PREFACE

Investigations on transition metal phases with $B$ subgroup elements of the Periodic Table play a vital role in modern research. Their solid solutions and phases have attracted the attention of a number of workers due to their numerous applications in science and industry. With the advancement of time more and more will be known about their crystal structures and physical properties, and their fruitfulness will be established further. Semi-conducting property, super conducting behaviour and recently anti-superconductivity phenomenon have been observed in these phases. The discovery of metallic glasses open a new exciting and expanding field of considerable scientific as well as technological interest. The chevrel-phases, which are considered as typical representatives for mixed ionic-covalent metallic bonded crystals, provide an interesting field of research for solid state chemists.

When two metals are alloyed together the product is either a primary solid solution or an intermediate phase. A compound formation or a solid solution is.

The structure of both the metallic elements be similar. Sometimes, a continuous solid solid also observed. This phase is a
on the composition of the alloys and the temperature, provided the alloy is at equilibrium. The relationships between different phases are represented on a map known as the thermal equilibrium diagram, also called phase diagram or constitution diagram.

Constitution diagrams make it possible to classify alloys into groups according to their microstructures and to study them as groups with regard to their general properties, and to the variations in these properties that result from variations in composition, condition of heat treatment, extent of mechanical working etc. A thorough knowledge of the construction, significance and interpretation of phase diagrams is the major prerequisite for understanding of internal structure of alloys and their behaviour, and of the effects of impurities upon the properties of metals and alloys in general.

The mechanical properties of solid solutions show a gradual and continuous change as the concentration of solute is increased: the strength increases and the ductility usually decreases. Recrystallization temperatures and grain growth rates are affected by impure state concentration and purity. A solute atom acts as a dislocation sink and at the critical concentration a gathering centre for dislocation activity.
The electrical resistivity shows a very marked drop when ordering occurs in a disordered solid solution. Solid solution alloys have low values of temperature coefficient of resistance and thermal conductivity, on the other hand, they have improved corrosion resistance as compared to component metals. These typical properties of solid solution alloys are being utilized in many ways, now and a days.

The applications of Hume-Rothery's rule for intermediate phases and primary solid solutions have been extended to alloys of transition elements and B sub group elements. There is, however, need of extensive work on these systems to visualize their structure and to see whether it fits in element, better of structures of brasses. For new structure, it is desirable to discuss the relationship with the structures occurring in Cu-Zn intermetallic systems. With this idea, the structural aspects of the four different ternary systems viz; Ni-Sn-In, Ni-Sn-B, Ni-Sn-As, Ni-Sn-Sb and Ni-Sn-Si have been investigated. Fundamental work on these systems could give a better understanding of these systems and would center on the systematic investigation of the conditions of formation of alloys containing transition and B sub group elements.
The occurrence of a large number of intermetallic phases as well as amorphous compounds in Ni-Zr system, has led us to investigate this binary system. Further, the non-availability of thermal expansion data of intermediate phases of this system, has become the nucleus for the present study of determining the linear thermal expansion coefficient of some intermetallic phases.

In an alloy system if a stable phase exists at a given temperature, pressure and composition, it is that with the lowest Gibb's free energy. However, the crystal structure of such a phase is governed by the environments geometrical, size, chemical bond and electrochemical factors. These factors have been briefly described in Chapter - I.

Intermetallic phases in an alloy system are different from intermetallic compounds which resemble the chemical compounds. Their phase structures have quite characteristic patterns of atomic sites. The difference is to be found in the nature of forces which hold the structures together. Intermetallic phases usually do not follow the normal valence concept of chemistry and new types of relationships are to be searched for the explanation of their structures. In Chapter - I, some of the important alloy theories viz. Hume-Rothery,
Brillouin zone theory for electron compounds, Schubert's model of spatial correlation of electrons and Engel-Brewer's theory have been reviewed and the mechanism of stabilizing new structures has been discussed.

Chapter III deals with the principle and working of a "Enraf-Nonius FR 552" Guinier camera which has been used in most of the present study. Further, a short description of the different modified techniques employed for rapid cooling along with some details of the present method of under cooling have been given.

X-ray investigation of Ni-Sn-In ternary system has been dealt in Chapter IV. The crystal structure of intermetallic phase Ni$_3$Sn has been found as hexagonal with lattice constants, \(a=5.34\) \(\text{Å}\) and \(c=4.259\) \(\text{Å}\), in agreement with the earlier reported work. This phase undergoes a transformation at high temperatures. The high temperature modification of this phase has been found as orthorhombic Cu$_3$Ti type with \(a=9.275\) \(\text{Å}\), \(b=4.600\) \(\text{Å}\) and \(c=4.254\) \(\text{Å}\). This structure is also observed on splat cooling the alloy, Ni$_3$Sn$_5$.

Comparison of unit cell parameters usually obtained from XRD and ex-splat cooling indicates better packing of atoms on splat cooling.

An appreciable solubility of indium in Ni$_3$Sn and nickel in Ni$_3$In is expected due to the existence of electron rich phases at low temperatures.
This fact has been observed in the present investigation where the ternary alloys in the \( \text{Ni}_3\text{Sn}-\text{Ni}_3\text{In} \) line show the presence of single solid solution phase at low temperatures which is of \( \text{Ni}_3\text{Sn(r)} \) form. Both the lattice parameters are found to increase, on replacement of tin by indium atoms, which can be accounted by the large atomic size of indium atoms. Further, comparison of variations in lattice parameters indicate that the random substitution is more in the basal plane than in the prismatic plane. The linear relationship between mean atomic volume (M.A.V.) and compositions in \( \text{Ni}_3\text{Sn}-\text{Ni}_3\text{In} \) system shows that there is no large concentrations of lattice vacancies at some definite compositions.

The favourable size-factor is responsible for the miscibility of indium in tin. Inspite of restricted size-factor, the extent of maximum solid solubility of indium in nickel is related perhaps more with the extent of distortion that the indium atom produce on the solvent lattice.

Chapter V consists of two parts. Investigation on Ni-Sn-Si ternary system has been reported in part A of this chapter and work on Ni-Sn-Be system has been included in part B.

Both Ni-Si and Ni-Be systems are known to form intermetallic compounds at composition \( \text{A}_2\text{B} \), viz. \( \text{Ni}_3\text{Si} \) and \( \text{Ni}_3\text{Sn} \). The phase \( \text{Ni}_3\text{Si} \) is known to exist in
three different modifications while Ni₃Sn usually exist in two forms. None of the modifications are isostructure in the two systems. Therefore, it is expected that there will not be any appreciable solid solubility of tin in Ni₃Si or of silicon in Ni₃Sn phase. The present investigation confirms the above prediction and all the alloys melted on the quasi binary system Ni₃Si-Ni₃Sn are found to contain two phases (upto 500°C) in equilibrium condition.

The electrochemical factor is responsible for the complete miscibility of silicon in tin. The high solid solubility value of silicon in nickel has been explained on the basis of the difference of the atomic radii (neutral and CN-12) of the silicon atom and the CN-12 radius of nickel atom and its effect on the thinning characteristics of the electron cloud of the assembly.

The structure of Ni₃Ge phase has been found as cubic, Cu₃Au type with lattice constant, a=3.563 Å in agreement with the past reported work. This phase is also found to occur at elevated temperatures. For stabilizing this phase, the electrochemical nature of forces seems to be responsible.

The alloy Ni₃Ge₁₂ has shown an interesting result after splat co-casting. The powder photograph shows a different pattern from the binary ones and it can be very well indexed on the orthorhombic lattice.
with, \(a=7.261\ \text{Å}\), \(b=3.260\ \text{Å}\) and \(c=6.536\ \text{Å}\). The unit

cell seems to be related to the unit cell of \(\text{Ni}_3\text{Sn}(h)\) phase where one axis has been doubled and that the face
diagonal corresponding to other two axes can account for
the other two lattice constants with some contraction/
dilatation. However, to resolve the structure fully,
single crystal data is required.

Splat-cooled \(\text{Ni}_{75}\text{Sn}_{15}\text{Ge}_{10}\) alloy shows the
possibility of a new metastable ternary phase, as the
complex X-ray powder pattern of this sample could not
be indexed. An extensive work on this sample is needed.

The present investigation has established that
the phase \(\text{Ni}_3\text{Sn}\) is stable up to the composition \(\text{Ni}_{75}\text{Sn}_{20}\text{Ge}_{10}\)
Crystal structures of this phase at low and high
temperatures are found to be hexagonal and orthorhombic
respectively. Similarly, \(\text{Ni}_3\text{Ge}\) phase shows the stability
range up to about \(\text{Ni}_{75}\text{Sn}_{20}\text{Ge}_{10}\) composition. The alloys in
between these compositions contain two phases
viz. \(\text{Ni}_3\text{Ge}(\text{Sn})\) and \(\text{Ni}_3\text{Sn}_2\).

The solid solubility of tin in \(\text{Ni}\text{Ge}\) phase is
found to be five atomic percent.

Chapter VI has been divided into three parts.
Part A is devoted to the work \(\text{Ni-Sn-As}\) system. The
system \(\text{Ni-Sn-Sb}\) has been dealt in part B, whereas the
system \(\text{Ni-Sb}\) is found in part C of this chapter.
The structure of Ni₅As₂ phase has been confirmed to be hexagonal with lattice constants, a=6.813 Å and c=12.501 Å. Splat-cooled Ni₇₁.₄As₂₈.₆ alloy shows similar structure with increased concentration of lattice vacancies.

The present investigation has established that in Ni₃Sn(r) phase, tin can be replaced by arsenic up to 5 at. %. Beyond this composition, and up to 17 at. % arsenic all the ternary alloys show a mixture of two phases viz. Ni₃Sn(r) and Ni₅As₂. The Ni₃Sn(As) phase is found to undergo phase transformation at high temperatures. The high temperature form has been found as cubic with parametric value, a=5.846 Å. It is interesting to note that Ni₇₄Sn₂₅ alloy shows the high temperature form of Ni₃Sn as orthorhombic, Cu₃Ti type. However, with the small addition of arsenic (5 at. %) the high temperature modification changes into cubic lattice. Splat-cooled Ni₇₄Sn₂₅As₅ alloy also exhibits cubic structure with slight higher parametric value, which can be attributed to the larger concentration of lattice vacancies in the splat-cooled alloy. In the Ni₃Sn(h) phase the ordering leads to orthorhombic structure. The atomic volume of the cubic structure is found to be higher than that of orthorhombic structure. This is obvious because the c-c structure is a disordered lattice and therefore has a larger atomic volume.
The random distribution of atoms will lead to cubic symmetry.

The solubility of arsenic in nickel and tin seems to be affected by the electrochemical factor.

The aim of the present investigation is to resolve the controversy regarding the existence of \( \text{Ni}_{15}\text{Sb} \) phase and the uncertainty of the crystal structures of \( \text{Ni}_{5}\text{Sb}_2 \) phase at low and high temperatures. The alloy \( \text{Ni}_{94}\text{Sb}_6 \) shows the existence of \( \text{Ni(Sb)} \) solid solution phase at high temperatures. However, the phase \( \text{Ni}_{15}\text{Sb} \) occurs along with nickel solid solution phase at low temperatures. The phase \( \text{Ni}_{15}\text{Sb} \) could not be isolated at this composition. Formation of this phase is an order-disorder transformation. The high temperature phase is f.c.c. and the ordered phase is based on f.c.c structure with doubling of the lattice constant.

The low temperature form of \( \text{Ni}_{5}\text{Sb}_2 \) phase has been found as tetragonal with lattice constants, \( a=8.766 \text{ Å} \) and \( c=12.535 \text{ Å} \). This phase undergoes a transformation at elevated temperatures. The high temperature form of \( \text{Ni}_{5}\text{Sb}_2 \) phase has been observed as orthorhombic with cell parameters:
\[ a=11.450 \text{ Å}, \ b=5.423 \text{ Å}, \ c=9.065 \text{ Å} \]

The phases \( \text{Ni}_{3}\text{Sn}(h) \) and \( \text{Ni}_{3}\text{Sb}(h) \) are isostructural and therefore complete miscibility in the solid state is expected, which has been observed.
in all the selected ternary alloys of Ni-Sn-Sb system during the present investigations. A continuous solid solution phase in the Ni$_3$Sn-Ni$_3$Sb line of the system has been seen. All the three lattice parameters of orthorhombic cell vary linearly with composition. This is due to replacement of tin atoms by the atoms of antimony which has comparatively larger atomic radius. The variation in 'a' parameter is found to be quite large as compared to 'b' and 'c' parameters. The MAV vs. composition curve also represents a linear relationship thereby showing that at specified compositions there will not be any large concentrations of lattice vacancies.

For the solid solubility of antimony, in nickel and tin, the favourable size-factor is responsible.

The widely differing atomic sizes of nickel and bismuth atoms restrict the formation of solid solution. In case of nickel and tin atoms the size factor is favourable. In the present investigation the ternary alloys show simultaneous occurrence of three phases viz. Ni$_3$Sn(r), NiBi and Ni(Sn) in equilibrium condition. Tin atoms can not be replaced by bismuth atoms in nickel solid solution phase due to above reason. Ni$_3$Sn phase is based on close packed structure and close packing for substitution requires the atoms within favourable size-factor. Though the electronegativity values for the
two elements are not very different, it seems that the size factor plays a predominant role in the formation of alloys. In view of this, extension of solid solution of \( \text{Ni}_3\text{Sn(r)} \) phase is not expected. The results are in close agreement with the above mentioned fact and the ternary alloys investigated are a mixture of three phases in accordance with the equilibrium diagrams.

Chapter VII consists of two parts. In part A, the work on Ni-Zr binary system has been summarised. The alloy Ni\(_{55}\)Zr\(_{45}\) shows the presence of Ni\(_{11}\)Zr\(_9\) phase. The tetragonal lattice parameters of this phase are found as:

\[
a = 10.299 \text{ Å} \quad \text{and} \quad c = 6.936 \text{ Å}
\]

Comparison of crystal structure of this phase with the phase Pt\(_{14}\)Zr\(_9\) in Pt-Zr system shows that they are isostructural phases. In the range from 65 to 80 at. \% nickel existence of a phase following three new intermetallic phases has been discovered:

1. The alloy Ni\(_{55}\)Zr\(_{45}\) shows the presence of nickel solid solution with a new phase Ni\(_{11}\)Zr\(_9\) with Co\(_{11}\)Zr\(_9\) phase. The lattice parameter has been found as \(a = 10.07 \text{ Å}\).

2. The phase Ni\(_{51}\)Zr\(_6\) (c = 3.37 Å, \(a = 10.11 \text{ Å}\)) has a tetragonal structure with unit cell parameters, \(a = 10.11 \text{ Å}, c = 3.37 \text{ Å}\).
The hexagonal lattice of $\text{Ni}_{11}\text{Zr}_5(h)$ phase has parametric values, $a=6.277\,\text{Å}$ and $c=13.182\,\text{Å}$. The occurrence of this phase has been observed in $\text{Ni}_{70}\text{Zr}_{30}$ alloy.

The mean atomic volume (MAV) values of above new phases also fit well in the MAV vs. composition curve.

Chapter VII B has been devoted to the work on determination of thermal expansion coefficient of some intermetallic phases viz. $\text{Ni}_{11}\text{Zr}_9$, $\text{Ni}_{23}\text{Zr}_6$ and $\text{Ni}_3\text{Zr}$ in Ni-Zr system. A brief description of the importance of thermal expansion coefficient, its relationship with the crystal structure and other properties of solids and the different macroscopic methods for its determination has been given. Under the X-ray diffraction method, which has been employed for the present study, the Extrapolation and Least Squares methods for accurate determination of unit cell parameters along with the method for computation of standard errors in parametric values, have been dealt at length. The results of the thermal expansion measurement are as under:

(a) Phase $\text{Ni}_{11}\text{Zr}_9$: The tetragonal lattice parameter of this phase vary linearly with temperature $(730-1220^\circ\text{C})$. The value of $\chi_c = 28.8\times10^{-6}/\text{°C}$ is found to be slightly higher than $\chi_a = 27.2\times10^{-6}/\text{°C}$. 
(b) Phase Ni$_2$Zr$_6$: A linear relationship between lattice parameter of cubic structure and temperature has been observed. A nearly constant value ($\approx 12.86 \times 10^{-6}/°C$) of $\alpha_a$ is obtained throughout the temperature range (730-1220°C).

(c) Phase Ni$_3$Zr: The hexagonal lattice parameters of this phase increase in a non-linear manner over the entire range of temperature (380-820°C). The variation has been expressed by a quadratic relation. The non-linear variation is associated with the anharmonicity and vacancy concentration. The marked decrease in $\alpha$ values with increasing temperature can be predicted from the nature of bonding forces between the constituent atoms and the temperature variation of the Gruneisen parameter, $\gamma$. Further, the large variation in $\alpha$ with temperature in comparison to $\alpha_0$ shows that atoms are loosely bounded in the basal plane.

The aim of the present investigation is to get knowledge of $\alpha$ values of these compounds. As they are being studied for the first time, the accuracy of the results may be further confirmed by using high temperature X-ray camera or by other standard macroscopic techniques.