An Estimation of Enthalpy of Amorphous Alloys using Differential Thermal Analysis (DTA) Technique

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Summary: The enthalpy energies are calculated by using exothermic peaks of differential (thermal analysis (DTA) on Cobalt-Boron liquid quenched amorphous alloys. The endothermic peaks are not distinctly recorded. The diffusional recovery processes in Co-B LQA alloys occur at about 693K and temperatures less than 800K; which suggests that the polymorphic transformation of cobalt is responsible for diverse diffusion recovery processes such as interstials and vacancy formations, Cottrell-Lomer locks, point defects due to free covalent bonds (dangling bonds), edge/edge and screw/screw annihilations through forced climb due to thermal stresses and indeed due to non-operative slip systems of cobalt (both basal and pyramidal slips). Structural changes in Co-B LQA alloys occur at above 800K mainly due to operative slip systems in Cobalt (both basal and pyramidal) which cross each other (cross-slip) due to thermal stresses and annealing. The cross-slip in c p.h. metals (cobalt) particularly at low temperatures is indeed difficult.

Introduction

An unusual, but already recognised method was adopted to calculate enthalpy energies. The samples used for this purpose are LQA alloys of Co-B. Preparation details of the samples is described elsewhere [1]. The DTA analysis of Co-B samples [2] was performed and sharp exothermic peaks were considered for calculations of enthalpy energies.

$$\Delta H = m \int_{T_1}^{T_2} c(T)\, dT \text{ or } \Delta H = mc\Delta T \text{ Joules}$$

where 'm' is the sample mass in micro kilogram (10^{-6} kg)

Δ T is the width of exothermic peak in Kelvin,

c(T) is me specific heat.

Usually, the chemists consider the masses in grams but the physicists follow SI units in which mass is taken in kilogram and temperature in Kelvin. The specific heat ,.i.e., c(T) in SI units is measured in cal/kg-K.

There are two types of chemical reactions,.i.e.exothermic in which energy is required and endothermic in which energy is released due to any physical or chemical changes preferably in this case due to solute atoms,.i.e., boron in cobalt. Our results indicate that there is no endothermic peak which shows that structural changes are not associated with energy releasing processes such as thermal stresses due to continuous heating and annealing. Moreover, enthalpy energies are always associated with exothermic chemical reactions (there is no Gibb's free energy).

For specific heat we considered a general universal formula, mostly used by chemical engineers [3] ,.i.e.,

$$c(T) = c = 0.132 + 1.56 \times 10^{-4}\, Tp + 2.64 \times 10^{-7}\, Tp^2$$

where Tp is the exothermic peak temperature observed in DTA.

Table shows details of Co-B alloys alongwith calculated enthalpy energies for each corresponding exothermic peak in the temperature range 673-1073K.

We compared our results from phase diagram of Co-B alloys [4] and then reached to some conclusive results.

Table of Calculated Enthalpy Energies

Samples	Mass of Sample (μkg)	Peak No.	Peak Temp. Tp(k)	Peak Width ΔT(k)	Specific Heat c (cal/kgK)	Enthalpy ΔH (μJ)	Process Description
$CO_{70.5}B_{23}$	0.55	1	781	285	0.4148657	272	Diffusional recovery process
		2	847	281	0.4535279	293	Structural changes (Orthorhombic)
$CO_{77}B_{23}$	0.50	1	863	285	0.463247	276	Structural changes (Orthorhombic)
$CO_{76}B_{24}$	0.40	1	757	289	0.4013769	194	Diffusional recovery process
		2	1029	281	0.572058	269	Structural changes (b.c.Tetragonal)
$CO_{75}B_{25}$	0.30	1	1049	289	0.5861498	213	Structural changes (b.c-Tetragonal)
$CO_{73}B_{27}$	0.25	1	841	289	0.4499181	136	Structural changes (Orthorhombic)
$CO_{71.5}B_{28.5}$	0.20	1	837	289	0.4468216	108	Structural changes (Orthorhombic)
$CO_{71}B_{29}$	0.20	1	693	289	0.3668937	89	Diffusional recovery process
		2	857	281	0.4595865	108	Structural changes (Orthorhombic)
$CO_{70}B_{30}$	0.20	1	707	285	0.3742521	89	Diffusional recovery process
		2	1047	285	0.5847311	140	Structural changes (b.c. Tetragonal)

Results and Discussion

Structural changes occur in between about 837-1053K temperature range such as body centred, tetragonal and orthorhombic for Co_2B and CoB, respectively.

We conjecture that the body centred tetragonal structural changes should occur at relatively high temperature as compared to orthorhombic. This evidence is supported by the exothermic peaks commensurate with temperatures for structural changes observed *via* dynamic temperature x-ray diffraction..i.e., DTXD [1].

Cobalt is basically a close packed hexagonal crystal. It has two slip systems, *i.e.*, basal and pyramidal. At above 800 K, basal and pyramidal slip systems become operative and cross each other due to thermal stresses as a consequence of which two different types of structural changes occur such as body centered tetragonal and orthorhombic for different alloys of Co-B depending on the boron concentration , indeed. At below 800 K, the slip systems of cobalt, *i.e.*, basal and pyramidal become non-operative due to which interlocking of dislocations produces other kinds of defects such as interstials of boron or vacancies of boron, screw and edge dislocations, etc. This manifests itself due to diffusional recovery processes.

The data is not plotted but the table shows an evidence that the enthalpy energy decreases with increasing concentration of boron. In other words if the increase of boron goes beyond a threshold then we may expect the occurrence of endothermic peaks (a process different than enthalpy energy because it will include a free Gibb's energy).

Enthalpy energies decrease for diffusional recovery processes with increasing boron percentage

and then becomes constant at and greater than 29 atomic percentage of boron in Co-B (LQA) which shows inhibition of diffusional recovery processes. The same type of behaviour is observed for orthorhombic structural changes [Table]. The orthorhombic structural changes are inhibited due to increasing concentration of boron at and above 28.5 atomic percent of boron. Diffusional recovery processes occur at temperatures below about 800K as it is observed in our case for Co-B (LQA) alloys [Table].

Enthalpy energies for such processes,.i.e., for diffusional recovery processes at below about 800K and for structural changes (.i.e,, body centred, tetragonal and orthorhombic) in the temperature range, 800-1060K are determined. The enthalpy energies also show a decreasing trend for body centred tetragonal structural change with increasing atomic concentration of boron. The body centred tetragonal structural changes in our Co-B (LQA) alloys occur at above 1000K.

The temperature of the polymorphic transformation of Cobalt is above 693K. Surprising enough the diffusional recovery process in Co-B (LQA alloys occur at about 693K and at temperature less than 800K which suggests that the polymorphic transformation of Cobalt is responsible for diverse diffusional recovery process such as interstials and vacancy formation. Cottrell-Lomer locks, point defects due to free covalent bonds (dangling bonds), edge/edge and screw/screw annihilations through forced climb due to thermal stresses and indeed due to non-operative slip systems of cobalt (both basal and pyramidal slips). Structural changes in Co-B LQA alloys occur at above 800K mainly due to operative slip systems in Cobalt (both basal and pyramidal) which cross each other (cross-slip) due to thermal stresses and annealing. The cross-slip in

c.p.h. metals (cobalt) particularly at low temperatures is indeed difficult.

The orthorhombic structural changes in Co-B (LQA) alloys occur in the temperature range 800-1000K and that the body centred tetragonal structural changes above 1000K. It is a new finding which explains the micromechanisms for structural changes only associated with enthalpy energies.

References

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