Sintering Aids in Powder Metallurgy

THE ROLE OF THE PLATINUM METALS IN THE ACTIVATED SINTERING OF REFRACTORY METALS

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When a metallic powder is subjected to a sufficiently high pressure a certain amount of adhesion takes place between individual particles. If this compact is then sintered the bond is improved by diffusion and intergranular grain growth. The earliest known platinum objects were fabricated by such a powder metallurgical process, and when European scientists first addressed the problem of manufacturing platinum bars they also used powder metallurgy to overcome their inability to melt the metal. Now powder metallurgical methods are widely used for fabricating a variety of materials, and this paper reviews studies made of the sintering of refractory metals when this process is promoted by the addition of a minor amount of a platinum group metal activator.

The manufacture of engineering metals and alloys in fabricated forms generally commences with the melting and casting of ingot material for subsequent shaping by mechanical techniques, such as forging, rolling and extrusion, although in many instances molten metal can be cast directly to a final shape. However, in the case of the refractory elements, such as tungsten, molybdenum and rhenium, their very high melting points (in excess of 2000°C), as well as their resistance to deformation, generally precludes the melting approach as a practical route to material and component manufacture. This has led to the development of processes in which consolidation of powder materials is achieved by sintering at temperatures below their melting points.

To promote and assist the sintering process, two techniques have been developed which involve the use of metallic sintering additives. These are known as Liquid Phase Sintering and Activated Sintering. In Liquid Phase Sintering the refractory metal powders are sintered in the presence of one or more metals—generally transition metals such as copper or iron—at temperatures **above** the melting point of the additive, so that sintering occurs in a molten binder phase which may be present in substantial amounts, for example up to 40 per cent by weight.

In contrast, Activated Sintering is performed in the presence of small amounts of metal additives, again often transition metals, but in the solid state at temperatures **below** the melting point of the additive. Thus, as can be seen from Table I, Activated Sintering can be accomplished at lower temperatures than Liquid Phase Sintering, although not necessarily so, depending on the particular metal additive used. In both cases, however, the temperatures employed are substantially lower than would otherwise be required if the refractory powders were sintered without additives. Kurtz, for example, showed in 1946 that 99 per cent dense tungsten parts could be achieved by sintering below 1400°C with less than 1 wt. per cent addition of nickel (1), whereas temperatures above 2800°C are required to achieve a comparable density in untreated tungsten powder.

Activated Sintering

Since Vacek reported the enhancement of sintering by additions of small quantities of transition metals to tungsten in 1959 (2),

Table I

Typical Sintering Temperatures for Activated Sintering and Liquid Phase Sintering of Refractory Metals

Refractory element	Melting point, °C	Activated sintering		Liquid phase sintering	
		Additive	Sintering temperature, °C	Additive	Sintering temperature, °C
Tungsten	3410	Nickel	1100	Nickel	1550
		Palladium	1100	Copper	1100
Molybdenum	2610	Nickel	1200	Nickel	1460
		Palladium	1200		
Tungsten carbide	—	—	—	Cobalt*	>1350

*The tungsten carbide-cobalt eutectic temperature is 1320°C

making it possible to lower the sintering temperature substantially, a great deal of work has been carried out into the activated sintering of tungsten and other refractory metals, particularly with additions of Group VIII transition metals. Much of this work has involved the use of platinum group metals which have been shown to be very effective as sintering activators. This paper reviews the published work on the effect of the platinum group metals on the activated sintering of tungsten and other refractory metals, in particular on the kinetics and mechanisms of sintering. The properties and microstructure of the sintered materials are also examined. Finally, the scientific basis for the beneficial effect of the platinum group metals in the activated sintering of the refractory metals is examined in terms of current theories and phenomenological models.
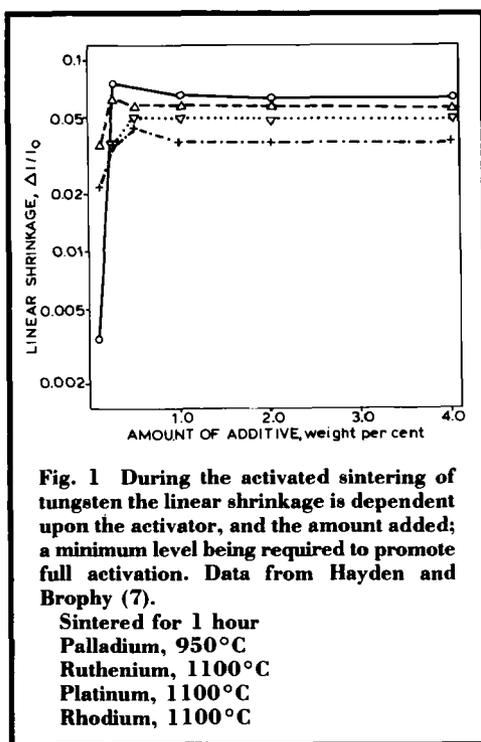
Tungsten

Much of the early work on the activated sintering of tungsten was carried out by Brophy, Hayden and co-workers (3–7). Their initial work focused on the sintering of tungsten powder coated with nickel. They found that, on sintering at 1100°C, the tungsten underwent rapid densification to more than 90 per cent theoretical density. Moreover, they found that the amount of nickel required to promote this accelerated sintering was roughly equivalent to a nickel coating thickness of about 1 atom monolayer (3). Nickel coatings thicker than this

did not produce any further enhancement; indeed, there was a tendency for the sintering rate to decrease from the optimum. They also found that densification occurred in two stages, the second stage coinciding with the onset of grain growth in the tungsten (4).

In an attempt to clarify the mechanism of activated sintering, which they had earlier attributed to the activating metal acting as a carrier phase for the diffusion of tungsten to the interparticle "necks", Hayden and Brophy examined the influence of ruthenium, rhodium, platinum and palladium additions on the kinetics of sintering in the temperature range 850 to 1100°C (7).

As in their previous work, the platinum group metal sintering additives were added to the tungsten powder in the form of aqueous solutions of salts (chlorides and nitrates) in the requisite amount; this was dried at 150°C and prereduced in hydrogen at 800°C to form a metallic coating on the tungsten powder. Sintering was carried out under hydrogen.

For all the platinum group metals examined, Hayden and Brophy found that a minimum level of platinum group metal was required to promote full activation, see Figure 1, as had been observed in the case of nickel, and that larger amounts did not produce any further enhancement. Interestingly, palladium was the most effective element; this is clearly illustrated in Figure 2 which shows the temperature dependence of shrinkage for each platinum

Fig. 1 During the activated sintering of tungsten the linear shrinkage is dependent upon the activator, and the amount added; a minimum level being required to promote full activation. Data from Hayden and Brophy (7).

Sintered for 1 hour
Palladium, 950°C
Ruthenium, 1100°C
Platinum, 1100°C
Rhodium, 1100°C

group metal additive after sintering for 1 hour. Ruthenium was the least effective element. Significantly, the authors found that palladium was better than nickel in promoting densification. For example, the densities of samples sintered at 1100°C for 30 minutes and 16 hours were 93.5 and 99.5 per cent, respectively, in the case of palladium in tungsten compared to 92 and 98 per cent, respectively, for nickel in tungsten. Untreated tungsten would only be presintered at this temperature.

Analysis of the sintering kinetics in terms of the process controlling mechanism in their carrier phase model of activated sintering—which applies also to liquid phase sintering—showed that for all the platinum group metals examined, the sintering rate was not dependent upon composition, but was proportional to the cube root of time, except for rhodium in a low shrinkage regime. This time dependence was interpreted in terms of the diffusion controlled transport of tungsten in the interface between the tungsten and the platinum group metal

coating layer. In the case of rhodium there is a transition in the rate controlling process, from the dissolution of tungsten in the rhodium layer at low shrinkages to interface diffusion at large shrinkages. Table II summarises these results, the slope, S, being the time dependence of the sintering curves.

Also shown in Table II are the calculated activation energies for each platinum group metal additive. These lie in the range 86 to 114 kcal/mol, which the authors believed to be comparable to the activation energy for tungsten grain boundary self-diffusion.

The effectiveness of the platinum metals and nickel in promoting enhanced sintering of tungsten were found to be in the order:

Pd > Ni > Rh > Pt > Ru

The reason for the platinum group metals being such effective activators for the sintering of tungsten was not established in this work, although it was suggested that it may be linked to their relatively high (10 to 20 per cent) solubility for tungsten and their low solubility in tungsten.

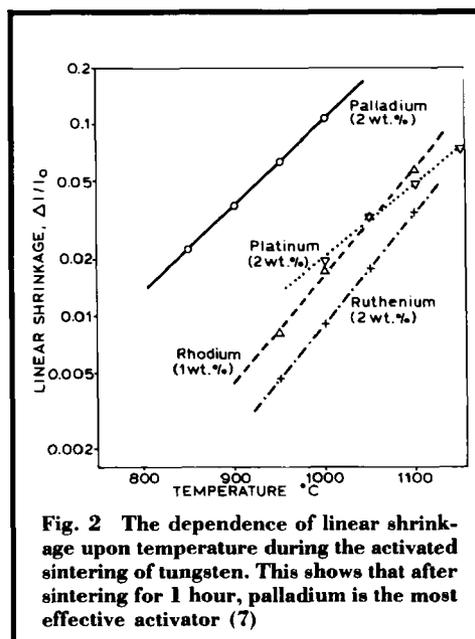Subsequently Hayden and Brophy extended their work on platinum group metal activators

Fig. 2 The dependence of linear shrinkage upon temperature during the activated sintering of tungsten. This shows that after sintering for 1 hour, palladium is the most effective activator (7)

Table II

**Summary of the Effect of Platinum Group Metal Additives
on the Sintering of Tungsten (Data from References 7 and 3)**

| Additive	Slope 'S'	Control of process	Activation energy, kcal/mol
Palladium	0.33	Diffusion	86
Ruthenium	0.39	Diffusion	114
Platinum	0.33	Diffusion	92
Rhodium [a]	0.5	Solution	85
Rhodium [b]	0.33	Diffusion	98
Nickel	0.5	Solution	68

(a) Rhodium : low shrinkage regime
(b) Rhodium : high shrinkage regime

to the sintering of tungsten with iridium additions (8). In contrast to the other platinum metals, they found that iridium actually decreased the rate of densification of tungsten, the effect reaching a minimum value at about 2 wt. per cent iridium, larger additions having no further effect. The measured activation energy of 133 kcal/mol was close to that for volume self-diffusion of tungsten (135 kcal/mol).

Further work on the activated sintering of tungsten by palladium and nickel additions was carried out by Toth and Lockington, who also found that there were optimum concentrations of both palladium and nickel for maximum densification during sintering at 1000°C (9). Calculations showed these optimum concentrations to correspond approximately to a monolayer of the activating element on the tungsten surface, as also found earlier by Brophy, Shepherd and Wulff (3). Once again, palladium was found to be more effective than nickel, especially at and below a temperature of 950°C. Toth and Lockington found the time dependence of the densification to be 0.5 for both palladium and nickel, in contrast to the value of 0.33 for palladium found by Brophy (7). The apparent activation energies were lower, 62.5 kcal/mol compared to 86 kcal/mol for palladium and 50.6 kcal/mol as against 68 kcal/mol for nickel. Microprobe analysis of the fracture surfaces of sintered specimens showed segregation of the activating elements on grain boundary surfaces. The authors concluded that Brophy's model for activated sintering was not

applicable; rather, they favoured a mechanism in which the surface diffusion of tungsten on the activator surface is the controlling step; both are shown schematically in Figure 3.

The influence of a wide range of transition metal additions, including all the platinum group metals, on the sintering of tungsten at temperatures between 1000 and 2000°C was studied by Samsonov and Jakowlev (10). They found, in agreement with earlier findings, that additions of Group VIII elements—including the platinum group metals—promoted densification of tungsten, with the exception of osmium which was neutral. Iridium had a small beneficial effect at the highest temperature studied, 2000°C, which is not inconsistent with the earlier work of Hayden and Brophy (8), since extrapolation of their Arrhenius plots predicts a transition from a detrimental to a beneficial effect at temperatures above about 1400°C. The effectiveness of the platinum group metals in enhancing sintering was found to be in the order:

$$Ru < Rh < Pd$$
$$and \quad Os < Ir < Pt$$
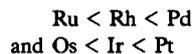
with the upper row of elements being superior to the lower row. This is shown in Table III, which also gives the measured values of compressive strength, hardness and grain size. On this basis, nickel appears to be slightly more effective as an activator than palladium, in contrast to the earlier work, but this is based on results obtained at higher sintering temperatures than those of the earlier studies.

Fig. 3 These two models show different representations of the sintering of tungsten particles which have been coated with a metallic activator.
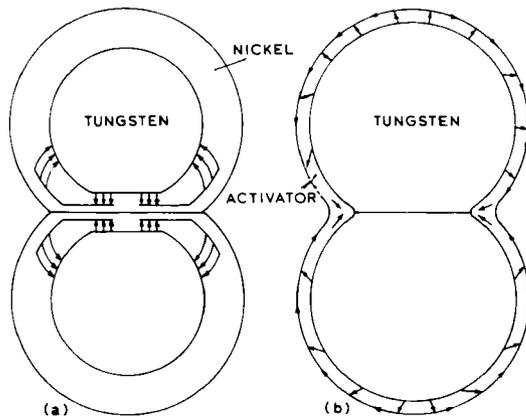
(a) The model of Brophy, Hayden and Wulff (3) has tungsten diffusing through the carrier (activator) phase, away from the line joining the centres of adjacent particles, to be redeposited elsewhere on the particles as indicated by the arrows. (b) The model of Toth and Lockington (9), where dissolution of tungsten at the activator-tungsten interface is followed by volume diffusion outwards through the activator layer and subsequent surface diffusion, this being the rate controlling step. Diffusion through the activator layer to the contact point between adjacent particles results in the formation of sintering "necks"

These results show that the stronger activators also enhance the associated grain growth in the final stage of sintering. The higher densities (lower porosity) achieved are also reflected in higher values of compressive strength and hardness.

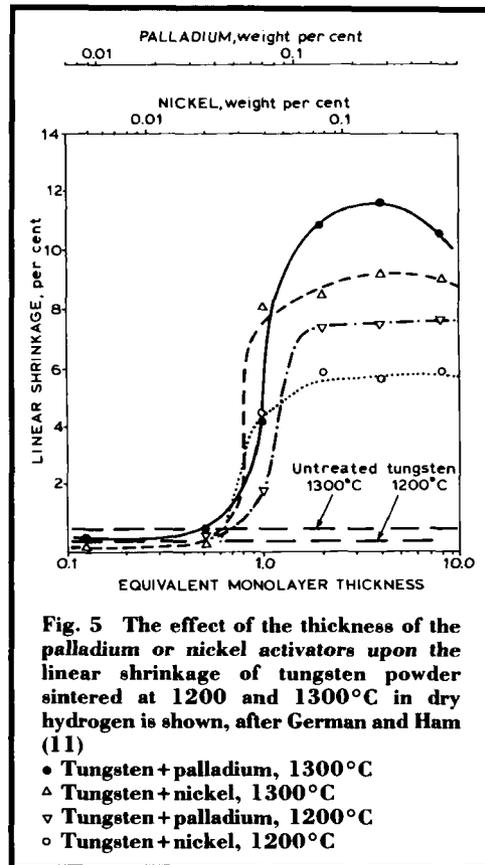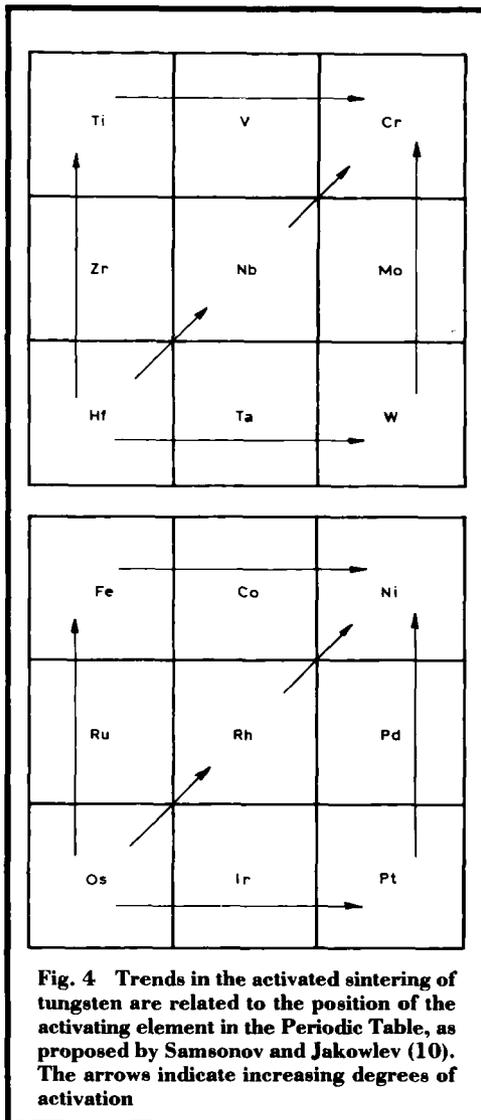Samsonov and Jakowlev summarised their findings in terms of the position of the activating element in the Periodic Table, Figure 4. The arrows indicate an increasing degree of activation. They interpreted these results in terms of the electron structure of the activators and tungsten; an increase of the stable d-bonds in the system lowers the free energy, activating the sintering process in which diffusion is accelerated by the activators for which tungsten acts as an electron donor.

More recently, German and his co-workers

Table III					
Dependence of the Properties of Tungsten on the Activating Element at the Optimum Concentration and Sintering Temperature (10)					
Activator, weight per cent	Sintering temperature, °C	Density, g/cm³	Compressive strength, kg/mm²	Hardness, kg/mm²	Tungsten grain size, μm
W	2000	16.1	80	181	5–7
Fe (0.5–1.0)	1600	17.4–17.95	92–96	310–390	12–15
Co (0.3–0.4)	1600	17.4–17.95	83–87	277–282	20–25
Ni (0.2–0.4)	1400–1600	18.1–18.4	91–95	280–306	100–120
Ru (1.0)	1600–1800	17.4	77	309	15–20
Rh (0.5)	1600	17.8	71	290	10–15
Pd (0.3–0.4)	1400–1600	18.1–18.35	83–90	290–300	20–25
Os (1.0)	2000	16.1	80	181	5–7
Ir (1.0)	2000	16.7	98	238	5.5–7
Pt (1.0)	1800–2000	17.6–17.9	88–93	305–330	20–30

have investigated the activated sintering of tungsten in more detail (11–13). German and Ham (11) confirmed that palladium is the best metallic activator for the sintering of tungsten in the range 1100 to 1400°C, as shown in Figure 5. This shows that, for both palladium and nickel, enhancement of sintering starts at approximately 1 monolayer thickness of additive and peaks at a thickness of 4 monolayers. Sintering in a moist hydrogen atmosphere was found to be detrimental to palladium activation

Fig. 5 The effect of the thickness of the palladium or nickel activators upon the linear shrinkage of tungsten powder sintered at 1200 and 1300°C in dry hydrogen is shown, after German and Ham (11)
• Tungsten + palladium, 1300°C
△ Tungsten + nickel, 1300°C
▽ Tungsten + palladium, 1200°C
○ Tungsten + nickel, 1200°C

Fig. 4 Trends in the activated sintering of tungsten are related to the position of the activating element in the Periodic Table, as proposed by Samsonov and Jakowlev (10). The arrows indicate increasing degrees of activation

for one tungsten powder, but beneficial for a second. The apparent activation energy is lowered on sintering in a moist atmosphere.

German and Munir (12) extended this work to other Group VIII elements including platinum, and confirmed that enhanced sintering commenced at about 1 monolayer thickness and peaked at 4 monolayers. They found the effectiveness of the activator to be in the order:

Pd > Ni > Pt = Co > Fe > Cu

Below 1300°C, iron was more effective than platinum and cobalt. In the case of palladium and nickel, where sintering progressed to the second stage, extensive tungsten grain growth was observed. The onset of grain growth was associated with a decline in the shrinkage rate. The authors found a time dependence of the shrinkage for all activators, similar to that found by Toth and Lockington, favouring

volume diffusion of tungsten through the activator layer as the rate controlling mechanism. The addition of 0.4 weight per cent palladium was found to increase the apparent grain boundary diffusion rate by about 6 orders of magnitude, corresponding to a decreased activation energy. The measured activation energies decreased in the order of increasing activator effectiveness, palladium having the lowest value. This was related to the electron structure modifications as postulated by Samsonov and Jakowlev (10), that is the transition metals with unfilled d-shells are the optimal activators for tungsten. Based on this concept, the authors suggest that palladium and nickel are optimum activators for all refractory metal powders.

Later work by Li and German examined the properties of palladium- and nickel-activated tungsten sintered with optimum activator content in the temperature range 1200 to 1600°C (13). Hardness levels were in the order Pd > Ni > Co > Fe at lower temperatures, as can be seen in Figure 6, but were closer together at the higher temperatures. In the case of transverse rupture strength, nickel-activated tungsten was stronger than palladium-activated tungsten, the strength decreasing with increasing sintering temperature above 1400°C due to rapid grain coarsening. For the 0.43 weight per cent palladium-activated material, the grain size increased from 4.5μm at 1200°C to 18.0μm at 1400°C and to 28.5μm at 1600°C.

Recent work on activated secondary recrystallisation of heavily-drawn doped tungsten wire has provided additional evidence for the influence of the activators during sintering (14). In this work the tungsten wire was coated with palladium, platinum or nickel prior to annealing and the rate of secondary recrystallisation measured. The highest rate of recrystallisation was found in the presence of palladium, followed by nickel and then platinum, grain growth being induced at temperatures several hundred degrees lower than uncoated tungsten wire. The process was controlled by the penetration of the activating elements into the wire. The diffusivities of these were found to be

much higher than in prerecrystallised tungsten, which is attributed to the high diffusivity paths through an intergranular phase formed by the activator which segregates to the grain boundaries. Auger electron spectroscopy revealed this layer to be about 2nm thick for both palladium and nickel. The measured diffusivities of the activators were in the order:

$$Pd > Ni > Pt > Co$$

Studies by Gessinger and Buxbaum on electron emission from thoriated tungsten cathodes has shown that platinum can also activate enhanced diffusion of thorium to the surface along grain boundaries, enabling the temperature limit for electron emission to be extended
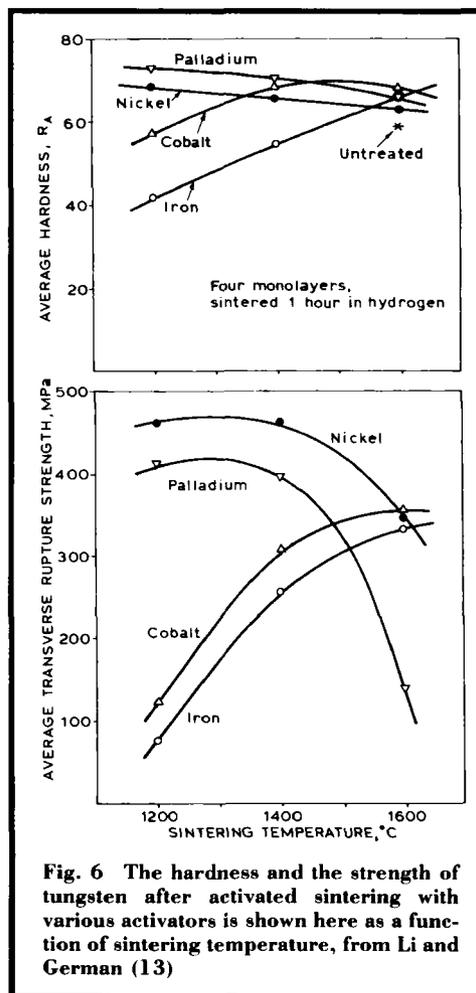

Fig. 6 The hardness and the strength of tungsten after activated sintering with various activators is shown here as a function of sintering temperature, from Li and German (13)

from 1950 to 2150K and the maximum emission current to be increased from 3 to 7.5 A/cm² (15). This work demonstrates that platinum group metals not only enhance the diffusion of tungsten, but can also enhance the diffusion of other elements in the tungsten grain boundaries.

Molybdenum and Other Refractory Metals

As with tungsten, several investigators have shown that both palladium and nickel can enhance the sintering of molybdenum, for example see References 16 to 18. Further, more detailed work on the activated sintering of molybdenum by platinum group metal additions has been carried out by German and his co-workers in the U.S.A. (19, 20). Their work on the heterodiffusion modelling of tungsten was extended to molybdenum where the effect of 13 transition metal additions including rhodium, palladium, iridium and platinum was examined in the temperature range 1000 to 1350°C (19). Again, they found that activation of sintering commenced at activator concentrations equivalent to 1 monolayer thickness and reached the maximum effect at about 10 monolayers' thickness, although this plateau shifted to greater thicknesses with increasing sintering temperature. They confirmed that palladium was the best activator for molybdenum, with the degree of effectiveness being in the order:

Pd > Ni > Rh > Co > Pt > Au > Fe

As in the case of tungsten, iridium was detrimental to the sintering of molybdenum. The activation energy for sintering decreased with increasing effectiveness of the activator, that for palladium-activation being 280 kJ/mol (66.9 kcal/mol) compared to 405 kJ/mol (96.8 kcal/mol) for untreated molybdenum. This decrease in activation energy for palladium, nickel and platinum was observed to be concentration dependent, a rapid decrease occurring at about 1 monolayer thickness and reaching a minimum value at the optimum concentration of about 10 monolayers. The authors concluded that the sintering process was in accord with the grain boundary heterodiffusion model developed earlier for tungsten (21).

Later studies by German and Labombard (20) on palladium, nickel and platinum additions to two different molybdenum powders of the same particle size sintered at low temperatures (1050 to 1150°C) confirmed the earlier findings, namely that palladium is the best activator, followed by nickel and platinum, and that sintering behaviour conformed to the heterodiffusion model.

German and Munir also studied the activated sintering of hafnium (22) and tantalum (23) with transition metals as part of their broader investigation into the mechanisms, particularly the d-electron exchange model proposed by Samsonov (10). In the case of hafnium, the activators were added to a thickness equivalent of 4 monolayers. Isothermal sintering experiments in the range 1050 to 1450°C showed densification after 1 hour in the following order of enhancement:

Ni > Pd > Co > Pt
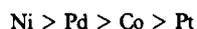
Cobalt and platinum were only beneficial at temperatures above about 1300°C. Unusually, a non-Arrhenius temperature dependence was found for the activated sintering, and this was confirmed by constant heating rate experiments which showed sharp peaks for some activators at varying temperatures. These peaks occurred at about 1375°C for palladium and about 1240°C for nickel, for example, and are indicative of an optimum sintering temperature for maximum densification enhancement. It was concluded that the activated sintering of hafnium does correlate with the electron structure model, although the activators only impart a limited benefit.

In their study of the activated sintering of tantalum in the range 1250 to 1700°C, German and Munir found only slight enhancement with platinum, palladium and rhodium (23). The poor enhancement of palladium was particularly surprising, but examination of fractured surfaces suggested that palladium enhanced only surface diffusion, not bulk diffusion.

The use of palladium and nickel as activators in the sintering of chromium has been studied

Fig. 7 This geometric model of the heterodiffusion controlled activated sintering process shows the activator layer wetting the interparticle grain boundary, after German and Munir (29)
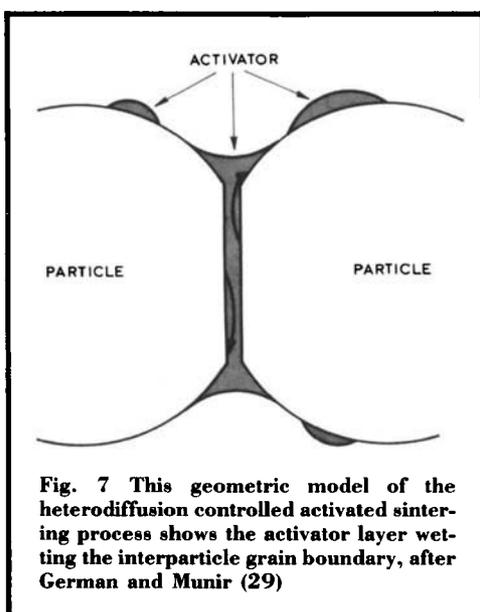
at the Tokohu University in Japan (24). It was found that palladium enhanced sintering considerably, the degree of enhancement reaching a plateau at about 0.8 wt. per cent palladium over the range 1050 to 1200°C. Above 1200°C, on sintering for 1 hour, the extent of enhancement became suppressed; this was mainly an effect of the higher density levels achieved at the higher temperatures and a reflection of the retardation due to grain growth in the second stage. In contrast, nickel had little activating effect. The relative behaviour of palladium and nickel was interpreted by the authors in terms of the mutual solubility criterion suggested earlier by Hayden and Brophy (7). Palladium-chromium fulfils this requirement whereas nickel-chromium does not.

The activated sintering of rhenium and tungsten-rhenium mixtures has been studied by several investigators (25–28). Dushina and Nevskaya found that on sintering rhenium for 2 hours in the range 1300 to 2000°C, substantial enhancement of sintering occurred with palladium contents of 0.1 to 0.5 weight per cent (25). Maximum enhancement was found in the range 0.2 to 0.4 wt. per cent palladium. This enhancement was observed to be accompanied

by substantial grain growth, grain sizes of 10 to 15μm being observed compared to 1 to 2μm for untreated rhenium. Sintering at 1800°C produced densities of 92 per cent in 0.2 wt. per cent palladium-activated rhenium and only 81 per cent for untreated rhenium.

In their study on the sintering of rhenium, German and Munir found that at 1000°C only platinum enhanced sintering, while elements such as palladium, nickel, iron and cobalt inhibited densification (26). The enhancement effect of platinum commenced at a thickness of about 1 monolayer, reaching a peak at about 2 monolayers. At 1400°C, both platinum and palladium enhanced sintering, platinum becoming effective at about 1 monolayer, rising to a plateau of maximum effectiveness at about 4 monolayers. Palladium acts less rapidly, reaching that of platinum at about 10 monolayers thickness, which suggests that palladium would be better than platinum at higher concentrations. The results of this study were considered to correlate with the electron structure model reasonably well.

The study of palladium additions to co-reduced tungsten-rhenium powders by Shnaiderman and Skorokhod again illustrates the beneficial effect of palladium in activated sintering of refractory metals, although in this instance palladium-rich alloy interlayers are formed at the grain boundaries (28).

Models of Activated Sintering

As we have seen, the activation of sintering refractory metal powders by transition metal elements has been interpreted in terms of several models, which are generally qualitative in nature. The results of the many studies on several refractory metals have shown a reasonably consistent pattern in that the most beneficial activators are palladium, nickel and platinum, generally in that order. Since these three elements sit in the same column of the Periodic Table, it is reasonable to assume that their role is related to their electronic structure and its ability to promote rapid diffusion of the refractory element. The time, temperature and activator concentration dependencies are also

Fig. 8 The position of the activator in the Periodic Table affects the densification of the tungsten. There is good agreement between the predictions of the heterodiffusion model (29) and experimental consensus

similar for all the refractory metals studied, which suggests that there is a common basis for a generalised model (29).

The initial model postulated by Hayden and Brophy was based on a solution-precipitation approach in which the relative solubilities of the activator in the refractory element and the refractory metal in the activating element should be low and high, respectively (7). In this model, illustrated schematically in Figure 3(a), the refractory element diffuses away from the interparticle boundary and is redeposited elsewhere on the particle surface—as indicated by the arrows in the Figure. Experimentally the rate controlling step is found to be either refractory metal diffusion at the interface with the activator layer, or refractory metal solution in the activator layer.

Later, Samsonov and Jakowlev proposed that activated sintering was a consequence of the electronic structure stabilisation of the refractory metal caused by the additive metal (10). They based this approach on the argument that a metallic system containing partially filled d-subshells becomes more stable as the number of d^5 and d^{10} electron configurations increase. The refractory element acts as an electron donor, and this ease of electron transfer gives

rise to the high solubility in the activating element.

A more recent proposal by German and Munir takes this model further (21) and applies the Engel-Brewer theory (30) to the prediction of the activation energies for the diffusion of refractory metals through the activator layer. In this quantitative model the activator has a role in providing enhanced grain boundary diffusion of the refractory metal. This is shown schematically in Figure 7, with the activator layer wetting the interparticle grain boundary. This is taken from Reference 29, where a more detailed description of these models is given. The relative solubility criterion is a prerequisite for enhanced diffusion of the refractory metal. Enhanced mass transport, and hence densification, results from the lowering of the activation energy for the refractory metal in the activator.

German and Munir have shown (29) that their calculated values of activation energy for diffusion of molybdenum agree well with experimentally determined values (19). These calculations indicate that palladium, nickel and platinum are the best activators, as shown experimentally for several refractory metals. The predicted shrinkages for molybdenum also

agree well with experiment, as shown in Table IV (29). Figure 8 shows the good agreement between their predictions and the experimental consensus for tungsten in terms of the position of the activator in the Periodic Table. This clearly demonstrates the superiority of palladium as an activator, with rhodium and platinum also in significant positions.

More recently, Miodownik has proposed a quantitative figure of merit for assessing the potential of additive elements as activators (31). This parameter, ϕ, has been derived by combining the relevant heats of solution, surface energies and the energy of vacancy formation in the activator, and is based on the underlying thermodynamic parameters that are responsible for the phase equilibria; the solubility criterion of the earlier models is an aspect of the latter:

$$\phi = \Delta H_1 + \Delta H_2 + \Delta H_3$$

where ΔH_1, ΔH_2 and ΔH_3 are thermodynamic functions related to solubility, segregation and diffusion, respectively. Using calculated values of ϕ for the sintering of tungsten, Miodownik's predictions are correct for 12 out of 14 activator elements shown in Figure 8, the only discrepancies being manganese and gold. Once again palladium is predicted to be the most effective activator.

Properties of Sintered Materials

While there has been a considerable number of studies into the phenomenon of activated sintering, relatively few studies have measured the properties of the sintered materials. Fracture is generally intergranular in nature, suggesting that the activator-rich grain boundaries are paths of easy fracture. Strength and hardness are very density dependent and the effectiveness of the activator on densification clearly plays a major role. Thus, both type and concentration of the activator influence sintered strength, as shown in Table III and Figure 6. Strengths as high as 1050 MPa have been shown for palladium-activated tungsten (10).

No data have been presented for high temperature creep properties, but the enhancement of grain boundary diffusion in the

Table IV

Comparison of Predicted and Measured Shrinkage for the Activated Sintering of Molybdenum Powder (29)

2.2μm size: sintered 1 hour at 1250°C in hydrogen

Activator	Shrinkage, per cent	
	Predicted	Measured
Untreated Mo	1.6	2.1
Pd	8.9	8.2
Ni	6.9	7.2
Pt	4.7	3.6
Co	4.6	4.3
Fe	3.5	2.2
Cr	1.1	1.1

presence of activators would be expected to promote diffusional creep of the Coble type.

As stated above, the use of platinum group activators can promote enhanced electrical properties: Gessinger and Buxbaum have utilised the increased grain boundary diffusivity in platinum-activated thoriated-tungsten emitters to improve electron emission (15).

Summary

This paper has reviewed the numerous studies of the activated sintering of refractory metals by transition metal additions and has shown that the platinum group metals, and particularly palladium and platinum, even at amounts of less than 1 per cent by weight, are very effective in promoting densification at temperatures several hundred degrees lower than would otherwise be required. The models developed to describe the phenomenon have been examined and those of German and Munir (29) and Miodownik (31) have been shown to predict the order of effectiveness remarkably well. Significantly, palladium is predicted to be the best activator element for several refractory metals including tungsten and molybdenum, in accord with experimental findings. The enhanced densification that results from the use of platinum group metal activators leads to improved strength properties.

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Oxidation Behaviour of Some Platinum Alloys

For a limited number of specialised applications, such as for jewellery, the aesthetic appearance of a material is a crucial factor. Clearly the appearance must be pleasing at the time of purchase, and for precious metal items it is equally important that they should not lose their appeal with use or the passage of time.

Recently the results of a study sponsored by Rustenburg Platinum Mines Limited into the oxidation behaviour of a number of commercially available platinum-rich and 18 carat gold alloys has been reported (A. Wells and I. Le R. Strydom, *J. Mater. Sci., Lett.*, 1986, **5**, (7), 743–746). The reactivity of the alloys was assessed by examining them in both the as-received condition and after heating at 150°C for 24 hours under a flow of oxygen.

After this treatment it was observed that both the gold alloys had undergone a colour change, but no changes were perceived on the four platinum alloys, which contained 5 weight per cent cobalt, 10 and 15 palladium, and 7 palladium plus 3 cobalt.

Auger electron spectroscopy detected surface segregation of alloying elements on all samples, except for the alloy containing cobalt, an element for which the technique is insensitive. In general, the platinum alloys showed no significant changes as a result of the oxidation treatment, although minimal oxidation-enhanced copper enrichment was observed on the surface of the platinum-15 palladium alloy, in which a small amount of copper is incorporated.

From this study it was concluded that the platinum alloys examined were significantly less environmentally reactive than the two gold alloys, under oxidising conditions at near ambient temperatures.