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THE EFFECT OF CHROMIUM ON THE SINTERABILITY OF WC-Ni-Cr

by

FREDERICK W.K. WONG, B. Eng.

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of

Master of Engineering

Department of Mechanical and Aeronautical Engineering

Carleton University

Ottawa, Ontario

April, 1989

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submitted by Frederick Wong, B. Eng.
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the degree of Master of Engineering

Thesis Supervisor

Chair, Department of Mechanical and Aeronautical Engineering

Carleton University
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Abstract

From the viewpoint of sinterability, Cr has a tendency to inhibit grain growth. The effect of Cr additions to WC-Ni cemented carbides is that it significantly reduces the amount of solid state shrinkage. As well, increasing Cr content reduces the eutectic temperature of the binder phase. However, significant amounts of Cr are required to noticeably alter the densification of Ni bonded WC. One weight percent Cr of the overall binder content has no significant effect on densification in either the solid or liquid phases of sintering. Thus, whereas low Cr grades show a high degree of densification during solid state sintering, high Cr alloys behave in exactly the opposite manner, with most of the compact shrinkage occurring during liquid phase sintering. Even so, low Cr grades were found to densify to a greater extent than high Cr alloys under similar conditions. As well, the activation energy for compact shrinkage during solid state sintering was found to increase with increasing Cr content.

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List of Symbols

A	cross sectional area
D	diffusion coefficient of the solid phase in the liquid
d	diameter
H_c	coercivity
I	current
K	constant
k_r	rate constant for the transfer of solid to liquid across the interface
L	length
l	distance between voltage contact points
p	resistivity
Q	activation energy for compact shrinkage
R	Universal gas constant, resistance
r	particle radius
S	solubility of the solid in the liquid
T	absolute temperature
t	time
V	molar volume of the solid
v	voltage
W_a	work of adhesion
τ	interfacial energy/unit area
θ	contact angle

CHAPTER I INTRODUCTION

The use of nickel as the binder phase in tungsten carbide hardmetals has been rather limited to date. The material of choice has almost exclusively been cobalt due to its outstanding wetting and adhesion as well as to its advantageous mechanical properties. The use of tungsten carbide as the dominant hard material is also extensive with more than 95% of all cemented carbide production involving the use of tungsten carbide, more than half of which are straight tungsten carbide-cobalt grades^[1]. Thus, it is not difficult to understand why tungsten carbide-cobalt grades are the best studied hardmetals.

Nickel or nickel plus chromium has replaced cobalt as the binder for tungsten carbide when corrosion/oxidation resistance and/or high hot hardness is required. The sintering of tungsten carbide hardmetals with straight nickel binder phases has lacked study over the years. Information regarding nickel binders has mainly resulted from studies surrounding the titanium carbide-nickel system^[2,3], the tungsten-nickel system^[4,5,6,7], and parallel inferences made from the tungsten carbide-cobalt system in general. More recently, there has been some study done on the partial replacement of Co with Ni in a WC based hardmetal^[8,9,10]. Only a small number of

published papers focus on the tungsten carbide-nickel system itself^[11,12].

The use of nickel rather than cobalt in tungsten carbide hardmetals is of greater importance than just the small specialty market of corrosion/oxidation resistance and where high hot hardness is required. In the past, nickel appears to have been used when cobalt supplies were limited, such as in the German cemented carbide industry during the Second World War. Today, the nickel market is generally more stable because the world output of nickel is of an order of magnitude greater than cobalt, and is mined in areas more widespread and which are more politically stable^[11]. As well, nickel is a cheaper material than cobalt, enhancing its attractiveness to cemented carbide producers.

The effect of chromium on the sintering of WC-Ni-Cr is even less understood. It is known, however, that the chromium additions do significantly improve the corrosion resistance of straight tungsten carbide-nickel grades^[11] as well as inhibit grain growth of tungsten carbide particles^[13]. Although WC-Ni-Cr grades are used in only a relatively small number of applications, such as seal rings, bearings nozzles, plungers and cylindrical liners where a erosive and/or corrosive fluid is present, their application in some cases may be quite critical. Such is the case of WC-Ni having found limited use in nuclear applications^[11].

For these reasons, this thesis will address the WC-Ni-Cr alloy with the primary point of interest being the effect of chromium additions on the sinterability of WC-Ni-Cr alloys. A straight WC-Ni alloy is also employed as a means of direct comparison so as to determine the effect of Cr additions. The investigation of the effect of Cr additions on the densification processes considers the solid state sintering stage as well as the liquid phase sintering stage. Within the liquid phase stage, special interest is given to grain growth behaviour of the WC grains.

The specific WC-Ni-Cr grades that will be used in this investigation will all contain 10% binder with varying amounts of chromium. These cemented carbide grades are:

1) WC-10wt%Ni	or 10 Ni	} Low Cr Grades
2) WC-9.9wt%Ni-0.1wt%Cr	or 1 Cr	
3) WC-9wt%Ni-1wt%Cr	or 10 Cr	} High Cr Grades
4) WC-8wt%Ni-2wt%Cr	or 20 Cr	
5) WC-5wt%Ni-5wt%Cr	or 50 Cr	

For the remainder of this thesis, percentage (%) will be assumed to be weight percentage. All others will be specified.

One of the most common methods of investigating sintering phenomena is dilatometry^[14,15]. Dilatometry allows the measuring of the

change in length of a compact during thermal treatment, especially during isothermal temperatures so as to characterize sintering behaviour. With the five cemented carbide grades, their various shrinkage characteristics were determined by dilatometry at a slow heating rate (15 C/min.). As well, isothermal tests were carried out at various temperatures for which shrinkage-time measurements were made. These isothermal tests are used to determine activation energies for the five compositions. Other experiments carried out with the dilatometer are for sintering of the five cemented carbide grades at 15 C/min. to various temperatures followed by He quenching to provide an *in-situ* binder phase composition and particle arrangement. These He-quenched samples are then to be measured for electrical resistivity to determine the extent of binder diffusion and spreading. This is reflected by the formation of a continuous conductive path. As well, for the 10 Ni and 10 Cr specimens, these samples will be sectioned, polished and photographed with a Scanning Electron Microscope. A brief analysis of the binder phase with EDAX (energy dispersive analytical x-ray) should give some idea as to the effect of Cr additions on the solubility of W in Ni. Transmission Electron Microscopy will also be carried out on slowly sintered, near full-density 10 Cr and 20 Cr specimens, to determine the distribution of chromium.

CHAPTER II

SINTERING THEORY

For centuries, mankind has been sintering ceramics and metals. We have progressed from simple pottery ceramics to the present day's powder metallurgical components whose superior properties overwhelm those of wrought products. This advancement in sintering technology, however, is more the result of empiricism and trial-and-error rather than through our understanding of the sintering sciences. Our knowledge in the basic science of sintering is quite limited and is plagued with disagreements among various investigators. As an overview of the basic sintering theory surrounding cemented carbides which this chapter is dedicated to, much reference will be directed at the WC-Co system due to the relatively large amount of research done on this particular alloy.

The sintering of metal powders basically involves the diffusion of atoms among powder particles in a pressed compact so as to achieve a denser, more consolidated compact of greater strength and rigidity. With some materials, in order to quicken the diffusion rate to attain a reasonable sintering time without significantly increasing the sintering temperature, it may be necessary to add a second phase to lower the energy barrier for transport. This second phase should have a considerably lower eutectic

temperature than the primary phase and be able to take the primary phase into solution. Thus, by sintering at a temperature where the secondary phase forms a melt, rapid diffusion of the primary phase is possible through the liquid. Such is the case of cemented carbides. With WC based hard materials, the high temperature properties of WC make it very difficult to fabricate. However, with the addition of a Fe-group metal (ie. Fe, Ni or Co) binder phase as the sintering aid to enhance diffusion rates, more realistic fabrication temperatures are possible, as well as more favourable mechanical properties due to the binder phase's ductility. Thus, the introduction of the Fe-group metal reduces the activation energy for diffusion by providing a short-circuit mass transport path for atoms between WC particles. This is possible due to the good solubility of W and C in Fe group metals and the lack of solubility of these metals in WC^[1].

With cemented carbides, sintering occurs in two major steps. The first step is the sintering of the powder compact below the binder's melting temperature, known as solid state sintering. The other step is called liquid phase sintering and occurs after the binder phase has melted. The latter of the two processes is the more important one regarding cemented carbides. These two processes will be introduced in greater depth in the following sub-sections of this chapter. As well, information regarding the effect of

Cr as well as other factors affecting the sinterability of cemented carbides will be presented.

2.1 Atomic Diffusion/Solid State Sintering

The driving force for sintering is the excess interfacial and surface free energy of a compact of powder particles, with the sintering process trying to bring about the reduction in the total free energy of the system. This is possible through the diffusion of atoms so as to join particles together since interfacial boundaries possess a lower free energy than free surfaces. At the same time, particles grow in size to minimize surface and interfacial free energy. This movement of atoms takes place in three forms: 1) surface diffusion; 2) grain boundary/interfacial diffusion; and 3) volume diffusion.

Surface diffusion occurs when atoms along the gas/solid interface relocate to another area on the gas/solid interface (see Figure 1). Atom movement is usually from convex surfaces to concave ones. Surface diffusion is a coarsening process that does not lead to pore reduction of the specimen but does reduce surface energy.

Grain boundary diffusion or interfacial diffusion is the process whereby atom movement is from the solid/solid grain boundary interface to a gas/solid surface. A similar diffusion process is volume diffusion in

which interior atoms of a particle diffuse to the gas/solid interface (see Figure 1). Both grain boundary diffusion and volume diffusion are termed densification processes since they reduce the centre-to-centre distances between particles and therefore decrease porosity levels.

Of the three mechanisms, only surface diffusion and grain boundary diffusion play a large role in sintering of cemented carbides. Grain boundary diffusion, unlike volume diffusion, occurs due to the low energy grain boundary path the atoms move along. However, grain boundary diffusion is limited due to surface diffusion which is occurring simultaneously. Surface diffusion reduces surface energy which is the driving force behind densification processes.

Solid phase sintering takes place below the eutectic temperature of the binder phase. For a WC-Ni system, for example, it consists mainly of surface and grain boundary diffusion of W and C through the Ni binder phase. Since W and C are quite soluble in Ni, the activation energy for W and C diffusing via the Ni binder to an adjacent WC particle is considerably less than for atomic diffusion between two contacting carbide particles without a sintering aid present.

Although cemented carbides are almost always sintered at temperatures above the eutectic temperature, solid phase sintering still plays a major role in the process. Significant shrinkage does occur in the solid

phase^[3,16,17]. In fact, Snowball and Milner^[17], have shown that through solid phase sintering alone, a WC-9% Co mixture could be sintered to equally high densities and with comparable mechanical properties at 1250 C compared with those sintered above the eutectic temperature (>1320 C). However, the sintering time required to reach these equivalent densities was approximately ten times that of the liquid phase sintered specimens. The high densification attained during solid state sintering alone is the result of the diffusion of the binder material into carbide interfaces to promote enhanced diffusion of the carbide particles.

2.2 Liquid Phase Sintering

Two of the main reasons Co is the preferred binding material in WC based hardmetals is because of the high solubility of WC in it, and its good wetting properties. The importance of solubility of the solid particles in the binder can be shown through work carried out by Snowball and Milner^[17]. In their study, they had sintered compacts of WC-9% Cu (in which WC has negligible solubility in Cu) and WC-6% Co. Both contained the same volume percent of liquid upon melting of the binder phase (approximately 18 vol.%) at their respective sintering temperatures. The amount of shrinkage was considerably less with Cu (at 1130 C) than with Co (at 1340 C). The shrinkage of the WC-Cu compact did increase

when the sintering temperature had been raised to 1400 C, but the amount of shrinkage was comparable to sintering WC without any binder phase. The high solubility of the solid in the liquid phase of the WC-Co system enables substantial particle smoothing to occur on melt formation, making it easier and faster for rearrangement to occur.

The solubility of WC in Co and Ni according to Edwards and Raine^[18] are 22% and 12% respectively. These values were assessed after 24 hours at 1250 C and quenching in water. However, Hoffmann and Mohs^{19]} work showed that the solubility of WC in Co at approximately 1250 C is much lower, at about 9.5% WC. As well, the eutectic temperature of the WC-Co system is reported to be 1320 C^[20] while the eutectic temperature of the WC-Ni system is 1370 C^[9].

Strong chemical bonds exist at the interface between carbides and the Fe-group metals. Chemical bonding is especially favourable in the case of WC and Co. This results in a very low solid/liquid interfacial energy resulting in nearly perfect wetting, and consequently a very good adhesion in the solid state. Thus, spreading of the Co liquid phase occurs readily, due to capillarity. Nickel binder, though effective does not wet carbide particles as readily as Co^[9]. For the case of poor wetting, there may be an exuding of the liquid from the compact. This results in the formation of

small balls of the liquid on the compact surface. The compact will retain a solid structure but will be quite porous.

During liquid phase sintering, three phases generally exist, a solid, liquid and vapour phase. The liquid will wet the solid as dictated by the equilibrium between the interfacial energies of the three phases. The concept of good and poor wetting is illustrated in Figures 2a & 2b. The degree of wetting is characterized by the contact angle or wetting angle. For the point of solid-liquid-vapour contact to be in equilibrium, the horizontal components of the three interfacial energy vectors in Figure 2c must equal zero. Thus,

$$\tau_{sv} = \tau_{sl} + \tau_{lv} \cos \theta$$

where τ = interfacial energy
 θ = contact angle
 s = solid
 l = liquid
 v = vapour

The work of adhesion, W_a (ie. the bonding force between the liquid and the solid phases) is defined as :

$$W_a = \tau_{sv} + \tau_{lv} - \tau_{sl}$$

This equation can be rewritten as :

$$W_a = \tau_{lv} (1 + \cos \theta)$$

The bonding force between the solid and liquid phases is now expressed in terms of the wetting angle and the interfacial energy of the liquid/vapour

interface (ie. the surface tension of the liquid). Thus, wetting is associated with a chemical reaction at the solid/liquid interface.

For good wetting, an attractive force will exist between two particles wetted by the liquid eventually leading to zero separation between the particles (Figure 3a). Alternatively, poor wetting represents a repulsive force between the two particles (see Figure 3b).

2.2.1 Rearrangement

Liquid phase sintering of cemented carbides occurs above the binder's eutectic temperature and consists of two stages. The first stage starts immediately after mass liquid formation of the binder and is called the rearrangement process. This process occurs rather rapidly and is the result of repositioning solid carbide particles resulting in higher compact densities. Movement of the solid carbide particles is due to the capillary forces of the wetting liquid pulling the carbide particles together. However, the mere presence of a liquid is not all that is required. The liquid will act as a lubricant between particles if it has good wetting characteristics and is able to wet all particle surfaces. If not, the liquid will tend to form balls of liquid instead of spreading in between particles, since the presence of the liquid on the solid surface is unfavourable. As well, if the solubility of the solid in the liquid phase is high, sharp corners

on the solid particles will be dissolved resulting in rounding of the solid particles. Both will result in decreased restriction of particle movement resulting in greater densification rates and higher levels of densification.

Rearrangement occurs in two stages. Primary rearrangement involves the original particles and is rapid due to the capillary forces of the spreading liquid phase between particles as already discussed. Secondary rearrangement consists of clustering and penetration. Clustering occurs when there is insufficient liquid volume to enable 100% densification to occur during primary rearrangement. Capillary forces pull carbide particles together forcing the liquid out from between them to fill surrounding voids and over unwetted particles. This spreading liquid in turn pulls more carbide particles towards the initial cluster of carbide particles. Penetration will occur only if the solubility of the solid in the liquid is high. The advancing melt will not only surround solid particles, but will penetrate particle grain boundaries by attacking and dissolving the particle interfaces that may have been created during solid state sintering. This leads to disintegration of the solid and subsequent rearrangement of the small fragments. However, fragmentation is usually accompanied by swelling as carbide grains are forced apart by the penetrating liquid. Subsequent densification occurs as repacking and solution-precipitation begins. The process of WC rearrangement has been documented by Nelson and

Milner^[21] who have studied the WC-Cu system. Since WC has almost no solubility in Cu, the rearrangement process could be studied in isolation.

2.2.2 Solution-Precipitation

The second stage of liquid phase sintering is solution-precipitation. With this second stage, as the rounding of large carbide particles and the total dissolution of smaller ones progresses, the solubility limit of the solid in the liquid will be reached and the liquid will be saturated. At this point, WC will be precipitated out of the liquid binder phase. The WC precipitated out will preferentially attach themselves to the larger existing WC particles instead of forming new particles. This is due to the fact that the system is trying to attain a minimum free surface energy. Expanding existing grains instead of forming new grains adheres to this minimum energy state. This results in the slow grain growth of WC particles.

As well, surface and interfacial diffusion resulting in coalescence of carbide grains co-exists with the solution-precipitation mechanism. However, grain growth due to coalescence in this manner is considered to be an insignificant contribution. It is generally accepted that solution-precipitation is the dominant mechanism in grain growth of cemented carbide^[22].

LSW Theory

Models governing the solution-precipitation process can be described by the LSW (Lifshitz, Slyozov and Wagner) theory as discussed by Sarian and Weart^[23]. The equations governing the process are:

$$\bar{r}^3 - \bar{r}_0^3 = \frac{8 \tau_{sl} V^2}{9 RT} D S t \quad (\text{eq'n. 1})$$

$$\bar{r}^2 - \bar{r}_0^2 = \frac{64 \tau_{sl} V^2}{81 RT} k_r S t \quad (\text{eq'n. 2})$$

where $\bar{r}$ is the mean particle radius after time, t , and $\bar{r}_0$ is the initial mean particle radius; τ_{sl} is the interfacial energy/unit area of the solid/liquid interface; D , the diffusion coefficient of the solid phase constituent in the liquid; S , the solubility of the solid in the liquid (at a plane interface); k_r , the rate constant for the transfer of solid to liquid across the interface; V , the molar volume of the solid; R , the universal gas constant; and T , the absolute temperature.

Both equations model the solution-precipitation process. However, equation (1) is applied when the process is controlled by the diffusion of the solid in the liquid, while equation (2) governs when the process is limited by the solid/liquid interfacial reaction. These two equations have been found to apply, to a good approximation, with experimental results^[24].

It should be noted that the LSW theory is based on spherical solid particles and does not take in to account grain surface anisotropy.

The general form of equations (1) and (2) may be written as:

$$\bar{r}^n - \bar{r}_0^n = Kt \quad (\text{eq'n. 3})$$

Thus, for an interfacial reaction controlled solution-precipitation process,

$$n = 2$$

$$\text{and } K = \frac{64 V^2}{81 RT} \tau_{sl} k_r S$$

$$\text{or } K = A_1 \tau_{sl} k_r S \quad (\text{eq'n. 4})$$

For a diffusion controlled process,

$$n = 3$$

$$\text{and } K = \frac{8 V^2}{9 RT} \tau_{sl} D S$$

$$\text{or } K = A_2 \tau_{sl} D S \quad (\text{eq'n. 5})$$

If the solution-precipitation process were controlled by diffusion, then for cemented carbides, those with low binder contents (low volume fraction of liquid) should exhibit greater grain growth than those with higher binder contents. This is due to the closer interparticle spacing as a result of less liquid binder phase separating them. However, experimental results supplied by Rudiger et al.^[25] show that for both fine and coarse WC

powder particles over various sintering times, the WC-15% Co clearly shows greater grain growth over the WC-8% Co grade. In addition, it has been shown that the growth behaviour of WC-Co alloys is in better agreement with interfacial reaction controlled solution-precipitation than diffusion controlled^[21].

Therefore, if the solution-precipitation process of WC based hardmetals is interfacial reaction controlled, then according to equation (4), grain growth is related to either the solid/liquid interfacial energy (τ_{sl}) and/or the solubility of WC in the liquid binder phase (S). The reaction constant (k_r) may be neglected since it is dependent upon τ_{sl} and S at the particular temperature of interest.

Isotropic/Anisotropic Grain Growth

With isotropic substances, solid particles tend to become more spherical as a means of attaining a minimum surface energy. Grain growth in an isotropic system comes about as a result of diffusion gradients whereby interfaces grow at the expense of surfaces, and surfaces with large radii of curvature grow at the expense of those with small radii. The diffusion gradient is the result of variations in interfacial and surface curvature. Thus, an isotropic system is one in which diffusion takes place according to the criterion of minimization of interfacial and surface areas,

and thus energies. Particles join together because interfacial boundaries possess a lower free energy than free surfaces, while at the same time particles grow in size to minimize surface and interfacial free energy. In isotropic systems, neck growth takes place from initial points of contact between particles while particles become rounded to attain a minimum area configuration. Surface and interfacial diffusion of material during neck growth and interfacial expansion between particles must be redistributed over particle surfaces so as to maintain minimum surface area requirements. The effect of the liquid phase is mainly to increase the rates of diffusion.

According to Meredith and Milner^[3], an anisotropic system is one in which low energy surface and interfacial planes form. Tungsten carbide is an anisotropic substance with anisotropic surface energies that favour grain growth along these lower energy surfaces or interfacial planes. This results in WC's characteristic prismatic shape in its sintered form, overriding the criterion of minimum surface area, but still maintaining the criterion of minimum surface energy. In the compact's green state, WC particles are generally spherical. However, at points of contact between two neighbouring carbide particles, a boundary comprising of low energy surfaces or interfacial planes can form. These low energy surfaces or interfacial planes will form if binder phase has diffused between the contacting carbide particles. The enhanced atomic mobility due to the

presence of the binder not only enables rapid diffusion from the particle's high energy regions to low energy surfaces and interfacial planes, but is also aided by the WC's anisotropic surface energy. Since atoms in the low energy surfaces and interfacial planes have low activity, a diffusion gradient is set up from the high energy regions where atomic activity is high to the low atomic activity surfaces and planes. Due to this diffusion gradient and the presence of the binder phase, more rapid diffusion is possible than with isotropic systems leading to rapid initial densification of the powder. Thus, material will tend to diffuse towards and expand only these more favourable low energy orientations, resulting in grain growth and leading to prismatic grain shapes. The rapid initial densification is possible since from the initial points of contact between two WC particles, instead of forming a neck between the two WC particles as in an isotropic material, the spherical contact flattens out to a low energy surface or interfacial plane. This enables the centre-to-centre distance between the two carbide particles to be decreased.

2.3 Effect of Cr Additions

The principal results of chromium additions to the WC-Ni system are an improvement of the material's corrosion resistance and inhibition of grain growth. The improvement in corrosion resistance of WC-Ni-Cr

grades over WC-Ni and WC-Co grades is due to the alloying of Cr in the Ni binder phase since a corrosive environment attacks the binder phase of a cemented carbide. The finer grain size resulting from chromium's grain growth inhibition increases the cemented carbide's low temperature wear resistance and hardness.

According to Edwards and Raine^[18], the solubility of Cr_3C_2 in Ni for a Cr_3C_2 -Ni system is of the order of 12%. The solubility of WC in Ni in a WC-Ni system is reported to be the same (12%) by these same investigators. However, some doubt has been cast by Hoffmann and Mohs^[19] on the accuracy of these values.

Tungsten carbide and chromium carbide have no affinity for one another^[16]. As well, the heat of formation of Cr_3C_2 is approximately half that of WC. This is reflected by the dissociation temperatures of 2800 C and 1800 C for WC and Cr_3C_2 respectively. Thus, Cr is believed to go in to solid solution, along with W and C, in the Ni binder phase in a WC-Ni-Cr system^[1].

There have been studies that have noted grain growth inhibition as a result of certain additions to the binder phase^[3,13,22,26]. However, very few studies of the mechanisms involved in grain growth inhibition exist. One exception is a study conducted by Kim and Accary^[22]. Their study centred around the WC-11% Co system and the grain growth inhibition caused by

0.5% TaC additions. The solution-precipitation process controlled by the interfacial reaction model (equation 4 of Section 2.2.2) had been used in their investigation. Kim and Accary reasoned that if the TaC additions were responsible for depressing the solubility of WC in the liquid binder phase, then the observed mean carbide size reduction of approximately 3 of the WC-11% Co-0.5% TaC over the WC-11% Co observed would require a ten-fold reduction in the solubility of WC in the liquid binder phase at the sintering temperature. If this were the case, then in the WC-Co-TaC specimen, only 5% W and C should exist in the binder phase at the sintering temperature. However, 10% W and C was found in a WC - 11%Co - 5%TaC specimen at room temperature. Besides Kim and Accary, Grewe et al.^[27] have also refuted the suppression of WC solubility in the binder. Since the greater TaC content showed a higher W and C content in the binder phase than would be expected, Kim and Accary concluded that the dominant factor governing grain growth in a WC-Co-TaC system was due to a decrease in the solid/liquid interfacial energy. They had observed that WC-Co-TaC specimens showed a lower degree of anisotropic grain growth compared with straight WC-Co's more angular carbide grain structure. Thus, it was reasoned that the interfacial energy's anisotropy had been lessened resulting in the diminution of the grain growth driving force.

Kim and Accary suggested that the decrease in interfacial energy anisotropy was due to a mismatch between the liquid binder phase structure and the structure of the WC solid, this mismatch being the result of Ta dissolved in the Co binder and its atomic size difference. The fact that the system behaves in a more isotropic manner seems to support this theory.

2.4 Other Factors Affecting Shrinkage and Grain Growth of Cemented Carbides

There are many factors that affect the shrinkage of cemented carbides. Among them are the influences of binder content/liquid-phase volume on shrinkage, carbide particle size and carbon content. The effect of increasing the binder content with all other parameters held constant in a hardmetal would result in greater shrinkage. From results obtained from a study by Froschauer and Fulrath^[20], the variation in binder content showed no significant difference in densification below the eutectic temperature. Meredith and Milner^[3] have also noted this in their study on the TiC-Co system. Only above the eutectic temperature were the effects of the greater binder content/liquid volume evident, resulting in quicker densification through rearrangement.

The influence of the carbide particle size on shrinkage is that the densification decreases with increasing particle size. Again, from

Froschauer and Fulrath's study^[20], almost full densification was achieved with the finer carbide particle sizes. Their results showed that although a noticeable amount of densification occurs below the eutectic temperature with the finer particle sizes compared with the larger ones in which almost no solid state densification occurred, the majority of the densification occurs just above the eutectic temperature. This is expected due to the greater powder flow during pressing and the subsequently higher packing density of the finer particles.

As well, Froschauer and Fulrath's results on particle size show the effect of ball milling 2.5 μm carbide particle sizes over non-ball milled 2.2 μm particle size. Ball milling of the starting cemented carbide powders enable an even distribution of the binder material throughout the powder mixture and will reduce the carbide particle size due to the crushing from the hardmetal mixing balls in the milling drums to some extent. The effect of the smaller carbide particle size due to crushing, however, is minimal due to the already fine initial particle size. Thus, the even distribution of the binder among the carbide particles has a greater effect at these particle sizes.

The influence of particle size on the shrinkage has a greater effect than the liquid volume in a hardmetal. Froschauer and Fulrath demonstrated that a fine powdered material with a low liquid volume

densifies much quicker than a coarse material in a substantially greater liquid volume.

Regarding carbide grain growth, Rudiger et al.^[25], found that liquid volume influenced the final grain size more so than did initial carbide particle size. Their studies showed that a coarse material in a low binder content resulted in considerable smaller carbide grains after prolonged sintering than did fine powdered material with a high binder content.

In general terms, it is desirable for the microstructure of WC-Co cemented carbides to be composed of two phases, the WC phase and the binder phase. However, if the carbon content is not controlled adequately, a third phase will appear that will have detrimental effects on the mechanical properties of the cemented carbide. This third phase is the result of either a carbon deficiency (eta phase, Co_3W) or an excess of carbon (free carbon). The range for which only the WC phase and the binder phase exist was determined by Suzuki and Kubota^[28] to lie between 6.04 and 6.22% C for WC-10% Co. Even within this two phase range, there is a significant variation in properties between the upper and lower carbon values. The precise stoichiometric value is 6.13% C.

The reason for this change in properties due to slight carbon variations is that the dissolved tungsten content in the binder phase is

higher in a low carbon alloy and lower in a high carbon alloy. This inverse relationship has been quantified by Exner^[1] as:

$$[W] \cdot [C] = \text{constant}$$

where $[W]$ and $[C]$ are the dissolved W and dissolved C respectively, in the binder phase.

In Suzuki and Kubota's study, 1.3 μm WC powder and 1.2 μm Co powder were wet ball milled, compacted and vacuum sintered at temperatures between 1370 and 1450 C for one hour and then cooled slowly. The carbon content was controlled by controlling the carbon content of the ball milled powder. The sintered WC-10% Co specimens showed W contents between 2 to 3% in high carbon alloys and 9 to 10% in low carbon alloys. The variation in mechanical properties within the two phase region of the WC-Co system due to differences in C levels has been discussed by several investigators^[25,28,29].

CHAPTER III EXPERIMENTAL PROCEDURES

3.1 Powder Compact Preparation

3.1.1 Starting Powders

Commercial high purity WC powder with a Fisher grain size of 5.8 μm was used for this work. The total carbon content of the WC powder was 6.15%. Nickel powder used was of a 1.7 μm Fisher grain size of 99.6% purity. Chromium contents in the WC-Ni-Cr cemented carbides were introduced as Cr_3C_2 powder. The Cr_3C_2 powder had a Fisher grain size of 1.7 μm , a purity level of 99.12% and a total carbon content of 13.12%. Tungsten powder was also used to maintain stoichiometric powder mixes. All powder types were each from a single processing batch. Thus, any variations in starting powder characteristics between one processing batch and another of a single powder type are avoided. The initial powder properties and the compositions of the five cemented carbide grades are summarized in Tables I to III.

3.1.2 Ball Milling

With stoichiometric proportions of the starting powders measured out to within ± 0.1 g, nominal 6 kg powder batches were wet ball milled in

3 litres of acetone with a WC-Co ball charge of 18 kg. The milling drums were made of stainless steel. To provide adequate mixing of the starting powders, milling times for the five powder grades were as follows:

Grade		Milling Time (hrs.)
WC-10%Ni	(10 Ni)	48
WC-9.9%Ni-0.1%Cr	(1 Cr)	60
WC-9%Ni-1%Cr	(10 Cr)	72
WC-8%Ni-2%Cr	(20 Cr)	72
WC-5%Ni-5%Cr	(50 Cr)	72

3.1.3 Powder Drying

Upon completion of the wet ball milling, the slurry was poured through two sieves, the first (9 mm) to remove the 18 kg ball charge and the second of a much finer mesh size (45 μ m) to remove any large contaminants (ie. flakes) contributed by the WC-Co balls or milling drum lining. The slurry was then poured into an enclosed container kept under vacuum, and partially immersed in a hot water bath regulated at 38 C for two hours to evaporate the acetone. The dried powder was then cooled to room temperature under vacuum and rescreened through a 74 μ m sieve.

3.1.4 Waxing

To increase green compact strength, the cemented carbide powders were waxed. Paraffin wax, 2 wt.%, was dissolved in hexane (1 litre per 5

kg of powder) and then the powder added to the wax/hexane mixture. One kilogram of powder was waxed at a time. The slurry was constantly stirred while partially immersed in a hot water bath to evaporate the hexane. The dry waxed powder was then sieved to obtain granules in the range of -30 to +100 mesh size. The granules that fell through the 100 mesh screen were then pressed into small blocks and re-screened to obtain -30/+100 mesh size granules. This process was repeated until almost all the waxed powdered granules were of -30/+100 mesh size.

3.1.5 Pressing

The test specimens were compacted using the -30/+100 mesh size waxed powder at 150 MPa in a single action cylindrical die set. Cylindrical dilatometer test specimens in their green state were 9.55 mm in diameter and of a nominal height of 10 mm. Test blocks for fully sintered microstructural evaluation were also pressed under the same conditions as the cylindrical compacts. However, with the test blocks, a rectangular single action die set was used to produce 52.22 mm x 11.41 mm x 16.7 mm nominal size green compacts.

3.1.6 De-Waxing/Pre-Sintering

To rid the green compacts of the wax before final sintering, the green test blocks were packed in a carbon powder and heated to 600 C surrounded by a flowing H_2 atmosphere. The heating and cooling cycle of the de-waxing process is shown in Figure 4. After a one hour hold time at 600 C, the carbon filled tray with the cemented carbide compacts, still under a flowing H_2 atmosphere, was introduced inside a water-cooled jacket. The flowing H_2 atmosphere was maintained until the temperature fell to about 70 C, upon which the H_2 is flushed out with N_2 until room temperature was reached. Upon removal of the de-waxed cemented carbide compacts from the carbon powder, the compacts were then ready for sintering.

De-waxing of the cylindrical dilatometric compacts was carried out at 500 C for one hour, as shown in Figure 5. A lower de-waxing temperature was used in order to maximize the information obtained from heating in the dilatometer.

3.2 Sintering of Test Blocks

Sintering of cemented carbide test blocks had been carried out in an induction furnace. These fully sintered test blocks were used to evaluate

the microstructural properties of their respective grades. Two test runs were carried out. Both involved the sintering of the five cemented carbide grades to 1520 C for 30 minutes. However, one test run involved gas treatment of the cemented carbides during the sintering cycle in an attempt to control the carbon loss that occurs during de-waxing. This is done through the introduction of a flowing hydrogen/methane (53 li./0.219 li.) gas mixture at approximately 1150 C and held constant for two hours. The hydrogen gas is used to increase the pressure of the gas treatment atmosphere and acts as a carrier for the low volume of methane gas introduced. At 1150 C, the methane gas (CH_4) introduced cracks, and if the hydrogen/methane mixture is correct, a carburization of the cemented carbide compacts should take place. At the higher sintering temperatures, an argon atmosphere (0.9 torr) is introduced to help reduce binder loss due to evaporation.

The second test run was similar to the first one except there was no gas treatment of the cemented carbides. The gas treatment and non-gas treatment sintering cycles are shown in Figures 6 and 7.

For each test run, 10 Ni, 1 Cr, 10 Cr, 20 Cr, and 50 Cr test blocks were sintered, providing a gas treated and non gas treated specimen of each grade. The analysis of these test blocks included density, hardness and coercivity measurements, as well as determination of porosity, carbide grain

size and third phase presence. The analysis followed standard ISO procedures outlined in:

ISO 3326	"Hardmetals - Determination of (the Magnetization) Coercivity"
ISO 3369	"Impermeable Sintered Metal Materials and Hardmetals - Determination of Density"
ISO 3878	"Hardmetals - Vickers Hardness Test"
ISO 4499	"Hardmetals - Metallographic Determination of Microstructure"
ISO 4505	"Hardmetals - Metallographic Determination of Porosity and Uncombined Carbon"

To further investigate the effect of carbon content in the cemented carbides, test blocks were *dry* pressed without waxing agents so that de-waxing and its corresponding carbon loss is eliminated. Test blocks pressed at 150 MPa from each of the five cemented carbide grades were then sintered at 1520 C for 30 minutes without gas treatment. Density, coercivity, porosity levels and general observations of the test blocks were then taken.

3.3 Dilatometric Testing

For these tests, a MMC Deformation Dilatometer was used. This machine makes use of induction heating and provides linear shrinkage/expansion vs. temperature as well as linear shrinkage/expansion

vs. time charts. The linear shrinkage/expansion is determined through the movement of one of the quartz platens (refer to Appendix 1). The cylindrical cemented carbide compacts are placed with their flat circular ends against the quartz platens that hold them under a slight spring pressure. This spring pressure decreases as the compact shrinks, so that at high temperatures where liquid phase is present, the spring force is negligible.

To prepare the cylindrical powder compacts for the dilatometer tests, a small hole, approximately 4 mm in depth, was drilled into the side of each compact to accommodate the insertion of the tip of a Pt/Pt+10% Rh thermocouple. The tips of the thermocouple had been melted together and the end dipped into a zirconia paste. The zirconia layer on the thermocouple tip was allowed to dry before use. Its purpose was to protect the thermocouple wire from breaking due to reaction with the liquid binder phase. Although zirconia is a thermal insulator, the thin layer applied should have a negligible effect on temperature readings.

To gain insight into the characteristic shrinkage of the various hardmetal grades, namely 10 Ni, 1 Cr, 10 Cr, 20 Cr, and 50 Cr, each compact was heated from room temperature to 450 C in ten minutes under a vacuum of approximately 10^{-5} torr. The temperature range from room temperature to 450 C was chosen for rapid heating because no further

shrinkage was expected below the pre-sintering (de-waxing) temperature. The compact was then heated at 15 C/min. to between 1000 C and 1100 C while still under vacuum, after which argon was introduced into the sintering chamber (10 in. Hg absolute) to help prevent binder evaporation. The heating continued at 15 C/min. until significant shrinkage ceased (approx. 1500 C). The choice of 15 C/min. was chosen to correspond to the conditions for the fully sintered test blocks. The sintered specimen was then allowed to slowly cool to room temperature still under the Ar atmosphere.

Similar dilatometric tests to the continuous heating tests were performed for the He quench runs. For each of the five hardmetal grades under investigation, a series of runs was performed whereby the compact was heated as outlined for the continuous heating tests, except upon reaching a set temperature, the power to the induction coil was shut off and the specimen He quenched. The quenching was uniform around the circumference of the specimen since the He emanated from small holes in the induction coil that surrounded the specimen. As an example, cooling from 1500 C to 1000 C would take approximately two seconds.

The purpose of quenching the cemented carbides at various temperatures was to preserve the microstructure and compositional characteristics of that temperature for resistivity measurements and SEM

analysis. The quenching temperatures were 900 C, 1050 C, 1200 C, 1300 C, 1350 C, 1400 C, 1450 C, 1500 C and 1550 C. A separate specimen was used for each temperature.

A third array of dilatometer tests involved isothermal sintering of the five cemented carbide grades at various isothermal temperatures (1100 C, 1150 C, 1200 C...1450 C). The results of these tests were used to determine the activation energies of the various cemented carbide grades (see Appendix 2).

The sintering cycle for the isothermal tests was similar to those outlined in the continuous heating tests. However, instead of maintaining a heating rate of 15 C/min. after the Ar introduction at between 1000 C and 1100 C, the compact was rapidly heated at 10 C/sec. to the isothermal temperature and held from 1 to 5 hours. The test run was then terminated by simply allowing the specimens to cool to room temperature on their own.

In order to determine the liquidus temperature of the binder phase, rapid heating of sintered 10 Ni, 1 Cr, 10 Cr, 20 Cr and 50 Cr cylindrical specimens was carried out in a dilatometer and charted on a shrinkage-temperature graph. By watching for the sudden decrease in the specimen's height, an approximate liquidus temperature may be obtained. The sudden shrinkage in the compact is due to the rearrangement process. The initial

sintering of the cemented carbide specimens was carried out at a heating rate of 15 C/min. from room temperature. The heating rate was maintained until any significant shrinkage had stopped. The furnace was then shut down and the specimen allowed to cool to room temperature. The re-heating of the sintered compact was carried out at 200 C/min.

3.4 Resistivity Measurements

Resistivity measurements were accomplished with a *home-made* set up schematically shown in Figure 8. The principle of this piece of apparatus is that a constant current is driven through the specimen from contact points on both ends of the cylindrical sample. Fixed distance contact points were used to measure the voltage across them at the surface of the compact. Several measurements of this sort were carried out at various locations around the circumference of the cylindrical specimen to avoid local surface irregularities (ie. Ni rich surfaces due to Ni migration).

Simple calculations were then carried out to determine the resistivity of the sample, as follows:

$$\begin{aligned}
 R &= v/I = P(l/A) \\
 \text{or } P &= v/I \times A/l \\
 &= v/(Il) \times (\pi d^2/4)
 \end{aligned}$$

where R = resistance
v = voltage
I = current
l = length
A = cross sectional area
d = diameter
P = resistivity

3.5 Electron Microscopy

3.5.1 Scanning Electron Microscopy

A scanning electron microscope (SEM) was used to examine and photograph the microstructure, and EDAX (energy dispersive analytical x-ray) used to analyze the binder phase composition. Only the 10 Ni and 10 Cr He quenched samples were examined due to the limited SEM time available. Also, only the higher temperature specimens were selected (1200 C and higher) due to the high porosity of the lower temperature He quenched samples. High porosity makes it difficult to attain the high vacuum required in the SEM sample chamber due to *out-gassing* of the specimen. The binder compositions of the He quenched samples at 1300 C, 1350 C, 1400 C and 1450 C were also analyzed. This temperature range was chosen to coincide with the expected eutectic temperature of approximately 1380 C for the straight WC-Ni system. Unfortunately, this

particular EDAX system was not capable of detecting elements with atomic numbers less than 7 (ie. carbon).

Preparation of the SEM specimens required that the cemented carbide samples be cut in half and then polished with various diamond paste sizes down to 1/4 μm . The final polish was accomplished with Linde B (0.01 μm alumina). All polishing and cleaning of polished surfaces followed standard procedures for hardmetals.

3.5.2 Transmission Electron Microscopy

With transmission electron microscopy, a closer look at the binder phase and binder/carbide interface could be taken. As with the SEM work, binder contents were determined and only 10 Cr and 20 Cr specimens were analyzed due to the limited TEM time available. The 10 Cr and 20 Cr specimens were the He quenched samples at 1500 C and 1550 C respectively.

Preparation of the TEM thin foils involved cutting thin slices (200 μm) from the circular cross section of the cylindrical cemented carbides. These thin slices were then spark cut to obtain 3 mm diameter disks. Mechanical dimpling of both sides of the disk through a series of progressively finer diamond paste sizes resulted in a dimpled disk with a centre thickness of approximately 15 μm . The final diamond paste size

used on both faces was 1 μm . The dimpled disk was then ion beam thinned on both faces simultaneously until a small hole appeared in the centre. The thin foil was then ready for TEM analysis. Further information surrounding thin foil preparation of cemented carbides may be found in Appendix 3.

CHAPTER IV

EXPERIMENTAL RESULTS/ANALYSIS

4.1 Test Blocks

Measurements were made of the two sets of waxed test blocks that had been presintered at 600 C for 1 hour. One set had subsequently been gas treated and sintered at 1520 C for 30 minutes while the other was non-gas treated but still sintered at 1520 C for 30 minutes. Similar measurements had been made on dry pressed, non-gas treated test blocks sintered at 1520 C for 30 minutes as well. The results of the three sets of test blocks are shown in Table IV.

Between the low Cr grades (ie. 10 Ni and 1 Cr) and the high Cr grades (ie. 10 Cr, 20 Cr and 50 Cr), the size of the porosity became much finer, turning from B type porosity to A type (according to ISO standards). As well, there is a trend of increasing porosity levels with increasing Cr. Among the high Cr group only, *holes* or relatively large cavities appeared. The number of these holes increased significantly with increasing Cr content. The relative density measurements reflect this fact with noticeable decreases between the 1 Cr, 10 Cr and 20 Cr.

Regardless of whether the test blocks were gas treated or non-gas treated, or the pressed specimens were waxed or unwaxed, the general trend

has been for the density of the test blocks to decrease with Cr additions. This is to be expected due to the increasing porosity observed with increasing Cr content. There appears to be very little difference between the 10 Ni and 1 Cr, indicating that 1% of the overall binder content is insufficient to significantly alter any properties of the cemented carbides. Lardner and Iggstrom^[26] have stated that grain growth could be slowed through additions of certain carbide forming elements, the most effective being vanadium followed by chromium. As well, other elements such as tantalum, molybdenum and niobium have shown a lesser effect. Suzuki et al.^[30] have reported that to control WC grain growth, 5% VC or more of the overall binder content was required. However, Lardner and Iggstrom feel this is about three times more than necessary according to their own experience, and is due to differences in processing and grain size distribution in the carbide powder. This is shown in experiments comparing the effect of introducing chromium as Cr_2O_3 mixed with W and C, and then carburised, and simply wet ball milling Cr_3C_2 with WC and Co. It was determined that the former process resulted in greater grain growth inhibition^[13]. Thus, since chromium is less effective as a grain growth inhibitor than vanadium, consisting of only 1% of the overall binder content and added as carbide, it is understandable that no significant differences between the 10 Ni and 1 Cr were noted.

The microstructures do display some grain growth inhibition with significant Cr additions. This may be noted by comparing the micrographs taken of 10 Ni and 10 Cr alloys sintered at 1480 C for 30 minutes (see Plates 1 and 2). More importantly, however, is the absence of any eta phase or free carbon in any of the three sets of test blocks. Among the waxed test blocks, it would appear that very little difference between the gas treated and non-gas treated specimens of the same grade could be found. This is reflected in the density and porosity levels, hardness measurements, and coercivity values shown in Table IV for the gas treated and non-gas treated, waxed specimens.

This is not to say that gas treatment to control the C content is totally ineffective. It has been noted by Exner⁽¹⁾ that a high C content generally promotes the growth of WC grains. Thus, comparison of the micrographs of especially the low Cr, waxed grades that had been gas treated and non-gas treated, indicate slightly larger WC grains in the gas treated cases. This is evidently the result of slightly higher C contents as noted by Exner. As well, the fact that a coercivity reading was obtained for the gas treated 10 Ni specimen, while the non-gas treated 10 Ni indicated a coercivity value of zero implies indirectly that the C content in the gas treated 10 Ni alloy is slightly higher.

Although coercive force measurements are intended to provide insight into the *thickness* of the binder phase between carbide particles, these measurements do still reflect the magnetic properties of the binder phase. This is because coercive force is a measure of the resistance to changing the direction of magnetization of a specimen^[31]. The theory behind coercivity measurements is that tungsten is a non-magnetic substance while nickel is magnetic. Therefore, coercivity measurements should be directly proportional to the specific binder surface area^[32]. Thus, for a given Co content the average WC grain size may be determined. Knowing the average WC grain size, the binder thickness or *mean free path* may also be deduced. However, because coercivity measurements rely on the resistance to changing the direction of magnetization in the binder phase, W content in the binder phase does play a role. As well, since the W content is affected by the C content in the binder phase, coercivity values do reflect the level of C in the binder phase indirectly. Therefore, the fact that the gas treated 10 Ni specimen provided a coercive force value would indicate a higher C content within the binder phase as opposed to the non-gas treated 10 Ni.

Among the rest of the waxed, gas treated specimens, however, coercivity measurements were found to be zero. With the dry pressed, non-gas treated test blocks, modest coercivity values were found. This

seems to suggest that for the waxed, gas treated specimens, de-carburization during the de-waxing cycle was so extensive that the gas treatment process carried out was inadequate in its attempt to carburize the waxed, gas treated specimens to a stoichiometric C level. Except for the waxed, gas treated 10 Ni specimen, the rest of the waxed, gas treated test blocks seemed to indicate that since the Cr content in these grades was introduced as Cr_3C_2 in the powder milling, that these test blocks de-carburized to a greater degree. Chromium carbide has a heat of formation energy value approximately half that of $\text{WC}^{[1]}$. Thus, since the waxed 10 Ni specimen indicates de-carburization has occurred during the de-waxing cycle, those grades with Cr_3C_2 would surely de-carburize to an even greater extent. Among the waxed, non-gas treated specimens, coercivity measurements of zero were determined for all grades. This is not surprising due to the expected low carbon levels. Upadhyaya and Basu^[9], Brabyn et al.^[8] and Almond and Roebuck^[33] have found similar results when testing WC-Ni alloys.

In work carried out by Brabyn et al.^[8], they had found that a marked loss of carbon occurred during processing of cemented carbides. Through chemical analysis carried out at each stage of manufacture, it was found that the major loss in carbon occurred during the pre-sintering stage.

With the dry pressed test blocks, the higher C contents are reflected in their coercivity measurements. With the coercivity measurements obtained from the waxed compared with the dry pressed test blocks, Brabyn et al.'s findings of substantial carbon loss during pre-sintering is confirmed. As well, according to Brabyn et al., even slight decarburization of the WC-Ni alloy will result in zero magnetic saturation and coercivity values. If this is true then the fact that the dry pressed, non-gas treated test blocks provide coercive force values indicates that during sintering at 1520 C for 30 minutes, significant decarburization does not occur. As well, this may explain why among the waxed, gas treated low Cr alloys (ie. 10 Ni and 1 Cr) that the 1 Cr was found to have a coercive force value of zero while the 10 Ni showed a positive but modest value. Thus, it is possible that the slight Cr_3C_2 content in the 1 Cr may have been enough to allow de-carburization during de-waxing to progress to the extent whereby the gas treatment process applied was insufficient to re-carburize the specimen, so that a non zero coercivity value could be obtained.

From Table IV, it is also shown that for the dry pressed, non-gas treated test blocks, with increasing Cr content, the coercivity decreases. Since the microstructural differences in the WC grain size of the waxed test blocks indicated very subtle changes in grain size (see Plates 3 to 6 and Plates 7 to 10), the predominant cause of the decreasing coercivity

measurements with increasing Cr is believed not to be a result of grain size modification. Instead, the main cause may be the result of the non-magnetic Cr content in the binder phase increasing, as well as the greater degree of C loss in the higher Cr alloys, leading to high W content in the binder. The fact that the coercivity measurements among the high Cr alloys is relatively constant may indicate that an equilibrium between the Cr and W content in the binder has been reached.

In Brabyn et al.'s work^[8], they mentioned that only about 70% of the theoretical magnetic saturation could be achieved. This would account for the low coercive force values obtained for the dry pressed, non-gas treated test blocks. Upadhyaya and Basu^[9] made coercivity measurements on WC-10% Co that resulted in values of about 110 Oersted whereas WC-10% Ni specimens sintered under the same conditions resulted in coercive readings of zero. They attributed this to the fact that dissolved carbon has a significant effect on the magnetic properties of nickel, compared with its almost negligible effect in cobalt. Brabyn et al. have suggested an alternative explanation, that dissolved carbon does not displace tungsten in nickel to the same extent as it does in cobalt. In other words, the *solubility product* relationship between dissolved carbon and tungsten, as maintained by Hoffmann and Mohs^[19] and Rudiger et al.^[25], is not exhibited in Ni.

Brabyn et al.^[8] have stated that the greater solubility of W and C in the binder phase of WC-Ni relative to Co bonded grades resulted in a much wider compositional range of the two-phase region without precipitation of eta phase or free carbon. Ekemar et al.^[11] have also mentioned that eta phase is more difficult to obtain in the WC-Ni system than in the WC-Co system. The results of this investigation do agree with these findings since among all the test blocks, no eta phase was present. Even among the high Cr non-gas treated grades, no eta phase was found. However, Cr has been found to promote eta phase in WC-Co grades^[11].

It has been reported that hardness increases with W content in the binder^[28,33]. However, hardness is dependent on other factors besides W content in the binder, such as density and carbide grain size. From Table IV, it is apparent that density is not the dominating factor since as Cr contents increase, density decreases while hardness increases. This is shown in all three sets. If density were the predominant factor, a decrease in hardness would be expected. As well, among the gas treated and non-gas treated, waxed specimens, the slight changes in carbide grain size due to Cr addition is not expected to have the significant change on hardness as seen in these test results. For example, among the waxed, gas treated test blocks, it is obvious that the difference in WC grain size is greater between the 10 Ni and 1 Cr than between the 1 Cr and 10 Cr. Yet, a

greater increase in hardness is observed between the 1 Cr and 10 Cr alloys than between the 10 Ni and 1 Cr. The W level in the binder phase is also not believed to be the reason behind the increasing hardness values with increasing Cr additions. According to EDAX analysis of the binder phase of the 10 Ni and 10 Cr specimens quenched at 1400 C (Tables IX and X), which show higher W contents in the 10 Ni's binder phase than in the 10 Cr's, one would expect higher hardness values from the low Cr alloys. Instead, the higher Cr specimen has the higher hardness. Thus, the variation in hardness among the five cemented carbide grades appears to be strongly affected by neither the level of dissolved W in the binder phase, the sintered density, nor by its grain size.

Another possibility as to the cause for the increase in hardness with increasing Cr content is that among the high Cr grades, a (W,Cr) carbide is being precipitated out as is suggested by TEM results to be discussed later. These mixed carbide precipitates are associated with the binder phase and act as pinning points to dislocation movement. Thus, they would in effect precipitation harden the binder and increase its hardness. Since these precipitates were only found in the high Cr grades, this would seem to account for the notable increase in hardness between the low Cr and high Cr grades. The fact that there is little difference in hardness levels between the high Cr grades seems to suggest that increasing the number of

precipitates beyond a particular value has no effect on restricting dislocation movement.

4.2 Dilatometric Results

4.2.1 Liquidus Temperatures

From the dilatometric tests conducted on the five grades, the temperatures at which sudden shrinkage of the compacts occurred were 1370 C, 1380 C, 1330 C, 1300 C and 1270 C for the 10 Ni, 1 Cr, 10 Cr, 20 Cr and 50 Cr specimens, respectively (as shown in Table V). It would appear that the increasing Cr content decreases the liquidus temperature of the binder phase. As well, each grade was found to exhibit linear thermal expansion below the liquidus temperature of the binder phase.

The temperatures obtained reflect the approximate temperatures at which either primary or secondary rearrangement occurs. These liquidus temperatures are only approximate, due to the rapid heating rate (200 C/min.), the thermal coating on the thermocouple, less than ideal thermocouple-specimen contact, and interpretation of the shrinkage-temperature curves. However, the temperature the thermocouple senses should not lag the specimen's true temperature by much since the heating rate is constant and the thermal coating thin.

The liquidus temperature of the 10 Ni compares very well with published values of the eutectic temperature of WC-Ni (1370 C according to Upadhyaya and Basu^[9]). Therefore, it is assumed that the liquidus temperatures of the WC-Ni-Cr alloys represent their true liquidus temperatures closely as well. Indirect evidence of this is shown in the results attained by several researchers in the area of the Cr_3C_2 -Ni system. Vlasyuk et al.^[34] and Ramqvist^[35] have determined eutectic temperatures of 1180 C and 1255 C respectively, regarding the Cr_3C_2 -Ni system. Even with the disagreement between these investigators over the true eutectic temperature of the Cr_3C_2 -Ni system, the liquidus temperature of the 50 Cr specimen does compare fairly well (a liquidus temperature of 1270 C for the 50 Cr had been determined). Any discrepancies between the liquidus temperature of the 50 Cr and the Cr_3C_2 -Ni system may justifiably be explained as due to the W content in the 50 Cr's binder phase. As well, considering the lower eutectic temperature of the Cr_3C_2 -Ni system compared to the WC-Ni system, the fact that the liquidus temperature decreased with increasing Cr additions in the WC-Ni-Cr hardmetals, seems to adhere to this.

4.2.2 General Shrinkage Curves

The shrinkage ($(L-L_0)/L_0$) vs. temperature (T) curves for the five cemented carbide grades that had been slowly sintered at 15 C/min. from room temperature to between 1500 C and 1600 C are shown in Figures 9 & 10. It is apparent from these curves that as the Cr content increases, the *knee* of the curve where significant shrinkage begins, becomes sharper. As well, in all cases, at about 500 C, shrinkage of the compact begins. This agrees quite well with the fact that the dilatometric compacts had been pre-sintered at 500 C for 1 hour. Thus, any net shrinkage below 500 C would not be expected.

With both the 10 Ni and 1 Cr curves which exhibit similar characteristics, the shrinkage rate gradually increases from 500 C to 1250 C, with the middle of the *knee* at approximately 1150 C. Between the temperature range of 1250 C and 1420 C, the shrinkage rate is relatively constant. This is followed by near vertical increases in the $L-L_0/L_0$ vs. T curves at about 1425 C and 1445 C for the 10 Ni and 1 Cr, respectively. Above 1450 C, the $L-L_0/L_0$ vs. T plots indicate very slow shrinkage with the curves becoming nearly horizontal.

The 10 Cr curve indicates gradual shrinkage from about 500 C to 1250 C. The shrinkage rate then increases steadily at the *knee* of the curve which is centered at about 1340 C. Interestingly enough, the centre

of the knee almost coincides with the liquidus temperature of the 10 Cr (1330 C). Coming out of the *knee* the slope of the curve is steep and constant up until approximately 1425 C where an inflection in the curve shows a decreasing shrinkage rate with increasing temperature. Following this the shrinkage of the specimen falls to about zero at 1500 C.

The 20 Cr curve is similar to the 10 Cr curve except the *knee* is sharper and instead of the shrinkage rate decreasing at 1425 C, the inflection occurs at about 1400 C. As well, a second inflection in the curve occurs at about 1490 C in which the shrinkage rate increases. Significant shrinkage of the 20 Cr specimen stops at about 1550 C.

Like the 20 Cr curve, the 50 Cr specimen behaves in much the same manner. However, the *knee* is centered at about 1260 C and with the first inflection point at 1360 C. The second inflection point occurs at 1500 C. Significant shrinkage of the 50 Cr specimen stops at about 1550 C. As with the 10 Cr, the centers of the 20 Cr and 50 Cr knees occur at approximately their corresponding liquidus temperatures.

In dilatometric work conducted by Ogawa and Kataoka^[14] on WC-10% Co, similar shrinkage curves to the 10 Ni and 1 Cr were obtained. From their work, as well as work carried out earlier by Snowball and Milner^[17] and Meredith and Milner^[16], significant densification occurs in the WC-Co system below the eutectic temperature. This same conclusion may

be drawn for the 10 Ni and 1 Cr grades. However, the general shrinkage curves of the 10 Ni and 1 Cr appear to indicate that the liquidus temperatures are higher at 1420 C and 1440 C, respectively, than the values found by rapid heating of sintered compacts, 1370 C and 1380 C respectively. Similar findings were made by Ramqvist^[35] whose experiments apparently did not show any melt formation below 1453 C. He, however, had speculated that the eutectic temperature of the WC-Ni system to be about 1350 C nevertheless. One possible reason as to why the 10 Ni's and 1 Cr's liquidus temperature appears to be higher is due to significant solid state sintering. WC/WC contacts may have formed during solid state sintering leading to a rigid carbide skeleton. Upon formation of the liquid phase at 1370 C, sufficient time above the eutectic temperature is required for carbide dissolution and contact penetration. Thus, the rapid increase in compact shrinkage above 1400 C that corresponds to rearrangement is not a true reflection of the start of melt formation. This theory is supported by Warren^[36] which has suggested that, during the early stages of liquid phase sintering, a process of carbide de-agglomeration occurs.

In another paper, Warren and Waldron^[37] have suggested that the existence of contacts between carbide particles and the presence of an apparently continuous skeleton are not necessarily inconsistent with the

densification process of rearrangement. First, if the contacts that are present at the start of sintering develop during solid state sintering, then upon liquid phase formation, the contacts become stressed by the capillary forces. Thus, one set of contact areas will be broken up by the penetrating liquid and enhanced by dissolution of the solid. At the same time, however, a more stable new contact area formed after local particle rearrangement will develop. Such a process would allow progressive rearrangement of the compact by localized contact breaking, rearrangement, and subsequent re-attachment of carbide grains. If observed at any instant in time, however, a high degree of carbide contiguity exists.

In work conducted by Snowball and Milner^[17], they too had found that with WC-9% Co, the shrinkage rate remained nearly constant even above its eutectic temperature of 1320 C up until just below 1400 C where the sudden increase in densification occurred. Meredith and Milner^[16], having analyzed Snowball and Milner's data and their own experiments had, unlike Warren and Waldron, theorized that WC-Co densification involved three stages. The first stage involved rapid initial densification below the eutectic temperature in which carbide particles formed around Co particles. The diffusion of the Co to neighbouring WC surfaces would result in activated surface and interfacial diffusion among the WC particles leading to a dense aggregate. The densification of these aggregates was

the source of the rapid initial compact densification below the eutectic temperature. Stage II occurs when the eutectic temperature is reached. Further densification of the aggregates takes place through capillary forces that act on the aggregates, resulting in the liquid phase being squeezed out. This liquid then proceeds to fill aggregate void spaces. Since 9% Co binder does not provide enough liquid volume to allow immediate aggregate rearrangement during Stage II, the densification rate remains similar to Stage I since compact shrinkage is still the result of aggregate densification. The start of Stage III occurs when adequate liquid phase has seeped from the aggregates to fill aggregate void spaces, resulting in rearrangement of the aggregates among themselves. From Snowball and Milner's data on WC-9% Co, the start of Stage III represents the sudden increase in shrinkage at about 1400 C, while the eutectic temperature of the WC-Co system is known to be about 1320 C.

Meredith and Milner's theory, applied to the general shrinkage curve of 10 Ni would suggest that Stage I occurs below 1370 C, with Stage II occurring between 1370 C and 1420 C. Since inadequate liquid volumes exists between aggregates, the shrinkage rate remains approximately constant. Stage III signifies rearrangement of the aggregates among themselves.

From the SEM micrographs taken of the He quenched dilatometric specimens at various temperatures (see Plates 11 to 15), the appearance of apparent aggregates of WC particles held together by binder phase seems to indicate that densification is as predicted by Meredith and Milner^[16]. Thus, during solid state sintering the formation of WC aggregates held together by the diffusing binder phase leads to local aggregate densification through surface and grain boundary diffusion. Upon reaching the eutectic temperature, liquid from these near full density aggregates flows into aggregate void spaces. This would eventually lead to rearrangement of the aggregates themselves. Finally, densification resulting from sintering of the aggregate clusters would result in an even distribution of WC grains and WC grain growth. Smolej et al.^[38] have also noted a clustering of the solid particles around the binder phase during an investigation of the rearrangement process in the W-Cu system. Thus, the experimental results obtained in this investigation appear to follow Meredith and Milner's theory more so than Warren and Waldron's^[37].

Meredith and Milner had stated that break up within the aggregate must be possible for prismatic grain growth to occur in the aggregate. The possibility that Warren and Waldron's theory may be the explanation that is applied within aggregates would seem unlikely according to Krstic and Komac^[39] and Sharma et al.^[40]. Both believe that a thin binder phase coats

all carbide grains completely, preventing any direct carbide contact which Warren and Waldron's theory suggests does occur. Sharma et al. found thin layers of Co between WC grains that were about 20 angstroms thick with TEM. Thus, even at low binder contents, all carbide grains could still be covered with a layer of binder.

From the general shrinkage curves, it is shown that the 10 Cr, 20 Cr, and 50 Cr display very little solid state densification compared with the 10 Ni and 1 Cr. This results in considerably smaller aggregate size, as SEM micrographs indicate (see Plates 16 to 20). With the 10 Cr curve and a liquidus temperature of 1330 C, the rapid densification that starts at the liquidus temperature seems to indicate that the aggregates formed during solid state sintering are undergoing rearrangement. The reason the rearrangement process proceeds right after liquid formation is due to the smaller aggregate sizes and thus smaller aggregate void spaces that need to be filled. Froschauer and Fulrath^[20,41] and Meredith and Milner^[3] have both concluded that rearrangement occurs more readily and to a greater degree with smaller particle sizes. This is because a large number of small particles flow much more easily than does a small number of large particles. Among the high Cr alloys, the general shrinkage curves as well as the SEM micrograph of the 10 Cr (He quenched from 1300 C) (see Plate 18) all indicate that very little solid state sintering occurs. Thus,

although WC aggregates may have formed, the limited solid state sintering has not enabled these aggregates to grow in size to the same degree as the low Cr alloys. Therefore, unlike the low Cr specimens, the high Cr alloys upon approaching melt formation, consist of many small aggregates that represent the effective particle size during rearrangement. The smaller size of the aggregates in the high Cr specimens allows for more rapid and greater densification through the rearrangement process. Stage III appears to begin at about 1400 C where densification by rearrangement is decreasing. In its place, a solution-precipitation process begins to take place which is a much slower process than rearrangement.

The 20 Cr general shrinkage curve is similar to the 10 Cr except its liquidus temperature is 1300 C, and there is a second sudden increase in the shrinkage rate at about 1500 C. Again, Stage I occurs up until about 1300 C where Stage II begins. As with the 10 Cr, aggregate densification under capillary forces from the liquid phase result in aggregate rearrangement occurring. In this stage, rearrangement is the dominant process, thus the relatively high densification rate. Stage III begins at approximately 1425 C where, initially, densification of the compact is dominated by aggregate densification through solution-precipitation rather than by aggregate rearrangement. However, at about 1500 C, aggregate rearrangement once again dominates perhaps due to the break up of the

aggregates as described by Meredith and Milner^[16] and mentioned previously. This process would behave similarly to particle disintegration. At the end of this secondary rearrangement phase, the traditional process of carbide grain growth takes place.

The 50 Cr behaves in the same manner as the 20 Cr except its liquidus temperature is at about 1270 C, where Stage II begins. Stage III starts at about 1350 C and secondary rearrangement of the carbide particles occurs at about 1500 C.

Other experimental data that indirectly substantiates the theory of smaller aggregate sizes in high Cr alloys is the porosity size in the three sets of test blocks (gas treated, non-gas treated and dry pressed). A definite change from B-type porosity in the low Cr specimens (10 Ni and 1 Cr) to A-type porosity in the high Cr specimens (10 Cr, 20 Cr and 50 Cr) had been observed. This seems to imply that the larger B-type porosity was the result of the larger aggregate size and thus larger aggregate void spaces.

4.2.3 Isothermal Results/Activation Energies

The values of the activation energies obtained are shown in Table VI. While published activation energy values of WC-Ni are unavailable

due to the lack of study on this alloy, there have been several studies conducted in the past that have dealt with the activation energy of compact shrinkage for WC-Co. Exner^[42] has measured the linear shrinkage of WC-10% Co sintered below the eutectic temperature. He found an activation energy for densification of 60 kcal/mole. Froschauer and Fulrath^[20] have also studied the densification of WC-Co and found an activation energy for densification of 80 kcal/mole.

The eutectic temperature of the WC-Ni system has been reported to be 1370 C^[9] which is higher than the WC-Co system's 1320 C eutectic temperature^[20]. There have been several other reports that state that the WC-Ni eutectic is higher than the WC-Co's eutectic temperature as well^[11,35,43]. Besides the higher eutectic temperature of the WC-Ni system, poorer wetting of WC by Ni compared with Co has also been reported^[1,9]. Gabriel et al.^[10] have also reported that for a given weight percentage of binder, Ni forms less liquid volume than does Co. The higher eutectic temperature, poorer wetting capabilities, and smaller liquid volume formed by Ni all result in greater difficulty in sintering of WC-Ni compared with the WC-Co system.

It is not surprising then that the activation energy for densification of WC-Ni (125 kcal/mole) arrived at in this investigation is greater than the activation energy values for WC-Co (less than 100 kcal/mole).

Another point to address is whether the activation energy is the same above and below the eutectic temperature (ie. during solid state sintering and liquid phase sintering). The isothermal test results of the low Cr alloys seem to indicate a single activation energy value for both sintering states. This result stems from the fact that the range of the isothermal temperatures, while above and below the liquidus temperature, cover the portion of the general shrinkage curve where a relatively constant densification rate exists. This has already been explained as being due to the extensive amount of solid state sintering. Exner^[42], too, has found a constant activation energy above and below the eutectic temperature, while Froschauer and Fulrath were unable to determine an activation energy value above the eutectic temperature since a straight line could not be fitted to their data.

However, it does not seem realistic that similar activation energies should exist both above the eutectic and below it. If so, this would imply that the appearance of the liquid phase has no effect on sintering. For the low Cr alloys, this may be true for a short period after the liquidus temperature. Although activation energies were not specifically determined above the liquidus temperature for the 10 Ni and 1 Cr, they were determined for the high Cr grades. The activation energies determined

above the liquidus temperature do show a significant decrease in energy levels compared with their solid state activation energy values.

The activation energy values obtained in the temperature range immediately after the liquidus temperature ranges from 55 kcal/mole for the 10 Cr to 87 kcal/mole for the 50 Cr (see Table VI). It is believed that these activation energies represent the rearrangement process. These values do seem realistic in terms of absolute values since in isothermal experiments conducted by Sebastian and Tendolkar^[44], activation energies for the rearrangement process of W-Cu were determined. In their experiments, W powder with an average particle size of 3.5 μm and Cu powder with an average particle size of 20.0 μm were ball milled. Since Cu has no solubility for W, the measurements were fairly accurate of the rearrangement process alone. Sebastian and Tendolkar obtained activation energy values in the temperature range immediately after the eutectic temperature of about 40 kcal/mole for the W-40 vol.% Cu and W-50 vol.% Cu to 62 kcal/mole for the W-30 vol.% Cu. These values are in the same range as the activation energy values obtained for the high Cr alloys in the suspected rearrangement region.

Although it might be expected that the activation energy values for the high Cr alloys would be lower than the W-Cu activation energy values due to the solubility of WC in Ni that may supplement the rearrangement

process, other factors must be considered. For instance, with Sebastian and Tendolkar's work, an initial W particle size of 3.5 μm was employed whereas the WC's initial particle size was 5.8 μm . It is obvious that the finer W particles would facilitate rearrangement more readily than the larger WC particles. This has been confirmed in work conducted by Froschauer and Fulrath^[41]. As well, it is believed that in the 50 Cr specimen, for example, the same volume of liquid is not achieved as with the W-Cu specimens used in Sebastian and Tendolkar's work. This is due to the fact that only 5% Ni is used and supplemented by the dissolution of W and Cr. However, because of solubility limits of W and Cr in Ni and the low Ni content, even 30 vol.% liquid is probably not achieved. In other work conducted by Froschauer and Fulrath^[20] on the WC-Co system, they found through experiments on the variation of liquid volume and particle size, that fine particles with 9 vol.% liquid densifies quicker than coarse material with 22 vol.% liquid. Since the high Cr grades dealt with larger particle sizes as well as lower liquid volumes, it seems realistic that the larger activation energies for rearrangement would result.

It should be noted that the actual activation energies of the W-Cu alloys in Sebastian and Tendolkar's work presented above were not provided in their paper. These values were calculated by determining the slopes of the Arrhenius plots provided.

One observation that can be made is that the activation energies for compact shrinkage appear to be proportional to the rate of densification displayed in the general shrinkage curves. This seems logical since the activation values are for densification of the compact. Thus, the activation energy values obtained below the liquidus temperature appear to be correct. For the high Cr grades, substantially higher activation energy values were obtained compared with the low Cr alloys. Reference to Figure 9 shows that very little solid state densification has occurred in the high Cr alloys. Immediately after the liquidus temperatures of the high Cr alloys, the rapid shrinkage that occurs takes place at a high rate that is reflected by the low activation energies obtained for this particular stage. After the rapid shrinkage period in the liquid stage, the decrease in densification rates for the 20 Cr and 50 Cr shown in Figure 10 appear to be constant as well as equal to one another. This is reflected in the similar activation energies obtained for this temperature range.

The values for the activation energies are approximate due to the inability of the thermocouple to track and accurately control sudden temperature rises to isothermal temperatures. A heating rate of 10 C/sec. required, for example, 40 seconds for a 10 Ni dilatometric specimen to reach a 1400 C isothermal temperature. Heating rates quicker than 10 C/sec. resulted in unstable temperature oscillation at the isothermal

temperature. However, the trend of the activation energy values increasing with increasing Cr contents is quite clear.

4.3 Resistivity Results

The results of the electrical resistivity measurements are shown in Tables VII & VIII and are plotted in Figures 11 & 12. In Figure 11, the resistivity measurements were normalized with respect to the lowest resistivity value which corresponded to the highest quench temperature of the 10 Ni grade, which is as expected. In Figure 12, the plots were obtained by normalizing each grade with its own lowest resistivity measurement. From Figure 11, it appears that by about 900 C, adequate solid state sintering has occurred to the point where the resistivity of all compact grades has dropped substantially. This would appear to indicate a rapid increase in binder diffusion at this temperature, resulting in a connectivity of particles. This agrees well with Hellsing et al.'s work^[45] in which during cooling after sintering of a WC-Co compact, it was found that significant W diffusion had stopped at about 900 C. Figure 12 provides an enlarged plot of Figure 11's upper temperature region. The basic shapes of the resistivity-temperature curves in Figure 12 when compared to the general shrinkage-temperature curves in Figure 10 are quite similar with inflection points at approximately the same temperatures.

This is to be expected since resistivity is a function of the specimen's density.

It has been hoped that the resistivity measurements would have detected the appearance of a precipitate in the high Cr grades. This did not occur however. During He quenching of the dilatometric specimens used to measure resistivity, it had been observed that a precipitate was falling out of solution. This was observed as a *spike* in the shrinkage-time charts that occurred during cooling at around 1200 C (see Figure 14 in Appendix 2). This spike appeared only in the high Cr grades and when cooling from above the liquidus temperature of the cemented carbide. Therefore, the precipitate is most likely of Cr content that is precipitated out of the liquid binder phase. These Cr precipitates were observed on the strip charts of the dilatometer whether slow cooling or He quenching was employed. This leads to the situation whereby the room temperature resistivity measurements were not made on *in-situ* compositions as had been hoped.

4.4 SEM Results

SEM micrographs of the He quenched dilatometric specimens for 10 Ni are shown in Plates 11 to 15. The SEM micrographs of the 10 Cr are shown in Plates 16 to 20. These photographs of polished surfaces taken of

10 Ni and 10 Cr specimens He quenched at 1050 C, 1200 C, 1300 C, 1350 C and 1400 C show the extent of binder phase diffusion and spreading, WC grain growth and porosity size.

Although the microstructures of the 10 Ni and 10 Cr at 1050 C and 1200 C are not noticeably different from one another, the greater extent of binder diffusion within the 1200 C quenched specimens is still evident. This is verified by the relatively small decrease in resistivity from 1050 C to 1200 C. The micrographs taken of the 10 Ni at 1300 C and 1350 C do show greater degrees of solid state diffusion of the binder with temperature. However, there are still large gaps that appear to almost completely surround small clusters of WC grains held together by the binder phase. Within the 10 Ni quenched from 1400 C, which is above the 1370 C liquidus temperature, it is apparent that binder melt has occurred. The liquid spreading has resulted in a greater compaction of WC grains, larger porosity free regions and increased pore sizes. In comparing the succession of 10 Ni SEM micrographs (1300 C to 1400 C) with its general shrinkage curve, it is apparent that the relatively steady rate of densification displayed by the 10 Ni shrinkage curve is closely matched by the micrographs. A gradual and smooth degree of densification is displayed from one micrograph to the next, as the 10 Ni general shrinkage curve suggests.

Regarding the SEM micrographs of the 10 Cr specimens quenched from 1300 C, 1350 C and 1400 C, there appear to be only slight changes in the micrographs taken at 1300 C and 1350 C. The 10 Cr quenched from 1300 C does not seem to show any significant signs of WC grain clustering, with the WC particles appearing to be scattered evenly about. The 10 Cr quenched from 1350 C, however, is starting to show signs of WC grain clustering. Although the 10 Cr (1350 C He quenched) specimen was quenched from a temperature above its liquidus temperature, no significant liquid spreading seems to have occurred. Referencing the 10 Cr's general shrinkage curve does shed light on this however. From the 10 Cr's general shrinkage curve at 1350 C, the stage of densification appears to be only at the middle of the *knee* of the curve. As well, little shrinkage has occurred since the liquidus temperature of 1330 C had been reached. This seems to imply that while liquid phase may have appeared at 1300 C, its appearance was localized and not wide spread, even at 1350 C. By about 1375 C, significant liquid volume was available for significant shrinkage and liquid spreading. This is substantiated by the 10 Cr quenched from 1400 C. Large clusters of WC grains held together with binder phase shown in the SEM micrograph of this specimen verifies this.

Thus, for a given temperature above 1300 C, it is evident that the SEM micrographs of the 10 Ni quenched specimens show a higher degree

of densification over the 10 Cr specimens. This is also substantiated by the general shrinkage curves and the resistivity curves (ie. the low solid state diffusion of the 10 Cr at 1300 C to the high densification of the 10 Ni due to the appearance of liquid phase at this temperature).

As for the quantitative results obtained from the SEM work through energy dispersive x-ray analysis it should be mentioned that some error is possible, due to the possibility that a WC grain could exist below a thin layer of binder that lies on the surface. The concentrated electron beam used for compositional analysis aimed at such a binder phase region penetrates about 1 μm below the surface. If the binder phase were thin enough, an erroneously higher W reading would appear for the binder phase. Therefore, the compositional analysis through back scattering of electrons by EDAX involves a finite volume of material at the surface rather than of a finite area on the surface. Quantitative results obtained on the WC grains should be accurate due to their considerably larger size and volume.

From the energy dispersive x-ray analysis conducted on the 10 Ni and 10 Cr He quenched dilatometric specimens, it is clear that the WC grains have no affinity for either Ni or Cr. The weight percentages of Ni and Cr shown in Tables IX and X for 10 Ni and 10 Cr point this out. This has also been substantiated by Aronsson and Pastor^[46]. The analysis

of the binder phase of the 10 Cr suggest that since the Cr:Ni ratios follow the theoretical Cr:Ni ratio of 0.10 closely, then the Cr must be in solid solution in the Ni binder phase. Also, since W is a stronger carbide former than Cr and is found in solution in the Ni binder, then any Cr present would also be in solution in the Ni binder. This is supported by electron microscope analysis conducted by Oakes⁽⁴⁷⁾ on WC-Co-Ni-Cr alloys where he too concluded that the Cr was in solution with the binder.

The Cr:Ni ratios for the 10 Cr show that at 1400 C, well above the liquidus temperature of 1330 C, there is a slight deficiency of Cr. The Cr:Ni ratio of about 0.09 is slightly below the theoretical value of 0.10. This keeps well with the consensus that a precipitate containing Cr has fallen out of the binder solution as indicated in the dilatometry work. Thus, the missing Cr content in the Ni phase is probably a result of the missing Cr being part of the precipitates.

The fact that the 10 Cr quenched at 1350 C shows Cr:Ni ratios of about 0.10 even though liquid phase should have been present, supports the previous explanation that wide spread binder melting has not occurred. As well, the rather small amount of Cr that was involved in the precipitates at 1400 C seems to suggest that at 1350 C, a negligible amount of Cr would be precipitated out due to the fact that dissolution of the Cr in the Ni binder would not have occurred to the same extent. Thus, the rapid

quenching in this case may have kept precipitation from occurring. This is substantiated by the shrinkage-temperature dilatometric chart for this specimen which showed no precipitation occurring during the quenching cycle.

Whether Cr inhibits W solubility in the binder phase is inconclusive, even though the W:Ni ratios of the 10 Ni and 10 Cr appear to suggest this. Due to penetration of the electron beam as well as the small number of *spots* analyzed, no judgement with any high degree of certainty can be made. However, in tests conducted by Grewe et al.^[27], no evidence could be found to substantiate the claim that carbides of the Va group would inhibit W solubility in the binder phase (ie. no spike).

4.5 TEM Results

X-ray analysis through TEM of 10 Cr that had been gradually heated to 1550 C and then cooled to room temperature without any hold time at 1550 C, shows that the WC phase essentially contains no Ni or Cr. In both the 10 Cr and 20 Cr, the binder contains W at a level of the order of 30%. This value must be considered very approximate due to the lack of a standard that could be used for calibration of the X-ray detector. In fact, the W level in the binder phase may possibly be higher than it should be due to the rapid cooling rate hindering an equilibrium state in the binder

phase from being reached. This is possible due to the fact that heating was carried out through induction heating. Thus, when the power is shut off at the end of a test, the small cylindrical specimen tends to cool quite rapidly. A dilatometric specimen would cool from 1500 C to 1000 C in about 30 seconds after the power to the induction coil was turned off. The temperature decreased exponentially with time. Thus, if significant precipitation of the WC out of the binder phase ceases at about 900 C as the resistivity results suggest, then this would allow only about 45 seconds for WC to precipitate out.

X-ray analysis of 10 Cr and 20 Cr alloys with TEM concurs with the results determined by SEM. The TEM data shown in Table XI indicates that the WC phase has almost no solubility for either Ni or Cr. This agrees well with work by Sharma et al.^[40] in which <1% Co was found in WC grains. As well, the Cr appears to be in solid solution with the binder phase, with the exception of the Cr containing precipitates. From Table XI, it is apparent that with the 20 Cr, substantially more Cr containing precipitates exist compared with the 10 Cr alloy.

These findings were substantiated after viewing of the binder phase in 10 Cr and 20 Cr by TEM. Observation of the 10 Cr and 20 Cr thin foils by TEM revealed no chromium carbide in the binder or any Cr layer at the WC/binder interface. This agrees well with Oakes^[47] work as well.

However, TEM work done by Yust and Long^[48] on WC-6% Co-1% Cr with the chromium added as Cr_4C_7 (stable carbides), found Cr_{23}C_6 and/or Cr_7C_3 in the final sintered compact. Also, a search of the various binder areas in the 10 Cr revealed very few precipitates. However, the binder phase of the 20 Cr showed a significantly greater number of precipitates that were dispersed throughout the binder. They had been determined to be a mixed carbide, possibly a W-Cr carbide, of approximately 5 W:1 Cr and of the order of 0.25 μm in diameter. Again, the TEM data on the 10 Cr and 20 Cr is inconclusive as to whether Cr inhibits W solubility. However, it is believed to have no significant effect.

CHAPTER V

DISCUSSION

In terms of sinterability of the WC-Ni-Cr system, it is well known that Cr acts as a grain growth inhibitor^[11,13,26,33]. However, the question of why Cr inhibits grain growth is uncertain. Various reasons proposed to account for the grain growth inhibition are:

- 1) Cr displaces W in the binder phase and thereby reduces the solubility of W^[49]
- 2) Cr segregates to WC-binder interfaces to form a diffusion barrier^[13]
- 3) Cr is in solid solution with the binder phase but alters the liquid/solid interfacial energy^[22]

From the results obtained from the test blocks, it is obvious that increasing Cr additions to the binder content adversely affects the sinterability of the WC-Ni-Cr alloy. The reasons behind the difficulties in sintering WC-Ni-Cr cemented carbides are unknown as well. However, possible reasons for the effect of increasing Cr content may be the result of:

- 1) reduction in the liquid surface tension forces
- 2) reduction in the amount of liquid formed
- 3) increase in the liquidus temperature of the WC-Ni-Cr system

- 4) promotion of WC/WC sintering in solid state so that capillary forces of the liquid phase are unable to further densify the virtually as sintered compact.

5.1 Solid State Sintering

The shrinkage-temperature dilatometric plots of the five cemented carbide grades has shown that significantly less shrinkage occurs in the high Cr grades during solid state sintering compared with the low Cr specimens. However, the overall densification (ie. after liquid phase sintering) of the high Cr alloys compared to the low Cr grades is significantly less. This would indicate that extensive solid state sintering does not hinder overall densification. As well, SEM micrographs taken of the 10 Cr quenched from temperatures below its eutectic temperature (see Plates 16 to 18) show no evidence of extensive WC/WC sintering. Thus, it is unlikely that Cr promotes WC contiguity during solid state sintering resulting in a rigid carbide skeleton during liquid phase sintering.

During solid state sintering of cemented carbides, densification occurs through activated surface and grain boundary diffusion^[13,16]. The binder phase enhances solid state sintering by reducing the activation energy for diffusion. Since the overall binder weight fraction is kept the same, the addition of Cr reduces the Ni content. In experiments carried out by Meredith and Milner^[16], they had found that the addition of 1 vol.% of any

of the Fe-group metals to WC resulted in significantly enhanced densification. However, 1 vol.% Cr added to WC had no effect on densification. Thus, it was proposed that solubility of WC in the binder was essential for densification in the solid state. It was reasoned that a WC solubility in the binder enticed W and C atoms to leave their carbide surfaces at the carbide/binder interface. The prospect that W has no solubility in Cr and that Cr is a good carbide former like W resulted in almost no atomic mobility.

The possibility that the reduction in solid state densification of the high Cr alloys compared to the low Cr alloys is a direct result of the lower Ni contents, and thus the overall amount of W and C dissolved in the binder phase, does not seem likely though. Meredith and Milner^[3] had also conducted experiments on TiC based cemented carbides with varying Co binder contents. They found that solid state shrinkage was independent of the amount of binder phase. Therefore, WC solubility in the binder phase may be required for enhanced densification but is not directly responsible for the degree of densification. Thus, the decrease in densification below the eutectic temperature of the high Cr carbides compared to the low Cr alloys must be the result of the Cr additions.

Solid state densification within low Cr alloys resulted in activated diffusion of W and C atoms along WC-Ni interfaces. The high shrinkage

in the solid state is due to Ni diffusion to WC/WC interfaces as a result of the system trying to attain a minimum energy state^[17]. Thus, the binder diffuses to fill gaps between WC grains to minimize the free surface area. This leads to the subsequent lowering of the activation energy required for surface and interfacial diffusion of W and C along such interfaces due to the presence of Ni. With high Cr alloys, the Ni still diffuses along WC surfaces but will have absorbed significant Cr contents as well. Nickel has a high solubility for both W and Cr^[1]. However, it is expected that Cr would have a lower activation energy for diffusion into Ni since Cr₃C₂ is less stable than WC, with a heat of formation approximately one half that of WC's^[1]. However, it seems unlikely that the Cr content in the binder phase would displace W resulting in lower W diffusion rates and thus restricting both grain growth and densification. Although EDAX results seem inconclusive (see Tables IX & X), TEM results do appear to indicate that Cr does not hinder W solubility in the binder (see Table XI). Grewe et al.^[27] have also reached similar conclusions.

The Cr containing binder, may however, result in poorer chemical bonding with the WC surface because of the Cr atom's larger size perhaps^[22], resulting in greater interfacial energies and thus higher activation energies for W and C diffusion, as indicated in Table VI.

5.2 Liquid Phase Sintering

From the general shrinkage curves shown in Figure 10, it is obvious that the rearrangement stage occurs much sooner and to a larger degree in the high Cr alloys compared with the low Cr grades. This is due to the high degree of solid state densification that occurs in the low Cr grades. Since solid state densification has been so extensive, the size of the WC aggregates that Meredith and Milner^[16] have suggested, are quite large. However, in the high Cr grades where solid state densification is minimal, the size of the aggregates are much smaller than those in the low Cr alloys. Thus, when the eutectic temperature is reached, the alloys with the smaller aggregate sizes will densify through rearrangement to a greater degree and much sooner after the formation of the liquid phase. This is why the general shrinkage curves of the high Cr alloys show a rather sudden increase in the shrinkage rate shortly after the liquidus temperature is reached, indicating the rearrangement process is occurring. With the low Cr grades, the high degree of solid state densification has led to larger aggregate sizes which has resulted in a time lag after the eutectic temperature is reached. This is because of the larger aggregate void spaces that need to be filled, and then a break up of the aggregates before rapid rearrangement of the aggregates can take place. Secondary rearrangement through particle disintegration has been discussed by Kaysser and

Petzow^[50]. When this does occur, the degree of densification due to rearrangement is not as great as in the high Cr alloys due to the fact that much of the densification has already occurred during solid state sintering.

From Figure 9, it is obvious that while the degree of solid state shrinkage among the high Cr alloys is similar, the amount of compact shrinkage due to the rearrangement process is not. The 10 Cr alloy appears to have densified to a greater degree during the rearrangement stage than the 20 Cr and 50 Cr grades. This may be due to the fact that there exists less liquid volume in the 20 Cr and 50 Cr than in the 10 Cr. With increasing Cr content in the compacts, lower Ni levels are used to maintain an overall binder content of 10%. Thus, with the 10 Cr, enough Ni is available whereby all the Cr is taken into solution by the Ni melt all at once. However, in the 20 Cr and 50 Cr grades, inadequate Ni contents are present to fully hold in solution all the Cr available due to the solubility limit of Cr in Ni. Instead, the liquid phase becomes saturated with Cr and then precipitates Cr, perhaps as a (W,Cr) carbide at a corresponding rate it accepts undissolved Cr into solution. Thus, while there exists 10% binder content in all three of the high Cr alloys, only the 10 Cr takes all the Cr into solution at once while the 20 Cr and 50 Cr only take a portion of the available Cr content into solution at any one time. Thus, the liquid volume in the 20 Cr and 50 Cr is notably less than

in the 10 Cr. This lower liquid volume would lead to less rearrangement as noted by Nelson and Milner^[51].

Although not as evident in the 10 Cr, the 20 Cr and 50 Cr indicate that a third stage occurs after the rearrangement process. This stage being the solution-precipitation process. Nelson and Milner^[51] have suggested that this third stage only occurs when 100% densification has not been attained through rearrangement. Figure 10 seems to agree with Nelson and Milner's conclusions.

During the solution-precipitation stage, not only does the dissolution of solid material occur, in which the material is then transported via the melt and precipitated on particles at other sites, but grain boundary penetration by the melt also occurs. The disintegration of the solid particles leads to secondary rearrangement which is shown to appear in the 20 Cr and 50 Cr general shrinkage curves. As well, it is evident that some particle disintegration must occur since the microstructures of the 10 Ni sintered at 1480 C for 30 minutes (see Plate 1) shows noticeably larger WC grains than similarly prepared 10 Ni sintered at 1520 C for 30 minutes (see Plate 7).

According to several authors^[8,10,33], Ni has a substantially higher solubility for W and C than Co does. However, Brabyn et al.^[8] have found that sintering of WC-10% Co and WC-10% Ni at 1400 C and 1440 C

respectively, to account for the higher eutectic temperature of the WC-Ni system, resulted in no significant variation in the WC grain size. Thus, it would appear that grain growth, and thus W and C diffusion above the eutectic temperature, is not a strong function of solubility of WC in the liquid phase. Since grain growth in the liquid phase is due to the solution-precipitation process, the Cr in solid solution may possibly be decreasing the W and C diffusion rates. Again, as in solid state sintering, this may be due to a decrease in chemical bonding between the liquid phase and WC as a result of the larger Cr atoms in the binder liquid as Kim and Accary^[22] have suggested during their experiments on the grain growth inhibition of WC-Co by TaC.

Meredith and Milner^[3] agree with Kim and Accary that grain growth during liquid phase sintering is an interfacial reaction controlled process. However, they attribute the cause of reduced W and C diffusion to the solid/liquid interface to be due to a different mechanism. In previous work, Meredith and Milner^[16] found that only the Fe-group metals added to WC exerted a major effect on densification. The use of carbide-forming elements such as Mo or Cr as the additive, however, had no effect on densification. Thus, Meredith and Milner concluded that only those additions in which the WC had some solubility were effective. This was because the solubility of WC in the additive created an in-flow of W and

C atoms at the WC/binder interface which decreases the activation energy for atomic movement, and thereby giving rise to greater atomic mobility. With Mo and Cr, however, no in-flow of W and C into the Mo or Cr takes place and so densification occurs at the rate pure WC would sinter at.

In Meredith and Milner's^[3] study of the liquid phase sintering of TiC-Co with Mo additions, they had concluded that grain growth and densification were both reduced due to the Mo additions. Considering their previous work on Mo and Cr additions to WC^[16], they suggested that this was due to the fact that with the chemical bonding that occurs with additives such as Mo, the Ti and C atoms were less mobile. Thus, a reduced flux of Ti and C to the carbide/binder interface resulted, leading to slower densification and reduced grain growth.

The other possibility that could change the carbide/binder interface resulting in lower densification and grain growth is that Cr segregates to these interfaces to act as a diffusion barrier. However, from TEM analysis of the 10 Cr and 20 Cr, no Cr diffusion barrier was found at the WC/binder interface. Thus, the predicted alteration in interfacial energy resulting in lower W and C diffusion rates to the WC/binder interface is not caused by Cr segregation.

The alteration in surface interfacial energy resulting from the Cr content in solution in the liquid phase may in fact lead to an increase in

the contact angle between the liquid/vapour interface and the liquid/solid interface. This reduces contact forces that are responsible for particle rearrangement and the extent of densification. In other words, the Cr content in the liquid degrades wettability, compared with a Ni melt with no Cr content.

It has been stated^[43] that the minimum criteria for good liquid phase sintering are :

- 1) low eutectic temperature
- 2) solubility of WC in the binder phase
- 3) good wetting

For the high Cr alloys, it has been shown in Table V that lower liquidus temperatures are realized over the low Cr alloys. Thus, this point is met by the high Cr carbides and refutes the possibility that densification is hindered in WC-Ni-Cr alloys due to the Cr increasing the liquidus temperature. The requirement of solubility of WC in the binder phase is quite evident from the electron microscopy work done (refer to Tables IX to XI). Thus, the high Cr alloys' poor densification must be to some degree attributed to the poor wettability of the Ni melt containing Cr. Since wetting depends on a chemical reaction taking place between the liquid and carbide, the Cr content in solid solution in the binder phase hinders such a reaction from occurring, resulting in poorer wetting capabilities.

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CHAPTER VI

SUMMARY AND CONCLUSIONS

The effect of Cr additions to WC-Ni cemented carbides is that it significantly reduces the amount of solid state shrinkage, as well as reduces the eutectic temperature of the binder phase with increasing Cr content. However, significant amounts of Cr are required to noticeably alter the densification of Ni bonded WC. One weight percent Cr of the overall binder content has no significant effect on densification in either the solid or liquid phases of sintering. Thus, whereas the low Cr grades (ie. 10 Ni and 1 Cr) show a high degree of densification during solid state sintering, the high Cr alloys (ie. 10 Cr, 20 Cr, and 50 Cr) behave in exactly the opposite manner, with most of the compact shrinkage occurring during liquid phase sintering. Even so, the low Cr grades were found to densify to a greater extent than the high Cr alloys under similar conditions. As well, the activation energy for compact shrinkage during solid state sintering was found to increase with increasing Cr content.

The extensive and almost immediate rearrangement that occurs right after surpassing the eutectic temperature during heating of the high Cr alloys is due to the low degree of solid state densification which has led to small WC aggregates. Among the low Cr alloys, the extensive solid state

densification has resulted in larger WC clusters. These aggregates or clusters of WC particles bonded together by the binder phase now become the effective particle size for rearrangement. The smaller aggregates enable densification to proceed at a much quicker rate and much sooner during this stage than the larger aggregates of the low Cr alloys.

Among the high Cr grades, a solution-precipitation process occurs when rearrangement has not resulted in 100% densification. During the solution-precipitation process, the predominant mechanism of compact shrinkage is aggregate break up leading to secondary rearrangement.

In the WC-Ni-Cr system, grain growth inhibition and the greater difficulty in sintering these alloys are somewhat interrelated. Grain growth is hindered due to the Cr in solution in the binder phase. This results in the Cr suppressing the atomic mobility of the W and C atoms at the carbide/binder interface. The reduction in W and C diffusion to the carbide/binder interface is the reason behind the significantly lower solid state densification in the high Cr grades. Grain growth during the solution-precipitation stage is hindered by this same mechanism.

During liquid phase sintering, the reduction in the liquid volume due to Cr replacing Ni content results in less densification through rearrangement. As well, Cr in the liquid phase reduces its wetting ability, resulting in lower capillary forces that cause rearrangement.

For further study on the WC-Ni-Cr system, greater and more reliable information could be obtained through further electron microscopy analysis. However, in order to confirm the stages that occur during liquid phase sintering, a hot stage scanning electron microscope should be used. This would enable observation of particle movement as well as growth or disintegration during liquid phase sintering at the elevated temperature. Thus, WC agglomeration, rearrangement of these clusters and subsequent break up could possibly be concluded with a high degree of certainty.

As well, further TEM work should be carried out using a calibrated machine to confirm the results already obtained. A slight change in procedure for the new TEM work that should be followed is that EELS be used so that C, along with W, Ni and Cr, may also be detected as well. With this ability, the effects of pre-sintering and gas treatment could be studied with respect to their interaction with C levels in the final sintered product, and thus mechanical properties.

Another form of analysis that could be carried out is Auger microscopy. With this electron microscope, true surface analysis could be made on fractured surfaces. This method could possibly enable one to determine whether or not binder phase exists between WC grains. As well, further proof of a Cr diffusion layer not existing at WC/binder interfaces could be provided.

APPENDICES

APPENDIX 1

Dilatometric Set Up Procedures

During the course of the preliminary dilatometric work with cemented carbides to determine proper dilatometric control settings, it was found that there was a heating rate limitation. This was due to the indirect thermocouple contact with the specimen. The MMC Deformation Dilatometer used in these experiments was originally designed for analysis of steels. Thus, thermocouple contact with the steel specimens was by spot welding the thermocouple leads directly to the surface of the steel specimen. This enabled heating rates of about 100 C/s to be carried out. With the cemented carbide powdered compacts, spot welding the thermocouple leads to the surface was not possible. Instead, the tips of the thermocouple wires were melted together and dipped into a zirconia paste (Ultra-Temp 516 from Aremco Products, Inc.) to guard against reacting with the liquid phase of the cemented carbide specimen. Although zirconia is a thermal insulator the thin coating is not expected to hinder temperature readings. Coating the thermocouple tip was found to be necessary since without it, the thermocouple wire exposed to the liquid binder would surely break. The zirconia coating was allowed to dry for 24 hours at room temperature. Since the thermocouple tip was inserted into a hole drilled

into the side of the compact, the semi-loose presence of the thermocouple tip did not seem to provide a secure enough contact to allow for very rapid heating followed by a isothermal hold at the upper temperature. A maximum heating rate, under such conditions, was found to be only 10 C/sec. For a heating rate greater than 10 C/sec, an unstable sinusoidal temperature fluctuation upon reaching the isothermal temperature would occur.

In drilling the hole in the compact for the thermocouple, care was taken to ensure the bottom of the hole coincided roughly with the centre of the compact. This enabled the thermocouple tip to provide temperature readings of the compact centre, where the temperature is highest. Drill bits approximately 0.8 mm in diameter were used.

Besides binder attack of the thermocouple, the liquid phase also resulted in bits of the quartz platens' contacting surfaces to be pulled away when removing the sintered compact. Thus, in order to extend the operational use of these quartz platens, a thin alumina disc was inserted at either ends of the cylindrical compacts to separate them from the quartz platens (see Figure 13). The alumina discs were obtained by cutting thin slices off a high density alumina milling cylinder with a diamond saw. Care was taken to ensure that both faces of the disc were parallel and flat.

APPENDIX 2

Determination of Activation Energies

From the isothermal dilatometric tests conducted on all five cemented carbide grades (10 Ni, 1 Cr, 10 Cr, 20 Cr and 50 Cr) at various temperatures, the resulting shrinkage-time charts (see Figure 14 for a typical example) were used to obtain data points for the determination of the *activation energies*. The rate of compact shrinkage is often considered to increase exponentially with temperature and is described by an Arrhenius equation :

$$K = K_0 \exp(-Q/RT)$$

$$\text{or } \ln K = \ln K_0 - (Q/R)(1/T)$$

where Q is the *activation energy*; R is the universal gas constant; T is the absolute temperature; K_0 is a constant; and K is a rate constant. Froschauer and Fulrath^[20] used the above Arrhenius equation with K representing the densification rate, $d(L-L_0/L_0)/dt$. Thus, their activation energy represents the compact shrinkage. Sebastian and Tendolkas^[44] and Warren^[36] used the Arrhenius equation as well but with $1/t$ as the rate constant, t being the time to reach a particular grain size. These latter cases represent the activation energies for grain growth. However, if t were the time to reach a particular compact shrinkage value, then the

were the time to reach a particular compact shrinkage value, then the resulting activation energy would represent the compact shrinkage.

To determine the activation energy for compact shrinkage, both methods of measuring $d(L-L_0/L_0)/dt$ and $1/t$ for $L-L_0/L_0 = 0.07$ were used. A value of $L-L_0/L_0 = 0.07$ was chosen since it was a compromise between the low temperature isothermal tests, where a shrinkage of 7% was small enough to limit the isothermal hold time to within reason, and large enough so that at the higher isothermal temperatures the shrinkage value of interest was not surpassed before the isothermal temperature was reached during the rapid heating. Time zero was taken as the start of the isothermal hold time.

In determining $d(L-L_0/L_0)/dt$ at $L-L_0/L_0 = 0.07$ for the various isothermal temperatures of the 10 Ni and 1 Cr cemented carbide grades, the slope of the shrinkage-time charts at $L-L_0/L_0 = 0.07$ was calculated. This was done by taking a point just before and a point just after the $L-L_0/L_0 = 0.07$ position on the shrinkage-time charts. The three shrinkage-time points were used to calculate $d(L-L_0/L_0)/dt$ for $L-L_0/L_0 = 0.07$. The intervals between the three points were chosen such that the segment of the shrinkage-time chart at $L-L_0/L_0 = 0.07$ could be closely approximated as a straight line. For each cemented carbide grade, the natural logarithms of the slopes at 7% shrinkage was plotted against the inverse of their absolute

isothermal temperatures (see Figures 15 & 16). The slope, $-Q/R$, of each of the cemented carbide grade's $\ln d(L-L_0/L_0)/dt$ vs. $1/T$ plot was used to calculate the activation energy, Q , for compact shrinkage. For the 10 Ni and 1 Cr alloys, the $\ln d(L-L_0/L_0)/dt$ vs. $1/T$ plots reveal activation energies for compact shrinkage of 120 kcal/mole and 112 kcal/mole, respectively. Due to the fact that the general shrinkage curves (see Figure 9) of the 10 Ni and 1 Cr are very similar, it is not surprising that similar activation energies for solid state sintering are obtained as well.

In the second method, the time (t) taken between when the isothermal temperature was first reached and when 7% shrinkage was attained was measured from the shrinkage-time charts at the various isothermal temperatures. The activation energies were then obtained from the slopes of the $\ln 1/t$ vs. $1/T$ plots of each of the cemented carbide grades (see Figures 17 to 26). The activation energies for compact shrinkage for solid state sintering, rearrangement and solution-precipitation are summarized in Table VI.

In comparing the activation energies of the two alloys at 7% shrinkage as provided by the $\ln d(L-L_0/L_0)/dt$ vs. $1/T$ and $\ln 1/t$ vs. $1/T$ plots, 120 kcal/mole and 125 kcal/mole, respectively, for the 10 Ni and 112 kcal/mole and 123 kcal/mole, respectively, for the 1 Cr, it appears that both methods result in similar activation energy values. However, of the two

methods, the $\ln 1/t$ vs. $1/T$ plots is believed to provided more reliable activation energy values due to the fact that direct measurements (ie. time taken from start of isothermal sintering for compact to shrink 7%) were made from the dilatometric shrinkage-time charts. The $d(L-L_0/L_0)/dt$ vs. $1/T$ plots, however, required indirect measurements to be made from the shrinkage-time charts (ie. determination of the slope of the tangent from the shrinkage-time curve at 7% shrinkage).

As well, in order to show that the activation energy is *independent* of the compact shrinkage within reason, $\ln 1/t$ vs. $1/T$ plots were made for 10 Ni at 5% and 10% compact shrinkages (see Figure 17). These resulted in activation energies of 125 kcal/mole and 121 kcal/mole, respectively. These compare very well to 125 kcal/mole, the activation energy at 7% shrinkage.

In calculating the shrinkage of the compact from the shrinkage-time charts, the thermal expansion of the compact was also considered. This was done by assuming a constant thermal expansion. This assumption was proven to be correct through dilatometric measurements taken of sintered WC-Ni-Cr specimens used to determine the liquidus temperatures. A constant thermal expansion is observed up to the eutectic temperature. The thermal expansion constant after the eutectic temperature was undetermined due to further liquid phase sintering. Therefore, the thermal expansion co-

efficient of each compact was determined from the initial slope of the shrinkage-time charts, at roughly between 75 and 200 C. At these temperatures, it is assumed no shrinkage exists and any change in the length of the compact is due to thermal expansion. This is a reasonable assumption since the powder compacts have been pre-sintered at 500 C for 1 hour. Thus, the overall thermal expansion at the isothermal temperature is subtracted from the chart value of the compact's shrinkage to obtain the change in length of the compact.

APPENDIX 3

TEM Thin Foil Preparation of Cemented Carbides

Cemented carbides, in particular WC with Ni binder, are very hard two-phase materials. The preparation of thin foils with these materials consists of cutting thin slices with a diamond saw from the bulk specimen, spark cutting 3 mm discs from these thin slices, mechanical dimpling of the discs, and finally ion beam thinning. In general, this appendix outlines the variations of the above procedures attempted as well as other techniques that were used but found to be not as effective.

In cutting thin slices of cemented carbide, the best results came from an Isomet Low Speed Saw (Model 11-1180) operating at *medium* speed and with a mass of approximately 225 g loaded on the saw arm. A 4 in. diamond wheel for nonferrous and ceramic materials (0.015 in. thick) was used and slices less than 100 μm were easily obtained. For TEM samples, slices less than 200 μm seemed best. Specimens greater than 200 μm required too long a dimpling time. With the Isomet saw, a cylindrical WC-Ni specimen 6 mm in diameter would take about 1 hour to cut through completely (using unagitated cutting oil).

A larger diamond saw machine was also used but with less success. A Jarrett Cut Off Saw operating at approximately 500 rpm and 300 g saw arm load had been used. Two types of diamond saw wheels, one for hard steels and one for nonferrous and ceramic materials, had been tested with this machine. Both were 5 in. wheels and 0.025 in. thick. The nonferrous and ceramic wheel performed much better than the wheel for hard steels in providing thin slices. However, with the nonferrous and ceramic diamond wheel slices less than 200 μm in thickness were difficult to achieve with parts of the slice breaking off before being completely cut off. Cutting time for the Jarrett saw with the nonferrous and ceramic wheel provided slightly faster cutting times than the Isomet saw with a similar wheel type. For example, for the same 6 mm diameter cylindrical WC-Ni sample, the cutting time is about 50 minutes with the Jarrett saw and nonferrous and ceramic wheel (using an unagitated cutting oil).

The next step in thin foil preparation is to cut out 3 mm diameter discs from the thin slices. An Agiepuls Spark Cutter was found to be quite successful. For a slice approximately 150 μm thick, the time required to cut through was about 25 minutes. An ultra sonic disc cutter had also been used but did not seem to cut well.

Mechanical dimpling of the 3 mm discs were found to work best for thinning of the centers to the point where the centers were about 15 μm in

thickness. To dimple all the way through was rather ineffective since achieving a very small hole size due to dimpling was extremely tedious and time consuming in that with 1 μm diamond paste, very frequent checks of the centre were required. In almost all cases attempted, dimpling all the way through created too large a hole for TEM application. Failure of this procedure was due to the inability to exactly determine the thickness of the dimple's centre. The advantage of this procedure would have been that ion beam thinning would be unnecessary.

In general, for specimens between 100 and 200 μm thick, it is best to dimple both sides. For discs less than 100 μm , hand polishing flat one side and then mechanically dimpling the other is permissible. In all cases, the final polish should be with a 1 μm diamond paste applied to some polishing cloth (such as Buehler's MicroCloth) attached to the grinding wheel. As an example of the dimpling technique used, assume a Gatan Dimple Grinder (Model 656) and a disc 200 μm in thickness to be dimpled on both sides. On the first side the dimpling would occur as such:

Dimple Depth	Diamond Paste (1)	Wheel Speed (2)
60 um	30 um (3)	4.5
80 um	9 um (3)	4.5
90 um	6 um (3)	4.5
93 um	3 um (3)	4.5
94 um	1 um (4)	6.5

- (1) with water lubricant
- (2) control knob setting
- (3) bronze wheel
- (4) polishing cloth on plastic wheel

The dimple depths would be determined using a calibrated microscope by focusing in on the centre and then at various positions around the unpolished edge of the disc. A similar procedure would be followed for the other side. Approximately 4 hours was required to dimple both sides. With the Gatan dimple grinder, a 30 g load was applied to the polishing wheel for both sides and all diamond pastes except for the second side for 3 and 1 um diamond pastes, which used 20 g loads.

Electrochemical thinning with a solution of NaCN (7 g), C₂H₅OH (30 ml), and H₂O (70 ml) had been attempted with some success. However, deposits around the hole's edges were found and required ion beam cleaning still. Electrochemical thinning does provide a viable alternative to mechanical dimpling for the first stage of thin foil preparation however.

With mechanical dimpling other techniques that were attempted was the use of 1 um paste with a bare plastic wheel. However, the polishing is

not as effective as when a polishing cloth is used. Also, 1/4 um paste on a polishing cloth was tested but found to give no noticeable improvement over the 1 um with cloth.

If the TEM sample at this point contained no hole or only a very small one in its centre, the sample was ion thinned in an Ion Tech Argon Ion Beam Thinning Machine. This machine incorporates two ion beam guns that bombard the surface of the TEM sample from both sides. Typical gun angles were approximately 13 to 14 degrees from the plane of the sample. Although for thick samples, 15 degrees was used initially to quicken the thinning and then 13 degrees at the end to erase the dislocations and other surface damage caused by ion beam thinning at 15 degrees.

REFERENCES

REFERENCES

- 1 Exner, H.E. "Physical and Chemical Nature of Cemented Carbides", Intern. Metals Reviews, Vol.24, No.4, 1979, p. 149.
- 2 Fukuhara, M.
Mitani, H. "Mechanisms of Grain Growth In Ti(C,N)-Ni Sintered Alloys", Powder Metallurgy, Vol. 25, No. 2. 1982, p. 62.
- 3 Meredith, B.
Milner, D. "The Liquid-Phase Sintering of Titanium Carbide", Powder Metallurgy, Vol. 19, No. 3, 1976, p. 162.
- 4 Huppman, W.
Riegger, H.
Petzow, G. "Liquid Phase Sintering of the Model System W-Ni", New Techniques In Sintering, p. 272.
- 5 Kaysser, W.
Puchert, F.
Petzow, G. "Recrystallization and Grain Boundary Migration During Sintering of W-Ni", Powder Metallurgy International, Vol. 12, No. 4, 1980, p. 188.
- 6 Kwon, O.
Yoon, D. "The Liquid Phase Sintering of W-Ni", Sintering Processes, Vol. 13., Ed. by G. Kuczynski, Plenum Press, New York, N.Y., 1979.
- 7 Riegger, H.
Pask, J.
Exner, H. "Direct Observation of Densification and Grain Growth In a W-Ni Alloy", Sintering Processes, Vol. 13, Ed. by G. Kuczynski, Plenum Press, New York, N.Y., 1979.
- 8 Brabyn, S.M.
Cooper, R.
Peters, C.T. "Effects of the Substitution of Nickel for Cobalt In WC Based Hardmetal", 10th Plansee Seminar, Reutte, Planseewerke, 1981, p. 675.

- 9 Upadhyaya, G.
Basu, D. "Nickel and Iron Substituted WC-10 Co Hard Metals", 11th Inter. Plansee Sem., Reutte, 1981, p. 559.
- 10 Gabriel, A.
Pastor, H.
Deo, D.M.
Basu, S.
Allibert, C. "New Experimental Data In the C-Co-W, C-Fe-W, C-Ni-W C-Fe/Ni-W & C-Co/Ni-W Systems and Their Applications To Sintering Conditions", Refract. and Hardmetals, Dec., 1986, p. 215.
- 11 Ekemar, S.
Lindholm, L.
Hartzell, T. "Nickel as a Binder In WC-Based Cemented Carbides", Refract. and Hard Metals, March 1982, p. 37.
- 12 Barlow, G. "Tungsten Carbide Bonded With Nickel", Fourth European Powder Metallurgy Symposium, Preprints Vol. 2, Grenoble 1975.
- 13 Anonymous "Cr₃C₂ Inhibits WC Grain Growth In Ultrafine Hard Alloy", Refractory and Hard Metals, Vol. 6, No. 1, March 1987, p. 19.
- 14 Ogawa, H.
Kataoka, Y. "A New Measurement For Sintering Of Several Cemented Carbides By High Temperature Sintering Dilatometer", 10th Plansee Seminar, 1981, p. 695.
- 15 Schreiner, H.
Tusche, R. "Description of Solid State Sintering Processes Based On Changes In Length of Compacts Made From Different Metal Powders", Metal Powder Report, 1978.
- 16 Meredith, B.
Milner, D. "Densification Mechanisms In the Tungsten Carbide-Cobalt System", Powder Metallurgy, Vol. 19, No. 1, 1976, p. 38.

- 17 Snowball, R.
Milner, D. "Densification Processes In the Tungsten Carbide-Cobalt System", Powder Metallurgy, Vol. 11, No. 21, 1968, p. 23.
- 18 Edwards, R.
Raine, T. "The Solid Solubilities of Some Stable Carbides in Cobalt, Nickel and Iron at 1250 C", Proceedings of the First Plansee Seminar, Ed. by R. Benesovsky Reutte/Tyrol, Planseewerke, 1952, p. 232
- 19 Hoffmann, A.
Mohs, R. Metall, 1974, Vol. 28, No. 7, p. 661
- 20 Froschauer, L.
Fulrath, R.M. "Direct Observation of Liquid-Phase Sintering In the System Tungsten Carbide-Cobalt", Journal of Materials Science, Vol. 11, 1976, p. 142.
- 21 Nelson, R.
Milner, D. "Liquid-Flow Densification In the Tungsten Carbide-Copper System", Powder Metallurgy, Vol. 14, No. 27, 1971, p. 39.
- 22 Kim, D.
Accary, A. "Mechanisms of Grain Growth Inhibition During Sintering of WC-Co Basted Hardmetals", Sintering Processes, Vol. 13.. Ed. by G. Kuczynski, Plenum Press, New York, N.Y., 1979.
- 23 Sarian, S.
Weart, H. "Kinetics of Coarsening of Spherical Particles In a Liquid Matrix", Journal of Applied Physics, Vol. 37, No. 4, March 1966, p. 1675.
- 24 Warren, R. "Carbide Grain Growth During the Liquid-Phase Sintering of the Alloys NbC-Fe, NbC-Ni, and NbC-Co", Journal of the Less Common Metals, Vol.17, 1969, p.65.

- 25 Rudiger, O.
Willbrand, J.
Hirschfeld, D.
Hoffmann, A.
Kolaska, J.
Ostermann, G. "Composition and Properties of the Binder Metal In Cobalt Bonded Tungsten Carbide", Modern Developments In Powder Metallurgy, Vol. 5: Materials and Properties, Ed. by H. Hausner, Plenum Press, New York, 1971, p. 215.
- 26 Lardner, E.
Iggstrom, S. "Properties and Applications of Sub-Micro' Hardmetals", 10th Intern. Plansee Sem., Reutte, 1981, p. 549.
- 27 Grewe, H.
Exner, H.
Walter, P. "Restriction of Grain Coarsening in Cemented Carbides of ISO-K 10-Type by Carbide Additions", Z. Metallkd., Vol. 64, No. 1, 1973, p. 85.
- 28 Suzuki, H.
Kubota, H. "The Influence of Binder Phase Composition On the Properties of WC-Co Cemented Carbides", Planseeberichte Fur Pulvermetallurgie, Vol.14, 1966, p. 96.
- 29 Exner, H.E.
Gurland, J. "A Review of Parameters Influencing Some Mechanical Properties Of Tungsten Carbide-Cobalt Alloys", Powder Metallurgy, Vol. 13, No. 25, 1970, p. 13.
- 30 Suzuki, H.
Fuke, Y.
Hayashi, K. "Grain Size of WC in Sintered WC-VC-Co Alloys", Powder and Powder Metallurgy (Japan), Vol. 19, No. 3, 1972, p. 106.
- 31 Stjernberg, K. "Some Relations Between the Structure and Mechanical Properties of WC-TiC-Co Alloys", Powder Metallurgy, Vol. 13, No. 25, 1970, p. 1.

- 32 Exner, H.E. "Methods and Significance of Particle and Grain-Size Control In Cemented Carbide Technology", Powder Metallurgy, Vol. 13, No. 26, 1970, p. 429.
- 33 Almond, E.
Roebuck, B. "Identification of Optimum Binder Phase Compositions for Improved WC Hardmetals", Proc. Int. Conf. Science of Hard Materials, 8-15 Nov., Preprint, 1987.
- 34 Vlasyuk, R.
Radomyselskii
Sotnik, A. "Dissolution of Cr_3C_2 In a Nickel Matrix During Sintering", Theory and Technology of Sintering, Thermal, and Chemicothermal Treatment Processes, 1985, p. 356.
- 35 Ramqvist, L. "Wetting of Metallic Carbides By Liquid Copper, Nickel, Cobalt and Iron", International Journal of Powder Metallurgy, 1965, p. 2.
- 36 Warren, R. "Microstructural Development During the Liquid-Phase Sintering of Two-Phase Alloys, with Special Reference to the NbC/Co System", Journal of Materials Science, Vol. 3, 1968, p. 471.
- 37 Warren, R.
Waldron, M. "Microstructural Development During the Liquid-Phase Sintering of Cemented Carbides", Powder Metall. Vol. 15, No. 30, 1972, p. 166.
- 38 Smolej, V.
Pejovnik, S.
Kaysser, W. "Rearrangement During Liquid Phase Sintering of Large Particles", Powder Metallurgy International, Vol. 14, No. 1, 1982, p. 34.

- 39 Krstic, V.
Komac, M. "Toughening In WC-Co Composites",
Philosophical Magazine A.,
Vol. 51, No. 2, 1985, p. 191.
- 40 Sharma, N.
Ward, I.
Fraser, H.
Williams, W. "STEM Analysis of Grain Boundaries In
Cemented Carbides", Journal of the
American Ceramic Society, Vol. 63,
No. 3-4, 1980, p. 194.
- 41 Froschauer, L.
Fulrath, R.M. "Direct Observation of Liquid-Phase
Sintering In the System Iron-Copper",
Journal of Materials Science,
Vol. 10, 1975, p. 2146.
- 42 Exner, H.E. Int. Pulvermet. Tagung, Bad Eisenach,
Vol. 13, 1965, p. 127.
- 43 German, R. Liquid Phase Sintering, Plenum Press,
New York, N.Y., 1985.
- 44 Sebastian, K.
Tendolkar, G. "Experimental Observations On the
Densification By Rearrangement In
Liquid Phase Sintering",
Powder Metallurgy International,
Vol. 11, No 2, 1979, p. 62.
- 45 Hellsing, M.
et al. "Atom-Probe Microanalysis of WC-Co
Based Cemented Carbides", Proc. Int.
Conf. Science of Hard Materials,
R.K. Viswanadham et al. (Eds.),
Jackson, Wyoming, 23-28 Aug., 1981,
Plenum, New York, p. 931.
- 46 Aronsson, B.
Pastor, H. "Cobalt in Cemented Carbide",
Metal Powder Report, July 1986,
p. 499.
- 47 Oakes, J. "The Effect of Cr and Mo Additions to
the Binder Phase of Cemented Carbides
Used For Rod Mill Rolls",
11th International Plansee Seminar,
Vol. I, 1985, p. 815.

- 48 Yust, C.
Long, E. Jr. "Optical and Electron Microscopy of WC-Co Alloys", American Ceramics Society Bulletin, Vol. 62, No. 9, 1983, p. 1039.
- 49 Palmqvist, S. Symposium On Powder Metallurgy, 1954, London, The Iron and Steel Institute, 1956, p. 305.
- 50 Kaysser, W.
Petzow, G. "Present State of Liquid Phase Sintering", Powder Metallurgy, Vol. 28, No. 3, 1985, p. 145.
- 51 Nelson, R.
Milner, D. "Densification Processes In the Tungsten Carbide-Cobalt System", Powder Metallurgy, Vol. 15, No. 30, 1972, p. 346.

TABLES

TABLE I: Initial Starting Powder Properties

Powder Type	Purity Level	Particle Size (Fisher Grain Size)	Total Carbon Content (wt.%)
WC	-	5.8 μm	6.15
Ni	99.60%	1.7 μm	-
Cr_3C_2	99.12%	1.7 μm	13.12

TABLE II: Intended Material Composition (wt.%)

Material	WC	Ni	Cr
10 Ni	90%	10%	0%
1 Cr	90%	9.9%	0.1%
10 Cr	90%	9.0%	1.0%
20 Cr	90%	8.0%	2.0%
50 Cr	90%	5.0%	5.0%

TABLE III: Weight Percentage of Starting Powders For Stoichiometric Composition

Material	WC	Ni	Cr_3C_2	W
10 Ni	89.65%	10.09%	0%	0.26%
1 Cr	89.62%	9.99%	0.11%	0.28%
10 Cr	89.53%	9.08%	1.15%	0.24%
20 Cr	89.49%	8.03%	2.30%	0.17%
50 Cr	89.18%	5.02%	5.75%	0.04%

TABLE IV: "Fully" Sintered Test Block Properties**Waxed, Non-Gas Treated (1520 C for 30 min.)**

	10 Ni	1 Cr	10 Cr	20 Cr
Density, %	.977	.977	.969	.956
HV30	1022	1150	1324	1382
Hc	0	0	0	0
WC Grain Size*	c-m	m	m-f	m-f
Porosity*	<B02	B03	A06 (a few holes)	A08 (several holes)

(note: see Plates 3 to 6)

Waxed, Gas Treated (1520 C for 30 min.)

	10 Ni	1 Cr	10 Cr	20 Cr
Density, %	.974	.974	.969	.947
HV30	1064	1106	1307	1303
Hc	17	0	0	0
WC Grain Size*	c-m	m	m	m-f
Porosity*	B02	A02/B02	A06 (a few holes)	A08 (several holes)

(note: see Plates 7 to 10)

Dry Pressed, Non-Gas Treated (1520 C for 30 min.)

	10 Ni	1 Cr	10 Cr	20 Cr	50 Cr
Density, %	.968	.970	.956	.938	-
Hc	34	26	15	16	14
Porosity*	A02/B02	<B02	A05	A07	>A08

* according to ISO standards

TABLE V: Liquidus Temperatures

Grade	Liquidus Temperature
10 Ni	1370 C
1 Cr	1380 C
10 Cr	1330 C
20 Cr	1300 C
50 Cr	1270 C

TABLE VI: Activation Engeries for Compact Shrinkage

	Solid State (kcal/mol)	Liquid Phase (kcal/mol)	
		Rearrangement	Sol'n-Precip.
10 Ni	125	-	-
1 Cr	123	-	-
10 Cr	208	55	-
20 Cr	236	64	158
50 Cr	266	87	163

**TABLE VII: Relative Electrical Resistivity, P/P_0 ,
(wrt 10 Ni quenched from 1450 C)**

Quench Temp (C)	10 Ni	1 Cr	10 Cr	20 Cr	50 Cr
1200	3.97	5.92	7.99	10.70	10.82
1300	2.79	3.76	6.25	8.61	6.18
1350	2.21	2.77	5.71	4.10	4.75
1400	1.93	2.39	2.71	2.79	4.50
1450	1.00	--	1.91	2.49	3.45
1470	--	1.56	--	--	--
1500	--	--	1.47	--	--
1550	--	--	--	1.83	1.91

where $P_0 = 12.6$ uohm-cm

**TABLE VIII: Relative Electrical Resistivity, P/P_x ,
(wrt each grade's highest quench
temperature resistivity measurement)**

Quench Temp (C)	10 Ni	1 Cr	10 Cr	20 Cr	50 Cr
700	80.99	98.35	121.89	168.71	175.07
900	19.75	15.31	41.08	37.77	47.96
1050	11.38	6.12	10.68	15.84	12.41
1200	3.97	3.79	5.44	5.84	5.68
1300	2.79	2.41	4.25	4.70	3.25
1350	2.21	1.77	3.89	2.24	2.49
1400	1.93	1.53	1.85	1.52	2.36
1450	1.00	--	1.30	1.36	1.81
1470	--	1.00	--	--	--
1500	--	--	1.00	--	--
1550	--	--	--	1.00	1.00

where $P_x =$ 12.6 uohm-cm for 10 Ni
 19.7 uohm-cm for 1 Cr
 18.5 uohm-cm for 10 Cr
 23.1 uohm-cm for 20 Cr
 24.0 uohm-cm for 50 Cr

**TABLE IX: SEM Compositional Results of
He Quenched 10 Ni Specimens**

10 Ni

Quenching Temperature = 1300 C

	W	wt.% Ni	Ratio W:Ni
1)	99.09	0.91	108.89
2)	98.53	1.47	67.03
3)	88.65	11.35	7.81
4)	89.36	10.64	8.40

Quenching Temperature = 1350 C

	W	wt.% Ni	Ratio W:Ni
1)	97.56	2.44	39.98
2)	96.50	3.50	27.57
3)	46.31	53.69	0.86
4)	36.20	63.80	0.57

Quenching Temperature = 1400 C

	W	wt.% Ni	Ratio W:Ni
1)	99.11	0.89	111.36
2)	98.28	1.72	57.14
3)	67.25	32.75	2.05
4)	66.62	33.38	2.00

**TABLE X: SEM Compositional Results of
He Quenched 10 Cr Specimens**

10 Cr

Quenching Temperature = 1300 C

	W	wt.% Cr	Ni	Ratios W:Ni	Cr:Ni
1)	99.51	0.00	0.49	203.08	0.000
2)	98.64	0.00	1.36	72.53	0.000
3)	47.59	4.78	47.62	1.00	0.100
4)	33.43	6.28	60.29	0.55	0.104

Quenching Temperature = 1350 C

	W	wt.% Cr	Ni	Ratios W:Ni	Cr:Ni
1)	99.23	0.00	0.77	128.87	0.000
2)	98.99	0.00	1.01	98.01	0.000
3)	49.86	4.65	45.49	1.10	0.102
4)	51.73	4.66	43.61	1.19	0.107

Quenching Temperature = 1400 C

	W	wt.% Cr	Ni	Ratios W:Ni	Cr:Ni
1)	98.88	0.00	1.12	88.29	0.000
2)	99.37	0.00	0.63	157.73	0.000
3)	36.86	5.15	57.99	0.64	0.089
4)	47.55	4.41	48.04	0.99	0.092

**TABLE XI: TEM Compositional Results of
10 Cr and 20 Cr Specimens**

10 Cr					
	W	wt.% Cr	Ni	Ratios	
				W:Ni	Cr:Ni
1)	99.29	0.00	0.71	140.41	0.000
2)	99.25	0.00	0.75	131.72	0.000
3)	90.94	0.00	9.06	10.04	0.000
4)	17.60	7.83	74.56	0.24	0.105
5)	21.30	6.69	71.97	0.30	0.093
6)	27.47	6.17	66.36	0.41	0.093
7)	24.24	6.70	69.06	0.35	0.097

20 Cr					
	W	wt.% Cr	Ni	Ratios	
				W:Ni	Cr:Ni
1)	97.93	0.45	1.62	60.36	0.276
2)	98.78	0.40	0.82	121.19	0.493
3)	31.07	8.25	60.68	0.51	0.136
4)	56.72	5.61	37.66	1.51	0.149
5)	99.13	0.87	0.00	-	-

FIGURES

Figure 1: The three diffusion mechanisms: a) surface diffusion; b) grain boundary/interfacial diffusion; and c) solid diffusion.

Figure 2: The solid-liquid-vapour equilibrium for: a) good wetting and b) poor wetting. The relation between the contact angle and the three interfacial energies is given in c). (Source: Reference 43)

Figure 3: The effect of the two extremes of contact angle: a) good wetting, leading to an attractive force and b) poor wetting, leading to a repulsive force. (Source: Reference 43)

Figure 4: De-waxing cycle of test blocks. Specimens are packed in carbon powder throughout the process.

Figure 5: De-waxing cycle of cylindrical dilatometric specimens. Specimens are packed in carbon powder throughout the process.

Figure 6: Sintering cycle of gas treated cemented carbide test blocks

$$\rho = (V/I) \times (\pi d^2/4)$$

Figure 8: Schematic of resistivity measurement set up

Figure 9: General Shrinkage Curves. Percent shrinkage of dilatometric specimens heated at 15 C/min. Shrinkage measurements corrected for thermal expansion.

Figure 10: Enlarged view of the upper temperature region of the general shrinkage curves indicating liquidus temperatures as well. Specimens heated to 15 C/min. Shrinkage measurements corrected for thermal expansion.

Figure 11: Relative electrical resistivity of dilatometric specimens measured after He quenching to R.T. Heating rate was 15 C/min. P_x = resistivity measurement of the highest quench temperature of the particular grade.

Figure 12: Enlarged view of upper temperature region of relative electrical resistivity. Specimens measured after He quenching to R.T.
 Heating rate was 15 C/min.
 P_0 = resistivity of the 10 Ni specimen quenched from 1450 C

Figure 13: Schematic of Interior of Dilatometric Sintering Chamber

Figure 14: Typical example of an isotherm chart. This shrinkage-time strip at 1410 C. Note the *spike* during falling out of the binder phase.

dilatometric shrinkage-time strip
 chart is for a 20 Cr specimen held
 cooling indicating precipitates

Figure 15: Activation energy plot of $\ln d(\Delta L/L_0)/dt$ vs. $1/T$ for 10 Ni at 7% gross shrinkage. Isothermal temperatures set below liquidus temperature, 1370 C (ie. solid state stage). Activation energy = 120 kcal/mole.

Figure 16: Activation energy plot of $\ln d(\Delta L/L_0)/dt$ vs. $1/T$ for 1 Cr at 7% gross shrinkage. Isothermal temperatures set below liquidus temperature, 1380 C (ie. solid state stage). Activation energy = 112 kcal/mole.

Figure 17: Activation energy plots of $\ln 1/t$ vs. $1/T$ for 10 Ni measured at 5%, 7% and 10% gross shrinkage. Isothermal temperatures set below liquidus temperature, 1370 C (ie. solid state stage). All three activation energy plots indicate similar values. Time zero taken at start of isothermal hold. Activation energies at 5%, 7% and 10% are 125, 125, and 121 kcal/mole, respectively.

Figure 18: Activation energy plot of $\ln 1/t$ vs. $1/T$ for 1 Cr at 7% shrinkage. Isothermal temperatures set below liquidus temperature, 1330 C (ie. solid state stage). Time zero taken at start of isothermal hold. Activation energy = 123 kcal/mole.

Figure 19: Activation energy plot of $\ln 1/t$ vs. $1/T$ for 10 Cr at 7% shrinkage. Isothermal temperatures set below liquidus temperature, 1330 °C (ie. solid state stage). Time zero taken at start of isothermal hold. Activation energy = 208 kcal/mole.

Figure 20: Activation energy plot of $\ln 1/t$ vs. $1/T$ for 20 Cr at 7% shrinkage. Isothermal temperatures set below liquidus temperature, 1300 C (ie. solid state stage). Time zero taken at start of isothermal hold. Activation energy = 236 kcal/mole.

Figure 21: Activation energy plot of $\ln 1/t$ vs. $1/T$ for 50 Cr at 7% shrinkage. Isothermal temperatures set below liquidus temperature, 1270 C (ie. solid state stage). Time zero taken at start of isothermal hold. Activation energy = 266 kcal/mole.

Figure 22: Activation energy plot of $\ln 1/t$ vs. $1/T$ for 10 Cr at 10% shrinkage. Isothermal temperatures set above liquidus temperature, 1330 C (ie. rearrangement stage). Time zero taken at start of isothermal hold. Activation energy = 55 kcal/mole.

Figure 23: Activation energy plot of $\ln 1/t$ vs. $1/T$ for 20 Cr at 10% shrinkage. Isothermal temperatures set below liquidus temperature, 1300 C (ie. rearrangement stage). Time zero taken at start of isothermal hold. Activation energy = 64 kcal/mole.

Figure 24: Activation energy plot of $\ln 1/t$ vs. $1/T$ for 50 Cr at 10% shrinkage. Isothermal temperatures set below liquidus temperature, 1270 C (ie. rearrangement stage). Time zero taken at start of isothermal hold. Activation energy = 87 kcal/mole.

Figure 25: Activation energy plot of $\ln 1/t$ vs. $1/T$ for 20 Cr at 10% shrinkage. Isothermal temperatures set below liquidus temperature, 1330 C (ie. sol'n-precip. stage). Time zero taken at start of isothermal hold. Activation energy = 158 kcal/mole.

Figure 26: Activation energy plot of $\ln 1/t$ vs. $1/T$ for 50 Cr at 10% shrinkage. Isothermal temperatures set below liquidus temperature, 1270 C (ie. sol'n-precip. stage). Time zero taken at start of isothermal hold. Activation energy = 163 kcal/mole.

PHOTOGRAPHIC PLATES

Plate 1: Microstructure of 10 Ni Gas Treated and Sintered at 1480 C for 30 Minutes (x 1500)

Plate 2: Microstructure of 10 Cr Gas Treated and Sintered at 1480 C for 30 Minutes (x 1500)

Plate 3: Microstructure of 10 Ni Non-Gas Treated and Sintered at 1520 C for 30 Minutes (x 1500)

Plate 4: Microstructure of 1 Cr Non-Gas Treated and Sintered at 1520 C for 30 Minutes (x 1500)

Plate 5: Microstructure of 10 Cr Non-Gas Treated and Sintered at 1520 C for 30 Minutes (x 1500)

Plate 6: Microstructure of 20 Cr Non-Gas Treated and Sintered at 1520 C for 30 Minutes (x 1500)

Plate 7: Microstructure of 10 Ni Gas Treated and Sintered at 1520 C for 30 Minutes (x 1500)

Plate 8: Microstructure of 1 Cr Gas Treated and Sintered at 1520 C for 30 Minutes (x 1500)

Plate 9: Microstructure of 10 Cr Gas Treated and Sintered at 1520 C for 30 Minutes (x 1500)

Plate 10: Microstructure of 20 Cr Gas Treated and Sintered at 1520 C for 30 Minutes (x 1500)

Plate 11: SEM Photograph of Cut and Polished 10 Ni
Specimen He Quenched from 1050 C (x 1500)

Plate 12: SEM Photograph of Cut and Polished 10 Ni
Specimen He Quenched from 1200 C (x 1500)

Plate 13: SEM Photograph of Cut and Polished 10 Ni
Specimen He Quenched from 1300 C (x 5000)

Plate 14: SEM Photograph of Cut and Polished 10 Ni
Specimen He Quenched from 1350 C (x 5000)

Plate 15: SEM Photograph of Cut and Polished 10 Ni
Specimen He Quenched from 1400 C (x 5000)

Plate 16: SEM Photograph of Cut and Polished 10 Cr Specimen He Quenched from 1050 C (x 1500)

Plate 17: SEM Photograph of Cut and Polished 10 Cr
Specimen He Quenched from 1200 C (x 1500)

Plate 18: SEM Photograph of Cut and Polished 10 Cr
Specimen He Quenched from 1300 C (x 5000)

Plate 19: SEM Photograph of Cut and Polished 10 Cr
Specimen He Quenched from 1350 C (x 5000)

Plate 20: SEM Photograph of Cut and Polished 10 Cr
Specimen He Quenched from 1400 C (x 5000)

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