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MAGNETISM AND SHORT RANGE ORDER IN MOLTEN CO\(_{1-x}\)B\(_x\) (0 \(\leq\) \(x\) \(\leq\) 0.33)

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Abstract. — We report on magnetic susceptibility measurements up to 2 200 K for studying the temperature and concentration dependence of atomic short range order in molten Co-B alloys. The magnetic properties change at well defined temperatures and around 20 at% B. The results are arranged in a "Phase diagram" of atomic associations in the melt.

Atomic short range order (SRO) stabilized by local chemical bonds has been suggested to be important for the formation and stability of metallic glasses [1]. Since the cohesive energy is large (e.g. Co: 425 kJ/mol) compared to the heat of melting (e.g. Co: 15.5 kJ/mol) one can expect the SRO to survive melting and decay by thermal fluctuations. The lack of transitional long range order and the high melting points of the transition metals make it difficult to study the structure of the melt by usual methods.

We tried to use the magnetic moment of 3d-metals as a sensitive convenient tool for studying the SRO in molten Co\(_{1-x}\)B\(_x\) glasses, because it is known to depend in solid disordered alloys on nearest neighbor coordinations [2]. We developed for this purpose a vibrating sample magnetometer, which has a sensitivity of 2.5 \(\times\) \(10^{-10}\) m\(^3\) / kg up to temperatures of 2 200 K. The samples of about 1.5 g weight are encapsulated in ceramic crucibles and then welded into Mo containers in order to avoid evaporation losses. Microprobe analysis of the sample surface after several runs to 2 200 K showed no traces of impurities or reaction with the crucible material.

We here present magnetic susceptibility (\(\chi\)) measurements between Co and the congruent melting compound Co\(_2\)B. In the crystalline or amorphous state around \(x\) = 0.2 the saturation moment and the ferromagnetic Curie temperature are reduced by the chemical bonds between B and Co atoms often described as charge transfer [3]. The \(\chi^{-1}\) curves plotted as a function of temperature are composed of pieces of straight Curie-Weiss (CW) lines separated by jumps or knees which indicate the occurrence of phase transformations or changes in SRO. The sharpness of the jumps at the structural phase transitions proves the suitability of this method as an excellent tool for determining transformation temperatures. The partial phase diagram Co-Co\(_2\)B, we have designed in this way, agrees well with the known data from literature [4]. The eutectic and peritectic temperature can be given more precisely as \(T_{\text{en}}\) = 1 393 ± 3 K and \(T_{\text{p}}\) = 1 414 ± 2 K, respectively. At melting \(\chi\) decreases in most alloys and in pure Co, whereas it increases at \(T_{\text{p}}\) and the melting point of Co\(_2\)B.

We derive from the CW behavior up to 2 200 K the paramagnetic Curie temperature \(\theta\), Curie constant and effective magnetic moment \(p_{\text{eff}}\) per Co atom in the usual way. The \(\chi^{-1}\) (\(T\)) curves show in addition to the jumps at the melting temperature \(T_{\text{L}}\) two knees at two critical temperatures \(T^*\) and \(T^{**}\) for \(x\) \(\leq\) 0.2, which we interpret as changes in SRO. At higher concentrations the change at \(T^{**}\) disappears. Figure 1 shows, how the Co moment varies with B concentration. For comparison the data for crystalline Co and Co\(_2\)B are included. Just above the melting point \(p_{\text{eff}}\) decreases linearly with concentration up to \(x\) = 0.2 and extrapolates to the value for solid Co\(_2\)B in a similar way as in the amorphous and crystalline materials, but with a reduced charge transfer of about 0.7 electrons. From this we conclude, that the melt closely above the melting point exhibits the same SRO as in crystalline and amorphous solids, i.e. Co tetrahedra which are decorated to an increasing number by B atoms. However the strength of the Co-B bonds may be about 50 % weaker in the melt than in the solid. This behavior changes for \(x\) > 0.2, where the Co moment surprisingly increases again when the B concentration increases. The B-B avoidance known to occur in glasses seems to

Fig. 1. — Paramagnetic moment per Co-atom of molten Co-B alloys.
be replaced by formation of B-B bonds so that Co-Co distances becomes larger, the moment increases whereas $\theta$ decreases (Fig. 2). The concentration dependence of $\theta$ for $x \leq 0.2$ just above the melting point also resembles the crystalline and amorphous situation [3], demonstrated by a dotted curve in figure 2.

When the temperature of the melt exceeds the critical value $T^* = 1.600 \pm 10$ K, the moment of Co changes to larger values, while the Curie temperature decreases. Figure 1 also shows typical values of $\rho_{\text{eff}}$ taken at 1 700 K. The independence of concentration and the similarity to the values of pure Co indicate that the Co-B bonds are now broken.

The magnetic behavior changes drastically for $x > 0.2$. The Co atoms become more separated due to the dominance of more stable B-B bonds. This causes more localized moments that weakly interact. At the concentration of Co$_2$B the value of $\rho_{\text{eff}}$ in the melt becomes temperature independent up to 2 200 K, but is much larger than in the crystal. That means, that the Co-B bonds, which reduce the moment in the crystalline state break already at melting.

There is another sudden increase of $\rho_{\text{eff}}$ for $x > 0.2$ at $T^{**} = 1900 \pm 20$ K which also decreases the Curie temperature. The points shown in figures 1 and 2 for $T > T^*$ refer to values taken at 2 000 K. It is interesting to note, that the transition at $T^*$ has been earlier observed in pure Co melts, where it can be suppressed by small additions of Y [5]. This indicates, that the transition at $T^{**}$ is related to a change in Co coordinations.

Another interesting feature is the irregularity around $x = 0.2$ for $T > T^*$, where the Co associations seem to be improved. A possible reason could be the stabilisation of Co icosahedra by strong forces to Frank-units, which often occur in the neighborhood of eutectics [6].

In figure 3 we try to sketch a "Phase diagram" for atomic associations in the melt. The sharpness of the transition temperatures $T^*$ and $T^{**}$ is encouraging for doing this, but one has to realize, that such associations are not rigid as in crystals and glasses, but fluctuate by thermal excitation. In area 1 we have a mixture of Co-B associations with Co tetrahedra. The first decay at $T^*$ and the latter at $T^{**}$ as in pure Co into a structure of randomly packed hard spheres (area 2). For $x > 0.2$ in area 3 the relatively strong B-B bonds dominate the structure of the melt. In area 4 the topological SRO may provide an additional stabilisation of more closely packed Co atoms, which gives a lower paramagnetic moment.

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