2 and the melt. As expected in this case, the area of both peaks decreases continuously with increasing KBr content.

The highest temperature peak belongs to the melting process. It starts for 0.66$\geq$ x_{KBr} $\geq$0.11 independently of concentration at 670±1⁰C. The temperature, where the melting process is completed increases almost linearly with composition from 670⁰C at x_{KBr}=0.12 to 708⁰C at x_{KBr}=0.665 as does the peak area. Here again, the end point temperatures of the peaks of the heating curves agree with the onset temperatures of the peaks of the cooling curves within ±1⁰C and in the reverse case within ±2⁰C. In addition, some first observations of the electrical resistance of KBr/KAu mixtures as a function of

temperature at some few compositions (ref. 13) in the range $0.04 < x_{KBr} < 0.51$ suggest, that there is a miscibility gap in the liquid phase with an upper critical point at about $880 \pm 20^\circ C$ and $x_{KBr} \sim 0.3$. The thermal effects related to this demixing were apparently to small to be detected by our DTA apparatus. Based on this suggestion, the composition dependence of the width of the "melting peak" and its composition independent onset temperature could be explained by a three phase equilibrium (despite the vapour phase) between two different liquid phases and crystalline KBr saturated with KAu and a four phase equilibrium at $670^\circ C$ with an additional gold rich solid phase such as pure Au or $KAu_{4...5}$ (refs. 10,14) but probably not KAu_2, since this compound decomposes peritectically already at $650^\circ C$ (ref. 10).

CONCLUSION

The mixing properties along the MBr/MAu sections of the ternary systems M/Au/MBr show a clear and systematic dependence on the alkali metal: Both, solid and liquid miscibility range decrease with decreasing atomic number of the alkali atom. Thus the Cs system shows complete miscibility in the liquid and in the solid state. In the Rb system complete miscibility in the liquid state is still preserved but the solid state solubility is limited as is expected due to different crystal structures of RbAu and RbBr despite the nonmetallic character of RbAu. In the K system finally, the crystal structure of the KAu compound differs strongly from that of KBr (ref. 10), leaving probably only a very limited solubility of KBr in KAu, whereas in the reverse case the solubility is substantial. Here even a limited solubility in the liquid is observed, although the exact shape of the miscibility gap still needs clarification. Thus whereas the limited mutual solid solibility of RbAu/RbBr and KAu/KBr corresponds to expectation due to the different crystal structures of the pure compounds, the strong influence of the electronic structure on the mixing properties of these systems is indicated by the mixing behaviour of the liquid state. Here no substantial deformation energies of the ionic structure can be caused by the accommodation of impurities, but instead the composition dependent transition from ionic to almost metallic like screening of the interparticle potential may cause a miscibility gap as has been demonstrated theoretically by Holzhey and Schirmacher (ref. 15).

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