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Author(s): B. Viswanathan
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Metallization of plastics by electroless plating

B. Viswanathan

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

Metallization of plastics is essential for a variety of applications like printed circuit boards, electromagnetic interference shielding, magnetic film devices and MICs. Electroless plating has gained considerable importance in the last 20 years and this review attempts to examine the scope of this process, the science behind each of the steps involved as well as outlines the electrochemical aspects of this plating process.

Of the available liquid state metallization processes for plastics, electroless process has gained remarkable importance in the last 20 years, even though, the administrator of the invention from NBS Dr Blum did not anticipate any tremendous commercial use for this process[1]. However, the following statements from P&SF report[2] that 'computer memory devices represent a growing market for electroless nickel plating.... The US government has saved the public several million dollars for the past few years by using electroless nickel.... Electroless copper baths without formaldehyde may be the wave of the future in circuit board plating' show that this anticipation was completely proved to be wrong. In fact plating of plastics has become an important segment of the metal-finishing industry in the US[3] and in many other developed and developing countries. Shipley[4] predicts that commercial usage of electroless plating will grow quite rapidly during the next 10 years (since 1984). Applications will increase in number as design engineers and advanced engineering groups learn more about the capabilities and advantages of electrolessly plated metals and alloys.

Starting from nickel electroless plating by hypophosphite by Brenner and Riddell[5], other metals and reducing agents have been used for the electroless deposition on plastics. The available data (Table 1) show that only a limited number of metals can be deposited by electroless method. However, this method has gained commercial applications in many sectors like aerospace, automotive, computers, electronics machinery and so on due to the unique properties of this deposition technique. The main reasons for using electroless method in preference to other methods,

Table 1. Typical metal coatings by electroless deposition — summary of available data

Deposit	Year	Medium	Reducing agent	First inventors	Ref.
Ni–P	1946		Sodium hypophosphite	Brenner and Riddel	51–53
Co–P	1947	Alkali			53
Ni			Hydrazine hydrosulphides		54
Ni–B	1958		Dimethylamineborane, borohydrides		54, 55
Co–Ni–P	1973		Sodium hypophosphite		53, 56
Ni–B–Th	1981			Matsuoka and Hayashi	57
Co–B		Acid/alkali	Dimethylamineborane		57
Cu	1947			Narcus	58, 12
		Alkali	Formaldehyde		59–66
		Alkali	dimethylamineborane		67
		Alkali			68, 69
Pd–P	1968	Alkali	Sodium hypophosphite		58, 70
Pd	1961	Alkali	Hydrazine ter.	Rhode	71
			amineboranes		72
Au	1970		Amineborane	Okino	73, 74
			borohydride		75
Au–Cu	1982		Formaldehyde	Molenaar	76
Ag	1974		Dimethylamine borane	Pearlstein	77
Sn	1980		Titanium trichloride	Warwick and Shirley	78
Alloy	1970			Malloy	79
Polyalloys	1965			Pearlstein and Weightman	80
Composites	1974			Parker	81

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especially electrolytic plating, are:

- the feasibility of obtaining uniform deposits over irregular surfaces
- the possibility of direct deposition on nonconductors
- the flexibility of depositing on isolated areas
- the desirable characteristics of the deposits namely, less porous and more corrosion-resistant and unique deposit properties
- the possibility of bulk plating and semibulk racking.

The electroless deposit is usually achieved by using a bath containing at least five functional components, namely

- a metal salt as the source for the deposited metal
- a reducing agent
- a complexing agent
- a pH adjusting agent
- a stabilizing agent and other functional additives.

For each one of these components, one has a variety of substances to choose from. Here we examine the science behind this process especially that of electroless copper and evaluate the relative merits of the choices, especially in the context of metallization of plastics.

Scope of electroless deposition

Riddell and Brenner invented this process during their investigations on the electrodeposition of nickel–tungsten and cobalt–tungsten alloys on the interior of a liner using an ammoniacal citrate–nickel–tungsten plating bath with an insoluble anode. In order to prevent the oxidation of organic components which affected the quality of the deposit they added various reducing agents to the bath. When hypophosphite was used as the reducing agent, they observed that the current efficiency was higher and, at the same time, the outside of the liner was also plated. This marked the beginning of the autocatalytic chemical plating, which is popularly known as 'electroless' plating today. Though Brenner called it electrodeless process, Blum coined the term 'electroless' to indicate that the process is similar to electroplating in that a metal coating is produced but the dissimilarity arises in that in the former process no external electric current is involved. It should be remarked that though the effect that sodium hypophosphite would reduce nickel and cobalt salts to the metallic powder was known even 30 years earlier to this invention, the achievement is that by a controlled autocatalytic process one could produce a smooth, coherent metal coating. This was followed by a series of investigations by Gutzeit and his group[6–9] on electroless deposition of Ni–P system, wherein the role of many other additives like chelates, exaltants, buffers, stabilizers was examined and operating conditions for obtaining a desirable rate of deposition were formulated[6–11]. In many aspects the electroless deposits exhibit different structures, physical and mechanical properties, fatigue strength and corrosion resistance compared to that of electrolytic deposits. A typical compilation[4] of the comparison of the properties of electroless Ni–P alloy and of electrodeposited nickel is given in Table 2.

Electroless copper has seen remarkable developments starting from Narcus[12] who reported the practical reduction of copper on nonconductors in 1947 and Cahill[13] who described autocatalytic chemical reduction of copper from alkaline copper baths using formaldehyde as the reducing agent. The success story of copper baths is mainly due to the introduction of effective stabilizing agents like mercaptobenzothiazole[14], thiourea[15], cyanide[16] and sulphur compounds[17,18]. Because of the better corrosion resistance and other favourable properties of electroless copper it is preferred over electroless nickel on plastics. The interest in electroless cobalt is mainly due to their magnetic

Table 2. Comparison of properties of deposits from electroless (Ni with approximately 8% P) and electrolytic nickel (ref. 4)

Properties	Electrolytic 99%+ Ni	Electroless average 92% Ni/8% P
Composition	99+ Ni	Average 92% Ni/8% P
Appearance	Dull to bright	Semibright
Structure	Crystalline	Amorphous
Density	8.9	Average 7.9
Thickness uniformity	Varies	±10%
Melting point	1455° C	890° C
Hardness as plated (kg/mm²)	150–400	500–600
Heat hardening (kg/mm²)	No effect	1000
Wear resistance corrosion	Fair	Excellent
Resistance	Good (porous)	Very good (few pores)
Relative magnetic susceptibility	36%	
Electrical resistivity (microohm/cm)	7	60–100
Thermal conductivity (cal/cm/sec/C)	0.16	0.01–0.02
Coefficient of thermal expansion (in/in/F × 10)	7.5	7.8
Modules of elasticity (Ksi)	30	10
Elongation	6–30%	2%
Internal Stress (ksi)	±10	±10
Friction coefficient vs steel		
Unlubricated	Galling	0.38
Lubricated	0.2	0.2

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properties which can be exploited for recording, storage and switching device applications. Attempts to produce electroless deposits of polyalloys[19] as well as composites[20] were successful in 1970 in addition to that of Au, Ag and tin.

Electroless gold plating continues to be an area of considerable activity. The studies pursued now involve formulation of baths with long-term stability, increased plating rate and improved throwing power. Carbonates of sodium and potassium in combination with amines like mono-, di-, and trialkanol amines and ethylene di- and tri-amines show higher throwing power in gold-plating baths[21]. Combined nickel and gold plating can also be achieved using dimethylamine borane and hydrazine hydrate as reducing agents[22].

General scheme of electroless plating

Normally electroless plating involves a number of steps carried out in sequence as shown in Figure 1. Normally the sequence of operations involves first sensitization followed by activation and then controlled electroless deposition using chemical reduction reaction with suitable additives for acceleration or retardation of the deposition rate. However, one should remember that there will be a number of rinsing and washing steps which are not explicitly shown in Figure 1.

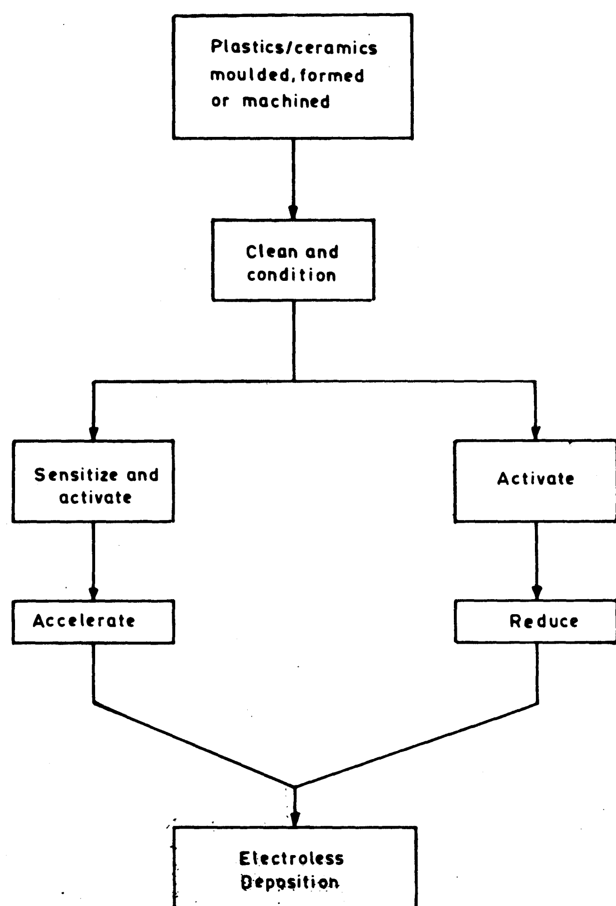

Figure 1. Sequence of general operations in electroless deposition.

Sensitization and activation

Normal commercial procedures of sensitization for hydrophobic surfaces involve two-step immersion sequence in acidic stannous chloride solution followed by immersion in acidic palladium chloride solution. The first bath is called the sensitizer and the second activator. The chemistry involved in this process of immersion is dispersion of finely divided palladium (0) which initiates the autocatalytic plating process. The nucleation of palladium (0) is achieved by the redox reaction taking place between Pd (II) ions in the solution as well as tin ions adsorbed on the substrate. This means one should achieve good adsorption of sensitizers. Schlesinger and Kisel[23] have examined the adsorption properties of acidified $SnCl_2$ solution with additives like hydroquinone, triton X-100, thiourea and showed a nonlinear relationship between the amount of sensitizer adsorbed and the number of metal islands deposited from electroless nickel bath (citrate bath) per unit area of the substrate. The effectiveness of commercially available sensitizing solutions for electroless copper deposition on hydrophobic substrates has been gauged by the measurement of the contact angles. Feldstein and Weiner[24] have demonstrated that controlled additions of stannic ions with or without sodium chloride especially with ageing could yield superior wetting and thus can yield uniform plating of hydrophobic substrates[25–27]. The ageing process in the stannic halide solutions probably favours the transformation of α-stannic acid to β-stannic acid form. The colloidal nature of stannic acid is consistent with the view that the sensitizers together with the activators form only colloids and not solution complexes[28]. Cohen and West[29,30] and Cohen and Meek[31] postulate that a complex between Sn (II) and Pd (II) is first formed in which the reduction of Pd (II) to Pd (0) occurs subsequently forming a nucleus for the growth of the colloid. The core of the colloid is a metallic alloy of Pd and tin surrounded by stabilizing layers of $SnCl_2$ and $Sn(OH)_2$. According to this model, one should expect the deposition of metallic tin on Pd. The cyclic voltammetric study by Jean Horkans[32], which aimed at identifying the chemical state of the catalyst on the activated surface, showed that in addition to the stabilizing stannous layer produced by the reduction of Sn (IV) metallic tin also constitutes to the core of the active colloid.

The structure and composition of the colloidal catalyst particles have been investigated by a variety of

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techniques though there is some convergence on the fcc structure of the active catalyst, there still seems to be some uncertainty regarding the composition of Pd–Sn alloy. It is certain that Pd/Sn ratio is greater than 1 (refs. 33, 34). The various values of the ratio reported in the literature could have arisen because the analysis of the data has been performed in the different regions of the active catalyst from the core to the outer layer depending upon the type of technique employed.

In the sensitizing and activating step, certain accelerators like NaOH and EDTA are added which are effective in removing the tin species from the surface and increasing the initial rate of metal deposition. The uniform distribution of the metal deposit is also dependent on the nature of the accelerator used, for example NaOH and EDTA are favourable for uniform deposition of copper[35].

In the sensitization step as stated earlier, various types of tin compounds including tin oxide (SnO_2) and stannous and stannic chlorohydroxides, oxyhydroxides and hydrated oxides have been identified. The formation of these compounds and hence the extent of sensitization are dependent on the pH of the solution[36]. The process sequence involves a rinsing step after the activation and sensitization. There seems to be some difference of opinion on the rinse water pH for the activation of plastics. Cohen and Meek[37] propose that acidic solution rinse provides a cleaner, more catalytic surface while Ghorashi[36] claims that a rinse water with pH 9 provides optimum conditions for obtaining a uniformly activated surface. It is to be remarked that the final rinse with appropriate pH provides the necessary type of species, hydroxide or chloride species on the outer layer of the activator–sensitizer combination which favours the catalytic reduction and deposition of the metal from the solution.

A new concept of the activation can be introduced based on the concept of anchoring the functional groups or ions on the polymer surfaces. For example, Pd^{2+} can be exchanged with polymer substrates with functional groups, especially carboxylic groups, which will avoid the formation of tin chloride shell over the activator and thus promote, in a facile manner, electroless deposition[38].

Electrochemistry of electroless copper

Electrochemical nature of the electroless deposition of metals has also received considerable attention[39–42]. Paunovic[39] started it with his mixed potential concept. According to this model, when at an electrode simultaneously two different electrode reactions

$$Ox_1 + n_1e \rightarrow Red_1 \quad (1)$$

$$Ox_2 + n_2e \rightarrow Red_2 \quad (2)$$

take place, both reactions strive to attain the equilibrium state with its own equilibrium potential E_{eq} but in this process attain a steady state mixed potential (E_{MP}). The characteristics of this mixed potential are that (i) both redox systems are removed from their equilibrium potentials governed by the equations

$$\eta_1 = E_{MP} - E_{1eq} \quad (3)$$

$$\eta_2 = E_{MP} - E_{2eq}, \quad (4)$$

(ii) net electrochemical reaction occurs as they are removed from their equilibrium by the establishment of the mixed potential, (iii) the condition that the sum of cathodic current densities is equal to the sum of the anodic current densities holds good, since net current cannot flow in the isolated system

$$\vec{i}_1 + \vec{i}_2 = \overleftarrow{i}_1 + \overleftarrow{i}_2, \quad (5)$$

(iv) since at the steady state mixed potential, the system is not in equilibrium and change in free energy is not equal to zero.

Extending this mixed potential concept to electroless plating wherein one of the redox couples is the metal electrode and the second one is the reducing agent applied in electroless plating, the corresponding reactions can be written as

$$M^{n+} + n_M e \rightarrow M \quad (6)$$

$$Ox + n_{red} e \rightarrow Red. \quad (7)$$

The establishment of mixed potential is shown in Figure 2, wherein it is seen that the potential of the redox couple is raised from its reversible value E_{red}^{eq} and the potential of the metal electrode is depressed cathodically from its reversible value E_M^{eq} to reach the

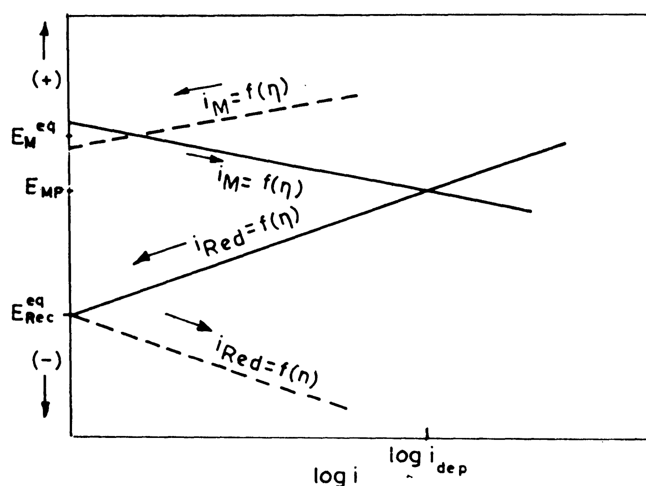

Figure 2. Current potential curves for the system with two different simultaneous electrochemical reactions-kinetic scheme [ref. 39].

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mixed potential E_{MP} value. The overall reaction at the electrode is represented as

$$M^{n+} + Red \rightarrow M + Ox. \quad (8)$$

In essence, the mixed potential can be considered to be the intersection points of i_M and i_R. This implies that at the steady state mixed potential, the rate of reduction of the metal is equal to the rate of oxidation of the reducing agent or

$$i_{electroless\ deposition} = \vec{i}_M = \overleftarrow{i}_{red}. \quad (9)$$

This implies that one can *a priori* calculate the values of E_{MP} and deposition rate i_{dep} if one knows the current potential functions $i=f(\eta)$ of the individual electrode processes. The parameters which determine the current potential curves for the partial electrode reactions (6) and (7) also determine E_{MP} and $i_{deposition}$. Parameters like the variation of the exchange current density, concentration of reactants (since $i_0 = nF\vec{k}s_{ox} = nF\overleftarrow{k}C_{red}$, where ks are rate constants and Cs are concentrations) temperature and the type of overvoltage (charge transfer, mass transport or reaction overvoltage) also control the values of E_{MP} as well as $i_{deposition}$.

The solution chemistry of electroless copper bath has been probed by a variety of electrochemical techniques. Using cyclic voltammetry technique below the mixed potential value (-0.7 V) Tam[43] identified that methyleneglycolate (CH_2OH_2) and its copper (II) complex are the electroactive species in solution. The methyleneglycolate anion is adsorbed on the copper sites with the C–H bonds adjacent to the copper surface which then undergoes electro-dehydrogenation to give rise to formate anion as well as molecular hydrogen evolution[44]. As seen from the data in Table 1 only a limited variety of reductants are used in electroless process namely hypophosphite, formaldehyde, borohydride, dialkylamine borane and hydrazine. Normally electroless plating is accompanied by hydrogen evolution though it is not directly related to metal deposition. Van den Meerakker[45] proposed a universal mechanism for electroless deposition which involves the dehydrogenation of the reductant as the first step.

$$RH \rightarrow R + H \quad (10)$$

$$R + OH^- \rightarrow ROH + e^- \quad (11)$$

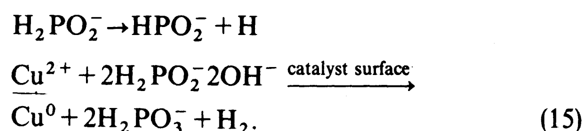
$$H + H \rightarrow H_2 \quad (12)$$

$$H + OH^- \rightarrow H_2O + e^- \quad (13)$$

$$M^{n+} + ne \rightarrow M, \quad (14)$$

where RH represents the reductant. It is seen from this mechanism that hydrogen atom combination step (12) indicates that metals with dehydrogenation–hydrogenation catalytic activity can promote this reaction step favourably. Extending this proposal Ohno *et al.*[46] proposed that the oxidation of the reductants proceeds mainly along with hydrogen evolution step on copper, silver and gold while hydrogen-ionization mechanism predominates on Co, Ni, Pd and Pt. The catalytic activity series of the metals for anodic oxidation of reductants does not coincide with that for hydrogen electrode reaction.

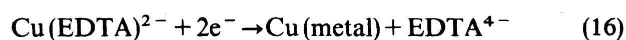
Electroless copper obtained using hypophosphite as reductant is supposed to proceed through the following steps



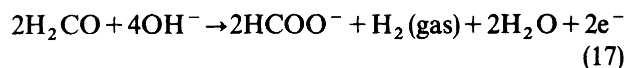
$$H_2PO_2^- \rightarrow HPO_2^- + H$$
$$Cu^{2+} + 2H_2PO_2^- 2OH^- \xrightarrow{\text{catalyst surface}} Cu^0 + 2H_2PO_3^- + H_2. \quad (15)$$

When complexing agents like EDTA are used, octaphedral complexes are formed while with ligands like oxalate, glycine square planar or square pyramidal type complexes are proposed. Multinuclear (usually dimeric) complexes are reported with citrate, tartrate, malate. Even though complexation is one of the essential steps in the electroless plating no definite relationship could be established between the plating rate and the stability constant of the possible complexes that are formed. However ligands that can form dimeric copper species exhibit higher plating rates.

The mixed potential theory proposed for electroless deposition does not seem to predict correctly the experimentally obtained mixed potential and the current potential (i/V) curve is not a simple sum of the half cell i/V responses in the case of copper electroless deposition by formaldehyde in presence of EDTA. When the two half cell reactions



$$Cu(EDTA)^{2-} + 2e^- \rightarrow Cu(metal) + EDTA^{4-} \quad (16)$$



$$2H_2CO + 4OH^- \rightarrow 2HCOO^- + H_2(gas) + 2H_2O + 2e^- \quad (17)$$

are strongly coupled then the assumption that the reduction of $Cu(EDTA)^{2-}$ is not perturbed by the presence of HCHO or vice versa does not hold good. It is therefore necessary to invoke in the reaction mechanism of formaldehyde-induced reduction of copper, the formation of a Cu(EDTA)/HCHO complex on the electrode followed by the reduction of the complex. This is one of the results reported in the literature which does not conform to the mixed potential model[47]. However, recent studies by Hung and Ohno[48] have shown that reactions involved in electroless copper deposition reduced by hypophosphite though complicated still follow the mixed potential theory.

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Conclusion

Electroless plating has thus been receiving considerable attention in recent times with respect to new bath formulations with improved features like long-term stability, increased plating rate, and increased throwing power from which purer deposits or deposits with consistent composition and quality can be obtained. Non-conventional methods like electroless gold plating on superconducting $YBa_2Cu_3O_{7-x}$ ceramic oxides from non-aqueous baths are also attempted for specific applications. Structural studies of the deposits still seem to interest scientists[50]. On the whole as expected, electroless deposition appears to have a challenging future.

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Tumour rejection antigens: Their role in spontaneous tumour regression

Girish Deshpande and Ashok Khar

Centre for Cellular & Molecular Biology, Uppal Road, Hyderabad 500 007, India
*Present Address: Department of Molecular Biology, Princeton University, New Jersey 08544, USA

Exploration of the cancer cell is akin to archaeology: 'We must infer the past from its remnants in the present, and the remnants are often cryptic.

J Michael Bishop: Les Prix Nobel, 1989.

The interaction between the tumour cell and the host immune system has attracted the tumour immunologists for a long time. Immunologists have chosen to concentrate on the surface associated or membrane bound antigens of tumours because of their ability to evoke a strong immune response. Based on their chemical nature, the type of immune response and the nature of the carcinogenic agent, tumour antigens have been classified into several categories, out of which the viral and the chemically induced antigens have been studied extensively. The focus of this article is on the tumour antigens that elicit tumour resistance by stimulating humoral or cellular immune response in a syngeneic host.

TUMOUR antigens, i.e. molecules which elicit immune response in a tumour-bearing host, have been referred by different terms in the history of immunology. Some of these terms like 'aberrant germs', 'factor responsible for regression' and 'new antigenic potentialities' have reincarnated over decades in various forms, e.g. viral antigens, histocompatibility antigens, oncofetal antigens, differentiation antigens, etc.

The long standing goal of cancer biologists has been to stimulate the immunological rejection of tumours. This goal is based on the hypothesis that a cancer cell which develops from its normal progenitor as a consequense of the transformation event, carries a foreign antigen which could be recognized by the host immune system. The focus of this article is on tumour antigens that elicit tumour resistance by stimulating humoral or cellular responses in a syngeneic host.

The capacity of a tumour-specific transplantation antigen to evoke an immune response is influenced by the interaction between the tumour and the host. Therefore, tumour antigens continue to be the interesting molecules to immunologists, primarily due to the role they play in modulating the immune response evoked[1], as well as the possible direct relationship they might have with molecular mechanisms of malignant transformation itself. Table 1 describes some of the tumour rejection antigens that have the ability to elicit an immune response in syngeneic host and thereby resist the tumour challenges.

The classical definition of tumour-specific antigens implied their presence only on tumours, but not on normal tissues. However, among the various tumour-specific antigens discovered so far, normal cellular proteins which can act as antigen and evoke an immune response in a syngeneic host have attracted considerable attention. More recently, the study of heat shock proteins (hsp's) has converged with immunology, more specifically with

Table 1. Tumour antigens defined by their ability to mount an immune response to tumour challenges

Tumour	Antigen	Reference
Murine sarcoma	Gp37	Steinmann *et al.*[81]
Rat hepatoma	p100	Srivastava and Das[82]
Murine B lymphoma	Gp80	Koch *et al.*[83]
Human melanoma	Gp90	Real *et al.*[84]
SV-40 transformed cells	p90–100 (T-antigen)	Anderson *et al.*[85]
C3H mouse sarcoma	Gp70	Zbar *et al.*[86]
Mouse sarcoma	Gp96	Srivastava *et al.*[27]
Mouse sarcoma	p84/86	Ullrich *et al.*[36]
B-16 mouse melanoma	B700	Hearing *et al.*[62]
Mouse mastocytoma	p60	DePlaen *et al.*[87]
BALB/c sarcoma	p75/82	DuBois *et al.*[88]
MuLV induced leukemia	Gp175	Rogers *et al.*[89]
A-MuLV transformed lymphoid cells	Gp95	Machida and Kabat[90]

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